

ENVIRONMENTAL PROTECTION AGENCY

40 CFR Part 425

[FRL 3304-6]

Leather Tanning and Finishing Industry Point Source Category Effluent Limitations Guidelines, Pretreatment Standards, and New Source Performance Standards

AGENCY: Environmental Protection Agency (EPA).

ACTION: Final rule.

SUMMARY: This final rule establishes effluent limitations guidelines and standards limiting the discharge of pollutants into navigable waters of the United States and the introduction of pollutants into publicly owned treatment works (POTW) by existing and new sources engaged in leather tanning and finishing. EPA is promulgating these amendments in accordance with a settlement agreement with the Tanners' Council of America, Inc. (The Tanners' Council of America, Inc., was redesignated the Leather Industries of America, Inc., in 1985). The agreement settles a dispute between the Council and EPA that was the subject of a petition for judicial review of the final leather tanning and finishing rule promulgated by EPA on November 23, 1982 (47 FR 52848).

This final rule, which was proposed on January 21, 1987 (52 FR 2370), (1) adds a new analytical method for the determination of the presence of sulfide in wastewaters for use in the Hair Save or Pulp, Non-Chrome Tan, Retan-Wet Finish Subcategory (Subpart C); (2) clarifies procedural requirements for publicly owned treatment works to follow in determining whether sulfide pretreatment standards are applicable; (3) revises certain of the effluent limitations for "best practicable control technology currently available" (BPT) and new source performance standards (NSPS); (4) changes the pH pretreatment standard for tanneries falling under the provisions of Subpart C; and (5) clarifies the production levels below which the chromium pretreatment standards for existing sources (PSES) do not apply. In addition, EPA clarifies in the preamble to this final rule its statements on median water use ratios, changes in subcategorization, tanneries with mixed subcategory operations, and composite samples of effluent discharges from multiple outfalls.

DATES: In accordance with 40 CFR 23.2 and 40 CFR 23.11, this rule shall be considered issued for the purposes of

judicial review at 1:00 p.m. eastern daylight time on April 4, 1988. This rule shall become effective May 4, 1988.

Under section 509(b)(1) of the Clean Water Act as amended by section 505(a)(2) of the Water Quality Act of 1987, judicial review of this rule may be made by filing a petition for judicial review in the United States Court of Appeals not later than 120 days after the rule is considered issued for purposes of judicial review. Under section 509(b)(2) of the Clean Water Act, the requirements in this rule may not be challenged later in civil or criminal proceedings brought by EPA to enforce these requirements.

ADDRESSES: Address questions on the final rule to Rexford R. Gile, Jr., Industrial Technology Division (WH-552), U.S. Environmental Protection Agency, 401 M Street SW., Washington, DC 20460, Attention: Leather Tanning and Finishing Industry Final Rule. The basis for this rule is detailed in the "Supplemental Development Document for Effluent Limitations Guidelines for the Leather Tanning and Finishing Point Source Category." A copy of this technical development document may be obtained from the National Technical Information Service, Springfield, Virginia 22161, (703) 487-6000. Technical information may be obtained by writing to Rexford R. Gile, Jr., Industrial Technology Division (WH-552), U.S. Environmental Protection Agency, 401 M Street SW., Washington, DC 20460 or by calling (202) 382-7146.

The record for the final rule will be available for public review not later than April 4, 1988, at the EPA Public Information Reference Unit, Room M2904 (Rear) (EPA Library). The EPA public information regulation (40 CFR Part 2) provides that a reasonable fee may be charged for copying.

FOR FURTHER INFORMATION CONTACT: Rexford R. Gile, Jr., (202) 382-7146.

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I. Legal Authority

These amendments to 40 CFR Part 425 are being promulgated under the authority of sections 301, 304(b), (c), (e), and (g), 306(b) and (c), 307(b) and (c), 308 and 501 of the Clean Water Act [the Federal Water Pollution Control Act Amendments of 1972 as amended by the Clean Water Act of 1977 and the Water Quality Act of 1987 (the "Act")]; 33 U.S.C. 1311, 1314(b), (c), (e), and (g), 1316(b) and (c), 1317(b) and (c), 1318, and 1361; 86 Stat. 816, *et seq.*, Pub. L. 92-500; 91 Stat. 1567, Pub. L. 95-217; and Pub. L. 100-4. These amendments to the regulation are also being promulgated in response to the Settlement Agreement in *Tanners' Council of America, Inc. v. U.S. Environmental Protection Agency*, No., 83-1191, (4th Cir.).

II. Background

A. Prior Regulations

EPA promulgated a regulation on April 9, 1974, establishing effluent limitations guidelines and standards for the leather tanning and finishing point source category based on the best practicable control technology currently available ("BPT"), the best available technology economically achievable ("BAT"), new source performance standards ("NSPS") for new direct dischargers, and pretreatment standards for new indirect discharges ("PSNS") (39 FR 12958; 40 CFR Part 425, Subparts A-F). The Tanners' Council of America, Inc., (TCA), challenged this regulation, and the U.S. Court of Appeals for the Fourth Circuit left BAT and PSNS undisturbed, but remanded the BPT and NSPS limitations and standards for several reasons (see *Tanners' Council of America, Inc. v. Train*, 540 F.2d 1188 (4th Cir. 1976)).

On March 23, 1977 (42 FR 15696), EPA promulgated pretreatment standards for existing sources ("PSES") for the leather tanning and finishing industry. This regulation established specific pH standards and other pretreatment standards for existing indirect dischargers to avoid interference with POTWs. This rule was not challenged.

EPA proposed a new regulation (44 FR 38746, July 2, 1979) establishing effluent limitations guidelines and standards for the leather tanning and finishing point source category based on revised BPT and NSPS to replace the remanded BPT and NSPS limitations and standards, new best conventional pollutant control technology ("BCT") limitations, and revised BAT, PSES, and PSNS limitations and standards. EPA accepted comments on the proposed regulation until April 10, 1980. The leather tanning and finishing industry commented that the data and supporting record material relied upon by EPA in proposing the regulation contained a large number of errors. The Agency responded by completely reviewing the entire data base and all documentation supporting the rulemaking, and by acquiring supplemental data during and after the comment period.

On June 2, 1982 (47 FR 23958), EPA made available for public review and comment supplementary technical and economic data and related documentation received after proposal of the regulation. The Agency also summarized the preliminary findings on how the supplementary record materials might influence the final rulemaking.

The final regulation for the leather tanning and finishing industry point source category was promulgated on November 23, 1982 (47 FR 52848) and established effluent limitations guidelines and standards to control specific toxic, nonconventional, and conventional pollutants for nine subcategories in the Leather Tanning and Finishing Category.

Subpart A—Hair Pulp, Chrome Tan, Retan-Wet Finish Subcategory (Subcategory 1)

Subpart B—Hair Save, Chrome Tan, Retan-Wet Finish Subcategory (Subcategory 2)

Subpart C—Hair Save or Pulp, Non-Chrome Tan, Retan-Wet Finish Subcategory (Subcategory 3)

Subpart D—Retan-Wet, Finish-Sides Subcategory (Subcategory 4)

Subpart E—No Beamhouse Subcategory (Subcategory 5)

Subpart F—Through-the-Blue Subcategory (Subcategory 6)

Subpart G—Shearling Subcategory (Subcategory 7)

Subpart H—Pigskin Subcategory (Subcategory 8)

Subpart I—Retan-Wet Finish-Splits Subcategory (Subcategory 9)

BPT effluent limitations guidelines were established for all subcategories based on high solids extended aeration activated sludge biological treatment. They included production-based effluent limitations (kg/kkg or lb/1,000 lb or raw material) for one toxic pollutant (total chromium), three conventional pollutants (BOD₅, TSS, oil and grease), and established an acceptable pH range. BPT production-based effluent limitations were derived using subcategory median water use ratios, attainable effluent concentrations, and variability factors.

BAT and BCT effluent limitations guidelines were also established for all nine subcategories in the leather tanning and finishing point source category. The technology basis and production-based effluent limitations guidelines for BAT and BCT were the same as those for the promulgated BPT effluent limitations guidelines. The BCT effluent limitations guidelines control three conventional pollutants (BOD₅, TSS, oil and grease), and established an acceptable pH range. The BAT effluent limitations guidelines controlled one toxic pollutant (total chromium).

