



**Supplemental                      Final**

**Development**

**Document for**

**Effluent Limitations**

**Guidelines and**

**Standards for the**

**Leather Tanning**

**and Finishing**

**Point Source Category**



SUPPLEMENTAL FINAL DEVELOPMENT DOCUMENT

FOR

EFFLUENT LIMITATIONS GUIDELINES  
NEW SOURCE PERFORMANCE STANDARDS

AND

PRETREATMENT STANDARDS

FOR THE

LEATHER TANNING AND FINISHING  
POINT SOURCE CATEGORY

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## SECTION I

### SUMMARY

The Environmental Protection Agency (EPA or the Agency) is amending 40 CFR Part 425 which limits effluent discharges to 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 agreed to promulgate these amendments in a settlement agreement with the Tanners' Council of America, Inc. [Tanners' Council of America Inc. v. U.S. Environmental Protection Agency, No. 83-1191, (4th Cir., filed March 2, 1983), entered on December 11, 1984]. (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 regulation promulgated by EPA on November 23, 1982 (47 FR 52848) as required by the Clean Water Act and the settlement agreement in Natural Resources Defense Council, Inc. v. Train, 8 ERC 2120 (D.D.C. 1976), modified, 12 ERC 1833 (D.D.C. 1979), and further modified by orders of the Court dated October 26, 1982, August 3, 1983, and January 6, 1984.

These amendments include: (1) a new analytical method for the determination of the presence of sulfide in wastewater for use in the Hair Save or Pulp, Non-Chrome Tan, Retan-Wet Finish Subcategory (Subcategory 3); (2) clarification of procedural requirements for POTW to follow in determining whether sulfide pretreatment standards are applicable; (3) revisions to certain of the effluent limitations guidelines for "best practicable control technology currently available" (BPT) and new source performance standards (NSPS); (4) a change in the pH pretreatment standard for tanneries falling under the provisions of the Hair Save or Pulp, Non-Chrome Tan, Retan-Wet Finish Subcategory (Subpart C of 40 CFR Part 425); and (5) clarification of the production levels below which the chromium pretreatment standards for existing sources (PSES) do not apply.

In addition, in the preamble to the promulgated amendments to 40 CFR Part 425, EPA clarifies its statements on median water use ratios, changes in subcategorization, tanneries with mixed subcategory operations, and composite samples of effluent discharges from multiple outfalls. These issues are addressed in Section VIII.



## SECTION II

### INTRODUCTION

#### LEGAL AUTHORITY

The Environmental Protection Agency promulgated amendments to 40 CFR Part 425 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. The amendments to the regulation are also promulgated in response to the Settlement Agreement in Tanners' Council of America, Inc. v. U.S. Environmental Protection Agency, No. 83-1191, (4th Cir., 1984).

#### PRIOR REGULATIONS AND CHALLENGES

EPA promulgated a regulation on April 9, 1974, establishing 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 dischargers ("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 let BAT and NSPS 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 for existing indirect dischargers specific pH standards and other pretreatment standards 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 (40 CFR Part 425).

- Subcategory 1 - Hair Pulp, Chrome Tan, Retan-Wet Finish Subcategory (Subpart A of 40 CFR Part 425)
- Subcategory 2 - Hair Save, Chrome Tan, Retan-Wet Finish Subcategory (Subpart B of 40 CFR Part 425)
- Subcategory 3 - Hair Save or Pulp, Non-Chrome Tan, Retan-Wet Finish Subcategory (Subpart C of 40 CFR Part 425)
- Subcategory 4 - Retan-Wet Finish-Sides Subcategory (Subpart D of 40 CFR Part 425)
- Subcategory 5 - No Beamhouse Subcategory (Subpart E of 40 CFR Part 425)
- Subcategory 6 - Through-the-Blue Subcategory (Subpart F of 40 CFR Part 425)
- Subcategory 7 - Shearling Subcategory (Subpart G of 40 CFR Part 425)
- Subcategory 8 - Pigskin Subcategory (Subpart H of 40 CFR Part 425)
- Subcategory 9 - Retan-Wet Finish-Splits Subcategory (Subpart I of 40 CFR Part 425)

BPT effluent limitations guidelines were established for all subcategories based on biological treatment, specifically high solids extended aeration activated sludge. They include

production-based effluent limitations (kg/kg or lb/1000 lb of raw material) for one toxic pollutant (total chromium), three conventional pollutants (BOD<sub>5</sub>, 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 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 (BOD<sub>5</sub>, 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 (BOD<sub>5</sub>, 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 1, 3, and 9 (Subparts A, C, and I to 40 CFR Part 425 respectively).

Concentration-based categorical pretreatment standards were also established for the control of sulfides in Subcategories 1, 2, 3, 6, and 8 (Subparts A, B, C, F, and H to 40 CFR Part 425 respectively) 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 40 CFR 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.

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.

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. In the settlement agreement, EPA agreed to propose and promulgate amendments to the leather tanning and finishing regulation and solicit comments regarding the proposed amendments. In addition, EPA agreed to propose and promulgate specific preamble language. Copies of the settlement agreement were promptly sent to EPA Regional Offices and State NPDES permit-issuing authorities on December 21, 1984.

If, after EPA takes final action under the settlement agreement, 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, TCA will move to dismiss its petition for judicial review and voluntarily withdraw the "Petition for Reconsideration."

In the settlement agreement, EPA agreed to propose and promulgate preamble changes and amendments to 40 CFR Part 425 to (1) allow the 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 effluent limitations guidelines and standards based on corrected and more complete water use ratio information, and (4) allow the small tannery exemption without restriction as to the number of working days per week.

## SECTION III

### SULFIDE ANALYTICAL METHODS

#### 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. 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.

1. The method described in the promulgated regulation 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.
2. The titrant equivalence statement, as set forth in the promulgated regulation, 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.
3. 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 existing approved method to delete glass wool as an alternative rapid filtration medium. EPA is also amending the previously approved method to specify use of coarse filter paper.

In response to the second problem, EPA is amending the SLM 4/2 method to express the results of the titrant equivalence statement in terms of mg./liter of sulfide which is the basis for the pretreatment standards.

In response to the third problem, EPA and TCA initiated a cooperative sampling and analytical methods development program for vegetable tanning wastewaters in November 1983 to evaluate the SLM 4/2 procedure and a modification of the Monier-Williams method for sulfite to allow measurement of sulfide. The SLM 4/2

procedure was modified slightly to standardize analytical procedures and to facilitate the measurement of sulfide in tannery wastewater. The iodometric titration procedure was not included in the evaluation program because of analytical interferences which led to the original selection of the SLM 4/2 procedure.

As part of the evaluation, raw and pretreated wastewaters were collected at seven tanneries, including two vegetable tannin tanneries, for analyses by two separate laboratories. The analytical data showed that the modified Monier-Williams method was able to measure sulfide in vegetable tannery wastewaters when wastewater color prevented detection of the endpoint color change of the ferricyanide titration procedure which was based on the SLM 4/2 procedure. The data also showed that the method produced considerably better spike recoveries than the ferricyanide titration procedure. The modified Monier-Williams method, thus, is an acceptable procedure for pretreatment standard compliance monitoring in the leather tanning industry. The ferricyanide titration procedure will be acceptable for use in all cases in which wastewater color does not interfere with detection of the endpoint color change and acceptable performance is achieved. It is not suitable for use in tannery wastewaters containing a high level of vegetable tannins. The methodologies of the ferricyanide titration procedure and modified Monier-Williams procedure are described in Appendixes A and B respectively. EPA is promulgating the modified Monier-Williams method for tanneries with vegetable tanning wastewaters and as an alternative sulfide analytical procedure for other tanneries.

In accordance with the settlement agreement, 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 above. Rather, the 1982 Methods document describes a procedure known as the Method Detection Limit (MDL) which is now also described in Appendix B to 40 CFR Part 136, Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act. EPA interprets MRC to be synonymous with the MDL 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. The definition and procedure for the determination of the Method Detection Limit is in Appendix C.

#### SUMMARY OF ANALYSIS FOR SULFIDE ANALYTICAL METHODS EVALUATION

The results obtained during the sulfide analytical methods evaluation by the E.C. Jordan Company and the Tanners' Council of America, Inc., are presented in Tables III-1 through III-10 and Figure III-1. As reflected by the data, the modified Monier-



Williams procedure was able to measure sulfide in vegetable tannery wastewater when wastewater color prevented detection of the endpoint color change of the ferricyanide titration procedure (SLM 4/2). Further, the modified Monier-Williams method provided more accurate measurement of sulfide concentrations than the ferricyanide titration procedure, which yields lower concentrations than actually present. This is because the modified Monier-Williams method produced considerably better spike recoveries in the 0 to 25 mg./l. range of sulfide concentrations. The modified Monier-Williams method thus was shown to be an acceptable procedure for pretreatment standard compliance monitoring of Leather Tanning and Finishing Industry wastewater. Based on the tabulated results, the use of the modified Monier-Williams procedure may be used instead of the ferricyanide titration method for measurement of sulfide in all tannery wastewaters.

The results obtained by the E.C. Jordan Company laboratory during clean water precision and accuracy trials are shown in Table III-1 and Figure III-1. The Tanners' Council of America, Inc., did not report clean water precision and accuracy data. As can be seen in Table III-1 and Figure III-1, the modified Monier-Williams procedure provided considerably better spike recoveries at sulfide concentrations in the range of 0 to 25 mg./l. than did the ferricyanide titration procedure. The percent recoveries decreased rapidly, however, when the spike levels exceeded approximately 50 mg./l. The explanation for this is that the amount of oxidant ( $H_2O_2$ ) present in the second trap is a limiting factor regarding the maximum amount of sulfide recoverable by the procedure set forth in the precision and accuracy protocol and used during the clean water portion of the study. The maximum recoverable amount of sulfide is between 10 and 20 milligrams. Therefore, in accordance with standard EPA procedures for other inorganic parameters, smaller sample volumes (i.e., diluted samples) were used where sulfide concentrations exceed 50 mg./l. This procedure was followed by the E.C. Jordan Company laboratory during subsequent analyses. TCA used a larger trap and 200 ml. of peroxide solution instead of the 50 ml. used by the E.C. Jordan Company and obtained analytical results comparable with the E.C. Jordan Company without cutting back on sample volume. (See Table III-3 for Irving Tanning and Table III-4 for A.C. Lawrence.)

Tables III-2 through III-9 present data obtained by TCA and the E.C. Jordan Company during subsequent precision and accuracy trials using wastewater collected at seven tanneries. Table III-10 identifies these tanneries and gives a description of the wastewater sampled. As evidenced by Table III-10, the sampled tanneries employ a variety of pretreatment options. The collected wastewater is considered a realistic presentation of what could be expected at other U.S. tanneries. The following comments apply to Tables III-2 through III-9.

1. The ferricyanide titration procedure was not applied to

measure sulfide in wastewater samples from Hermann Oak (Table III-2) and Scholze (Table III-7) tanneries. This was due to masking of the endpoint of the procedure by the deep brown color of the wastewater. The E.C. Jordan Company laboratory observed this phenomenon previously when using the method to analyze a wastewater containing vegetable tannins from the A.C. Lawrence Leather Company in Hazelwood, North Carolina.

