State of Wisconsin \ DEPARTMENT OF NATURAL RESOURCES

Scott McCallum, Governor
Darrell Bazzell, Secretary

101 S. Webster St.
Box 7921
Madison, Wisconsin 53707-7921
Telephone 608-266-2621
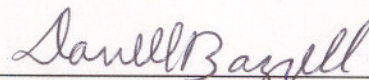FAX 608-267-3579
TTY 608-267-6897

**WISCONSIN
DEPT. OF NATURAL RESOURCES**

STATE OF WISCONSIN   )
)   ss

DEPARTMENT OF NATURAL RESOURCES   )

TO ALL TO WHOM THESE PRESENTS SHALL COME, GREETINGS:

I, Darrell Bazzell, Secretary of the Department of Natural Resources and custodian of the official records of said Department, do hereby certify that the annexed copy of Natural Resources Board Order No. WT-8-99 was duly approved and adopted by this Department on January 24, 2001. I further certify that said copy has been compared by me with the original on file in this Department and that the same is a true copy thereof, and of the whole of such original.

IN TESTIMONY WHEREOF, I have hereunto set my hand and affixed the official seal of the Department at the Natural Resources Building in the City of Madison, this _20 th_ day of March, 2001.

Darrell Bazzell

Darrell Bazzell, Secretary

(SEAL)

www.dnr.state.wi.us
www.wisconsin.gov

*Quality Natural Resources Management
Through Excellent Customer Service*

Printed on
Recycled
Paper

The Wisconsin Natural Resources Board proposes an order to amend NR 252.02(12), 252.11, 252.15. 252.25, 252.31, 252.35, 252.41, 252.44, 252.51, 252.61, 252.64, 252.65, 252.71, 252.85, 252.91 and 252.95(2); to repeal and recreate NR 252.03; and to create NR 252.035, 252.036, 252.0365 and 252.04(4) relating to effluent limitations and pretreatment standards for the leather tanning and finishing industry.

WT-8-99

Analysis Prepared by the Department of Natural Resources

Statutory authority: ss: 283.11(1), 283.19(1), 283.21(1), and 227.11(2)(a), Stats.
Statutes interpreted: ss: 283.11, 283.13, 283.19, and 283.21, Stats.

The Federal Water Pollution Control Act amendments of 1972 established a comprehensive program to "restore and maintain the chemical, physical, and biological integrity of the Nation's waters." (33 USC s. 1251(a)). To implement the act, the U.S. Environmental Protection Agency issues effluent limitation guidelines, pretreatment standards, and new source performance standards for industrial wastewater discharges. The Clean Water Act of 1977 expanded the federal pollution control program by setting different types of effluent limitations: "best practicable technology" (BPT), "best available technology" (BAT), "best conventional technology" (BCT), "new source performance standards" (NSPS), "pretreatment standards for existing sources" (PSES), and "pretreatment standards for new sources" (PSNS). The Clean Water Act stresses control of toxic pollutants, including 65 "priority" pollutants and classes of pollutants in 21 major industries.

The Wisconsin Department of Natural Resources instituted the Wisconsin pollutant discharge elimination system in 1976. This system included regulation of effluent discharges from various industries. The Wisconsin Department of Natural Resources is amending ch. NR 252, Wis. Adm. Code, to regulate the leather tanning and finishing industry. The provisions of this chapter are based upon the U.S. Environmental Agency's regulations in 40 CFR 425.

The purpose of these amendments is to specify effluent limitations for BPT, BCT, BAT, and NSPS for the direct discharge of pollutants to waters of the state and to establish pretreatment standards for the introduction of pollutants into publicly owned treatment works. The effect of amending ch. NR 252, Wis. Adm. Code will be to amend state standards and limitations for industrial wastewater discharges from the leather tanning and finishing industry. The Code will reflect these changes made by the United States Environmental Protection Agency under authority of sections 301, 304, 306, 307, 308 and 501 of the Clean Water Act. (33 USC ss. 1311, 1314, 1316, 1318, and 1361).