The production-based NSPS for all nine subcategories limited one toxic pollutant (total chromium) and three conventional pollutants (BOD₅, TSS, oil and grease), and established an acceptable pH range. NSPS were based on the same technology, effluent concentrations, and variability factors as BAT, but the production-based limitations for NSPS were different from those for BAT because the NSPS limitations were based on reduced water use ratios.

The final regulation established concentration-based categorical pretreatment standards for existing and new source indirect dischargers for one toxic pollutant (total chromium) for all nine subcategories except for existing small indirect dischargers in subcategories in Subparts A, C, and I.

Concentration-based categorical pretreatment standards were also established for the control of sulfides in subcategories in Subparts A, B, C, F, and H where unhairing operations are included. However, the regulation included a provision which allows a POTW to certify to the Regional Water Management Division Director of EPA in the appropriate Regional Office, in accordance with § 425.04, that the discharge of sulfide from a particular facility does not interfere with its

treatment works. If this certification is made, and EPA determines that the submission is adequate, EPA will publish a notice in the *Federal Register* identifying the facility where the sulfide pretreatment standard would not apply.

The cost of pretreatment technology can be minimized by reducing to the maximum extent feasible the volume of wastewater treated. Therefore, the Agency used reduced water use ratios to calculate the costs of PSES/PSNS technology for indirect dischargers instead of median water use ratios for existing sources.

B. Challenge to the 1982 Regulation by the Tanners' Council of America, Inc.

The Tanners' Council of America, Inc. (TCA), filed a petition for judicial review of several aspects of the final regulation in the U.S. Circuit Court of Appeals for the Fourth Circuit on March 2, 1983 (*Tanners' Council of America, Inc. v. U.S. Environmental Protection Agency*, No. 83-1191), and followed this by filing with EPA an administrative Petition for Reconsideration on May 9, 1983. The Agency responded by completely reviewing the entire data base and all documentation supporting the rulemaking, and by acquiring supplemental data. After extensive discussions, TCA and EPA resolved the issues raised by the Council through a settlement agreement.

C. Settlement Agreement

On December 11, 1984, TCA and EPA entered into a comprehensive settlement agreement which resolved all issues raised by TCA in its petitions. EPA agreed to propose regulatory amendments and preamble language to the leather tanning and finishing regulation and to solicit comments on the regulatory and preamble language. TCA agreed to move to dismiss its petition for judicial review and voluntarily withdraw the "Petition for Reconsideration" if each provision of the final leather tanning and finishing industry regulation and each preamble statement is substantially the same as that called for by the settlement agreement.

Copies of the settlement agreement were sent to EPA Regional Offices and State NPDES permit-issuing authorities on December 21, 1984. In accordance with the settlement agreement, EPA proposed regulatory amendments and preamble language to the leather tanning and finishing regulation on January 21, 1987 (52 FR 2370) and solicited comments regarding these proposed amendments. The comment

period on the proposal closed on February 20, 1987.

As part of the settlement agreement, TCA and EPA jointly requested the U.S. Court of Appeals for the Fourth Circuit in *Tanners' Council of America, Inc. v. EPA* to stay the effectiveness of the sections of 40 CFR Part 425 which EPA had agreed to propose to amend, pending final action by EPA on each proposed amendment. On February 22, 1985, the Court entered an Order staying the following sections of the regulation promulgated on November 23, 1982: § 425.02(a); § 425.03; § 425.11, except for the pH limitations; § 425.15(b); § 425.31, except for the pH limitation; the pH limitation in § 425.35(a); § 425.35(b); § 425.41, except for the pH limitation; § 425.44, except for the pH limitation; § 425.51, except for the pH limitation; § 425.61, except for the pH limitation; § 425.64, except for the pH limitation; § 425.71, except for the pH limitation; § 425.91, except for the pH limitation; and § 425.95(b). EPA is amending these sections in this final rule in accord with the settlement agreement.

All effluent limitations guidelines and standards contained in the final leather tanning and finishing industry regulation promulgated on November 23, 1982, which are not specifically listed in these amendments to the regulation, were not stayed by the Order entered by the Court. In addition, EPA is not deleting or modifying any of the effluent limitations guidelines and standards not affected by the settlement agreement or Order.

III. Amendments to the Leather Tanning and Finishing Point Source Category Regulation

In the final rule, EPA is amending Part 425 in accordance with the settlement agreement to (1) allow use of a new alternative sulfide analytical method, (2) clarify the procedures to be followed by a POTW when changed circumstances justify application of sulfide pretreatment standards where previously waived, or a certification by a POTW that the discharge of sulfide will not interfere with the operation of the POTW, (3) revise BPT effluent limitations guidelines and NSPS standards based on corrected and more complete information, and (4) allow the small tannery exemption without restriction as to the number of working days per week. These amendments are discussed in this section.

A. Alternative Sulfide Analytical Method

1. *TCA Concerns and EPA Response.* EPA had promulgated a categorical sulfide pretreatment standard and required all facilities to use the Society

of Leather Trades' Chemists' "Method for Sulfide Analysis SLM 4/2" in which the sulfide solution is titrated with standard potassium ferricyanide solution in the presence of a ferrous dimethylglyoxime ammonia complex (§ 425.03). TCA and some industry members conducted testing to determine the validity of this analytical method. These test results revealed the following problems with the SLM 4/2 method.

a. The method described in the previously promulgated § 425.03(c)(1) provides for the removal of the suspended matter by rapid filtration through *either* glass wool *or* coarse filter paper. The lack of standardization of glass wool could potentially cause inconsistent analytical results.

b. The titrant equivalence statement as set forth in the previously promulgated § 425.03(c)(4) will lead to confusion in the reporting of analytical results because it expresses the results in terms of sodium sulfide instead of sulfide upon which the pretreatment standards are based.

c. Colored tannery wastewater, especially vegetable tanners' wastewater, makes it difficult to detect the destruction of the pink color at the end point. Additionally, certain simple phenolic substances (pyrogallol and pyrocatechol), which are model substances for the nontannins of vegetable tanning materials, consume the ferricyanide titrant under the prescribed SLM 4/2 conditions. These interfering substances may yield false results.

In response to the first problem, EPA is amending the promulgated approved method to delete glass wool as an alternative rapid filtration medium. EPA is also amending the previously promulgated method to specify use of a coarse filter paper. In response to the second problem, EPA is amending the method to express the results of the titrant equivalence statement in terms of mg. per liter of sulfide which is the basis for the pretreatment standards.

In response to the third problem, EPA and TCA conducted a cooperative sampling and analytical methods development program for vegetable tanning wastewaters using both the promulgated SLM 4/2 method and a method suggested by TCA, the modified Monier-Williams method. Raw and pretreated wastewaters were collected at seven tanneries, including two vegetable tanning tanneries, for analysis by EPA and TCA. The analytical data showed that the modified Monier-Williams method was able to measure sulfide in vegetable tannery wastewater when wastewater color prevented detection of the end point color change

using the SLM 4/2 procedure. The data also showed that the method produced considerably better spike recoveries than the SLM 4/2 procedure. These data and EPA's summary of the results are part of the record of this rulemaking. The modified Monier-Williams method, thus, is an acceptable procedure for pretreatment standard compliance monitoring in the leather tanning and finishing industry. EPA is amending Part 425 by including the modified Monier-Williams method as a sulfide analytical procedure for facilities with vegetable tanning wastewaters and as an alternative sulfide analytical procedure for other tanneries.

2. *Amendment to § 425.02 General Definitions.* EPA is making two minor changes to the general definitions sections to address analytical methods issues. EPA is defining "sulfide" in § 425.02(a) as total sulfide as measured by either the potassium ferricyanide titration procedure ("Method for Sulfide Analysis SLM 4/2") in Appendix A to Part 425 or the modified Monier-Williams procedure described in Appendix B to Part 425. This is a technical change required to allow use of the new procedures. These two analytical procedures are moved to appendixes to the final rule for the convenience of the user.