2. Analysts from both laboratories reported difficulties in detecting the ferricyanide titration endpoint color change, even in the absence of vegetable tannins.
3. Comparison of results obtained using the modified Monier-Williams procedure with those obtained using the ferricyanide titration for chromium tanneries shows that in eight out of nine instances the modified Monier-Williams procedure gave a higher estimate of sulfide concentration in unspiked samples than the ferricyanide titration. In eight out of 11 instances the modified Monier-Williams procedure provided better spike recoveries than the ferricyanide titration. Inclusion of recovery data from vegetable tannin tanneries also favors the modified Monier-Williams procedure: 12 out of 13 instances and 12 out of 15 instances, respectively.
4. The modified Monier-Williams procedure gave lower recoveries in wastewater from Hermann Oak Tanning Co. (Table III-2) and Scholze Tannery (Table III-7) than in wastewater from other tanneries. In both cases, the initial concentration of sulfide was very low, and  $\text{MnSO}_4$  had been added at Hermann Oak to catalyze sulfide oxidation. The ferricyanide titration procedure gave low spike recoveries in wastewater from Midwest Tanning (Table III-5). In this instance, the initial sulfide concentration was also low, and  $\text{MnSO}_4$  had also been added to help oxidize sulfides.
5. The available data do not provide a clear explanation for these observations. One possibility is that there may have been a sulfide consuming substance present in each of these samples in sufficient quantity to affect spike recoveries. This is especially likely in the case of Hermann Oak and Midwest Tanning where  $\text{MnSO}_4$  had been added to catalyze sulfide oxidation. It is noteworthy that this phenomenon was observed only in wastewaters with low sulfide concentrations.

6. It has been suggested that filtration of wastewater samples in accordance with the ferricyanide titration procedure might reduce the measured concentration of sulfide. The results of a modest research program utilizing the modified Monier-Williams procedure indicate that filtration in accordance with ferricyanide titration procedure did not significantly affect sulfide concentrations in wastewater from Hermann Oak and Irving Tanning Company.

TABLE III-1  
CLEAN WATER PRECISION AND ACCURACY RESULTS

Modified Monier-Williams Procedure			Ferricyanide Titration Procedure		
Spike Concentration mg/l	Sulfide Measured mg/l	Percent Recovery	Spike Concentration mg/l	Sulfide Measured mg/l	Percent Recovery
0	0	---	0	0.16	---
0	0	---	0	0.16	---
0	0	---	0	0.16	---
0	0	---	0	0.16	---
5.1	5.1	100	4.4	2.8	64
5.1	4.2	82	4.4	2.8	64
5.1	4.5	88	4.4	2.8	64
5.1	4.6	85	4.4	2.7	61
			4.4	2.1	48
			4.4	2.1	48
			4.4	2.0	45
			4.4	2.1	48
			8.8	4.6	52
			8.8	4.9	56
			8.8	4.9	56
			8.8	4.6	52
15	16	106	13	8.4	65
15	15	100	13	9.0	69
15	15	100	13	9.2	71
16	14	88	13	9.1	70
25	25	100	22	20	91
25	23	92	22	20	91
25	25	100	22	19	86
25	23	92	22	19	86
			26	17	65
			26	17	65
			26	17	65
			26	17	65
50	43	86	44	41	93
50	43	86	44	41	93
50	44	88	44	41	93
50	46	92	44	42	96

TABLE III-1 (continued)  
CLEAN WATER PRECISION AND ACCURACY RESULTS

<u>Modified Monier-Williams Procedure</u>			<u>Ferricyanide Titration Procedure</u>		
<u>Spike Concentration mg/l</u>	<u>Sulfide Measured mg/l</u>	<u>Percent Recovery</u>	<u>Spike Concentration mg/l</u>	<u>Sulfide Measured mg/l</u>	<u>Percent Recovery</u>
135	59	44	110	99	90
135	59	44	110	98	89
135	59	44	110	94	86
135	56	42	110	90	82
269	56	21	221	214	97
269	59	22	221	210	95
269	59	22	221	205	93
269	58	22	221	205	93

FIGURE III-1

SPIKE RECOVERY VERSUS CONCENTRATION IN CLEAN WATER

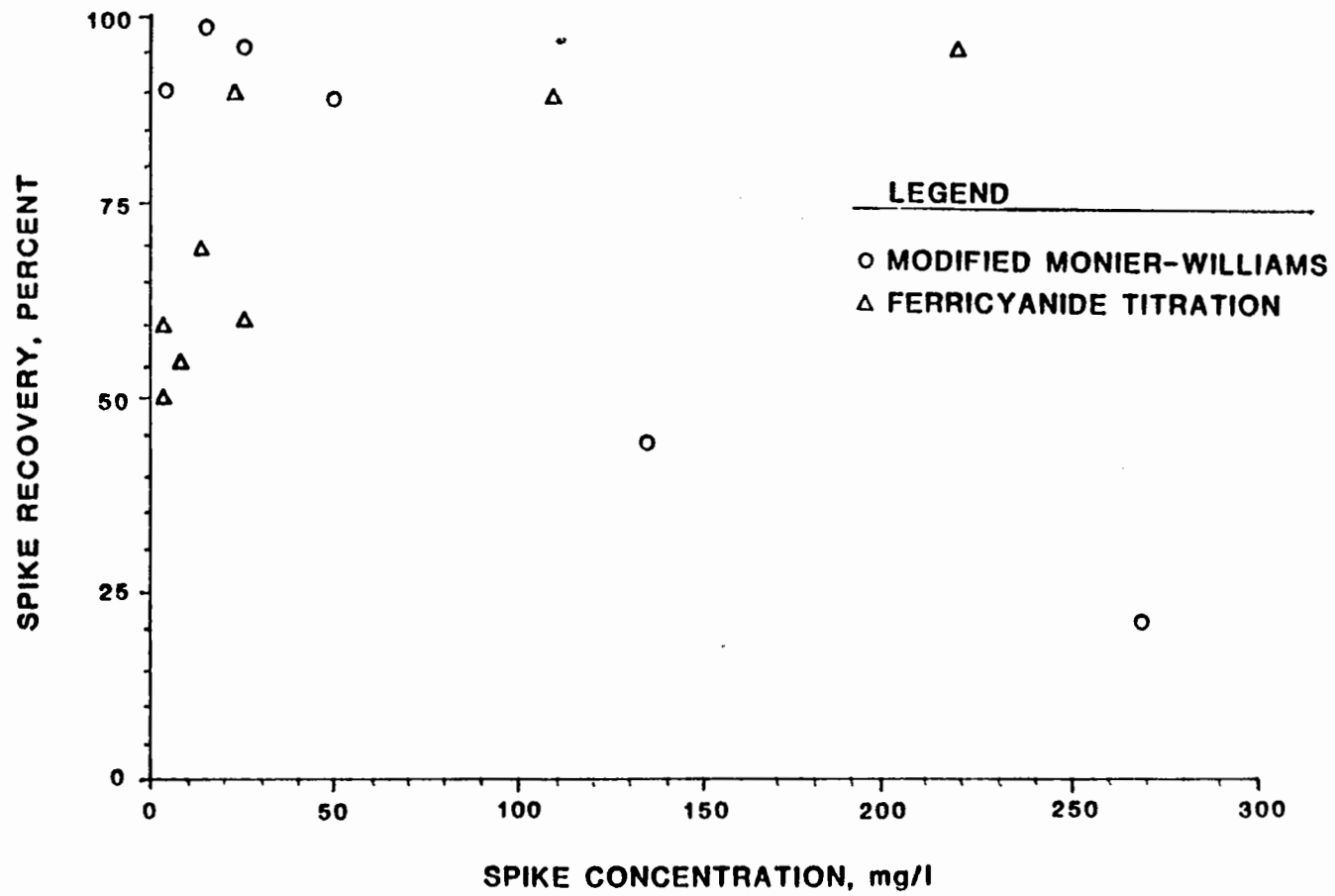


TABLE III-2

## COMPARISON OF ANALYTICAL RESULTS - HERMANN OAK LEATHER CO.

<u>Modified Monier-Williams Procedure</u>			<u>Ferricyanide Titration Procedure</u>		
<u>Spike Concentration mg/l</u>	<u>Sulfide Measured mg/l</u>	<u>Percent Recovery</u>	<u>Spike Concentration mg/l</u>	<u>Sulfide Measured mg/l</u>	<u>Percent Recovery</u>
<u>Tanners' Council Laboratory</u>					
0	0.35	---	0	*	*
0	0.1	---	0	*	*
0	0.28	---	0	*	*
0	0.1	---	0	*	*
0	0.35	---	0	*	*
0	0.52	---	0	*	*
0	0.21	---	0	*	*
0	0.31	---	0	*	*
<u>E.C. Jordan Co. Laboratory</u>					
9.3	----	61			
9.3	----	61			
9.3	----	67			
9.3	----	72			
23	----	65			
23	----	70			
24	----	71			
24	----	67			
93	----	42			
93	----	48			
93	----	50			
93	----	47			

\* Unable to determine due to wastewater color interference.

TABLE III-3

## COMPARISON OF ANALYTICAL RESULTS - IRVING TANNING COMPANY

<u>Modified Monier-Williams Procedure</u>			<u>Ferricyanide Titration Procedure</u>		
<u>Spike Concentration mg/l</u>	<u>Sulfide Measured mg/l</u>	<u>Percent Recovery</u>	<u>Spike Concentration mg/l</u>	<u>Sulfide Measured mg/l</u>	<u>Percent Recovery</u>
<u>Tanners' Council Laboratory</u>					
0	75	---	0	78	---
0	65	---	0	75	---
0	72	---	0	75	---
0	74	---	0	76	---
			0	73*	---
			0	73*	---
0	88	---	0	30**	---
0	66	---	0	29**	---
0	73	---	0	30**	---
			0	28**	---
<u>E.C. Jordan Co. Laboratory</u>					
46	---	86	42	---	100**
46	---	81	42	---	101**
46	---	84	42	---	97**
46	---	86	42	---	98**
118	---	97	105	---	91**
118	---	97	105	---	89**
118	---	91	105	---	89**
118	---	52	105	---	86**
236	---	85	210	---	79**
236	---	83	210	---	79**
236	---	90	210	---	78**
236	---	94	210	---	79**

\* Analysis performed on a 50 ml sample volume.

\*\* Analysis performed approximately 30 days after receipt of sample. Because of a laboratory delay, precision and accuracy analyses using the ferricyanide titration were not run until approximately 30 days after sample collection. As expected, the sample, preserved only by pH adjustment, lost a significant amount of volatile sulfide during this holding period. Spike recoveries were good, however, ranging between 78 and 101 percent, and are considered suitable for consideration with other data as part of this study. The observed loss of sulfide emphasizes the need for prompt analysis of samples preserved by pH adjustment alone.



TABLE III-4

## COMPARISONS OF ANALYTICAL RESULTS - A.C. LAWRENCE LEATHER CO.

<u>Modified Monier-Williams Procedure</u>			<u>Ferricyanide Titration Procedure</u>		
<u>Spike Concentration mg/l</u>	<u>Sulfide Measured mg/l</u>	<u>Percent Recovery</u>	<u>Spike Concentration mg/l</u>	<u>Sulfide Measured mg/l</u>	<u>Percent Recovery</u>
<u>Tanners' Council Laboratory</u>					
0	181	---	0	143	---
0	180	---	0	150	---
0	189	---	0	151	---
0	187	---	0	150	---
0	157	---	0	106	---
0	182	---	0	105	---
0	120	---	0	104	---
0	178	---	0	105	---
<u>E.C. Jordan Co. Laboratory</u>					
110	---	93	110	---	75
110	---	96	110	---	75
110	---	93	110	---	75
110	---	86	110	---	73
219	---	85	219	---	72
219	---	85	219	---	72
219	---	82	219	---	70
219	---	89	219	---	68

TABLE III-5  
COMPARISON OF ANALYTICAL RESULTS - MIDWEST TANNING CO.

