

STATE OF MONTANA AIR QUALITY CONTROL IMPLEMENTATION PLAN	Subject: Yellowstone County Air Pollution Control Program
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BEFORE THE BOARD OF ENVIRONMENTAL REVIEW
OF THE STATE OF MONTANA

In the Matter of the Application of)
 the Department of Environmental)
 Quality for Revision of the Montana)
 State Air Quality Control Implementation)
 Plan relating to Control of Sulfur Dioxide)
 Emissions in the Billings/Laurel Area,)
 Affecting the Following Industries:)
 Cenex, Inc. (Laurel); Conoco, Inc.; Exxon)
 Company, USA; Montana Power Company)
 (J.E Corette and F. Bird Plants); Montana)
 Sulphur & Chemical Company; and)
 Yellowstone Energy Limited Partnership.)

**STIPULATION OF
DEPARTMENT
AND CENEX
HARVEST STATES
COOPERATIVES**

The Department of Environmental Quality ("Department"), and Cenex Harvest States Cooperatives ("Cenex"), formerly Cenex, Inc., hereby stipulate to the following paragraphs 1 through 12, including the attachment, in regard to the above-captioned matter and present the same for consideration and adoption by the Board of Environmental Review ("Board").

1. On June 9, 1998, the Department and Cenex executed a document entitled "Stipulation of Department and Cenex Harvest States Cooperatives," which included an Exhibit A and Attachments 1 and 2 (collectively "1998 Cenex Stipulation"). The 1998 Cenex Stipulation contained the sulfur dioxide control plan for Cenex, as part of the state's efforts to revise the State Implementation Plan for the control of sulfur dioxide (SO₂) emissions in the Billings/Laurel area ("Billings/Laurel SIP").

2. On March 4, 1993, the United States Environmental Protection Agency (EPA) notified the Governor of Montana that it had determined that the existing implementation plan for the control of SO₂ emissions in the Billings/Laurel area was substantially inadequate to attain and maintain the SO₂ National Ambient Air Quality Standards ("NAAQS"). The letter further called for a revision to the implementation plan for the Billings/Laurel area, to assure attainment and maintenance of the SO₂ NAAQS.

3. The express purpose of the 1998 Cenex Stipulation was to "establish an emission control strategy for Cenex which, together with similar control strategies for the

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other Billings/Laurel industries, will assure attainment and maintenance of the primary and secondary SO₂ NAAQS." (1998 Cenex Stipulation, para. 7). As part of the 1998 Cenex Stipulation, Exhibit A contained emission limitations and other conditions, including but not limited to: methods for determining compliance with emission limitations, requirements by which such emission limitations are made quantifiable and enforceable by the Department, and facility modification requirements. Attachment 1 addressed performance specifications for stack flow rate monitors, fuel oil flow meters, and fuel oil sulfur analysis, and Attachment 2 addressed analytical methods for analyzing sour water stripper overheads for hydrogen sulfide, and precision and accuracy methods for the sour water stripper flow meter. The 1998 Cenex Stipulation was approved and made enforceable by Board Order, dated June 12, 1998. On July 29, 1998, the 1998 Cenex Stipulation was submitted to EPA as a revision to the existing Billings/Laurel SIP, in response to the March 1993 SIP Call.

4. In a letter to the Department dated January 15, 1999, EPA identified a concern with the 1998 Cenex Stipulation. (Letter from Richard Long, to Mark Simonich, dated 1/15/99). Specifically, EPA noted that there were several questions regarding the methodology proposed in Attachment 2, relating to analytical methods for analyzing sour water stripper overheads for hydrogen sulfide. In a letter dated March 24, 1999, Governor Marc Racicot committed the Department to revise the Billings/Laurel SIP to address this concern.

5. The purpose of this Stipulation is to revise Attachment 2 of the 1998 Cenex Stipulation, as necessary to fulfill the Department's commitment to EPA to address the issue described above in paragraph 4. Unless expressly stated otherwise, this document does not in any way supercede or alter the provisions of the 1998 Cenex Stipulation, and except as expressly revised by this document, the 1998 Cenex Stipulation, including Exhibit A and Attachments 1 and 2, remain in full force and effect, as part of the Department's control plan for SO₂ emissions in the Billings/Laurel area.

6. The parties agree that Method #6A of Attachment 2 to the 1998 Cenex Stipulation, entitled "Analytical Method for Analyzing the Sour Water Stripper Overheads (SWSOH) for Hydrogen Sulfide (H₂S)," is superceded in its entirety, and is replaced by the updated Method #6A-1, entitled "Analytical Method for Analyzing the

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Sour Water Stripper Feed for Hydrogen Sulfide (H₂S) (October 1999)." The updated Method #6A-1 is attached to this Stipulation.

7. This Stipulation, including the attachment ("Stipulation"), shall become effective immediately upon the issuance of an order by the Board in this proceeding.

8. It is the intent of the parties that this Stipulation, after adoption and incorporation by Board Order, shall be submitted to the EPA for review and approval as revisions to the Cenex control strategy for the attainment and maintenance of the primary and secondary SO₂ NAAQS in the Billings/Laurel area, as part of the State Implementation Plan. The revised requirements in this Stipulation shall supersede any less stringent corresponding conditions pertaining to SO₂ sources in any existing permit currently issued to Cenex.

9. The 1998 Cenex Stipulation, as revised by this Stipulation, is intended to assure attainment and maintenance of the primary and secondary NAAQS for SO₂, but is not intended to address attainment or maintenance of the Montana Ambient Air Quality Standards.