Under the settlement agreement, EPA agreed to propose that the Minimum Reportable Concentration (MRC) should be determined periodically in each of the two sulfide analytical procedures by each participating laboratory in accordance with the procedures specified in "Methods for Chemical Analysis of Municipal and Industrial Wastewater," EPA-600/4-82-057, July 1982, EMSL, Cincinnati, OH 45268. The term MRC is not explicitly defined in the settlement agreement or in the 1982 "Methods" document cited. Rather, the 1982 "Methods" document describes the Method Detection Limit (MDL) procedure which is also described in Appendix B to 40 CFR Part 136. EPA interprets MRC to be synonymous with the MDL procedure described in Appendix A to the 1982 "Methods" document and Appendix B to 40 CFR Part 136. Therefore, the MDL procedure is used as the MRC method. For the convenience of the user, the definition and procedure for the determination of the Method Detection Limit is contained in Appendix C to Part 425.

3. *Amendment to § 425.03 Sulfide Analytical Methods.* The previously promulgated § 425.03 describes the potassium ferricyanide titration (SLM 4/2) method in detail. As explained above, this method and the modified Monier-

Williams method are described in new appendixes to Part 425. Section 425.03 is amended to provide that the potassium ferricyanide method is approved for analysis of sulfide except for those tanneries covered by Subpart C (Hair Save or Pulp, Non-Chrome Tan, Retan-Wet Finish Subcategory). For these tanneries, the modified Monier-Williams method is the approved method; tanneries in other subcategories may also use the modified Monier-Williams method to detect sulfide.

3. Applicability of Sulfide Pretreatment Standard

1. TCA Concern and EPA Response. The previously promulgated § 425.04 provided that, until October 13, 1983, POTWs may take steps to certify that sulfide pretreatment standards do not apply. (40 CFR 425.04(c)). The previous rule did not provide a procedure by which POTWs could revoke a previously issued certification of inapplicability. TCA criticized the provision of § 425.04 under which, after October 13, 1983, a POTW is precluded from certifying that the sulfide pretreatment standards should not apply to a particular facility. TCA noted that there may be changed circumstances after that deadline under which it may still be appropriate for a POTW to allow such a certification. EPA agrees that there may be changed circumstances after the October 13, 1983 deadline which would justify both the issuance and revocation of a certification as to the applicability or inapplicability of the sulfide pretreatment standards, and is amending § 425.04 to permit a POTW to initiate proceedings, revoke, or issue certification on the inapplicability of the sulfide pretreatment standards subsequent to the October 13, 1983 deadline.

2. Amendment to § 425.04 Applicability of Sulfide Pretreatment Standard. EPA is amending § 425.04 by adding paragraphs (d)(1), (d)(2), and (e) to § 425.04. The amended §§ 425.04(d) (1) and (2) provide a procedure for POTWs to revoke a previously issued certification of inapplicability of the sulfide pretreatment standard. If, as a result of this revocation, the sulfide pretreatment standards are to be applicable to an indirect discharger, the discharger will be required to comply with these standards no later than 18 months from the publication date of the Federal Register notice announcing the revocation.

EPA is amending § 425.04(e) which authorizes POTWs to initiate proceedings to certify that sulfide

pretreatment standards should not apply to specified facilities after October 13, 1983. Under this subsection, a POTW may determine that circumstances have arisen since that date that justify a determination that the sulfide pretreatment requirements should not apply. The POTW may propose to certify that the pretreatment standard does not apply and may initiate proceedings to this end. This certification would be governed by the existing certification procedures and time intervals in §§ 425.04 (b) and (c).

C. Changes to Effluent Limitations Guidelines and Standards Based on Revised Water Use Ratios, pH Pretreatment Standard, and Changes to the Small Tannery Exemption

1. Changes to Effluent Limitations Guidelines and Standards. TCA criticized EPA's median flow ratios for three subcategories (Subparts D, F, and I) alleging that the flow ratios developed by EPA were erroneous based on new water use data submitted by TCA. EPA had developed median flow ratios for each subcategory to derive production-based effluent limitations for direct discharging facilities.

After reviewing the revised data base for the subcategory median and new source water use ratios, EPA determined that changes should be made in the median water use ratios for a number of subcategories. Table 1 reflects the revisions in median water use ratios for existing plants as well as revisions in the number of plants in the subcategory data bases and the number of plants achieving median water use ratios. Table 2 reflects the revisions in the new source water use ratios and in the number of plants achieving these water use ratios.

TABLE 1

Subcategory	Median water use ratio (gals/lb)	Plants in data base	
		Number of plants in subcategory data base	Number of plants in data base achieving water use ratios
1	6.6	34	17
2	5.8	4	3
3	4.8	11	6
4	6.3	7	4
5	5.7	10	5
6	2.3	3	2
7	10.7	2	1
8	5.0	2	1
9	4.1	6	3

TABLE 2

Subcategory	New source water use ratio (gals/lb)	Number of Plants in data base achieving water use ratio
1	4.3	6
2	4.9	1
3	4.2	4
4	4.6	2
5	3.8	3
6	2.1	1
7	9.4	1
8	4.1	1
9	2.5	2

As a result of the review of EPA's data base, supplemented by information supplied by TCA, and corrections to identified errors in the interpretation of existing water use data, the subcategory median and new source water use ratios used to establish BPT and NSPS limitations and standards were recalculated. These amendments will result in BPT effluent limitations guidelines for Subparts A, D, F, G, and I that are less stringent than those in the final regulation (47 FR 52848, November 23, 1982), while the BPT limitations for Subparts C and E will be more stringent than those in the final regulation. NSPS for subparts D and F will be less stringent than those in the final regulation. The Supplemental Development Document for Effluent Limitations Guidelines and Standards for the Leather Tanning and Finishing Industry Point Source Category documents the basis for the changes to effluent limitations guidelines and standards based on revised water use ratios.

2. PSES for pH. EPA established a pH range of 7.0 to 10.0 for leather tanneries with alkaline wastestreams in the 1982 final regulation. EPA established 10 as the uppermost level of the pH range because of the solubility of chromium at pH levels in excess of 10. TCA argued that EPA should establish a waiver procedure to allow relief for tanneries with a pH in excess of 10 in certain circumstances.

After careful consideration, EPA concluded that a waiver from the higher standard would be unduly complicated. In response to TCA's request, EPA did agree to delete the higher (alkaline) pH standard for vegetable tanneries in Subpart C only (§ 425.35(a)). EPA is less concerned about the chromium solubility for vegetable tanneries since these tanneries typically discharge low levels of chromium. The higher pH pretreatment standards for the other subcategories will remain as

promulgated because they will reduce the probability of chromium solubility. The low (acid) pH standard has been retained to ensure that the formation of hydrogen sulfide gas is minimized.

3. *Small Tannery Exemption.* The pretreatment standards for the leather tanning and finishing industry provide that chromium standards are now inapplicable to small plants in Subparts A, C, or I which discharge to publicly owned treatment works if these plants produce less than a specified number of hides/splits per day and a specified weight of hides/splits per year in their respective subcategories. In a correction notice dated June 30, 1983, the Agency specified the annual weight basis as well as the number of working days per year underlying the specified hide and split limits (48 FR 30115). Subsequent to discussing this matter with TCA, the Agency has reconsidered this issue. The Agency is deleting all references to the annual weight basis and the number of working days per year underlying the specified hide and split limits. Accordingly, tanneries with a seven-day workweek could qualify for the exemption.

Therefore, EPA is amending Subpart A (§ 425.15(b)), Subpart C (§ 425.35(b)), and Subpart I (§ 425.95(b)) by deleting references to the annual weight basis and the number of working days per year that were specified in the correction notice (48 FR 30115, June 30, 1983) to the final regulation for the small tannery exemption from pretreatment standards for chromium. The Agency has not, however, made any changes to the underlying exemption based on numbers of hides or splits per day.

IV. Clarifications

In addition to the amendments discussed in Section III, EPA is clarifying several issues: Changes in subcategorization, classification of tanneries with mixed subcategory

operations, and multiple outfalls. These issues are addressed below.

A. Changes in Subcategorization

Under 40 CFR 403.6(a) of the general pretreatment regulations, an existing industrial user or a POTW may seek written certification from the Approval Authority as to whether the industrial user falls within a particular subcategory of a promulgated categorical pretreatment standard. Existing users must make the request within 60 days after the effective date of a pretreatment standard for a subcategory under which the user may be included or within 60 days after the Federal Register notice announcing the availability of the technical document for the subcategory. New sources must request this certification prior to commencing discharge.