<u>Modified Monier-Williams Procedure</u>			<u>Ferricyanide Titration Procedure</u>		
<u>Spike Concentration mg/l</u>	<u>Sulfide Measured mg/l</u>	<u>Percent Recovery</u>	<u>Spike Concentration mg/l</u>	<u>Sulfide Measured mg/l</u>	<u>Percent Recovery</u>
<u>Tanners' Council Laboratory</u>					
0	3.3	---	0	0.16	---
0	4.2	---	0	0.16	---
0	4.1	---	0	0.16	---
0	3.9	---	0	0.16	---
<u>E.C. Jordan Co. Laboratory</u>					
0	7.5	---	0	0.3	---
0	7.7	---	0	0.3	---
0	8.7	---	0	0.3	---
0	10.3	---	0	0.3	---
13	---	86	8.3	---	52
13	---	95	8.3	---	49
13	---	86	8.3	---	49
13	---	64	8.3	---	46
22	---	87	25	---	40
22	---	77	25	---	40
22	---	65	25	---	40
22	---	71	25	---	40

TABLE III-6  
COMPARISON OF ANALYTICAL RESULTS - GUTMAN AND COMPANY

<u>Modified Monier-Williams Procedure</u>			<u>Ferricyanide Titration Procedure</u>		
<u>Spike Concentration mg/l</u>	<u>Sulfide Measured mg/l</u>	<u>Percent Recovery</u>	<u>Spike Concentration mg/l</u>	<u>Sulfide Measured mg/l</u>	<u>Percent Recovery</u>
<u>Tanners' Council Laboratory</u>					
0	17	---	0	15	---
0	21	---	0	16	---
0	20	---	0	15	---
0	21	---	0	14	---
<u>E.C. Jordan Laboratory</u>					
0	25	---	0	13	---
0	25	---	0	13	---
0	23	---	0	13	---
0	22	---	0	13	---
22	---	91	38	---	79
22	---	86	38	---	79
22	---	82	38	---	79
22	---	91	38	---	79
30	---	77	63	---	79
30	---	80	63	---	79
30	---	77	63	---	79
30	---	77	63	---	79

TABLE III-7  
COMPARISON OF ANALYTICAL RESULTS - SCHOLZE TANNERY

<u>Modified Monier-Williams Procedure</u>			<u>Ferricyanide Titration Procedure</u>		
<u>Spike Concentration mg/l</u>	<u>Sulfide Measured mg/l</u>	<u>Percent Recovery</u>	<u>Spike Concentration mg/l</u>	<u>Sulfide Measured mg/l</u>	<u>Percent Recovery</u>
<u>Tanners' Council Laboratory</u>					
0	0	---	0	*	*
0	0	---	0	*	*
0	0	---	0	*	*
0	0.8	---	0	*	*
<u>E.C. Jordan Laboratory</u>					
0	1.1	---	0	*	*
0	0.9	---	0	*	*
0	1.1	---	0	*	*
0	1.4	---	0	*	*
4.6	---	53			
4.6	---	70			
4.6	---	40			
4.6	---	51			
12	---	60			
12	---	92			
12	---	66			
12	---	56			

\* Unable to determine due to wastewater color interference.

TABLE III-8

## COMPARISON OF ANALYTICAL RESULTS - COEY TANNING COMPANY, INC.

<u>Modified Monier-Williams Procedure</u>			<u>Ferricyanide Titration Procedure</u>		
<u>Spike Concentration mg/l</u>	<u>Sulfide Measured mg/l</u>	<u>Percent Recovery</u>	<u>Spike Concentration mg/l</u>	<u>Sulfide Measured mg/l</u>	<u>Percent Recovery</u>
<u>Tanners' Council Laboratory</u>					
0	34	---	0	32	---
0	43	---	0	34	---
0	44	---	0	34	---
0	44	---	0	34	---
<u>E.C. Jordan Laboratory</u>					
0	45	---	0	32	---
0	41	---	0	32	---
0	44	---	0	32	---
0	47	---	0	32	---
48	---	100	48	---	79
48	---	103	48	---	79
48	---	94	48	---	80
48	---	100	48	---	80
93	---	92	97	---	79
93	---	92	97	---	79
93	---	100	97	---	79
93	---	93	97	---	79

TABLE III-9  
COMPARISON OF ANALYTICAL RESULTS  
FILTERED AND UNFILTERED SAMPLES

	Spike Concentration mg/l	Sulfide Measured mg/l	
		Filtered	Unfiltered
Hermann Oak Leather Co.	0	0.31	0.35
	0	0.52	0.52
	0	0.38	0.21
	0	0.52	0.31
Irving Tanning Co.	0	95	88
	0	103	66
	0	115	73
	0	119	---
* Results from E.C. Jordan Laboratory using modified Monier-Williams procedure.			

TABLE III-10  
IDENTIFICATION OF SAMPLED TANNERIES

Tannery	Subcategory	Wastewater Sampled
Hermann Oak Leather Co. St. Louis, Missouri	3	Total tannery effluent following aerated equal- ization and $MnSO_4$ addition
Irving Tanning Co. Hartland, Maine	1	Total tannery effluent following segregated stream pretreatment
A.C. Lawrence Leather Co.* South Paris, Maine	1	Total tannery effluent following equalization and $FeCl_3$ addition
Midwest Tanning Co. South Milwaukee, Wisconsin	1	Total tannery effluent following aerated equal- ization and $MnSO_4$ addition
Gutman and Company Chicago, Illinois	1	Total tannery effluent following equalization and pH adjustment
Scholze Tannery Chattanooga, Tennessee	3	Total tannery effluent following equalization and pH adjustment
Coey Tanning Company, Inc. Wartrace, Tennessee	1	Total tannery effluent following segregated stream pretreatment
*Sample collected at Paris Utilities District POTW which receives the tannery discharge.		





## SECTION IV

### SUBCATEGORY WATER USE RATIO DETERMINATION

During the development of the 1982 effluent limitations guidelines and standards for the leather tanning industry, the Agency assembled water use data for as many facilities as possible in each of the nine leather tanning industry subcategories. Individual facility data was normalized on a production basis and averaged. The normalized facility means were subsequently ranked in order of increasing value within each subcategory. Three water use ratio values were then selected from each array of subcategory data.

1. Median Ratio. The Agency concluded that for the purposes of calculating production-based BPT effluent limitations guidelines and the cost of BPT control technology, a flow ratio which best represented the central tendency of each subcategory was the median value of the individual tannery means. The median flow ratio is that value at which half of the individual tannery means are higher and half are lower. The median water use ratios were achieved by at least half the tanneries in each subcategory. The dominant factor which determined the range of water use within subcategories was the extent to which tanneries have implemented water conservation practices.
2. Reduced Ratio. In developing more stringent BAT control technologies for existing sources, the Agency incorporated in-plant controls to reduce water use. Since tanneries that meet reduced water use ratios within each subcategory were found to use the same raw materials and major groups of subprocesses as plants which exhibited higher water use ratios, the Agency concluded that reduced water use ratios are achievable for all tanneries within the individual subcategories. Therefore, the "reduced" water use ratio is based on the median of the lower 50 percent of the tannery water use means within each subcategory.
3. New Source Ratio. New tanneries generally have a distinct advantage over existing tanneries in achieving water use reduction and conservation. By emphasizing these items in the design of a new tannery, a tanner has more opportunity and flexibility than does an existing tanner. Therefore, it is reasonable that new tanneries can achieve further reductions in water use than can existing tanneries. To establish realistic and achievable new source flow ratios, the median flow ratio was based on the water use means of those tanneries that are currently meeting or bettering the reduced flow ratio identified by the methodology described above.

Table IV-1 presents the subcategory water use ratios used in calculating the 1982 effluent limitations guidelines.

TABLE IV-1  
SUBCATEGORY WATER USE RATIOS USED IN DEVELOPMENT  
OF 1982 EFFLUENT LIMITATIONS

Subcategory	Median (gal/lb)	Reduced (gal/lb)	New Source (gal/lb)
1	6.5	5.4	4.3
2	5.8	5.0	4.9
3	4.9	4.8	4.2
4	4.8	4.6	4.5
5	5.8	4.0	3.8
6	2.1	1.4	1.4
7	9.4	9.4	9.4
8	5.0	5.0	4.1
9	3.0	2.5	2.5

In its challenge of the regulations, the TCA identified specific instances in which it claimed errors had been made in determination of tannery mean water use ratios, thus creating subcategory water use ratios which were too low. In some cases, TCA supplied additional data to document water use at certain facilities. EPA conducted an extensive review of both the existing water use ratio data base and the new data submitted by TCA. The existing data base was examined to make sure that all data included in the development of final subcategory water use ratios satisfied the applicable criteria set forth in the Development Document. These criteria are summarized below:

1. For a tannery's data to be utilized to characterize water use, at least 80 percent of the tannery's production must be in one subcategory, or data from each processing operation representing a separate subcategory must be from a segregated and measurable wastewater stream.
2. Both production and flow values must have been reported.
3. Production data must have been reported on the basis specified by EPA for raw material for each subcategory.

The new data were also examined to make certain that these criteria were met. In addition, a fourth criterion was applied to these recent data:

4. The data must correct errors in interpretation or use of data submitted previously during the Agency's data collection program or during the public comment periods on the proposed regulation and the notice of availability.

Any data submitted that covered a time period outside that described in the fourth criterion (i.e., after promulgation) were not considered. Changes in individual facility water use ratios resulting from the data review are discussed in the following paragraphs.

Subcategory 1: Hair Pulp, Chrome Tan, Retan-Wet Finish

(Table IV-2)

Tannery No. 432: Review of the existing data base indicated that the water use ratio for Tannery No. 432 was based on a letter submitted as a comment on the proposal. The value of 7.8 gal/lb was accepted and used without production or flow data for backup. Therefore, this tannery is dropped from the water use ratio data base.

Tannery No. 87: Review of the existing data base revealed that Tannery No. 87 submitted a comment letter on the Notice of Availability which stated that its water use ratio should be increased from 11.5 gal/lb to 12.8 gal/lb.

Although flow and production backup were provided, the change was not made. Because all the criteria for use of the data are satisfied, a water use ratio of 12.8 gal/lb is assigned to this tannery and it is included in the data base.

Tanneries Nos. 60, 183, 279, 403, 413, 509: These six subcategory 1 tanneries were dropped from the water use ratio data base following the June 2, 1982 Notice of Availability because they process either all or a portion of their splits on site, and therefore were interpreted to be mixed subcategory tanneries (subcategories 1 and 9). However, review of the typical raw material weights for these subcategories indicated that an error in calculation was made in arriving at the conclusion that these were mixed subcategory tanneries. The weight of the split as received, before shaving, trimming, and resplitting, was used in 1982. However, the Agency should have used the material weight placed into the first wet process. Using this weight, more than 90 percent of raw material falls in subcategory 1. Therefore, these tanneries satisfy the 80 percent criterion and water use data for these six tanneries also are included in the subcategory 1 data base.

Tannery No. 5500: A water use ratio of 9.2 gal/lb, based on 1979-1980 data, was assigned to this tannery for the Notice of Availability. However, in its comment on the Notice, the tannery presented average flow and production values for 1981 that yield a water use ratio of 7.7 gal/lb. Following the Notice of Availability this tannery was dropped from the water use ratio data base because either all or a portion of its splits are processed on-site. A review of the typical raw material weights for these subcategories, however, indicates that an error in calculation was made in arriving at the conclusion that this was a mixed subcategory tannery (subcategories 1 and 9). The weight of the split as received, before shaving, trimming, and resplitting, was used. However, use of the split weight into wet process reveals that more than 90 percent of raw materials falls in subcategory 1. Therefore, this tannery satisfies the 80 percent criteria and its water use ratio of 7.7 gal/lb is included in the subcategory 1 data base.

