SCAQMD METHOD 315-91

DETERMINATION OF HYDROGEN SULFIDE AND MERCAPTANS IN OIL AND SLUDGE SAMPLES

1. Principle

1.1 Oil or sludge samples are acidified in a wet impingement train containing cadmium sulfate. Evolved sulfur gases are reacted to form cadmium sulfide and are quantified by iodometric titration.

2. Equipment

2.1 Midget gas impingers

2.2 Pipettes, volumetric, class A

2.3 Personal sampler vacuum pump

2.4 Tubing, 1/4 inch, Tygon^{R} or Silastic^{R}

2.5 Bottles, polyethylene, 125 mL

2.6 Graduated cylinders with stoppers

2.7 Buret, 50 mL

2.8 Iodine titration flasks, w/caps, 125 mL

2.9 Pipette, 10 mL graduated, quick delivery

3. Reagents

3.1 Cadmium sulfate solution, 0.1 M $3CdSO_4 \cdot 8H_2O$,

pH = 4.0$\pm$0.2 (pH adjusted with H_2SO_4 and/or NaOH)

3.2 Cadmium sulfate solution, 0.1 M $3CdSO_4 \cdot 8H_2O$,

pH = 6.0 $\pm$0.2 (pH adjusted with H_2SO_4 and/or NaOH)

3.3 Water, deionized

3.4 Hydrochloric acid, concentrated

3.5 Apiezon^{R} M grease or equivalent

3.6 Silica gel

3.7 Sodium thiosulfate solution, approximately 0.05 N $Na_2S_2O_3$

3.8 Iodine solution, 0.1 M I_2

3.9 Standard potassium dichromate solution, 0.05 N $K_2Cr_2O_7$

3.10 Potassium iodide, pellets

3.11 Starch indicator, powdered

4. Procedure

4.1 Preparation of Sample

4.1.1 Refer to Figure 1 to assemble nine midget impingers in a series as follows:

Impinger	Contents
1	10 mL sample or 10 g sample
2	Empty
3	10 mL Cadmium sulfate solution, pH4
4	10 mL Cadmium sulfate solution, pH4
5	Empty
6	10 mL Cadmium sulfate solution, pH6
7	10 mL Cadmium sulfate solution, pH6
8	Empty
9	Approximately 10 mL silica gel

Note: If SO_2 is present in the sample, an impinger containing 10 mL of 3 percent hydrogen peroxide solution should be placed between impingers 1 and 2 to remove the SO_2 as an interfering species.

4.1.2 Seal each impinger with a small amount of Apiezon^{R} M grease.

4.1.3 Connect the impingers with Tygon^{R} or silastic^{R} tubing. The last impinger is connected to the personal sampler vacuum pump.

4.1.4 Ensure that there are no leaks in the system

4.1.4.1 Close off the free tubing at point A in Figure 1 and turn on the personal sampler vacuum pump. The rotameter ball of the personal sampler vacuum pump should fall to nearly zero.

4.1.4.2 When the rotameter ball has been at nearly zero for 1 minute, close the line between the last impinger and the personal sampler vacuum pump (at point B in Figure 1) for 1 minute.

4.1.4.3 Open the line between the last impinger and the personal sampler vacuum pump (point B in Figure 1). If there is a leak in the system, the rotameter ball position will change and bubbles will occur in the solutions.

4.1.4.4 Release the vacuum by slowly opening the tubing at point A in Figure 1.

4.1.5 Turn on pump and set at 0.5 L/min. Add 1 mL concentrated HCl to impinger 1.

4.1.6 After 1 hour, the amount of yellow precipitate (CdS) in impinger 4 should be less than that of impinger 3. Also the amount of CdS in impinger 7 should be less than that of impinger 6.

4.1.7 The concentrations of either H_2S or mercaptans is too high when the amount of precipitate in the second impinger of each set approaches that of the first impinger. Discard the run and prepare another sample preparation beginning with Section 4.1 but either reduce the sample volume or add additional impingers containing the appropriate cadmium sulfate absorbing solution.

4.1.8 Transfer, quantitatively, each set of cadmium sulfate absorbing solutions to separate stoppered graduated cylinders. Also rinse the empty impinger following each set of cadmium sulfate absorbing solutions into the appropriate stoppered graduated cylinder. Residual films of cadmium sulfide should be scraped with a rubber policeman and rinsed into the appropriate stoppered graduated cylinder.

4.1.9 Make up to a known volume, then transfer to a polyethylene bottle and store in the dark at room temperature.

4.1.10 Titration of solutions must be performed within 24 hours of sample preparation.

4.2 Standardization of sodium thiosulfate solution

4.2.1 Note: Titration flasks must remain closed as much as possible to avoid air oxidation and I_2 volatilization. Standardize the sodium thiosulfate solution the same day that the samples are analyzed.

4.2.2 To each of two iodine flasks add the following: approximately 3 g KI, exactly 20 mL 0.05N $K_2Cr_2O_7$ and 50 mL water. Cap immediately.