These amendments add new analytical methods for the measurement of sulfide in wastewaters at certain tanneries, clarify procedural requirements for POTWs to follow in determining whether sulfide pretreatment standards are applicable, revise effluent limitations for BPT and NSPS, and clarify the production levels below which the chromium PSES do not apply. Finally the amendments remove the upper pH limit for PSES at certain tanneries.

This proposed rule is essentially identical to 40 C.F.R. Part 425 for purposes of s. 227.14(1m)(b), Stats. However, changes have been made in the text of the federal regulation to make the rule useful

to Wisconsin citizens, industry, and regulating authorities. These changes are consistent with the current state regulatory framework and reflect the conventions of state rule drafting. Where possible, Wisconsin Administrative Code references were substituted in the text for reference to the Code of Federal Regulations.

SECTION 1. NR 252.02(12) is amended to read:

NR 252.02(12) "Sulfide" means total sulfide as measured by the ~~Society of Leather Trades' Chemists method SLM 4/2 as described in s. NR 252.03.~~ potassium ferricyanide titration method described in s. NR 252.035 or the modified Monier- Williams method described in s. NR 252.036.

SECTION 2. NR 252.03 is repealed and recreated to read:

NR 252.03 Sulfide analytical method. (1) The potassium ferricyanide titration method described in s. NR 252.035 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 section in s. NR 252.30. In all other cases, the modified Monier-Williams method as described in s. NR 252.036 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 sections except ss NR 252.30.

(2) The modified Monier-Williams method as described in s. NR 252.036 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 pursuant to s. NR 252.30.

SECTION 3. NR 252.035 is created to read:

NR 252.035 Potassium ferricyanide titration method. The following 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 and is to be used for the determination of sulfide in alkaline wastewater.

(1) OUTLINE OF METHOD. (a) 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 shall be precipitated with barium chloride. Thiosulfate is not titrated under the conditions of the determination.

(b) Apparatus: burrette, 10 ml.

(2) REAGENT. (a) 0.1 Preparation of 0.02 N potassium ferricyanide; -32.925 g. per liter - this solution must be kept in the dark. Weigh to the nearest tenth of a gram 6.6 g. of analytical reagent grade potassium ferricyanide and dissolve in one 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 one g., mix gently to dissolve, add one ml. of 6N hydrochloric acid, stopper the flask, and swirl gently. Let stand for 2 minutes, add 10 ml. of a 30% 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-

2

0.050N. Add one 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:

$$\text{Normality of Potassium Ferricyanide} = \frac{\text{(ml of thiosulfate added)} \times \text{(normality of thiosulfate)}}{\text{Ml of } K_3 Fe(CN)_6}$$
$K_3 Fe(CN)_6$

(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 one liter with distilled water. The buffer may 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 one liter of distilled water.

(e) Preparation of ferrous dimethylglyoxime indicator solution: Mix 10 ml. 0.6 percent ferrous sulfate, 50 ml. one 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 one 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.

(g) Preparation of 10N NaOH: Dissolve 400 g. of analytical reagent grade NaOH in one liter distilled water.

(h) Sample preservation and storage: samples are to be field filtered by either gravity or pressure with coarse filter paper, such as 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 degrees C until analysis. Samples shall 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 shall provide documentation of sample integrity.

(3) 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 HC1.

(c) Add 20 ml. of 6M ammonium chloride buffer (pH 9.3), one ml. of ferrous dimethylglyoxime indicator, and 25 ml. of 0.05M 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.

(e) Calculation and reporting of results.

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

where A = volume in ml. of potassium ferricyanide solution used, and B = normality of potassium ferricyanide solution. Report results to 2 significant figures.

(4) 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 shall 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 shall demonstrate the ability to generate acceptable precision and accuracy with this method by performing the following operations.

1. Perform 4 replicate analyses of a 20 mg/l sulfide standard prepared in distilled water. See sub. (2)(f).

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

b. 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 4 replicate analyses shall be within the range of 50 to 110% of the true value.

(c) The method detection limits or MDL may 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 s. NR 252.0365.

(d) A minimum of one spiked and one duplicate sample shall be performed for each analytical event, or 5% spikes and 5% duplicates when the number of samples per event exceeds 20. Spike levels are to be at the MDL and at x where x is the concentration found if in excess of the MDL. See par. (c) for MDL samples. Spike recovery shall be 40 to 120% 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 shall be repeated using the modified Monier-Williams procedures described in s. NR 252.036.