TABLE IV-2

WATER USE RATIO DEVELOPMENT FOR SUBCATEGORY 1  
HAIR PULP, CHROME TAN, RETAN-WET FINISH

Tannery	November 1982 Value (gal/lb)	Revised Value (gal/lb)
248	3.0	3.0
383	3.1	3.1
520	3.2	3.2
274	3.8	3.8
413	---	4.0*
246	4.3	4.3
525	4.5	4.5
438	5.4	5.4
245	5.4	5.4
80	5.5	5.5
237	5.7	5.7
235	6.0	6.0
60	---	6.0*
425	6.1	6.1
262	6.2	6.2
206	6.4	6.4
13	6.5	6.5
403	---	6.7*
103	6.8	6.8
431	7.0	7.0
509	---	7.0*
626	7.5	7.5
6	7.6	7.6
5500	---	7.7*
432	7.8	Dropped*
632	7.9	7.9
231	8.9	8.9
31	8.9	8.9
279	---	9.2*
183	---	9.2*
58	9.7	9.7
37185	9.9	9.9
57	10.5	10.5
409	10.7	10.7
87	11.5	12.8*
Median ratio	6.5	6.6*
Reduced ratio	5.4	5.4
New source ratio	4.3	4.3

\* Changed value

Subcategory 2: Hair Save, Chrome Tan, Retan-Wet Finish

There were no changes to the water use ratio data base for this subcategory.

TABLE IV-3

WATER USE RATIO DEVELOPMENT FOR SUBCATEGORY 2  
HAIR SAVE, CHROME TAN, RETAN-WET FINISH

Tannery	November 1982 Value (gal/lb)	Revised Value (gal/lb)
7	[4.9]	[4.9]
8	5.0	5.0
236	5.8	5.8
320	6.8	6.8
Median ratio	5.8	5.8
Reduced ratio	5.0	5.0
New source ratio	4.9	4.9

[ ] These values used only for new source water use ratio development. The basis for this is discussed in the 1982 Development Document (EPA 440/1-82/016).

Subcategory 3: Hair Save or Pulp, Non-Chrome Tan, Retan-Wet Finish (Table IV-4)

Tannery No. 404: EPA's criteria for inclusion of data from a mixed subcategory tannery, such as Tannery No. 404, requires that data representing each subcategory must be obtained from a segregated and measurable wastewater stream. At the time of data base development, documentation in a comment letter appeared to properly addresss this issue; however, TCA included in its petition a letter from the tannery stating that these criteria were not in fact met. Based on these facts, this facility is dropped from the water use ratio data base for this subcategory and subcategory 4.

Tannery No. 239: In its comment on the Notice of Availability, Tannery No. 239 stated that the ratio of record, 7.9 gal/lb, was too low and should be increased to 9.6 gal/lb. Although average 1982 flow and production values of 130,000 gpd and 13,500 lbs/day were supplied as backup, the assigned ratio was not changed. Because all the criteria for use of the data are satisfied, an updated water use ratio of 9.6 gal/lb is assigned to this tannery.

TABLE IV-4

WATER USE RATIO DEVELOPMENT FOR SUBCATEGORY 3  
HAIR SAVE OR PULP, NON-CHROME TAN, RETAN-WET FINISH

Tannery	November 1982 Value (gal/lb)	Revised Value (gal/lb)
385	(2.3)	(2.3)
415	(3.0)	(3.0)
47	(3.1)	(3.1)
397	4.2	4.2
46	4.8	4.8
186	4.8	4.8
388	4.9	4.9
399	4.9	4.9
404	7.7	Dropped*
239	7.9	9.6*
24	8.2	8.2
376	9.6	9.6
Median ratio	4.9	4.8*
Reduced ratio	4.8	4.5*
New source ratio	4.2	4.2

\* Changed value

( ) Value used only for median water use ratio development. The basis for this is discussed in the 1982 Development Document (EPA 440/1-82/016).

Subcategory 4: Retan-Wet Finish-Sides (TABLE IV-5)

Tannery 224: Information received by EPA, in a comment letter on the Notice of Availability, indicated that the water use ratio assigned to Tannery 224 was based on incorrect data. This tannery indicated that the correct ratio was 8.1 gal/lb based upon data provided in a letter of clarification submitted as backup. Therefore, the water use ratio for this tannery is increased from 5.6 gal/lb to 8.1 gal/lb.

Tannery No. 404: See discussion for this tannery in Subcategory 3 above.

Tannery No. 5000: During the development of subcategory water use ratios for the 1982 regulations, EPA assigned a water use ratio of 4.5 gal/lb to Tannery No. 5000. Information subsequently supplied to EPA clarified the original data and indicated that the water use ratio at this tannery is 6.3 gal/lb. Therefore, a water use ratio of 6.3 gal/lb is assigned to this tannery.

TABLE IV-5  
WATER USE RATIO DEVELOPMENT FOR SUBCATEGORY 4  
RETAN-WET FINISH-SIDES

Tannery	November 1982 Value (gal/lb)	Revised Value (gal/lb)
389	(1.7)	(1.7)
404	(2.4)	Dropped*
3	4.6	4.6
4937	4.9	4.9
5000	4.5	6.3*
625	6.4	6.4
224	5.6	8.1
191	11.4	11.4
Median ratio	4.8	6.3*
Reduced ratio	4.6	4.8*
New source ratio	4.5	4.6*

\* Changed value.

( ) Value used only for median water use ratio development. The basis for this is discussed in the 1982 Development Document (EPA 440/1-82/016).

#### Subcategory 5: No Beamhouse (Table IV-6)

Tannery No. 75: Review of the existing data base indicated that the water use ratio of 5.5 gal/lb assigned to Tannery No. 75 was based on a letter from TCA which stated that water use ranged from 5 to 6 gal/lb. No flow or production data was provided as backup. Review also indicates that this is a mixed subcategory tannery (60 percent chrome tanning, 40 percent vegetable tanning). In light of these facts, this tannery is dropped from the water use ratio data base.

Tannery No. 169: Review of the existing data base indicated that Tannery No. 169 is a mixed subcategory tannery (subcategories 1 and 5). In addition, raw material conversion factors used by the tannery were not supported by data. Therefore, this tannery is dropped from the water use ratio data base.

Tannery No. 220: Review of the existing data base indicates that the water use ratio of 13.5 gal/lb assigned to Tannery No. 220 was based on a letter submitted as a comment on the proposal. That letter stated that water use was in the range of 13 to 14 gal/lb. Because no production data was provided for backup, this tannery is dropped from the water use ratio data base.



TABLE IV-6

WATER USE RATIO DEVELOPMENT FOR SUBCATEGORY 5  
NO BEAMHOUSE

Tannery	November 1982 Value (gal/lb)	Revised Value (gal/lb)
88	(3.5)	(3.5)
700	3.8	3.8
285	(3.8)	(3.8)
51	4.0	4.0
75	(5.5)	Dropped*
615	5.6	5.6
92	5.8	5.8
380	6.6	6.6
556	7.4	7.4
522	7.8	7.8
319	8.5	8.5
169	11.0	Dropped*
220	13.5	Dropped*
Median ratio	5.8	5.7*
Reduced ratio	4.0	4.0
New source ratio	3.8	3.8

\* Changed value.

( ) Value used only for median water use ratio development. The basis for this is discussed in the 1982 Development Document (EPA 440/1-82/016).

Subcategory 6: Through-the-Blue (Table IV-7)

Tannery No. 444: The Agency assigned a water use ratio of 1.4 gal/lb to Tannery No. 444 during the development of the 1982 regulation. Information was subsequently provided to EPA which indicated that production and flow data available previously, but not used because of misinterpretation, met the necessary criteria for consideration. This additional data indicated that the water use ratio for this tannery should be changed to 2.1 gal/lb.

Tannery No. 559: The Agency assigned a water use ratio of 1.4 gal/lb to Tannery No. 559 during the development of the 1982 regulation. Information was subsequently provided to EPA which indicated that the water use ratio was based on winter hide weights and thus not representative of average conditions. Therefore, the Agency reevaluated the water use ratio reported previously by this tannery by averaging the summer and winter hide weights. Accordingly, the production value for this tannery decreased and the flow ratio increased from 1.4 gal/lb to 2.3 gal/lb.

TABLE IV-7

WATER USE RATIO DEVELOPMENT FOR SUBCATEGORY 6  
THROUGH-THE-BLUE

Tannery	November 1982 Value (gal/lb)	Revised Value (gal/lb)
444	1.4	2.1*
559	2.1	2.3*
502	2.6	2.6
Median ratio	2.1	2.3*
Reduced ratio	1.4	2.1*
New source ratio	1.4	2.1*
* Changed value.		

Subcategory 7: Shearling (Table IV-8)

Tannery No. 54: A review of the technical record indicates that no usable wastewater data was available for Tannery No. 54 at the time of the proposal or the Notice of Availability. However, in its comment on the Notice, another tannery, of which Tannery No. 54 is an affiliate, supplied production and flow data which indicated that Tannery No. 54's water use ratio should be 11.9 gal/lb. This data inadvertently was not added to the data base. A water use ratio of 11.9 gal/lb is assigned to this tannery.

TABLE IV-8

WATER USE RATIO DEVELOPMENT FOR SUBCATEGORY 7  
SHEARLING

Tannery	November 1982 Value (gal/lb)	Revised Value (gal/lb)
500	9.4	9.4
54	---	11.9
Median ratio	9.4	10.7*
Reduced ratio	9.4	9.4
New source ratio	9.4	9.4
* Changed value.		

Subcategory 8: Pigskin (Table IV-9)

No changes.

TABLE IV-9  
WATER USE RATIO DEVELOPMENT FOR SUBCATEGORY 8  
PIGSKIN

Tannery	November 1982 Value (gal/lb)	Revised Value (gal/lb)
185	(4.1)	(4.1)
233	5.8	5.8
Median ratio	5.0	5.0
Reduced ratio	5.0	5.0
New source ratio	4.1	4.1

( ) Value used for median water use ratio development and new source ratio. The basis for this was discussed in the 1982 Development Document (EPA 440/1-82/016).

Subcategory 9: Retan-Wet Finish-Splits (Table IV-10)

Tannery No. 622: Review of the technical record indicates that Tannery No. 622 submitted a comment letter on the Notice of Availability containing flow and production backup which supported a water use ratio of 4.7 gal/lb. EPA did not utilize the data because we believed that that the backup data were maximum design values rather than average values. When we reviewed the comment letter and data, we realized that average values were given. Therefore, a water use ratio of 4.7 gal/lb is assigned to Tannery No. 622.

Tannery No. 26560: Review of the Technical Record indicates that Tannery No. 26560 was not included in water use ratio development for the Notice of Availability because the only information available at that time concerning this tannery's water use was a statement, without flow or production data, that long-term water use was 8.3 gal/lb. In its comment on the Notice of Availability, the tannery again stated that long-term water use was 8.3 gal/lb, and that under recent "non-optimum conditions," water use had increased to 9.79 gal/lb. Flow and production figures were provided to back up the short-term ratio of 9.79 gal/lb. The short-term ratio was not used because it was stated to reflect "non-optimum" conditions and was significantly higher than the long-term value. After reconsideration of the documentation supplied by this plant, a water use ratio of 9.8 gal/lb is assigned to this tannery.