10. This Stipulation may be subject to modification as provided in paragraphs 16 and 17 of the 1998 Cenex Stipulation.

11. Cenex does not waive and expressly reserves its right to contest any Board order or federal action which, without the written consent of Cenex, modifies this Stipulation.

12. Accordingly, the parties agree that the Board shall issue an order adopting the terms of this Stipulation. Upon adoption in a Board Order, this Stipulation shall be enforceable by the Department.

Cenex Harvest States Cooperatives

Montana Department of
Environmental Quality

By Ronald E. Oltz

By Mark Simonich
Mark Simonich
Director

Date 12/22/99

Date 2/14/00

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Approved as to form:

Approved as to form:

By David A. Hodges
Attorney

By Tracy R. Bell
Attorney

Date 1/6/2000

Date 2/14/02

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METHOD #6A-1

**ANALYTICAL METHOD FOR ANALYZING THE SOUR WATER STRIPPER FEED FOR
HYDROGEN SULFIDE (H₂S)
(October 1999)**

1.0 SCOPE AND APPLICATION

This method is applicable to the measurement of total and dissolved sulfides in sour water produced by the refinery. Acid insoluble sulfides are not measured by the use of this test. (Copper sulfide is the only common sulfide in this class).

2.0 SUMMARY OF METHOD

Excess iodine is added to a sample which has been treated with zinc acetate to produce zinc sulfide. The iodine oxidizes the sulfide to sulfur under acidic conditions. The excess iodine is back titrated with sodium thiosulfate.

3.0 COMMENTS

Reduced sulfur compounds, such as sulfite, thiosulfate and hydrosulfite, which decompose in acid may yield erratic results. Also, volatile iodine-consuming substances such as mercaptans will give high results.

The sample source is hot and under pressure.

The volumes of preservative and the normality of the reagents have been modified from the referenced methods. The modifications are to make the method appropriate for the expected high concentrations of sulfide in the samples. The method calculations are also modified to correct for the sample dilution from the preservative.

4.0 APPARATUS

- 4.1 Ordinary laboratory glassware.
- 4.2 130 ml HDPE bottles. These bottles are pre-charged with preservative. For the sour water stripper feed inlet the bottle contains 5 ml of zinc acetate and 10 ml of sodium hydroxide.

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5.0 REAGENTS

- 5.1 Hydrochloric acid, HCl, 6 N
- 5.2 Standard iodine solution, 0.1000 N: Dissolved 20 to 25 g KI in a little water in a liter volumetric and add 12.8 g iodine. Allow to dissolve. Dilute to 1 liter and standardize against 0.1000 N sodium thiosulfate using a starch indicator.
- 5.3 Sodium thiosulfate 0.1000N: Dissolve 24.82 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in water. Add 1 ml of chloroform and dilute to 1000 ml.
- 5.4 Starch indicator: Dissolved 10 g soluble starch and 10 mg Hg_2I in hot water and dilute to 4 liters.
- 5.5 Standardize the sodium thiosulfate against KIO_3 . Adjust the concentration to 0.1000 N. Use this sodium thiosulfate to standardize the iodine solution.
- 5.6 Zinc acetate solution, 2N: Dissolve 220 g $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ in water and dilute to one liter.
- 5.7 Sodium hydroxide, 6N: Dissolve 240 grams of sodium hydroxide in 800 ml of water, Dilute to one liter. Caution: much heat will be liberated.

6.0 SAMPLING

- 6.1 The sample bottles (4.2) are pre-charged with zinc acetate and sodium hydroxide preservative and labeled. The sample bottle sample contains 5 ml of preservative and 10 of sodium hydroxide.
- 6.2 The sample is obtained by carefully filling the appropriate bottle. Fill the bottle slowly to prevent the sample from splashing the preservative out or overflowing the bottle. The bottle should be completely filled with no headspace air. If necessary, the sides of the bottle can be squeezed while screwing on the lid to exclude the remaining air.
- 6.3 Experience shows that the pH of these samples, taken and preserved as described, are above 9. No further pH adjustment is required.

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7.0 PROCEDURE

- 7.1 Shake the container to suspend all solids and remove the sample. Measure the volume of sample. This is used to correct the results for the dilution due to the preservative. Check the pH of the sample using pH test paper to confirm that it is 9 or higher.
- 7.2 Place 20 ml of standard iodine solution (5.2) into a 500 ml iodine titration flask.
- 7.3 Add 15 ml of 6N HCl (5.1).
- 7.4 Thoroughly mix the sample and quickly take a 25 ml aliquot and place it in the flask.
- 7.5 If the iodine color disappears, add more iodine until the color remains. Record the total number of milliliters of standard iodine used steps 7.2 and 7.5.
- 7.6 Titrate with the reducing solution (0.1 N sodium thiosulfate) to a pale straw color. Add the starch indicator and titrate until the blue color disappears. Record the volume used.

8.0 CALCULATIONS

8.1 Sulfide as H₂S, mg/l = $\frac{(A - B) \times 17.01 \times 1000}{\text{sample aliquot, ml} \times K}$

Where: A = Volume of Iodine, ml * Normality of Iodine

B = Volume of Thiosulfate, ml * Normality of Thiosulfate

K = $\frac{\text{ml of sample} - \text{ml of preservative}}{\text{ml of sample}}$

This is a correction for the preservative volume. The volume of sample is the total volume in the sample container including the preservative. The volume of preservative is the volume added to the container before the sample was obtained.

9.0 REFERENCES

- 9.1 Standard Methods for the Examination of Water and Wastewater, 19th Edition, p 4-127, Method 4500-S₂ F, (1995)
- EPA Method 376.1

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