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

SECTION 4. NR 252.036 is created to read:

NR 252.036 Modified Monier-Williams method. (1) OUTLINE OF METHOD. (a) Hydrogen sulfide is liberated from an acidified sample by distillation and purging with nitrogen gas (N₂). 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)).

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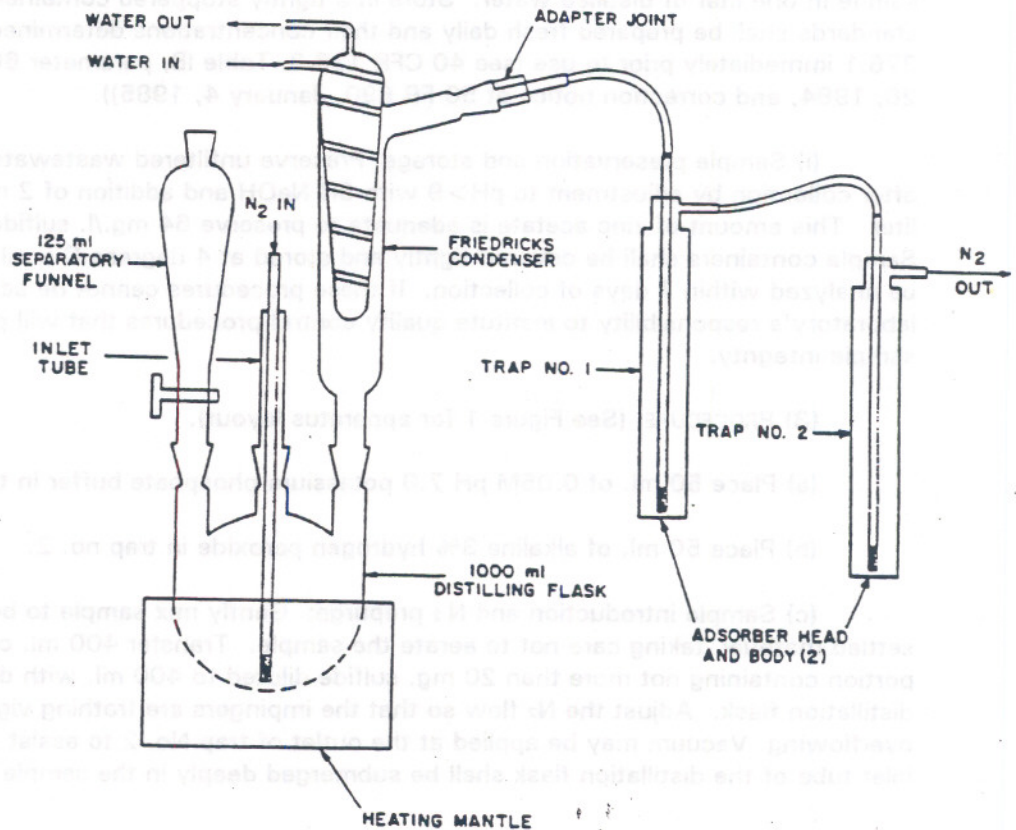Inlet tube with 24/40 joint (VWR Cat. No. 33057-105)
Adapter joint 24/40 to 19/38 (VWR Cat. No. 62905-26)
Adsorber head (2 required) (Thomas Cat. No. 9849-R29)
Adsorber body (2 required) (Thomas Cat. No. 9849-R32)
Laboratory vacuum pump or water aspirator

FIGURE 1
EQUIPMENT ASSEMBLY

(2) REAGENTS. (a) Potassium hydroxide, 6N: Dissolve 340 g. of analytical reagent grade KOH in one liter distilled water.

(b) Sodium hydroxide, 6N: Dissolve 240 g. of analytical reagent grade NaOH in one liter distilled water.

(c) Sodium hydroxide, 0.03N: Dilute 5.0 ml. of 6N NaOH to one liter with distilled water.