4.2.3 Add 10 mL concentrated HCl to each iodine flask, cap immediately.

4.2.4 Water seal the cap and place in a dark cabinet for 15 minutes.

4.2.5 Titrate with 0.05 N $Na_2S_2O_3$ until pale yellow.

4.2.6 Add approximately 0.05 g of starch and continue to titrate until clear. A very pale clear green color is also an acceptable end point. The titration values for standards prepared in Section 4.2.2 should agree within 0.05 mL.

4.2.7 Blanks are analyzed by substituting 20 mL water for 20 mL 0.05 N $K_2Cr_2O_7$. Duplicate blank determinations should agree with 0.05 mL.

4.3 Titration of cadmium sulfate absorbing solutions

4.3.1 To each of two iodine flasks add the following: Approximately 3 g KI, an aliquot of cadmium sulfate absorbing solution (amount depends upon the amount of CdS generated), 10 mL 0.1 M I_2 and 50 mL water. Cap immediately.

4.3.2 Follow sections 4.2.3 to 4.2.6 except that solutions are placed in a dark cabinet for 30 minutes. The titration values obtained for the solutions prepared in Section 4.3.1 should agree within 0.05 mL.

4.3.3 Blanks are analyzed by substituting appropriate fresh cadmium sulfate solution for the volume of sample. Duplicate blank determinations should agree within 0.05 mL.

4.4 Determine the density of the sample by ASTM D 1475-90. Density need not be determined if sample was weighed.

5. Calculations

5.1 Normality of sodium thiosulfate solution

$$\text{Normality of } Na_2S_2O_3 = \frac{N \times V}{V1 - V0}$$

Where

N = Normality of $K_2Cr_2O_7$ standard solution
V = Volume of $K_2Cr_2O_7$ standard solution, mL
V1 = Average titration volume used in titration of standard, mL (Sec. 4.2.6)
V0 = Average titration volume used in titration of blank, mL (Sec. 4.2.7)

5.2 Weight of hydrogen sulfide trapped by cadmium sulfate solution at pH 4.

$$\text{mg } H_2S = 17.04 \times (V0 - V1) \times N \times \frac{T}{Q}$$

Where:

V0 = Average titration volume used in titration of blank, mL (Sec. 4.3.3)
V1 = Average titration volume used in titration of sample, mL (Sec. 4.3.2)
N = Normality of sodium thiosulfate solution (Sec. 5.1)
T = Total volume absorbing solution, mL (Sec. 4.1.9)
Q = Aliquot volume of sample used in titration, mL (Sec. 4.3.1)

Note: The equivalent weight of H_2S is 17.04 grams per equivalent.

5.3 Weight percent hydrogen sulfide in oil or sludge sample.

$$\text{Wt \% } H_2S = \frac{M \text{ X } 0.1}{D \text{ X } VS}$$

Where:

M = H_2S, mg (Sec. 5.2)
VS = Volume of sample used for extraction, mL (Sec. 4.1.1)
D = Density of sample, g/mL (Sec. 4.4)

Note: If sample was weighed, substitute grams of sample for D X VS

5.4 Weight of mercaptans (calculated as methyl mercaptan) trapped by cadmium sulfate solution at pH 6.

$$\text{mg mercaptan } (CH_3SH) = 24.05 \text{ X } (V0\text{-}V1) \text{ X } N \text{ X } \frac{T}{Q}$$

Where:

V0 = Average titration volume used in titration of blank, mL (Sec. 4.3.3)
V1 = Average titration volume used in titration of sample, mL (Sec. 4.3.2)
N = Normality of sodium thiosulfate solution (Sec. 5.1)
T = Total volume of absorbing solution, mL (Sec. 4.1.9)
Q = Aliquot volume of sample used in titration, mL (Sec. 4.3.1)

Note: The equivalent weight of CH_3SH is 24.05 grams per equivalent.

5.5 Weight percent mercaptan (as methyl mercaptan) in oil or sludge sample

$$\text{Wt. \% mercaptan (As methyl mercaptan)} = \frac{M \text{ X } 0.1}{D \text{ X } VS}$$

Where:

M = Mercaptan (as methyl mercaptan), mg (Sec. 5.4)
VS = Volume of sample used for extraction, mL (Sec. 4.1.1)
D = Density of sample, g/mL (Sec. 4.4)

Note:If sample was weighed, substitute grams of sample for D X VS

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

APPLIED SCIENCE & TECHNOLOGY DIVISION

LABORATORY SERVICES BRANCH

SCAQMD METHOD 315-91

DETERMINATION OF HYDROGEN SULFIDE AND MERCAPTANS IN OIL AND SLUDGE SAMPLES

Approved June 1, 1991
Revised November 1996

SCAQMD METHOD 315-91

DETERMINATION OF HYDROGEN SULFIDE AND MERCAPTANS IN OIL AND SLUDGE SAMPLES

This method covers the determination of hydrogen sulfide and mercaptans in oil and sludge samples by iodometric titration. It is applicable to samples regulated under Regulation IV.

CONTENTS