

**§ 425.92 Effluent limitations representing the degree of effluent reduction attainable by the application of the best conventional pollutant control technology (BCT).**

Except as provided in 40 CFR 125.30 through 125.32, any existing point source subject to this subpart must achieve the following effluent limitations representing the degree of effluent reduction attainable by the application of the best conventional pollutant control technology (BCT): The effluent limitations are those for BOD<sub>5</sub>, TSS, Oil and Grease, and pH contained in § 425.91.

**§ 425.93 Effluent limitations representing the degree of effluent reduction attainable by the application of the best available technology economically achievable (BAT).**

Except as provided in 40 CFR 125.30 through 125.32, any existing point source subject to this subpart must achieve the following effluent limitations representing the degree of effluent reduction attainable by the application of the best available technology economically achievable (BAT): The effluent limitations are those for Total Chromium contained in § 425.91.

**§ 425.94 New source performance standards (NSPS).**

Any new source subject to this subpart must achieve the following new source performance standards (NSPS):

Pollutant or pollutant property	NSPS	
	Maximum for any 1 day	Maximum for monthly average
	Kg/kgk (or pounds per 1,000 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 .....	( <sup>1</sup> )	( <sup>1</sup> )

<sup>1</sup> Within the range 6.0 to 9.0.

**§ 425.95 Pretreatment standards for existing sources (PSES).**

(a) Except as provided in 40 CFR 403.7 and 403.13, any existing source subject to this subpart that introduces process wastewater pollutants into a publicly owned treatment works must comply

with 40 CFR part 403, and must achieve the following pretreatment standards:

Pollutant or pollutant property	PSES	
	Maximum for any 1 day	Maximum for monthly average
	Milligrams per liter (mg/l)	
Total Chromium .....	19	12
pH .....	( <sup>1</sup> )	( <sup>1</sup> )

<sup>1</sup> Within the range 6.0 to 10.0.

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

[47 FR 52870, Nov. 23, 1982; 48 FR 30117, June 30, 1983, as amended at 53 FR 9183, Mar. 21, 1988]

**§ 425.96 Pretreatment standards for new sources (PSNS).**

Except as provided in 40 CFR 403.7, any new source subject to this subpart that introduces process wastewater pollutants into a publicly owned treatment works must comply with 40 CFR part 403, and achieve the pretreatment standards contained in § 425.95.

APPENDIX A TO PART 425—POTASSIUM FERRICYANIDE TITRATION METHOD

*Source*

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

*Outline of Method*

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

*Apparatus*

Burette, 10 ml.

*Reagents*

1. Preparation of 0.02N potassium ferricyanide; Weigh to the nearest tenth of a gram

6.6 g. of analytical reagent grade potassium ferricyanide and dissolve in 1 liter distilled water. Store in an amber bottle in the dark. Prepare fresh each week.

2. Standardization of ferricyanide solution: Transfer 50 ml. of solution to a 250 ml. Erlenmeyer flask. Add several crystals of potassium iodide (about 1 g.), mix gently to dissolve, add 1 ml. of 6N hydrochloric acid, stopper the flask, and swirl gently. Let stand for two minutes, add 10 ml. of a 30 percent zinc

sulfate solution, and titrate the mixture containing the gelatinous precipitate with standardized sodium thiosulfate or phenylarsine oxide titrant in the range of 0.025-0.050N. Add 1 ml. of starch indicator solution after the color has faded to a pale yellow, and continue the titration to the disappearance of the blue color. Calculate the normality of the ferricyanide solution using the equation:

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

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

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

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

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

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

#### Sample Preservation and Storage

Samples are to be field filtered (gravity or pressure) with coarse filter paper (Whatman

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

#### Procedure

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

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

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

4. After 10 minutes titrate with standardized potassium ferricyanide to disappearance of pink color. The endpoint is reached when there is no reappearance of the pink color after 30 seconds.

#### Calculation and Reporting of Results.

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

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

2. Report results to two significant figures.

*Quality Control*

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

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

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

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

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

3. The Method Detection Limits (MDL) should be determined periodically by each participating laboratory in accordance with the procedures specified in "Methods for Chemical Analysis of Municipal and Industrial Wastewater," EPA-660/4-82-057, July 1982, EMSL, Cincinnati, OH 45268. For the convenience of the user, these procedures are contained in appendix C to part 425.

4. A minimum of one spiked and one duplicate sample must be performed for each ana-

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

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

[53 FR 9183, Mar. 21, 1988]

APPENDIX B TO PART 425—MODIFIED  
MONIER-WILLIAMS METHOD

*Outline of Method*

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

*Apparatus\**

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

Heating 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)