(d) Hydrochloric acid, 6N: Dilute 500 ml. of concentrated HCl to one liter with distilled water.

(e) Potassium phosphate stock buffer, 0.5M: Dissolve 70 g. of monobasic potassium phosphate in approximately 800 ml. distilled water. Adjust pH to 7.0 0.1 with 6N potassium hydroxide and dilute to 1 liter with distilled water. Stock solution in stable for several months at 4 degrees C.

(f) Potassium phosphate buffer, 0.05M: Dilute one volume of 0.5M potassium phosphate stock buffer with 9 volumes of distilled water. Solution is stable for one month at 4 degrees C.

(g) Alkaline 3% hydrogen peroxide: Dilute one volume of 30 % 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 one liter of distilled water. Store in a tightly stoppered container. Diluted working standards shall 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)).

(i) Sample preservation and storage: Preserve unfiltered wastewater samples immediately after collection by adjustment to pH > 9 with 6N NaOH and addition of 2 ml. of 2N zinc acetate per liter. This amount of zinc acetate is adequate to preserve 64 mg./l. sulfide under ideal conditions. Sample containers shall be covered tightly and stored at 4 degrees C until analysis. Samples shall be analyzed within 7 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.

(3) 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% hydrogen peroxide in trap no. 2.

(c) Sample introduction and N_2 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 shall be submerged deeply in the sample to ensure efficient

6

agitation. Purge the sample for 30 minutes without applying heat. Test the apparatus for leaks during the prepurge cycle using snoop or soap water solution.

(d) Volatilization of H_2 S: 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, 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 shall be exercised in terminating the distillation cycle to avoid flash-over, draw-back, or violent steam release.

(e) 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.

(f)1. Calculations and reporting of results

2. Gravimetric procedure:

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

3. 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

4. Report results to 2 significant figures.

(4) QUALITY CONTROL. (a) Each laboratory that uses this method shall 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 shall maintain performance records to define the quality of data that is generated. Ongoing performance checks shall 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 shall demonstrate the ability to generate acceptable accuracy and precision by performing the following operations.

1. Perform 4 replicate analyses of a 20 mg./l. sulfide standard prepared in distilled water. Refer to par. (h) under "Reagents."

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

b. 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 4 replicate analyses shall be within the range of 72 to 114% of the true value.

(c) The method detection limit or MDL may be determined periodically by each participating laboratory in accordance with the procedures specified in "Methods for Chemical Analysis of Municipal and Industrial Wastewater," EPA- 600/4-82-057, July 1982, EMSL, Cincinnati, OH 45268. For the convenience of the user, these procedures are contained in s. NR 252.045.

(d) A minimum of one spiked and one duplicate sample shall be run for each analytical event, or 5% spikes and 5% duplicates when the number of samples per event exceeds 20. Spike levels are to be at the MDL and at x when x is the concentration found if in excess of the MDL. See sub. (c) of this section for MDL samples. Spike recovery shall be 60 to 120% for the analysis of a particular matrix type to be considered valid.

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

SECTION 5. NR 252.0365 is created to read:

NR 252.0365 Method detection limit method. (1) DEFINITION. "Method detection limit" or "MDL" means the minimum concentration of a substance that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero and determined from analysis of a sample in a given matrix containing analyte.

(2) SCOPE AND APPLICATION. This procedure is designed for applicability to a wide variety of sample types ranging from reagent or blank water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. All sample processing steps of the analytical method shall be included in the determination of the MDL. 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.

(3) PROCEDURE. (a) Make an estimate of the detection limit using one of the following:

1. The concentration value that corresponds to an instrument signal or 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 shall be considered in making the estimate.

2. The concentration value that corresponds to 3 times the standard deviation of replicate instrumental measurements for the analyte in reagent water.

8

3. The concentration value that corresponds to the region of the standard curve where there is a significant change in sensitivity at low analyte concentrations, such as a break in the slope of the standard curve.

4. The concentration value that corresponds to known instrumental limitations.

(b) Prepare reagent or 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 or interferent. The interferent concentration is presupposed to be normally distributed in representative samples of a given matrix.