Persons have inquired as to the procedures that existing leather tanning facilities should use to seek an Agency determination if the facility decides to change its subcategorization subsequent to the expiration of the 60-day deadline under 40 CFR 403.6(a). In fact, 40 CFR 403.6(a) does not preclude leather tanning and finishing facilities from changing operations which would in turn automatically change their subcategorization status. Facilities that are planning to change their subcategorization status and are unsure which subcategory they will fall into should request written certification from the Approval Authority as to whether the facility falls within a particular subcategory prior to commencing discharges which would fall within that subcategory.

B. Tanneries With Mixed Subcategory Operations

The pretreatment standards for chromium are not applicable to plants with mixed subcategory operations if the greatest part of the plant's production is in either subcategory 1, 3, or 9 and if the total plant production is less than the specified number of hides

or splits per day for the particular subcategory. The intent of this exemption is to exclude small plants from the chromium pretreatment standards, not to exclude processing operations at medium or large plants.

C. Multiple Outfalls

Most indirect discharging plants combine their process wastewaters and discharge them all through one outfall. The Agency has costed this approach by including costs for internal plant piping for wastewater collection, as well as contingency costs to account for any unforeseen site specific costs.

If, however, an indirect discharging plant does not choose to combine its process wastewaters for treatment and to discharge them through one outfall, a composite sampling of the multiple outfalls could be acceptable. A single composite sample for multiple outfalls must be comprised of representative process wastewaters from each outfall. A composite sample must be combined in proportions determined by the ratio of process wastewater flow in each outfall to the total flow of process wastewaters discharged through all outfalls. If nonprocess wastewater is combined with process wastewater or if a plant has operations in more than one subcategory, the plant would have to use the "combined wastestream formula" in 40 CFR 403.6(e) to make this calculation. Flow measurements for each outfall must be representative of the plant's operation. An analysis of the total sample would then be compared to the applicable categorical standard to determine compliance.

V. Environmental Impact of Amendments

EPA estimates that the industry-wide direct BPT discharge of conventional and toxic pollutants under the final leather tanning and finishing regulation as amended by these amendments will increase less than four percent by weight as reflected in Table 3.

TABLE 3.—COMPARISON OF INDUSTRY-WIDE DIRECT BPT DISCHARGES OF CONVENTIONAL AND TOXIC POLLUTANTS UNDER FINAL AND AMENDED REGULATIONS FOR LEATHER TANNING AND FINISHING

Pollutant	Discharge (lbs/yr)			Percent increase
	Final ¹ regulation	Amended regulation	Increase	
BOD ₅	913,000	949,000	36,000	3.9
TSS.....	1,330,000	1,380,000	50,000	3.8
Oil & grease.....	381,000	392,000	11,000	2.9
Total chromium.....	19,300	19,900	600	3.1

¹ Final regulation, 47 FR 52848, November 23, 1982.

VI. Economic Impact of Amendments

These amendments will not alter the recommended technologies for complying with the leather tanning and finishing regulation. The Agency considered the economic impact of the regulation when the regulation was previously promulgated (see 47 FR 52848). These amendments will not alter the determinations with respect to the economic impact to leather tanning and finishing facilities.

VII. Public Participation and Response to Comments

This regulation was proposed on January 21, 1987 (52 FR 2370). The comment period ended on February 20, 1987. Only one commenter, the Leather Industries of America, Inc. ("LIA"), formerly Tanners' Council of America, Inc., the principal trade association of the United States leather industry, submitted comments pointing out a few typographical errors in the proposed regulation to modify the effluent limitations guidelines and pretreatment standards for the leather tanning and finishing point source category. EPA has, in today's final rule, corrected these minor typographical errors. In their comments, LIA stated that, subject to these minor comments, the proposed rulemaking, if finally adopted, would substantially comply with the requirements of the settlement agreement. Moreover, in general, LIA voiced full support for the Agency's amended regulatory and preamble language as set forth in the proposal.

VIII. Executive Order 12291

Executive Order 12291 requires EPA and other agencies to perform regulatory impact analyses on major regulations. Major rules are defined as those which result in an annual cost of \$100 million or more, or meet other economic impact criteria, such as cause major increases in costs and/or prices, or significant adverse effects on the ability of domestic producers to compete with foreign enterprises, or on competition, investment, productivity, or innovations. The 1982 final regulation for the leather tanning and finishing industry was not a major rule according to these definitions, and, therefore, did not require a formal regulatory impact analysis. This rulemaking also satisfies the requirements of the Executive Order for a non-major rule.

IX. Regulatory Flexibility Analysis

Under the Regulatory Flexibility Act, 5 U.S.C. 601 *et seq.*, EPA must prepare a Regulatory Flexibility Analysis for all regulations that have a significant

impact on a substantial number of small entities. In the preamble to the 1982 final rule, EPA concluded that significant impacts on small entities had been eliminated by exempting small tanners from chromium PSES. That conclusion is equally applicable to these amendments. The Agency is not, therefore, preparing a formal analysis for these amendments.

X. OMB Review

This final rule was submitted to the Office of Management and Budget for review as required by Executive Order 12291. Any comments from OMB to EPA and any EPA response to those comments are available for public inspection at Room 2904, U.S. Environmental Protection Agency, 401 M Street SW., Washington, DC from 9:00 a.m. to 4:00 p.m. Monday through Friday, excluding Federal holidays.

List of Subjects in 40 CFR Part 425

Leather, Leather Tanning and Finishing, Water Pollution Control, Wastewater Treatment and Disposal.

Dated: March 2, 1988.

Lee M. Thomas,
Administrator.

For the reasons set out in the preamble, EPA is amending Part 425, Subchapter N, Chapter I, of Title 40, Code of Federal Regulations, as follows:

PART 425—[AMENDED]

1. The authority citation for Part 425 is revised to read as follows:

Authority: Sections 301, 304(b), (c), (e), and (g), 306(b) and (c), 307(b) and (c), 308 and 501 of the Clean Water Act (the Federal Water Pollution Control Act Amendments of 1972, as amended by the Clean Water Act of 1977) (the "Act"); 33 U.S.C. 1311, 1314(b), (c), (e), and (g), 1316(b) and (c), 1317(b) and (c), 1318, and 1361; 86 Stat. 816, Pub. L. 92-500; 91 Stat. 1567, Pub. L. 95-217.

General Provisions

2. Section 425.02 is amended by revising paragraph (a) to read as follows:

§ 425.02 General definitions.

* * * * *

(a) "Sulfide" shall mean total sulfide as measured by the potassium ferricyanide titration method described in Appendix A or the modified Monier-Williams method described in Appendix B.

* * * * *

3. Section 425.03 is amended by revising it to read as follows:

§ 425.03 Sulfide analytical methods and applicability.

(a) The potassium ferricyanide titration method described in Appendix A to Part 425 shall be used whenever practicable for the determination of sulfide in wastewaters discharged by plants operating in all subcategories except the hair save or pulp, non-chrome tan, retan-wet finish subcategory (Subpart C, *see* § 425.30). In all other cases, the modified Monier-Williams method as described in Appendix B to Part 425 shall be used as an alternative to the potassium ferricyanide titration method for the determination of sulfide in wastewaters discharged by plants operating in all subcategories except Subpart C.

(b) The modified Monier-Williams method as described in Appendix B to Part 425 shall be used for the determination of sulfide in wastewaters discharged by plants operating in the hair save or pulp, non-chrome tan, retan-wet finish subcategory (Subpart C, *see* § 425.30).

4. Section 425.04 is amended by adding paragraphs (d) and (e) to read as follows:

§ 425.04 Applicability of sulfide pretreatment standards.

* * * * *

(d) (1) If, after EPA and the POTW have determined in accordance with this section that the sulfide pretreatment standards of this Part are not applicable to specified facilities, a POTW then determines that there have been changed circumstances (including but not limited to changes in the factors specified in paragraph (b) of this section) which justify application of the sulfide pretreatment standards, the POTW shall revoke the certification submitted under paragraph (c) of this section. The POTW and EPA shall then adhere to the general procedures and time intervals contained in paragraph (c) of this section in order to determine whether the sulfide pretreatment standards contained in this Part are applicable.