TABLE IV-10

WATER USE RATIO DEVELOPMENT FOR SUBCATEGORY 9  
RETAN-WET FINISH-SPLITS

Tannery	November 1982 Value (gal/lb)	Revised Value (gal/lb)
507	(2.2)	(2.2)
97	2.5	2.5
116	3.4	3.4
622	---	4.7*
501	4.9	4.9
26560	---	9.8*
Median ratio	3.0	4.1*
Reduced ratio	2.5	3.0*
New source ratio	2.5	2.5*

\* Changed value.

( ) Value used only for median water use ratio development. The basis for this is discussed in the 1986 Development Document (EPA 440/1-82/016).

Tables IV-11 and IV-12 summarize the revised median and new source water use ratios respectively.

TABLE IV-11  
SUBCATEGORY MEDIAN WATER USE RATIOS

Subcategory	Number of Tanneries In Subcategory Data Base	Median Water Use Ratio (gal/lb)	Number of Tanneries In Data Base Achieving Water Use Ratio
1	34	6.6	17
2	4	5.8	3
3	11	4.8	6
4	7	6.3	4
5	10	5.7	5
6	3	2.3	2
7	2	10.7	1
8	2	5.0	1
9	6	4.1	3

TABLE IV-12  
SUBCATEGORY WATER USE RATIOS FOR NEW SOURCES

Subcategory	Number of Tanneries In Subcategory Data Base	Median Water Use Ratio (gal/lb)	Number of Tanneries In Data Base Achieving Water Use Ratio
1	34	4.3	6
2	4	4.9	1
3	11	4.2	4
4	7	4.6	2
5	10	3.8	3
6	3	2.1	1
7	2	9.4	1
8	2	4.1	1
9	6	2.5	2



## SECTION V

### BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE (BPT) LIMITATIONS

Revisions to the BPT effluent limitations guidelines for subcategories 1, 3, 4, 5, 6, 7, and 9 are based on the revised median water use ratios developed in Section IV and presented in Table IV-11. The following methodology was used to calculate the revised BPT effluent limitations guidelines.

The following equation was used to calculate maximum day and monthly average production-based effluent BPT guidelines in Tables V-1 through V-9.

$$\text{BPT limitations (lb/1,000 lbs raw material)} = 8.34CFQ \times 10^{-3}$$

where:

C = effluent concentration (mg/l)

F = variability factor

Q = subcategory median flow ratio (gal/lb raw material)

As described in the 1982 Development Document (EPA 440/1-82/016), EPA adopted the following long-term average final effluent concentrations ("C" in the above equation) for the leather tanning and finishing industry.

BOD <sub>5</sub>	40 mg/l
TSS	60 mg/l
Oil and Grease	20 mg/l
Chromium (total)	1 mg/l

The following variability factors ("F" in the above equation) were also developed by EPA in the 1982 Development Document (EPA 440/1-82/016).

	<u>Maximum for any one day</u>	<u>Maximum for monthly average</u>
BOD <sub>5</sub>	4.21	1.89
TSS	4.05	1.85
Oil and Grease	3.54	1.58
Chromium (total)	4.33	1.59

The revised median flow ratios ("Q" in the above equation) were developed in Section IV and are presented in Table IV-11.

The following tables present the revised production-based effluent BPT limitations and guidelines. BPT effluent limitations guidelines for subcategories 2 and 8 are also included.

TABLE V-1

Subcategory 1

Hair Pulp, Chrome Tan, Retan-Wet Finish Subcategory  
BPT Limitations

Pollutant or Pollutant Property	<u>BPT Limitations</u>	
	Maximum for any one day	Maximum for monthly average
	kg/kg (or pounds per 1000 lb) of raw material	
BOD <sub>5</sub>	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.



Table V-2

## Subcategory 2

Hair Save, Chrome Tan, Retan-Wet Finish Subcategory  
BPT Limitations

Pollutant or Pollutant Property	<u>BPT Limitations</u>	
	Maximum for any one day	Maximum for monthly average
	kg/kg (or pounds per 1000 lb) of raw material	
BOD <sub>5</sub>	8.2	3.7
TSS	11.8	5.4
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.

Table V-3

## Subcategory 3

Hair Save or Pulp, Non-chrome Tan, Retan-Wet Finish Subcategory  
BPT Limitations

Pollutant or Pollutant Property	<u>BPT Limitations</u>	
	Maximum for any one day	Maximum for monthly average
	kg/kg (or pounds per 1000 lb) of raw material	
BOD <sub>5</sub>	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.

Table V-4

## Subcategory 4

Retan-Wet Finish-sides Subcategory  
BPT Limitations

Pollutant or Pollutant Property	<u>BPT Limitations</u>	
	Maximum for any one day	Maximum for monthly average
	<u>kg/kkg (or pounds per 1000 lb) of raw material</u>	
BOD <sub>5</sub>	8.9	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.

Table V-5

## Subcategory 5

## No Beamhouse Subcategory BPT Limitations

Pollutant or Pollutant Property	<u>BPT Limitations</u>	
	Maximum for any one day	Maximum for monthly average
	<u>kg/kkg (or pounds per 1000 lb) of raw material</u>	
BOD <sub>5</sub>	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.

Table V-6

## Subcategory 6

## Through-The-Blue Subcategory BPT Limitations

Pollutant or Pollutant Property	<u>BPT Limitations</u>	
	Maximum for any one day	Maximum for monthly average
	kg/kg (or pounds per 1000 lb) of raw material	
BOD <sub>5</sub>	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.

Table V-7

## Subcategory 7

## Shearling Subcategory BPT Limitations

Pollutant or Pollutant Property	<u>BPT Limitations</u>	
	Maximum for any one day	Maximum for monthly average
	kg/kg (or pounds per 1000 lb) of raw material	
BOD <sub>5</sub>	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.

Table V-8

Subcategory 8  
Pigskin Subcategory BPT Limitations

Pollutant or Pollutant Property	<u>BPT Limitations</u>	
	Maximum for any one day	Maximum for monthly average
	kg/kg (or pounds per 1000 lb) of raw material	
BOD <sub>5</sub>	7.0	3.2
TSS	10.1	4.6
Oil & Grease	3.0	1.3
Total Chromium	0.18	0.07
pH	(1)	(1)

(1) Within the range of 6.0 to 9.0.

Table V-9

Subcategory 9  
Retan-Wet Finish-Splits Subcategory BPT Limitations

Pollutant or Pollutant Property	<u>BPT Limitations</u>	
	Maximum for any one day	Maximum for monthly average
	kg/kg (or pounds per 1000 lb) of raw material	
BOD <sub>5</sub>	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.

## SECTION VI

### NEW SOURCE PERFORMANCE STANDARDS

Revisions to the new source performance standards for subcategories 4 and 6 were calculated as the product of (a) long-term average final effluent concentrations, (b) appropriate variability factors for each pollutant (both of these were utilized in the development of BPT effluent limitations in Section V), and (c) reduced water use ratios achievable by new sources summarized in Table IV-12 using the equation presented in Section V. Tables VI-4 and VI-6 present the revised standards. NSPS are also included for the remaining subcategories.

Table VI-1

#### Subcategory 1

#### Hair Pulp, Chrome Tan, Retan-Wet Finish Subcategory NSPS

Pollutant or Pollutant Property	<u>NSPS Limitations</u>	
	Maximum for any one day	Maximum for monthly average
	<u>kg/kg (or pounds per 1000 lb) of raw material</u>	
BOD <sub>5</sub>	6.0	2.7
TSS	8.7	4.0
Oil & Grease	2.5	1.1
Total Chromium	0.16	0.06
pH	(1)	(1)

(1) Within the range of 6.0 to 9.0.

TABLE VI-2

Subcategory 2  
Hair Save, Chrome Tan, Retan-Wet Finish Subcategory NSPS

Pollutant or Pollutant Property	<u>NSPS Limitations</u>	
	Maximum for any one day	Maximum for monthly average
	kg/kg (or pounds per 1000 lb) of raw material	
BOD <sub>5</sub>	6.9	3.1
TSS	9.9	4.5
Oil & Grease	2.9	1.3
Total Chromium	0.18	0.06
pH	(1)	(1)

(1) Within the range of 6.0 to 9.0.

Table VI-3

Subcategory 3  
Hair Save or Pulp, Non-chrome Tan, Retan- Wet Finish  
Subcategory NSPS

Pollutant or Pollutant Property	<u>NSPS Limitations</u>	
	Maximum for any one day	Maximum for monthly average
	kg/kg (or pounds per 1000 lb) of raw material	
BOD <sub>5</sub>	5.9	2.7
TSS	8.5	3.9
Oil & Grease	2.4	1.1
Total Chromium	0.15	0.06
pH	(1)	(1)

(1) Within the range of 6.0 to 9.0.

Table VI-4  
Subcategory 4  
Retan-Wet Finish-Sides Subcategory NSPS

Pollutant or Pollutant Property	<u>NSPS Limitations</u>	
	Maximum for any one day	Maximum for monthly average
	kg/kg (or pounds per 1000 lb) of raw material	
BOD <sub>5</sub>	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.

Table VI-5  
Subcategory 5  
No Beamhouse Subcategory NSPS

Pollutant or Pollutant Property	<u>NSPS Limitations</u>	
	Maximum for any one day	Maximum for monthly average
	kg/kg (or pounds per 1000 lb) of raw material	
BOD <sub>5</sub>	5.3	2.4
TSS	7.7	3.5
Oil & Grease	2.2	1.0
Total Chromium	0.14	0.05
pH	(1)	(1)

(1) Within the range of 6.0 to 9.0.

Table VI-6  
Subcategory 6  
Through-the-Blue Subcategory NSPS

Pollutant or Pollutant Property	<u>NSPS Limitations</u>	
	Maximum for any one day	Maximum for monthly average
	kg/kg (or pounds per 1000 lb) of raw material	
BOD <sub>5</sub>	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.

Table VI-7  
Subcategory 7  
Shearling Subcategory NSPS

Pollutant or Pollutant Property	<u>NSPS Limitations</u>	
	Maximum for any one day	Maximum for monthly average
	kg/kg (or pounds per 1000 lb) of raw material	
BOD <sub>5</sub>	13.2	5.9
TSS	19.1	8.7
Oil & Grease	5.6	2.5
Total Chromium	0.347	0.12
pH	(1)	(1)

(1) Within the range of 6.0 to 9.0.



Table VI-8  
Subcategory 8  
Pigskin Subcategory NSPS

Pollutant or Pollutant Property	<u>NSPS Limitations</u>	
	Maximum for any one day	Maximum for monthly average
	kg/kg (or pounds per 1000 lb) of raw material	
BOD <sub>5</sub>	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.

Table VI-9  
Subcategory 9  
Retan-Wet Finish-Splits Subcategory NSPS

Pollutant or Pollutant Property	<u>NSPS Limitations</u>	
	Maximum for any one day	Maximum for monthly average
	kg/kg (or pounds per 1000 lb) of raw material	
BOD <sub>5</sub>	3.5	1.6
TSS	5.1	2.3
Oil & Grease	1.5	0.66
Total Chromium	0.09	0.03
pH	(1)	(1)

(1) Within the range of 6.0 to 9.0.



## SECTION VII

### PRETREATMENT STANDARDS FOR EXISTING AND NEW SOURCES

EPA's economic analysis for the 1982 regulation projected that the cost of chromium pretreatment would result in the potential closure of four to five of six small tanneries in subcategory 1; two of three small tanneries in subcategory 3; and four to five of nine small tanneries in subcategory 9. No less costly chromium control technology options or less stringent chromium standards could be identified for these facilities. Therefore, the PSES chromium standards were not applied to small tanneries which process less than 275 hides/day in subcategory 1, less than 350 hides/day in subcategory 3, and less than 3600 splits/day in subcategory 9. However, small facilities in subcategories 1 and 3 were still subject to sulfide pretreatment standards, and small facilities in subcategories 1, 3, and 9 were still required to comply with the general pretreatment regulations contained in 40 CFR Part 403.