(c)1. If the MDL is to be determined in reagent or blank water, prepare a laboratory standard such as an analyte in reagent water at a concentration which is at least equal to or in the same concentration range as the estimated MDL. It is recommended to be between one and 5 times the estimated MDL. Proceed to par. (d).

2. 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 5 times the estimated MDL, proceed to par. (d).

3. 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 5 times the MDL. In the case where an interference is coanalyzed with the analyte and the measured level of analyte is greater than 5 times the estimated MDL, there are 2 options:

a. Obtain another sample of lower level of analyte in same matrix if possible.

b. 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.

(d)1. Take a minimum of 7 aliquots of the sample to be used to calculate the MDL and process each through the entire anlaytical 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 anlayzed. The average blank measurement is subtracted from the respective sample measurements.

2. It may be economically and technically desirable to evaluate the estimated MDL before proceeding with subd.1. This will prevent repeating this entire procedure when the costs of analyses are high and 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 5 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 2 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 subd.1. Evaluate these data:

a. If these measurements indicate the sample is in the desirable range for determining the MDL, take 5 additional aliquots and proceed. Use all 7 measurements to calculate the MDL.

b. If these measurements indicate the sample is not in the correct range, reestimate the MDL, obtain new sample as in par. (c) and repeat either subd.1. or 2.

(e) 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.

(f)1. 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% confidence level and a standard deviation estimate with n-1 degrees of freedom as given in subd. 6.
S = standard deviation of the replicate analyses.

2. The 95% confidence limits for the MDL derived in par. (f)1. are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution (X2/df) and calculated as follows:

MDLLCL = 0.69 MDL
MDLUCL = 1.92 MDL where MDLLCL and MDLUCL are the lower and upper 95% confidence limits respectively based on 7 aliquots.

(g)1. Optional iterative procedure to verify the reasonableness of the estimated MDL and calculated MDL of subsequent MDL determinations.

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

3. 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.

10

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

if $\dfrac{S^2_A}{S^2_B}$ < 3.05

then compute the spooled standard deviation by the following equation:

$$^S\text{pooled} = \dfrac{[\ 6S_A{}^2 + 6S_B{}^2\ ]^{0.5}}{12}$$

if $\dfrac{S^2_A}{S^2_B}$ > 3.05

respike at the last calculated MDL and process the samples through the procedure starting with par. (d).

5. Use the ^{S}pooled as calculated in subd. 3. to compute the final MDL according to the following equation:

MDL = 2.681 (^{S}pooled)
where 2.681 is equal to t (12, 1-a = .99)

6. The 95% confidence limits for MDL derived in g.4. are computed according to the following equations derived from percentiles of the chi squared over degrees of freedom distribution.

MDLLCL = 0.72 MDL
MDLUCL = 1.65 MDL

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

(4) REPORTING. The analytical method used shall 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 shall be specified with the MDL value. The sample matrix used to determine the MDL shall 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.

(5) 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).

(6) TABLE OF STUDENTS' T VALUES AT THE 99% CONFIDENCE LEVEL

Number of replicates	Degrees of freedom (n-1)	t (n-1, 1-a = .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

SECTION 6. NR 252.04(4) is created to read:

NR 252.04(4)(a) Applicability of sulfide pretreatment standards. If, after EPA and the POTW have determined in accordance with this section that the sulfide pretreatment standards of this chapter are not applicable to specified facilities, a POTW then determines that there have been changed circumstances which justify application of the sulfide pretreatment standards, the POTW shall revoke the certification submitted under sub. (3). Circumstances include, but are not limited to, changes in the factors specified in sub. (2). The POTW and EPA shall then adhere to the general procedures and time intervals contained in sub. (3) in order to determine whether the sulfide pretreatment standards contained in this chapter are applicable.

(b) If pursuant to par. (a) the sulfide pretreatment standards of this chapter 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.

(c) At any time after October 13, 1983, if a POTW determines that there have been changed circumstances which include, but are not limited to, changes in the factors specified in sub. (2), it may initiate proceedings contained in sub. (3) to determine that the sulfide pretreatment standards of this section shall not be applicable. The POTW and EPA shall follow the procedures and time intervals contained in sub. (3) to make this determination. A final determination that the sulfide pretreatment standards are not applicable shall be made prior to the discharge of sulfide not in accordance with the standards set forth in this chapter.