(2) If pursuant to paragraph (d)(1) of this section, the sulfide pretreatment standards of this Part are applicable to a specified facility, the indirect discharger shall comply with the sulfide pretreatment standards no later than 18 months from the date of publication of the **Federal Register** notice identifying the facility.

(e) At any time after October 13, 1983, if a POTW determines that there have been changed circumstances (including but not limited to changes in the factors specified in paragraph (b) of this

section), it may initiate proceedings contained in paragraph (c) of this section to determine that the sulfide pretreatment standards of this Part shall not be applicable. The POTW and EPA shall follow the procedures and time intervals contained in paragraph (c) of this section to make this determination. A final determination that the sulfide pretreatment standards are not applicable must be made prior to the discharge of sulfide not in accordance with the standards set forth in this Part.

4a. Section 425.05 is revised to read as follows:

§ 425.05 Compliance dates.

The compliance date for new source performance standards (NSPS) and pretreatment standards for new sources (PSES) is the date the new source commences discharge. The compliance date for BPT effluent limitations and guidelines and pretreatment standards for existing sources to no later than March 31, 1989.

Subpart A—Hair Pulp, Chrome Tan, Retan-Wet Finish Subcategory

5. Section 425.11 is amended by revising the table of BPT limitations to read as follows:

§ 425.11 Effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT).

Pollutant or pollutant property	BPT limitations	
	Maximum for any 1 day	Maximum for monthly average
	kg/kg (or pounds per 1,000 pounds of raw material)	
BOD5.....	9.3	4.2
TSS.....	13.4	6.1
Oil & Grease.....	3.9	1.7
Total Chromium.....	0.24	0.09
pH.....	(¹)	(¹)

¹ Within the range of 6.0 to 9.0

6. Section 425.15 is amended by revising paragraph (b) to read as follows:

§ 425.15 Pretreatment standards for existing sources (PSES).

(b) Any existing source subject to this subpart which processes less than 275 hides/day shall comply with § 425.15(a), except that the total chromium limitations contained in § 425.15(a) do not apply.

Subpart C—Hair Save or Pulp, Non-Chrome Tan, Retan-Wet Finish Subcategory

7. Section 425.31 is amended by revising the table of BPT limitations to read as follows:

§ 425.31 Effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT).

Pollutant or pollutant property	BPT limitations	
	Maximum for any 1 day	Maximum for monthly average
	kg/kg (or pounds per 1,000 pounds) of raw material	
BOD5.....	6.7	3.0
TSS.....	9.7	4.4
Oil & Grease.....	2.8	1.3
Total Chromium.....	0.17	0.06
pH.....	(¹)	(¹)

¹ Within the range of 6.0 to 9.0

8. Section 425.35 is amended by revising the table of PSES standards in paragraph (a) and revising paragraph (b) to read as follows:

§ 425.35 Pretreatment standards for existing sources (PSES).

(a) * * *

Pollutant or pollutant property	PSES limitations	
	Maximum for any 1 day	Maximum for monthly average
	Milligrams per liter (mg/l)	
Sulfide.....	24	—
Total Chromium.....	12	8
pH.....	(¹)	(¹)

¹ Not less than 7.0.

(b) Any existing source subject to this subpart which processes less than 350 hides/day shall comply with § 425.35(a), except that the Total Chromium limitations contained in § 425.35(a) do not apply.

Subpart D—Retan-Wet Finish-Sides Subcategory

9. Section 425.41 is amended by revising the section heading and the table of BPT limitations to read as follows:

§ 425.41 Effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT).

* * *

Pollutant or pollutant property	BPT limitations	
	Maximum for any 1 day	Maximum for monthly average
	kg/kg (or pounds per 1,000 pounds) of raw material	
BOD5.....	6.9	4.0
TSS.....	12.8	5.8
Oil & Grease.....	3.7	1.7
Total Chromium.....	0.23	0.08
pH.....	(¹)	(¹)

¹ Within the range of 6.0 to 9.0.

10. Section 425.44 is amended by revising the table of NSPS to read as follows:

§ 425.44 New source performance standards (NSPS).

* * *

Pollutant or pollutant property	NSPS	
	Maximum for any 1 day	Maximum for monthly average
	kg/kg (or pounds per 1,000 pounds) of raw material	
BOD5.....	6.5	2.9
TSS.....	9.3	4.3
Oil & Grease.....	2.7	1.2
Total Chromium.....	0.17	0.06
pH.....	(¹)	(¹)

¹ Within the range of 6.0 to 9.0.

Subpart E—No Beamhouse Subcategory

11. Section 425.51 is amended by revising the table of BPT limitations to read as follows:

§ 425.51 Effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT).

* * *

Pollutant or pollutant property	BPT limitations	
	Maximum for any 1 day	Maximum for monthly average
	kg/kg (or pounds per 1,000 pounds) of raw material	
BOD5.....	8.0	3.6
TSS.....	11.6	5.3
Oil & Grease.....	3.4	1.5
Total Chromium.....	0.21	0.08
pH.....	(¹)	(¹)

¹ Within the range of 6.0 to 9.0.

Subpart F—Through-the-Blue Subcategory

12. Section 425.61 is amended by revising the table of BPT limitations to read as follows:

§ 425.61 Effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT).

* * * * *

Pollutant or pollutant property	BPT limitations	
	Maximum for any 1 day	Maximum for monthly average
	kg/kg (or pounds per 1,000 pounds) of raw material	
BOD5.....	3.2	1.5
TSS.....	4.7	2.1
Oil & Grease.....	1.4	0.61
Total Chromium.....	0.08	0.03
pH.....	(¹)	(¹)

¹ Within the range of 6.0 to 9.0.

13. Section 425.64 is amended by revising the table of NSPS to read as follows:

§ 425.64 New source performance standards (NSPS).

* * * * *

Pollutant or pollutant property	NSPS	
	Maximum for any 1 day	Maximum for monthly average
	kg/kg (or pounds per 1,000 pounds) of raw material	
BOD5.....	3.0	1.3
TSS.....	4.3	1.9
Oil & Grease.....	1.2	0.55
Total Chromium.....	0.08	0.03
pH.....	(¹)	(¹)

¹ Within the range of 6.0 to 9.0.

Subpart G—Shearling Subcategory

14. Section 425.71 is amended by revising the table of BPT limitations to read as follows:

§ 425.71 Effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT).

* * * * *

Pollutant or pollutant property	BPT limitations	
	Maximum for any 1 day	Maximum for monthly average
	kg/kg (or pounds per 1,000 pounds) of raw material	
BOD5.....	15.0	6.8
TSS.....	21.7	9.9
Oil & Grease.....	6.3	2.8
Total Chromium.....	0.39	0.14
pH.....	(¹)	(¹)

¹ Within the range of 6.0 to 9.0.

Subpart I—Retan-Wet Finish-Splits Subcategory

15. Section 425.91 is amended by revising the table of BPT limitations to read as follows:

§ 425.91 Effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT).

* * * * *

Pollutant or pollutant property	BPT limitations	
	Maximum for any 1 day	Maximum for monthly average
	kg/kg (or pounds per 1,000 pounds) of raw material	
BOD5.....	5.8	2.6
TSS.....	8.3	3.8
Oil & Grease.....	2.4	1.1
Total Chromium.....	0.15	0.05
pH.....	(¹)	(¹)

¹ Within the range of 6.0 to 9.0.

16. Section 425.95 is amended by revising paragraph (b) to read as follows:

§ 425.95 Pretreatment standards for existing sources (PSES).

* * * * *

(b) Any existing source subject to this subpart which processes less than 3,600

splits/day shall comply with § 425.95(a), except that the total chromium limitations contained in § 425.95(a) do not apply.

17. Part 425 is amended by adding Appendix A to read as follows:

Appendix A to Part 425—Potassium Ferricyanide Titration Method

Source

The potassium ferricyanide titration method is based on method SLM 4/2 described in "Official Method of Analysis," Society of Leather Trades' Chemists, Fourth Revised Edition, Redbourn, Herts., England, 1965.