The Agency further defined the applicability of the exemptions by specifying in a Federal Register notice dated June 30, 1983 (48 FR 30115) an annual weight limit based on 260 working days per year. The Agency has reconsidered this issue and is deleting all reference to the annual weight basis and number of working days per year because the weight limit penalized facilities which operate more than five days per week and where raw material weights do not correspond to those used by EPA to calculate the annual weight limitation.

In addition, EPA is deleting the upper pH bound of ten contained in the PSES Subcategory 3 (Hair Save or Pulp, Non-Chrome Tan, Retan-Wet Finish subcategory). This upper pH limit was originally included in the PSES for all subcategories to provide an additional tool for POTW's to use in their efforts to control the introduction of chromium into their collection and treatment systems. The inclusion was based on the fact that chromium hydroxide is amphoteric and dissolves at high pH. Placing an upper bound on pH thus helps control the discharge of dissolved chromium. However, because the tanneries affected by the PSES of Subcategory 3 do not use chromium as a primary tanning agent, the inclusion of an upper pH bound is unnecessary. The lower bound of pH 7 will remain in effect and the tanneries will continue to be subject to the general pretreatment regulations.



## SECTION VIII

### REMAINING ISSUES

#### 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 and are unsure which subcategory they will fall into should request written certification from the Agency as to whether the facility falls within a particular subcategory prior to commencing discharges which would fall within that subcategory.

#### 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 the Hair Pulp, Chrome Tan, Retan-Wet Finish Subcategory (Subcategory 1), the Hair Save or Pulp, Non-Chrome Tan, Retan-Wet Finish Subcategory (Subcategory 3), or the Retan-Wet Finish-Splits Subcategory (Subcategory 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.

## 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" [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.

Appendix A  
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  $[K_3Fe(CN)_6]$  =

$$\frac{(\text{ml of thiosulfate added}) (\text{normality of thiosulfate})}{\text{ml of } K_3Fe(CN)_6}$$

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 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 - 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 procedure 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.

Appendix B  
Modified Monier-Williams Method

Outline of Method

Hydrogen sulfide is liberated from an acidified sample by distillation and purging with nitrogen gas (N<sub>2</sub>). 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)

125 ml. separatory funnel with 24/40 joint (VWR Cat. No. 30357-102)

Inlet tube with 24/40 joint (VWR Cat. No. 33057-105)

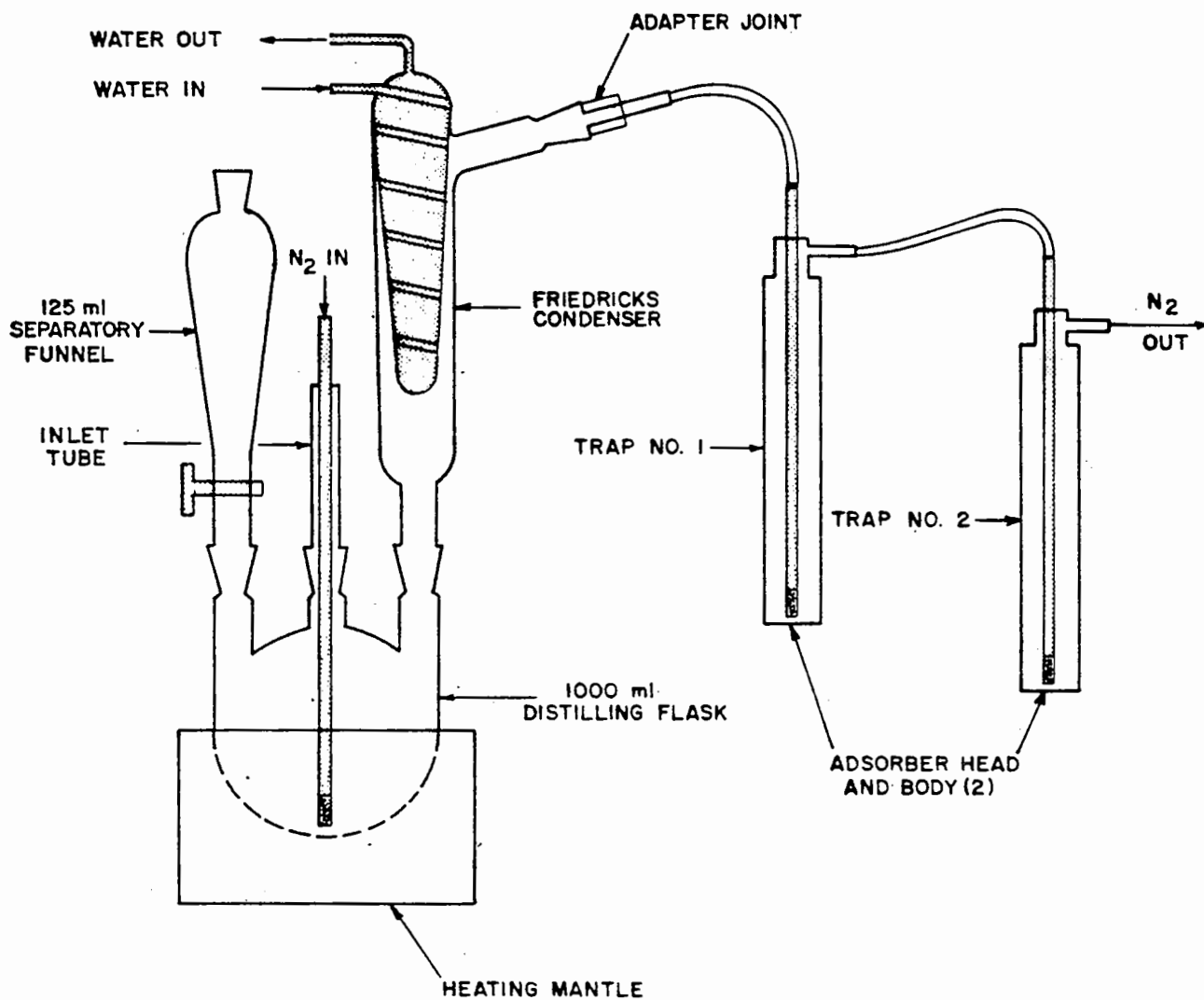
Adapter joint 24/40 to 19/38 (VWR Cat. No. 62905-26)

Adsorber head (2 required) (Thomas Cat. No. 9849-R29)

Adsorber body (2 required) (Thomas Cat. No. 9849-R32)

Laboratory vacuum pump or water aspirator

**FIGURE B-1**  
**EQUIPMENT ASSEMBLY**



## 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  $7.0 \pm 0.1$  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  $\text{pH} > 9$  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 N<sub>2</sub> 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 N<sub>2</sub> 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 N<sub>2</sub> 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 H<sub>2</sub>S: Interrupt the N<sub>2</sub> 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 N<sub>2</sub> flow for 30 minutes. Terminate the distillation cycle by turning off the heating mantle and maintaining N<sub>2</sub> flow through the system for 5 to 10 minutes. Then turn off the N<sub>2</sub> 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 for 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 if 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.



Appendix C  
Definition and Procedure for the Determination  
of the Method Detection Limit

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 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. (Recommend 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:

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

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

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:

$$MDL = t(n-1, 1-a = .99)(S)$$

where:

MDL = the method detection

$t(n-1, 1-a = .99)$  = the students'  $t$  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:

$$MDL_{LCL} = 0.69 MDL$$

$$MDL_{UCL} = 1.92 MDL$$

where  $MDL_{LCL}$  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  $S_A^2$  from the current MDL calculation and  $S_B^2$  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  $S_{\text{pooled}}$  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

TANNERS' COUNCIL OF AMERICA, INC.,  
Petitioner,  
v.  
U.S. ENVIRONMENTAL PROTECTION AGENCY,  
Respondent.

Petitioner Tanners' Council of America, Inc. ("TCA") and respondent U.S. Environmental Protection Agency ("EPA" or "the Agency"), intending to be bound by this agreement, hereby stipulate and agree as follows:

2. EPA agrees to propose and take final action on the amendments to the leather tanning regulations set forth in Exhibit A to this agreement and the accompanying preamble language set forth in Exhibit B to this agreement in accordance with the following schedule:

D-1

- (b) As expeditiously as possible, EPA shall submit the proposed amendments and preamble language (Exhibits A and B) to the Office of Management and Budget ("OMB") in accordance with the terms of Executive Order 12291. EPA shall request that OMB expeditiously review the proposed amendments and preamble language.
- (c) As expeditiously as possible after the completion of OMB review, EPA shall submit the proposed amendments and preamble language to the Federal Register for immediate publication.
- (d) The public comment period on the proposed amendments and preamble language shall be no longer than 30 days. EPA may extend this period for a maximum of 30 days if it receives a request for an extension based upon compelling circumstances not apparent at the time of execution of this agreement. If EPA extends the comment period, it shall immediately notify TCA of the cause or causes for the extension and the additional time allowed for comment. No extension shall exceed the time required by its cause.
- (e) As expeditiously as possible after the close of the public comment period on the proposed amendments and preamble language, EPA shall submit any final amendments and preamble language to OMB in accordance with the terms of Executive Order 12291. EPA shall request that OMB expeditiously review these amendments and preamble language.
- (f) As expeditiously as possible after the completion of OMB review, EPA shall submit any final amendments and preamble language to the Federal Register for immediate publication. Unless compelling circumstances arise not apparent on the date of execution of this agreement, EPA shall set the effective date of the final regulations no later than 44 days after publication in the Federal Register.

3. The parties agree that if, after EPA has taken final action under this agreement, any individual provision of the final leather tanning regulations or any preamble section is not substantially the same as or alters the meaning of the language set forth in Exhibits A and B, TCA reserves the right to proceed further with this litigation or file a new petition for judicial review with respect to: (a) any issue related



to that individual provision, and (b) all issues in the TCA Petition for Reconsideration filed before the Administrator on May 9, 1983, entitled "In Re Leather Tanning and Finishing Industry Effluent Limitations Guidelines, Pretreatment Standards and New Source Performance Standards" that are not addressed in Exhibits A and B, including issues numbered 6 (pretreatment pH lower limit), 7 (alkalinity pH pretreatment standard), 11 (pretreatment for chromium), 13 (variability factors) and 14 (PSES mass limitations), except that TCA may only challenge issues numbered 6 and 7 if EPA fails to amend the pH limitation in 40 C.F.R. § 425.35(a) as set forth in Exhibit A. EPA reserves the right to oppose such litigation on any grounds other than petitioner's execution of this agreement. TCA reserves the right to pursue such litigation on any grounds.

4. The parties agree that within 15 days after final EPA action under this agreement, with respect to each amendment and each preamble section which is substantially the same as and does not alter the meaning of the language set forth in Exhibits A and B to the agreement, TCA will voluntarily move to dismiss its petition for review and voluntarily withdraw the Petition for Reconsideration. EPA will support this TCA motion and neither party will seek to recover any litigation costs or fees from the other.

5. TCA will not seek judicial review of any amendment to the leather tanning and finishing regulations or preamble which is substantially the same as and does not alter the meaning of the language set forth in Exhibits A and B of this agreement.

6. The parties agree that, after the effective date of this Settlement Agreement, they will treat each amendment and preamble provision contained in Exhibits A and B as a duly promulgated rule or interpretation until the Agency takes final action on each proposed revision.

7. The parties agree to seek a stay of the portions of the leather tanning regulations that EPA has agreed to propose to amend. The parties will request that this

stay remain in effect until the Agency completes final action on the amendments and preamble language.