SECTION 7. NR 252.11 is amended to read:

NR 252.11 Effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT). Except as provided in 40 CFR 125.30-125.32, any existing point source subject to this subcategory shall achieve the following effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT):

Pollutant or pollutant property	BPT limitations kg/kkg (or pounds per 1000 lb) of raw material	
	Maximum for any 1 day	Maximum for monthly average
BOD5	~~9.1~~ 9.3	~~4.1~~ 4.2
TSS	~~13.2~~ 13.4	~~6.0~~ 6.1
Oil & grease	3.8 3.9	1.7
Total chromium	~~0.23~~ 0.24	0.09
pH	(¹)	(¹)

¹Within the range 6.0 to 9.0.

SECTION 8. NR 252.15 is amended to read:

NR 252.15 Pretreatment standards for existing sources (PSES). (1) Except as provided in s. NR 252.04 and 40 CFR 403.7 and 403.13, any existing source subject to this subcategory which introduces process wastewater pollutants into a publicly owned treatment works shall comply with 40 CFR Part 403, and achieve the following pretreatment standards:

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

1~~Within the range 7.0 to 10.0.~~ Not less than 7.0.

(2) Any existing source subject to this subcategory which processes less than 275 hides/day ~~(3.9 million pounds per year, at 260 working days per year)~~ shall comply with sub. (1), except that the total chromium limitations contained in sub. (1) do not apply.

SECTION 9. NR 252.25 is amended to read:

NR 252.25 Pretreatment standards for existing sources (PSES). Except as provided in s. NR 252.04 and 40 CFR 403.7 and 403.13, any existing source subject to this subcategory which introduces process wastewater pollutants into a publicly owned treatment works shall comply with 40 CFR Part 403, and achieve the following pretreatment standards:

Pollutant or pollutant property	PSES Milligrams per liter (mg/l)	
	Maximum for any 1 day	Maximum for monthly average
Sulfide..24		....
Total chromium...12		8
pH..(^{1})		(^{1})

^{1} ~~Within the range 7.0 to 10.0.~~ <u>Not less than 7.0.</u>

SECTION 10. NR 252.31 is amended to read:

NR 252.31 Effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT). Except as provided in 40 CFR 125.30-125.32, any existing point source subject to this subcategory shall achieve the following effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT):

Pollutant or pollutant property	BPT limitations kg/kkg (or pounds per 1000 lb) of raw material	
	Maximum for any 1 day	Maximum for monthly average
BOD5	~~6.9~~ 6.7	~~3.1~~ 3.0
TSS	~~9.9~~ 9.7	~~4.5~~ 4.4
Oil & grease	~~2.9~~ 2.8	1.3
Total chromium	~~0.18~~ 0.17	0.06
pH	(^{1})	(^{1})

^{1} Within the range of 6.0 to 9.0

SECTION 11. NR 252.35 is amended to read:

NR 252.35 Pretreatment standards for existing sources. (1) Except as provided in s. NR 252.04 and 40 CFR 403.7 and 403.13, any existing source subject to this subcategory which introduces process wastewater pollutants into a publicly owned treatment works shall comply with 40 CFR Part 403, and achieve the following pretreatment standards:

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

¹~~Within the range 7.0 to 10.0.~~ Not less than 7.0.

(2) Any existing source subject to this subcategory which processes less than 350 hides/day ~~(5.4 million pounds per year, at 260 working days per year)~~ shall comply with s. NR 252.35(1), except that the total chromium limitations contained in sub. (1) do not apply.