Outline of Method

The buffered sulfide solution is titrated with standard potassium ferricyanide solution in the presence of a ferrous dimethylglyoxime ammonia complex. The sulfide is oxidized to sulfur. Sulfite interferes and must be precipitated with barium chloride. Thiosulfate is not titrated under the conditions of the determination (Charlot, "Ann. chim. anal.," 1945, 27, 153; Booth; "J. Soc. Leather Trades' Chemists," 1956, 40, 238).

Apparatus

Burette, 10 ml.

Reagents

1. Preparation of 0.02N potassium ferricyanide: Weigh to the nearest tenth of a gram 6.6 g. of analytical reagent grade potassium ferricyanide and dissolve in 1 liter distilled water. Store in an amber bottle in the dark. Prepare fresh each week.

2. Standardization of ferricyanide solution: Transfer 50 ml. of solution to a 250 ml. Erlenmeyer flask. Add several crystals of potassium iodide (about 1 g.), mix gently to dissolve, add 1 ml. of 6N hydrochloric acid, stopper the flask, and swirl gently. Let stand for two minutes, add 10 ml. of a 30 percent zinc sulfate solution, and titrate the mixture containing the gelatinous precipitate with standardized sodium thiosulfate or phenylarsine oxide titrant in the range of 0.025–0.050N. Add 1 ml. of starch indicator solution after the color has faded to a pale yellow, and continue the titration to the disappearance of the blue color. Calculate the normality of the ferricyanide solution using the equation:

Normality of Potassium Ferricyanide $[K_3Fe(CN)_6] = \frac{\text{ml of thiosulfate added}}{\text{normality of thiosulfate}}$

Ml of $K_3Fe(CN)_6$

3. Preparation of 6M ammonium chloride buffer, pH 9.3: Dissolve 200 g. ammonium chloride in approximately 500 ml. distilled water, add 200 ml. 14M reagent grade ammonium hydroxide and make up to 1 liter with distilled water. The buffer should be prepared in a hood. Store in a tightly stoppered container.

4. Preparation of 0.05M barium chloride solution: Dissolve 12-13 g. barium chloride dihydrate in 1 liter of distilled water.

5. Preparation of ferrous dimethylglyoxime indicator solution: Mix 10 ml. 0.6 percent ferrous sulfate, 50 ml. 1 percent dimethylglyoxime in ethanol, and 0.5 ml. concentrated sulfuric acid.

6. Preparation of stock sulfide standard, 1000 ppm: Dissolve 2.4 g. reagent grade sodium sulfide in 1 liter of distilled water. Store in a tightly stoppered container. Diluted working standards must be prepared fresh daily and their concentrations determined by EPA test procedure 376.1 (see 40 CFR 136.3, Table IB, parameter 66 (49 FR 43234, October 26, 1984, with correction notice at 50 FR 690, January 4, 1985)) immediately prior to use.

7. Preparation of 10N NaOH: Dissolve 400 g. of analytical reagent grade NaOH in 1 liter distilled water.

Sample Preservation and Storage

Samples are to be field filtered (gravity or pressure) with coarse filter paper (Whatman 4 or equivalent) immediately after collection. Filtered samples must be preserved by adjustment to pH > 12 with 10N NaOH. Sample containers must be covered tightly and stored at 4 °C until analysis. Samples must be analyzed within 48 hours of collection. If these procedures cannot be achieved, it is the laboratory's responsibility to institute quality control procedures that will provide documentation of sample integrity.

Procedure

1. Transfer 100 ml. of sample to be analyzed, or a suitable portion containing not more than 15 mg. sulfide supplemented to 100 ml. with distilled water, to a 250 ml. Erlenmeyer flask.

2. Adjust the sample to pH 8.5-9.5 with 6N HCl.

3. Add 20 ml. of 6M ammonium chloride buffer (pH 9.3), 1 ml. of ferrous dimethylglyoxime indicator, and 25 ml. of 0.05M barium chloride. Mix gently, stopper, and let stand for 10 minutes.

4. After 10 minutes titrate with standardized potassium ferricyanide to disappearance of pink color. The endpoint is

reached when there is no reappearance of the pink color after 30 seconds.

Calculation and Reporting of Results.

$$1. \text{ mg./l. sulfide} = \frac{A \times B \times 16,000}{\text{vol. in ml. of sample titrated}}$$

where A = volume in ml. of potassium ferricyanide solution used, and B = normality of potassium ferricyanide solution.

2. Report results to two significant figures.

Quality Control

1. Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of replicate and spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within precision and accuracy limits expected of the method.

2. Before performing any analyses, the analyst must demonstrate the ability to generate acceptable precision and accuracy with this method by performing the following operations.

(a) Perform four replicate analyses of a 20 mg./l. sulfide standard prepared in distilled water (see paragraph 6 under "Reagents" above).

(b)(1) Calculate clean water precision and accuracy in accordance with standard statistical procedures. Clean water acceptance limits are presented in paragraph 2(b)(2) below. These criteria must be met or exceeded before sample analyses can be initiated. A clean water standard must be analyzed with each sample set and the established criteria met for the analysis to be considered under control.

(2) Clean water precision and accuracy acceptance limits: For distilled water samples containing from 5 mg./l. to 50 mg./l. sulfide, the mean concentration from four replicate analyses must be within the range of 50 to 110 percent of the true value.

3. The Method Detection Limits (MDL) should be determined periodically by each participating laboratory in accordance with the procedures specified in "Methods for

Chemical Analysis of Municipal and Industrial Wastewater," EPA-660/4-82-057, July 1982, EMSL, Cincinnati, OH 45268. For the convenience of the user, these procedures are contained in Appendix C to Part 425.

4. A minimum of one spiked and one duplicate sample must be performed for each analytical event, or five percent spikes and five percent duplicates when the number of samples per event exceeds twenty. Spike levels are to be at the MDL (see paragraph 3 above for MDL samples) and at x where x is the concentration found if in excess of the MDL. Spike recovery must be 40 to 120 percent for the analysis of a particular matrix type to be considered valid. If a sample or matrix type provides performance outside these acceptance limits, the analyses must be repeated using the modified Monier-Williams procedures described in Appendix B to this Part.

5. Report results in mg./liter. When duplicate and spiked samples are analyzed, report all data with the sample results.

18. Part 425 is amended by adding Appendix B to read as follows:

Appendix B to Part 425—Modified Monier-Williams Method

Outline of Method

Hydrogen sulfide is liberated from an acidified sample by distillation and purging with nitrogen gas (N_2). Sulfur dioxide interference is removed by scrubbing the nitrogen gas stream in a pH 7 buffer solution. The sulfide gas is collected by passage through an alkaline hydrogen peroxide scrubbing solution in which it is oxidized to sulfate. Sulfate concentration in the scrubbing solution is determined by either EPA gravimetric test procedure 375.3 or EPA turbidimetric test procedure 375.4 (see 40 CFR 136.3, Table IB, parameter 65 (49 FR 43234, October 26, 1984, and correction notice at 50 FR 690, January 4, 1985)).

Apparatus*

(See Figure 1.) * Catalogue numbers are given only to provide a more complete description of the equipment necessary, and do not constitute a manufacturer or vendor endorsement.