8. If for any reason the provisions of paragraphs 6 or 7 are not implemented by any federal or state regulating authority, TCA may seek relief in any appropriate forum.

9. TCA agrees to submit comments in support of all amendments and preamble language proposed in accordance with Exhibits A and B.

10. EPA agrees not to attempt to invoke this agreement as a bar in subsequent EPA administrative proceedings (other than the proceeding contemplated by this agreement) to revise or supplement limitations and standards addressed by the leather tanning regulations.

11. Although EPA commits itself to take the necessary implementing steps described in paragraph 2(a) immediately, this agreement shall not become effective until 14 days after it has been signed by both parties.

12. TCA is a national trade association representing the leather tanning and finishing industry. The undersigned attorney for TCA hereby certifies that he is authorized to enter into this agreement on behalf of TCA. TCA has notified all its members subject to the leather tanning regulations (those entities listed in Exhibit C to this agreement) of the terms of this agreement, and has requested that any member objecting to the terms of the agreement notify TCA immediately. None of these members has notified TCA of any objection to the terms of this agreement. Moreover, TCA has notified these members that EPA would not enter into this agreement unless TCA assured the Agency that the regulated members of TCA: (a) would treat the amendments and preamble provisions contained in Exhibits A and B as duly promulgated rules or interpretations after the execution of this Settlement Agreement; (b) would not petition for review of any amendment or preamble provision of the leather tanning

regulations promulgated consistent with Exhibits A and B; and (c) would not submit adverse comments on any proposed amendment or preamble provision to the leather tanning regulations substantially the same as or not altering the meaning of the language in Exhibits A and B. Based upon the responses, TCA has given EPA its reasonable assurance that its members will act in accordance with items (a) through (c) of this paragraph. EPA has entered into this agreement in reliance upon TCA's action and assurances.

13. Upon execution of this agreement, the parties agree to move promptly for a stay of this litigation pending final action by the Agency under this agreement.

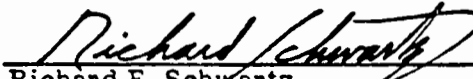
14. Nothing in this agreement shall operate to waive any legal right of either party unless such a waiver is expressly provided.

15. The pending applications for variances based on "fundamentally different factors" submitted by Ocean Leather Corporation, Richard Leather Company, Carr Leather Company, Badger State Tanning Corp., and Blackhawk Tanning Company, shall be unaffected by this Settlement Agreement.

16. This Settlement Agreement, including Exhibits A, B and C, represents the entire agreement between the Agency and TCA with respect to the leather tanning regulations published at 47 Fed. Reg. 52,848.

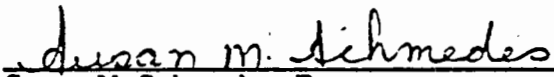
Respectfully submitted,

Dated: 11/27/84

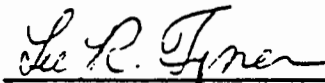
  
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## EXHIBIT A

### AMENDMENTS TO 40 C.F.R. PART 425

#### **I     SULFIDE ANALYTICAL METHODS.**

Amend 40 C.F.R. § 425.02(a) to read:

"Sulfide" shall mean total sulfide as measured by the potassium ferricyanide titration method or the modified Monier-Williams method described in § 425.03.

Amend 40 C.F.R. § 425.03 to read:

§ 425.03 Sulfide analytical methods.

##### **(a)   Applicability.**

The potassium ferricyanide titration method described in § 425.03(b) 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 § 425.03(c) 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.

The modified Monier-Williams method as described in § 425.03(c) 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).

##### **(b)   Potassium Ferricyanide Titration Method.**

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.

(1) 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).

(2) Apparatus. Burette, 10 ml.

(3) Reagents.

(A) 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.

(B) 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:

$$\text{Normality of Potassium Ferricyanide (K}_3\text{Fe(CN)}_6\text{)} = \frac{(\text{ml of thiosulfate added})(\text{normality of thiosulfate})}{\text{ml of K}_3\text{Fe(CN)}_6}$$

- (C) 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.
- (D) Preparation of 0.05M barium chloride solution: Dissolve 12-13 g barium chloride dihydrate in 1 liter of distilled water.
- (E) 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.
- (F) 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 376.1 immediately prior to use.
- (G) Preparation of 10N NaOH: Dissolve 400 g of analytical reagent grade NaOH in 1 liter distilled water.

(4) 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  $\text{pH} \geq 12$  with 10N NaOH. Sample containers must be covered tightly and stored at  $4^{\circ}\text{C}$  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.

(5) Procedure.

- (A) 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.
- (B) Adjust the sample to pH 8.5-9.5 with 6N HCl.
- (C) Add 20 ml of 6M ammonium chloride buffer (pH 9.3), 1 ml of ferrous dimethylglyoxime indicator, and 25 ml of 0.05 M barium chloride. Mix gently, stopper, and let stand for 10 minutes.
- (D) 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.

(6) Calculation and Reporting of Results.

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

where A = volume in ml of potassium ferricyanide solution used

and B = normality of potassium ferricyanide solution.

- (B) Report results to two significant figures.

(7) Quality Control.

- (A) 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.

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

- (i) Perform four replicate analyses of a 20 mg/l sulfide standard prepared in distilled water (see (3)(F)).
- (ii) Calculate clean water precision and accuracy in accordance with standard statistical procedures. Clean water acceptance limits are presented 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.

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.

(C) The Minimum Reportable Concentration (MRC) should be determined periodically by each participating laboratory in accordance with the procedures specified in Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater - EPA-600/4-82-057, July 1982, EMSL, Cincinnati, OH 45268.

(D) 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 MRC (see (7)(C)) for MRC samples, and at x where x is the concentration found if in excess of the MRC. 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 procedure described in § 425.03(c).

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

(c) Modified Monier-Williams Method

(1) 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 gravimetric (EPA 375.3) or turbidimetric (EPA 375.4) procedures.

(2) 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.

- (A) Heating mantle and control (VWR Cat. No. 33752-464)
- (B) 1000 ml distilling flask with three 24/40 joints (VWR Cat. No. 29280-215)
- (C) Friedrichs condenser with two 24/40 joints (VWR Cat. No. 23161-009)

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

(3) Reagents.

- (A) Potassium hydroxide, 6N: Dissolve 340 g of analytical reagent grade KOH in 1 liter distilled water.
- (B) Sodium hydroxide, 6N: Dissolve 240 g of analytical reagent grade NaOH in 1 liter distilled water.
- (C) Sodium hydroxide, 0.03N: Dilute 5.0 ml of 6N NaOH to 1 liter with distilled water.
- (D) Hydrochloric acid, 6N: Dilute 500 ml of concentrated HCl to 1 liter with distilled water.
- (E) Potassium phosphate stock buffer, 0.5M: Dissolve 70 g monobasic potassium phosphate in approximately 800 ml distilled water. Adjust pH to  $7.0 \pm 0.1$  with 6N potassium hydroxide and dilute to 1 liter with distilled water. Stock solution is stable for several months at 4°C.
- (F) 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 1 month at 4°C.

- (G) Alkaline 3 percent 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.
- (H) 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 376.1 immediately prior to use.

(4) Sample Preservation and Storage.

Preserve unfiltered wastewater samples immediately after collection by adjustment to pH  $\geq 9$  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.

(5) Procedure. (See Figure 1 for apparatus layout)

- (A) Place 50 ml of 0.05M pH 7.0 potassium phosphate buffer in Trap No. 1.
- (B) Place 50 ml of alkaline 3 percent hydrogen peroxide in Trap No. 2.
- (C) Sample introduction and N<sub>2</sub> 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  $N_2$  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  $N_2$  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).

(D) Volatilization of  $H_2S$ : Interrupt the  $N_2$  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  $N_2$  flow for 30 minutes. Terminate the distillation cycle by turning off the heating mantle and maintaining  $N_2$  flow through the system for 5 to 10 minutes. Then turn off the  $N_2$  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 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.

(E) Analysis: Analyze the contents of Trap No. 2 for sulfate according to EPA Method 375.3 (Gravimetric) or EPA Method

375.4 (Turbidimetric) and use result to calculate mg/l of sulfide in wastewater sample.

(6) Calculations and Reporting of Results.

(A) Gravimetric procedure:

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

(B) Turbidimetric procedure:

$$\frac{(\text{mg/l Sulfate in Trap No. 2}) \times (\text{liquid volume in l in Trap No. 2}) \times (333)}{\text{Volume in ml of waste sample distilled}} = \text{mg Sulfide/l}$$

(C) Report results to two significant figures.

(7) Quality Control

(A) 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 accuracy and limits expected of the method.

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

(i) Perform four replicate analyses of a 20 mg/l sulfide standard prepared in distilled water (see (3)(H)).

- (ii) Calculate clean water precision and accuracy in accordance with standard statistical procedures. Clean water acceptance limits are presented 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.

Clean water precision and accuracy acceptance limits:  
For distilled water samples containing from 5 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.

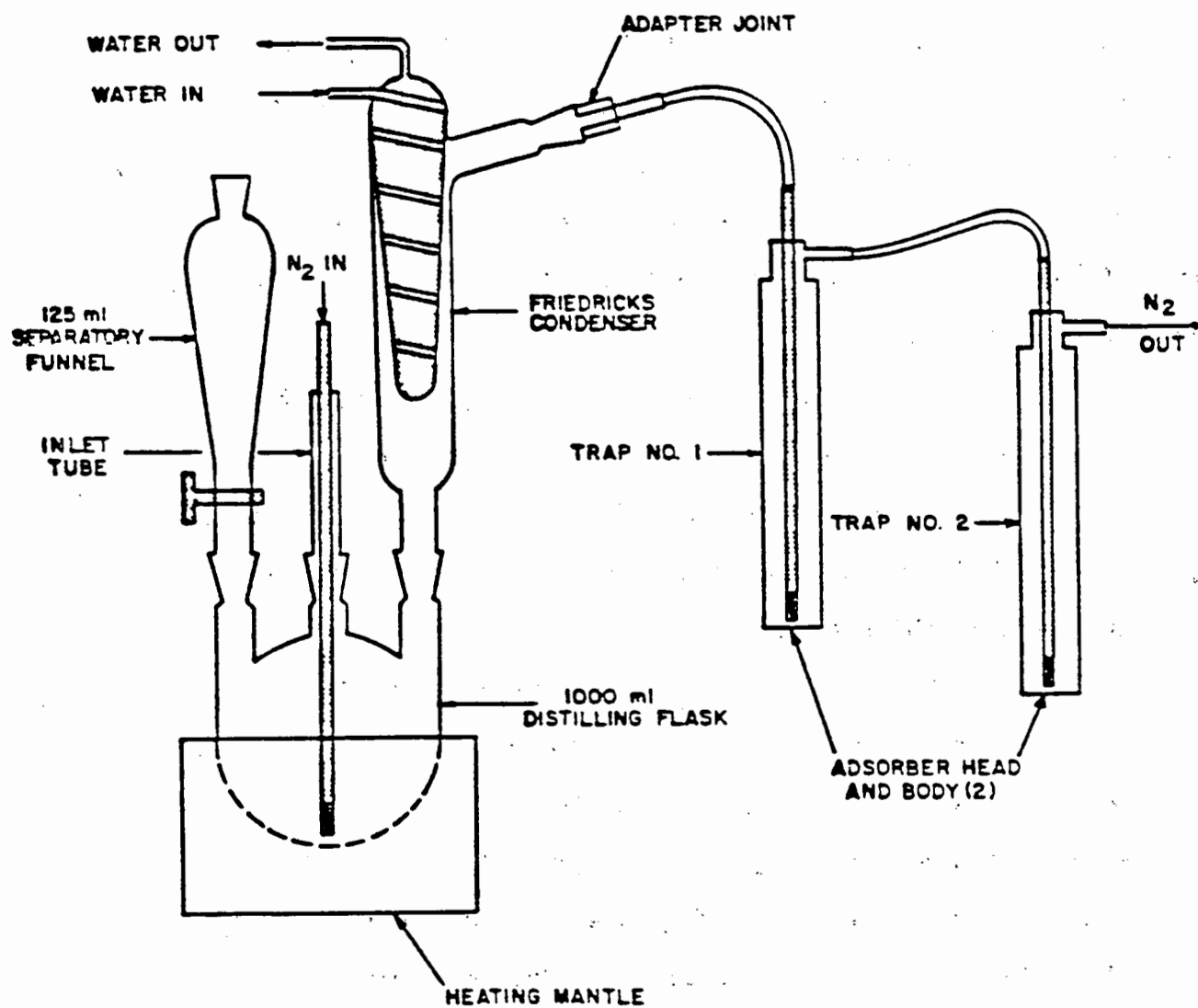
- (C) The Minimum Reportable Concentration (MRC) should be determined periodically by each participating laboratory in accordance with the procedures specified in Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater - EPA-600/4-82-057 July 1982, EMSL, Cincinnati, OH 45268.
- (D) A minimum of one spiked and one duplicate sample must be run with 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 MRC (See Section (7)(C)) for MRC samples, and at x when x is the concentration found if in excess of the MRC. Spike recovery

must be 60 to 120 percent for the analysis of a particular matrix type to be considered valid.