SECTION 12. NR 252.41 is amended to read:

NR 252.41 Effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT). Except as provided in 40 CFR 125.30-125.32, any existing point source subject to this subcategory shall achieve the following effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT):

Pollutant or pollutant property	BPT limitations kg/kkg (or pounds per 1000 lb) of raw material			
	Maximum for any 1 day		Maximum for monthly average	
BOD5	~~6.7~~	8.9	~~3.0~~	4.0
TSS	~~9.7~~	12.8	4.4	5.8
Oil & grease	~~2.8~~	3.7	~~1.3~~	1.7
Total chromium	~~0.17~~	0.23	~~0.06~~	0.08
pH	(¹)		(¹)	

¹ Within the range of 6.0 to 9.0

SECTION 13. NR 252.44 is amended to read:

NR 252.44 New source performance standards (NSPS). Any new source subject to this subcategory shall achieve the following new source performance standards (NSPS):

Pollutant or pollutant property	NSPS kg/kkg (or pounds per 1000 lb) of raw material			
	Maximum for any 1 day		Maximum for monthly average	
BOD5	~~6.3~~	6.5	~~2.8~~	2.9
TSS	~~9.1~~	9.3	~~4.2~~	4.3
Oil & grease		2.7		1.2
Total chromium	~~0.16~~	0.17		0.06
pH		(¹)		(¹)

¹ Within the range of 6.0 to 9.0

SECTION 14. NR 252.51 is amended to read:

NR 252.51 Effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT). Except as provided in 40 CFR 125.30-125.32, any existing point source subject to this subcategory shall achieve the following effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT):

Pollutant or pollutant property	BPT limitations kg/kkg (or pounds per 1000 lb) of raw material			
	Maximum for any 1 day		Maximum for monthly average	
BOD5	~~8.2~~	8.0	~~3.7~~	3.6
TSS	~~11.8~~	11.6	~~5.4~~	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

SECTION 15. NR 252.61 is amended to read:

NR 252.61 Effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT). Except as provided in 40 CFR 125.30-125.32, any existing point source subject to this subcategory shall achieve the following effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT):

Pollutant or pollutant property	BPT limitations kg/kkg (or pounds per 1000 lb) of raw material	
	Maximum for any 1 day	Maximum for monthly average
BOD5	~~3.0~~ 3.2	~~1.3~~ 1.5
TSS	~~4.3~~ 4.7	~~1.9~~ 2.1
Oil & grease	~~1.2~~ 1.4	~~0.6~~ 0.61
Total chromium	0.08	0.03
pH	(¹)	(¹)

¹ Within the range of 6.0 to 9.0

SECTION 16. NR 252.64 is amended to read:

NR 252.64 New source performance standards. Any new source subject to this subcategory shall achieve the following new source performance standards (NSPS):

Pollutant or pollutant property	NSPS kg/kkg (or pounds per 1000 lb) of raw material	
	Maximum for any 1 day	Maximum for monthly average
BOD5	~~2.0~~ 3.0	~~0.88~~ 1.3
TSS	~~2.8~~ 4.3	~~1.3~~ 1.9
Oil & grease	~~0.8~~ 1.2	~~0.4~~ 0.55
Total chromium	~~0.05~~ 0.08	~~0.02~~ 0.03
pH	(¹)	(¹)

¹ Within the range of 6.0 to 9.0

SECTION 17. NR 252.65 is amended to read:

NR 252.65 Pretreatment standards for existing sources (PSES). Except as provided in s. NR 252.04 and 40 CFR 403.7 and 403.13, any existing source subject to this subcategory which introduces process wastewater pollutants into a publicly owned treatment works shall comply with 40 CFR Part 403, and achieve the following pretreatment standards:

Pollutant or pollutant property	PSES Milligrams per liter (mg/l)	
	Maximum for any 1 day	Maximum for monthly average
Sulfide	24.0	....
Total chromium	12.0	8.0
pH	(¹)	(¹)

¹~~Within the range 7.0 to 10.0.~~ <u>Not less than 7.0.</u>

SECTION 18. NR 252.71 is amended to read:

NR 252.71 Effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT). Except as provided in 40 CFR 125.30-125.32, any existing point source subject to this subcategory shall achieve the following effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT):

Pollutant or pollutant property	BPT limitations kg/kkg (or pounds per 1000 lb) of raw material			
	Maximum for any 1 day		Maximum for monthly average	
BOD5	~~13.2~~	15.0	~~5.9~~	6.8
TSS	~~19.1~~	21.7	~~8.7~~	9.9
Oil & grease	~~5.6~~	6.3	~~2.5~~	2.8
Total chromium	~~0.34~~	0.39	~~0.12~~	0.14
pH		(¹)		(¹)