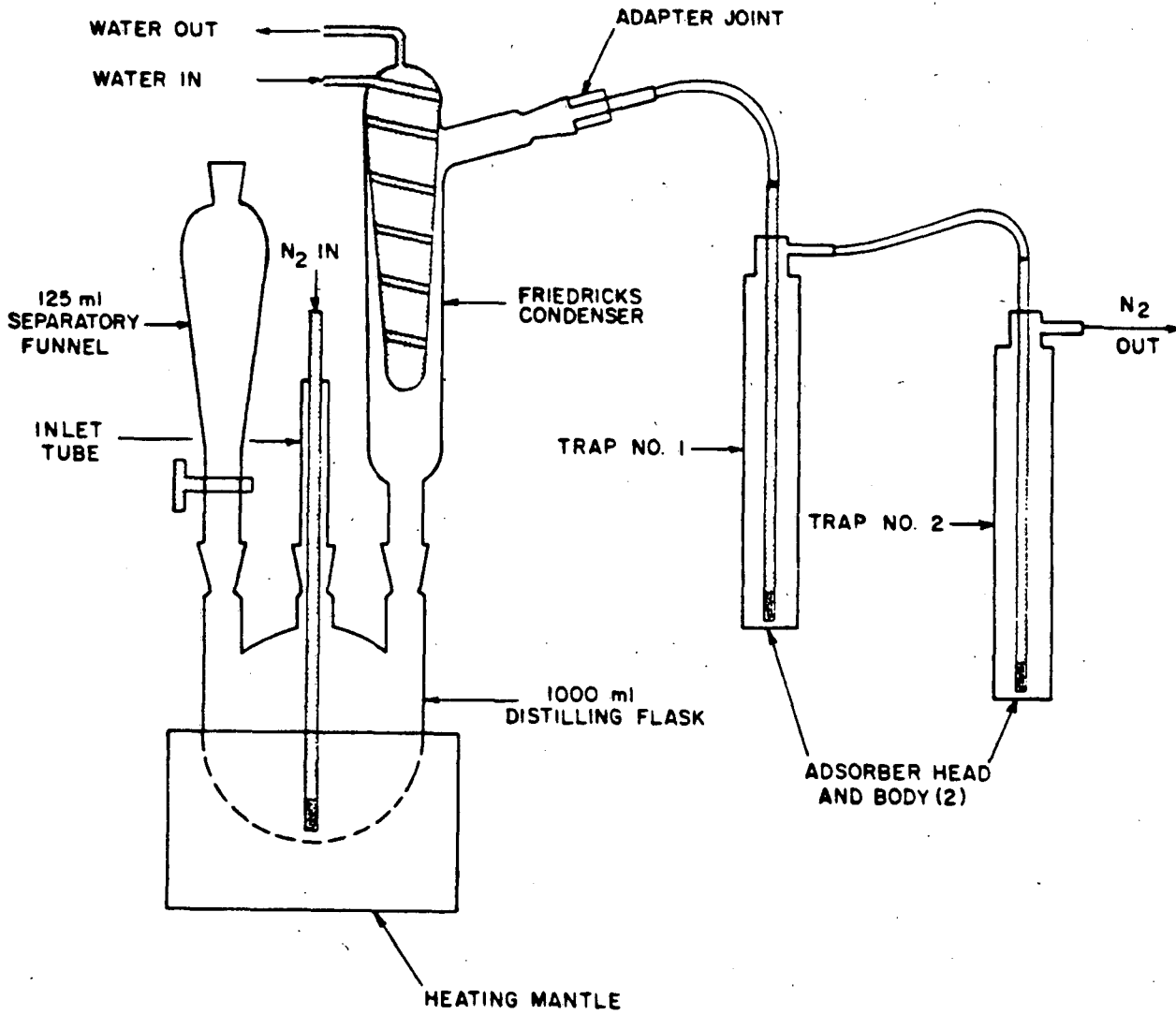
Heating mantle and control (VWR Cat. No. 33752-464)

1000 ml. distilling flask with three 24/40 joints (VWR Cat. No. 29280-215)

Friedricks condenser with two 24/40 joints (VWR Cat. No. 23161-009)

BILLING CODE 6560-50-M

FIGURE 1
EQUIPMENT ASSEMBLY



125 ml. separatory funnel with 24/40 joint (VWR Cat. No. 30357-102)
 Inlet tube with 24/40 joint (VWR Cat. No. 33057-105)
 Adapter joint 24/40 to 19/38 (VWR Cat. No. 62905-26)
 Adsorber head (2 required) (Thomas Cat. No. 9849-R29)
 Adsorber body (2 required) (Thomas Cat. No. 9849-R32)
 Laboratory vacuum pump or water aspirator

Reagents

1. Potassium hydroxide, 6N: Dissolve 340 g. of analytical reagent grade KOH in 1 liter distilled water.
2. Sodium hydroxide, 6N: Dissolve 240 g. of analytical reagent grade NaOH in 1 liter distilled water.
3. Sodium hydroxide, 0.03N: Dilute 5.0 ml. of 6N NaOH to 1 liter with distilled water.
4. Hydrochloric acid, 6N: Dilute 500 ml. of concentrated HCl to 1 liter with distilled water.
5. Potassium phosphate stock buffer, 0.5M: Dissolve 70 g. of monobasic potassium phosphate in approximately 800 ml. distilled water. Adjust pH to 7.0 ± 0.1 with 6N potassium hydroxide and dilute to 1 liter with distilled water. Stock solution is stable for several months at 4 °C.
6. Potassium phosphate buffer, 0.05M: Dilute 1 volume of 0.5M potassium phosphate stock buffer with 9 volumes of distilled water. Solution is stable for one month at 4 °C.
7. Alkaline 3% hydrogen peroxide: Dilute 1 volume of 30 percent hydrogen peroxide with 9 volumes of 0.03N NaOH. Prepare this solution fresh each day of use.
8. Preparation of stock sulfide standard, 1000 ppm.: Dissolve 2.4 g. reagent grade sodium sulfide in 1 liter of distilled water. Store in a tightly stoppered container. Diluted working standards must be prepared fresh daily and their concentrations determined by EPA test procedure 376.1 immediately prior to use (see 40 CFR 136.3, Table IB, parameter 66 (49 FR 43234, October 26, 1984, and correction notice at 50 FR 690, January 4, 1985)).

Sample Preservation and Storage

Preserve unfiltered wastewater samples immediately after collection by adjustment to pH > 9 with 6N NaOH and addition of 2 ml. of 2N zinc acetate per liter. This amount of zinc acetate is adequate to preserve 64 mg./l. sulfide under ideal conditions. Sample containers must be covered tightly and stored at 4 °C until analysis. Samples must be analyzed within seven days of collection. If these procedures cannot be achieved, it is the laboratory's responsibility to institute quality control procedures that will provide documentation of sample integrity.

Procedure (See Figure 1 for apparatus layout.)

1. Place 50 ml. of 0.05M pH 7.0 potassium phosphate buffer in Trap No. 1.
2. Place 50 ml. of alkaline 3 percent hydrogen peroxide in Trap No. 2.
3. Sample introduction and N₂ prepurge: Gently mix sample to be analyzed to resuspend settled material, taking care not to aerate the sample. Transfer 400 ml. of sample, or a suitable portion containing not more than 20 mg. sulfide diluted to 400 ml. with

distilled water, to the distillation flask. Adjust the N₂ flow so that the impingers are frothing vigorously, but not overflowing. Vacuum may be applied at the outlet of Trap No. 2 to assist in smooth purging. The N₂ inlet tube of the distillation flask must be submerged deeply in the sample to ensure efficient agitation. Purge the sample for 30 minutes without applying heat. Test the apparatus for leaks during the prepurge cycle (Snoop or soap water solution).

4. Volatilization of H₂S: Interrupt the N₂ flow (and vacuum) and introduce 100 ml. of 6N HCl to the sample using the separatory funnel. Immediately resume the gas flow (and vacuum). Apply maximum heat with the heating mantle until the sample begins to boil, then reduce heat and maintain gentle boiling and N₂ flow for 30 minutes. Terminate the distillation cycle by turning off the heating mantle and maintaining N₂ flow through the system for 5 to 10 minutes. Then turn off the N₂ flow (and release vacuum) and cautiously vent the system by placing 50 to 100 ml. of distilled water in the separatory funnel and opening the stopcock carefully. When the bubbling stops and the system is equalized to atmospheric pressure, remove the separatory funnel. Extreme care must be exercised in terminating the distillation cycle to avoid flash-over, draw-back, or violent steam release.

5. Analysis: Analyze the contents of Trap No. 2 for sulfate according to either EPA gravimetric test procedure 375.3 or EPA turbidimetric test procedure 375.4 (see 40 CFR 136.3, Table IB, parameter 65 (49 FR 43234, October 26, 1984, and correction notice at 50 FR 690, January 4, 1985)). Use the result to calculate mg./l. of sulfide in wastewater sample.

Calculations and Reporting of Results

1. Gravimetric procedure:

$$\text{mg sulfide/l.} = \frac{(\text{mg. BaSO}_4 \text{ collected in Trap No. 2}) \times (137)}{\text{volume in ml. of waste sample distilled}}$$

2. Turbidimetric procedure:

$$\text{mg. sulfide/l.} = \frac{A \times B \times 333}{C}$$

where A = mg./l. of sulfate in Trap No. 2
 B = liquid volume in liters in Trap No. 2
 and C = volume in ml. of waste sample distilled

3. Report results to two significant figures.

Quality Control

1. Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of replicate and spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to

define the quality of data that is generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within precision and accuracy limits expected of the method.

2. Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision by performing the following operations.

(a) Perform four replicate analyses of a 20 mg./l. sulfide standard prepared in distilled water (see paragraph 8 under "Reagents" above).

(b)(1) Calculate clean water precision and accuracy in accordance with standard statistical procedures. Clean water acceptance limits are presented in paragraph 2(b)(2) below. These criteria must be met or exceeded before sample analyses can be initiated. A clean water standard must be analyzed with each sample set and the established criteria met for the analyses to be considered under control.

(2) Clean water precision and accuracy acceptance limits: For distilled water samples containing from 5 mg./l. to 50 mg./l. sulfide, the mean concentration from four replicate analyses must be within the range of 72 to 114 percent of the true value.

3. The Method Detection Limit (MDL) should be determined periodically by each participating laboratory in accordance with the procedures specified in "Methods for Chemical Analysis of Municipal and Industrial Wastewater," EPA-600/4-82-057, July 1982, EMSL, Cincinnati, OH 45268. For the convenience of the user, these procedures are contained in Appendix C to Part 425.

4. A minimum of one spiked and one duplicate sample must be run for each analytical event, or five percent spikes and five percent duplicates when the number of samples per event exceeds twenty. Spike levels are to be at the MDL (see paragraph 3 above for MDL samples) and at x when x is the concentration found in excess of the MDL. Spike recovery must be 60 to 120 percent for the analysis of a particular matrix type to be considered valid.

5. Report all results in mg./liter. When duplicate and spiked samples are analyzed, report all data with the sample results.

19. Part 425 is amended by adding Appendix C to read as follows:

Appendix C to Part 425—Definition and Procedure for the Determination of the Method Detection Limit¹

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be identified, measured and reported with 99 percent confidence that the analyte concentration is greater than zero and determined from analysis of a sample in a given matrix containing analyte.

Scope and Application

This procedure is designed for applicability to a wide variety of sample types ranging

¹ Source: "Methods for Chemical Analysis of Municipal and Industrial Wastewater," EPA-600/4-82-057, July 1982, EMSL, Cincinnati, OH 45268

from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

Procedure

1. Make an estimate of the detection limit using one of the following:

(a) The concentration value that corresponds to an instrument signal/noise ratio in the range of 2.5 to 5. If the criteria for qualitative identification of the analyte is based upon pattern recognition techniques, the least abundant signal necessary to achieve identification must be considered in making the estimate.

(b) The concentration value that corresponds to three times the standard deviation of replicate instrumental measurements for the analyte in reagent water.

(c) The concentration value that corresponds to the region of the standard curve where there is a significant change in sensitivity at low analyte concentrations, i.e., a break in the slope of the standard curve.

(d) The concentration value that corresponds to known instrumental limitations.

It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferent concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferent). The interferent concentration is presupposed to be normally distributed in representative samples of a given matrix.

3. (a) If the MDL is to be determined in reagent water (blank), prepare a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated MDL. (Recommended between 1 and 5 times the estimated MDL.) Proceed to Step 4.

(b) If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated MDL, proceed to Step 4.

If the measured concentration of analyte is less than the estimated MDL, add a known amount of analyte to bring the concentration

of analyte to between one and five times the MDL. In the case where an interference is coanalyzed with the analyte:

If the measured level of analyte is greater than five times the estimated MDL, there are two options:

(1) Obtain another sample of lower level of analyte in same matrix if possible.

(2) The sample may be used as is for determining the MDL if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

4. (a) Take a minimum of seven aliquots of the sample to be used to calculate the MDL and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units. If blank measurements are required to calculate the measured level of analyte, obtain separate blank measurements for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.

(b) It may be economically and technically desirable to evaluate the estimated MDL before proceeding with 4a. This will: (1) Prevent repeating this entire procedure when the costs of analyses are high and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an incorrect MDL can be calculated from data obtained at many times the real MDL even though the background concentration of analyte is less than five times the calculated MDL. To insure that the estimate of the MDL is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower MDL. Take two aliquots of the sample to be used to calculate the MDL and process each through the entire method, including blank measurements as described above in 4a. Evaluate these data:

(1) If these measurements indicate the sample is in the desirable range for determining the MDL, take five additional aliquots and proceed. Use all seven measurements to calculate the MDL.

(2) If these measurements indicate the sample is not in the correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.

5. Calculate the variance (S^2) and standard deviation (S) of the replicate measurements, as follows:

$$S^2 = \frac{1}{n-1} \left[\sum_{i=1}^n x_i^2 - \frac{(\sum_{i=1}^n x_i)^2}{n} \right]$$

$$S = (S^2)^{0.5}$$

where: the x_i , $i = 1$ to n are the analytical results in the final method reporting units obtained from the n sample aliquots and

$$\sum_{i=1}^n x_i^2$$

refers to the sum of the X values from $i = 1$ to n .

6. (a) Compute the MDL as follows:

$$MDL = t_{(n-1, 1-\alpha = .99)} (S)$$

where:

MDL = the method detection

$t_{(n-1, 1-\alpha = .99)}$ = the student's t value appropriate for a 99 percent confidence level and a standard deviation estimate with $n-1$ degrees of freedom. See Table.

S = standard deviation of the replicate analyses.

(b) The 95 percent confidence limits for the MDL derived in 6a are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution (X^2/df) and calculated as follows:

$$MDL_{LCL} = 0.69 MDL$$

$$MDL_{UCL} = 1.92 MDL \text{ where } MDL_{LCL} \text{ and } MDL_{UCL}$$

are the lower and upper 95 percent confidence limits respectively based on seven aliquots.

7. Optional iterative procedure to verify the reasonableness of the estimated MDL and calculated MDL of subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimated MDL in Step 1, take the MDL as calculated in Step 6, spike in the matrix at the calculated MDL and proceed through the procedure starting with Step 4.

(b) If the current MDL determination is an iteration of the MDL procedure for which the spiking level does not permit qualitative identification, report the MDL as that concentration between the current spike level and the previous spike level which allows qualitative identification.

(c) If the current MDL determination is an iteration of the MDL procedure and the spiking level allows qualitative identification, use S^2 from the current MDL calculation and S^2 from the previous MDL calculation to compute the F ratio.

$$\text{if } \frac{S_A^2}{S_B^2} < 3.05$$

then compute the pooled standard deviation by the following equation:

$$S_{\text{pooled}} = \left[\frac{6S_A^2 + 6S_B^2}{12} \right]^{0.5}$$

$$\text{if } \frac{S_A^2}{S_B^2} > 3.05,$$

respike at the last calculated MDL and process the samples through the procedure starting with Step 4.

(d) Use the S_{pooled} as calculated in 7b to compute the final MDL according to the following equation:

$$\text{MDL} = 2.681 (S_{\text{pooled}})$$

where 2.681 is equal to $t(12, 1 - \alpha = .99)$

(e) The 95 percent confidence limits for MDL derived in 7c are computed according to the following equations derived from percentiles of the chi squared over degrees of freedom distribution.

$$\text{MDL}_{\text{LCL}} = 0.72 \text{ MDL}$$

$$\text{MDL}_{\text{UCL}} = 1.65 \text{ MDL}$$

where LCL and UCL are the lower and upper 95 percent confidence limits respectively based on 14 aliquots.

Reporting

The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with the MDL value. Report the mean analyte level with the MDL. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, report the mean recovery, and indicate if the MDL determination was iterated.

If the level of the analyte in the sample matrix exceeds 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.

Reference

Glaser, J.A., Foerst, D.L., McKee, G.D., Quave, S.A., and Budde, W.L., "Trace

Analysis for Wastewaters," Environmental Science and Technology, 15, 1426 (1981).

TABLE OF STUDENTS' t VALUES AT THE 99 PERCENT CONFIDENCE LEVEL

Number of replicates	Degrees of freedom (n-1)	$t(n-1, 1-\alpha=.99)$
7.....	6	3.143
8.....	7	2.998
9.....	8	2.896
10.....	9	2.821
11.....	10	2.764
16.....	15	2.602
21.....	20	2.528
26.....	25	2.485
31.....	30	2.457
61.....	60	2.390
		2.326

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