- (E) Report all results in mg/liter. When duplicate and spike samples are analyzed, report all data with the sample results.



FIGURE 1  
EQUIPMENT ASSEMBLY



## II. APPLICABILITY OF THE SULFIDE PRETREATMENT STANDARDS.

Amend 40 C.F.R. § 425.04 by adding a new section 425.04(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) in order to determine whether the sulfide pretreatment standards contained in this Part are applicable.

Amend 40 C.F.R. § 425.04 by adding a new section 425.04(d)(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.

Amend 40 C.F.R. § 425.04 by adding a new section 425.04(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 the 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.

### III. SUBCATEGORY WATER USE RATIOS.

Amend 40 C.F.R. § 425.11 by substituting:

Pollutant or Pollutant Property	BPT Limitations	
	Maximum for Any One Day	Maximum for Monthly Average
	Kg/KKg (or Pounds per 1,000 lb.) of Raw Material	
BOD <sub>5</sub>	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 6.0 to 9.0

Amend 40 C.F.R. § 425.15(b) by substituting:

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

Amend 40 C.F.R. § 425.31 by substituting:

Pollutant or Pollutant Property	BPT Limitations	
	Maximum for Any One Day	Maximum for Monthly Average
	Kg/KKg (or Pounds per 1,000 lb.) of Raw Material	
BOD <sub>5</sub>	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 6.0 to 9.0

Amend 40 C.F.R. § 425.35(a) by substituting:

PSES Limitations

Pollutant or Pollutant Property	Maximum for	Maximum for
	Any One Day	Monthly Average
	<u>Milligrams Per Liter (mg/l)</u>	
Sulfide	24	--
Total Chromium	12	8
pH	(1)	(1)

(1) Not less than 7.0

Amend 40 C.F.R. § 425.35(b) by substituting:

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

Amend 40 C.F.R. § 425.41 by substituting:

BPT Limitations

Pollutant or Pollutant Property	Maximum for	Maximum for
	Any One Day	Monthly Average
	<u>Kg/KKg (or Pounds per 1,000 lb.) of Raw Material</u>	
BOD <sub>5</sub>	8.9	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 6.0 to 9.0

Amend 40 C.F.R. § 425.44 by substituting:

NSPS Limitations

Pollutant or Pollutant Property	Maximum for	
	Any One Day	Monthly Average
	Kg/KKg (or Pounds per 1,000 lb.) of Raw Material	
BOD <sub>5</sub>	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 6.0 to 9.0

Amend 40 C.F.R. § 425.51 by substituting:

BPT Limitations

Pollutant or Pollutant Property	Maximum for	
	Any One Day	Monthly Average
	Kg/KKg (or Pounds per 1,000 lb.) of Raw Material	
BOD <sub>5</sub>	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 6.0 to 9.0

Amend 40 C.F.R. § 425.61 by substituting:

BPT Limitations

Pollutant or Pollutant Property	Maximum for	
	Any One Day	Monthly Average
	Kg/KKg (or Pounds per 1,000 lb.) of Raw Material	
BOD <sub>5</sub>	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 6.0 to 9.0

Amend 40 C.F.R. § 425.64 by substituting:

Pollutant or Pollutant Property	NSPS Limitations	
	Maximum for Any One Day	Maximum for Monthly Average
	Kg/KKg (or Pounds per 1,000 lb.) of Raw Material	
BOD <sub>5</sub>	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 6.0 to 9.0

Amend 40 C.F.R. § 425.71 by substituting:

Pollutant or Pollutant Property	BPT Limitations	
	Maximum for Any One Day	Maximum for Monthly Average
	Kg/KKg (or Pounds per 1,000 lb.) of Raw Material	
BOD <sub>5</sub>	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 6.0 to 9.0

Amend 40 C.F.R. § 425.91 by substituting:

Pollutant or Pollutant Property	BPT Limitations	
	Maximum for Any One Day	Maximum for Monthly Average
	Kg/KKg (or Pounds per 1,000 lb.) of Raw Material	
BOD <sub>5</sub>	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 6.0 to 9.0

Amend 40 C.F.R. § 425.95(b) by substituting:

Any existing source subject to this subpart which processes less than 3,600 splits/day shall comply with section 425.95(a), except that the Total Chromium limitations contained in section 425.95(a) do not apply.

EXHIBIT B

PREAMBLE LANGUAGE TO 40 C.F.R. PART 425

**I     SUBCATEGORY WATER USE RATIOS.**

    Add the following preamble language:

    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 as well as changes in the number of plants in the subcategory data bases and the number of plants achieving the 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

<u>Subcategory</u>	<u>Number of plants in subcategory data base</u>	<u>Median water use ratio (gallons per pound)</u>	<u>Number of plants in data base achieving water use ratio</u>
1	34	6.6	17
2	4	5.8	3
3	11	4.8	6
4	7	6.3	4
5	10	5.7	5
6	3	2.3	2
7	2	10.7	1
8	2	5.0	1
9	6	4.1	3



TABLE 2

<u>Subcategory</u>	<u>New source water use ratio (gallons per pound)</u>	<u>Number of plants in data base achieving water use ratio</u>
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

**II. SMALL TANNERY EXEMPTION.**

Add the following preamble language:

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 Fed. Reg. 30,115. Subsequent to discussing this matter with TCA, the Agency has reconsidered this issue. The Agency plans to delete 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 work week could qualify for the exemption.

Add the following preamble language:

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.

### **III. CHANGES IN SUBCATEGORIZATION.**

Add the following preamble language:

Under 40 C.F.R. § 403.6(a) of the general pretreatment regulations, an existing industrial user or a POTW may seek written certification from the Agency 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 C.F.R. § 403.6(a). In fact, 40 C.F.R. § 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 Agency as to whether the facility falls within a particular subcategory prior to commencing discharges which would fall within that subcategory.

### **IV. MULTIPLE OUTFALLS.**

Add the following preamble language:

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 the process wastewater flow in each outfall to the total flow of process wastewaters discharged through all outfalls. <sup>1/</sup> 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.

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<sup>1/</sup> If non-process 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" (40 C.F.R. § 403.6(e)) to make this calculation.

## EXHIBIT C

### TCA MEMBERS

Acme Sponge & Chamois Co.  
Allied Leather Co. (Feuer)  
Amdur Braude Riley, Inc.  
American Leather Mfg. Co.  
Armira Company  
Badger State Tanning Corp.  
Beatrice, Leather Div.  
Beggs & Cobb Corp.  
Berkshire Tanning Corp.  
Blackhawk Tanning Co., Ltd.  
The Blueside Companies, Inc.  
Baldwell Lace Leather Co.  
Calnap Tanning Company  
Camden Tanning Corp.  
Carr Leather Company  
Chaudhutta Tanning Company  
Classic Leather Corporation  
Coey Tanning Company, Inc.  
Collins-Johnsen, Inc.  
Conneaut Leather, Inc.  
Cromwell Leather Co., Inc.  
Del-Tan Corporation  
Delta Tanning Corporation  
Dreher Leather Mfg. Corp.  
Eagle Ottawa Leather Company  
Elithorp Tanning Company  
Fashion Tanning Company, Inc.  
Fermion Leather Company  
Feuer Leather Group  
Paul Flagg, Inc.  
John Flynn & Sons, Inc.  
J.B. Foot Tanning Co.  
The Fouke Company  
Fox Valley Leathers, Inc.  
Frontier Leather Co., Inc.  
J.F. Gallun & Sons Corp.  
Garden State Tanning  
Gerlin & Company, Inc.  
J.L. Gebhardt Company  
General Split Corporation  
Genesco, Inc.  
Gordon-Gruenstein, Inc.  
Granite State Leathers, Inc.  
Hunnison Brothers, Inc.  
Hermann Oak Leather Company  
Horizon Leather Company

Horween Leather Company  
Howes Leather Company, Inc.  
Hoyt & Worthen Tanning Corp.  
Huch Leather Company  
Irving Tanning Company  
JBF Industries, Inc.  
JEC Tanning Company, Inc.  
Kroy Tanning Company, Inc.  
Lackawanna Leather Company  
Lannom Tannery  
A.C. Lawrence Leather Co., Inc.  
Leather's Best, Inc.  
Liberty Leather Corp.  
Hermann Loewenstein, Inc.  
Los Angeles Tanning Company  
MTE Corporation  
Manasse-Block Tanning Company  
Mason Tanning Company, Inc.  
Master Inc.  
Middlesboro Tanning Co. of Del.  
Middlesboro Tanning Company  
Midwest Tanning Company  
Moench Tanning Company  
Moran Leather Company  
George Moser Leather Co., Inc.  
New Jersey Tanning Co., Inc.  
Norwich Leather Company  
Ocean Leather Corp.  
Pfister & Vogel Tanning Co.  
W.B. Place & Company  
Poetsch & Peterson  
Pollet Leather Co.  
Prime Tanning Company, Inc.  
Radel Leather Manufacturing Co.  
Remis Industries  
W.C. Reynolds Company, Inc.  
Richard Leather Co., Inc.  
John J. Riley Company  
A.H. Ross & Sons Co.  
Fred Rueping Leather Co.  
F. Rulison and Sons, Inc.  
Salz Leather, Inc.  
Sawyer Tanning Company  
Scholze Tannery  
Schwarz Leather Corp.  
Seidel Tanning Corp.

Seton Leather Corp.  
Shrut & Asch Leather Co., Inc.  
Stock Kojima  
The Sidney Tanning Company  
Sierra Pine Tanning Company  
Sigma Leather, Inc.  
Sirois Leather, Inc.  
Slip-Not Belting Corporation  
John Smidt Co. Inc.  
Steinberg Bros., Inc.  
Suncook Tanning Corporation  
Tanners' Council Laboratory  
Tennessee Tanning Company  
Texas Tanning  
Thiele Tanning Company  
Travel Leather Company, Inc.  
Twin City Leather Company, Inc.  
Vernon Leather Company  
Victory Tanning Corporation  
Volunteer Leather Company  
Western Leather Products Corp  
Whitehall Leather Company  
Wolverine Leather Division  
Wood and Hyde Leather Compa