¹ Within the range of 6.0 to 9.0

SECTION 19. NR 252.85 is amended to read:

NR 252.85 Pretreatment standards for existing sources (PSES). Except as provided in s. NR 252.04 and 40 CFR 403.7 and 403.13, any existing source subject to this subcategory which introduces process wastewater pollutants into a publicly owned treatment works shall comply with 40 CFR Part 403, and achieve the following pretreatment standards:

Pollutant or pollutant property	PSES Milligrams per liter (mg/l)	
	Maximum for any 1 day	Maximum for monthly average
Sulfide................................	24.0	....
Total chromium.....................	12.0	8.0
pH......................................	(^{1})	(^{1})

^{1}Within the range 7.0 to 10.0. Not less than 7.0.

SECTION 20. NR 252.91 is amended to read:

NR 252.91 Effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT). Except as provided in 40 CFR 125.30-125.32, any existing point source subject to this subcategory shall achieve the following effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT):

Pollutant or pollutant property	BPT limitations kg/kkg (or pounds per 1000 lb) of raw material			
	Maximum for any 1 day		Maximum for monthly average	
BOD5	4.2	5.8	1.9	2.6
TSS	6.1	8.3	2.8	3.8
Oil & grease	1.8	2.4	0.79	1.1
Total chromium	0.11	0.15	0.04	0.05
pH		(^{1})		(^{1})

^{1} Within the range of 6.0 to 9.0.

SECTION 21. NR 252.95(2) is amended to read:

NR 252.95(2) Any existing source subject to this subcategory which processes less than 3,600 splits/day (3.7 million pounds per year, at 260 working days per year) shall comply with s. NR 252.95 (1), except that the total chromium limitations contained in sub. (1) do not apply.

The foregoing rule was approved and adopted by the State of Wisconsin Natural Resources Board on January 24, 2001.
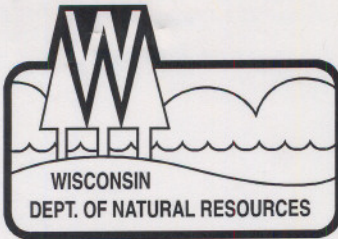
The rule shall take effect on the first day of the month following publication in the Wisconsin administrative register as provided in s. 227.22(2)(intro.), Stats.

Dated at Madison, Wisconsin ___March 20, 2001___

<div style="text-align:center">

STATE OF WISCONSIN
DEPARTMENT OF NATURAL RESOURCES

By _____
Darrell Bazzell, Secretary

</div>

(SEAL)

State of Wisconsin \ DEPARTMENT OF NATURAL RESOURCES
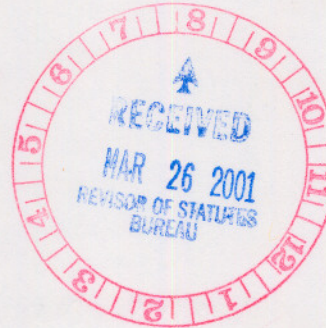
WISCONSIN
DEPT. OF NATURAL RESOURCES

Scott McCallum, Governor
Darrell Bazzell, Secretary

101 S. Webster St.
Box 7921
Madison, Wisconsin 53707-7921
Telephone 608-266-2621
FAX 608-267-3579
TTY 608-267-6897

March 19, 2001

Mr. Gary L. Poulson
Assistant Revisor of Statutes
131 West Wilson Street - Suite 800
Madison, WI

RECEIVED
MAR 26 2001
REVISOR OF STATUTES
BUREAU

Dear Mr. Poulson:

Enclosed are two copies, including one certified copy, of State of Wisconsin Natural Resources Board Order No. WT-8-99. These rules were reviewed by the Assembly Committee on Natural Resources and the Senate Committee on Environment pursuant to s. 227.19, Stats. Summaries of the final regulatory flexibility analysis and comments of the legislative review committees are also enclosed.

You will note that this order takes effect following publication. Kindly publish it in the Administrative Code accordingly.

Sincerely,

Darrell Bazzell
Secretary

Enc.