

Method 630.1
The Determination of
Dithiocarbamates Pesticides in
Municipal and Industrial
Wastewater

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1. SCOPE AND APPLICATION

- 1.1 This method covers the determination of certain dithiocarbamates pesticides after conversion to carbon disulfide. The following parameters can be determined by this method:

<i>Parameter</i>	<i>CAS No.</i>
Amobam	3566-10-7
Busan 40	51026-28-9
Busan 85	128-03-0
EXD	502-55-6
Ferbam	14484-64-1
KN Methyl	137-41-7
Metham	137-42-8
Nabam	142-59-6
Nabonate	138-93-2
Sodium dimethyldithiocarbamate	128-04-1
Thiram	137-26-8
Zineb	12122-67-7
Ziram	137-30-4

- 1.2 The compounds are decomposed to form carbon disulfide (CS₂) and the total dithiocarbamate concentration is measured from the amount of CS₂ produced by acid hydrolysis. Unless the sample can be otherwise characterized, all results are reported as ziram.
- 1.3 This is a total-residue gas chromatographic (GC) method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 *CFR* 136.1. Any modification of this method beyond those expressly permitted shall be considered a major modification subject to application and approval of alternative test procedures under 40 *CFR* 136.4 and 136.5.
- 1.4 The method detection limits (MDLs, defined in Section 14) for the parameters listed in Section 1.1 are listed in Table 1. The MDLs for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.
- 1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. SUMMARY OF METHOD¹

- 2.1** A measured 5-mL volume of sample is digested with acid to yield CS₂ by hydrolysis of the dithiocarbamate moiety. The evolved CS₂ is extracted from water into hexane. Gas chromatographic conditions are described which permit the separation and measurement of CS₂ in the extract by gas chromatography with a Hall detector in the sulfur mode.
- 2.2** This method provides a cleanup procedure involving purging of any indigenous CS₂ from the sample at pH 12 to 13. This procedure is performed using a vortex evaporator.

3. INTERFERENCES

- 3.1** Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample-processing apparatus that lead to discrete artifacts or elevated baselines in gas chromatograms. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.5.

3.1.1 Glassware must be scrupulously cleaned.² Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water, drain dry, and heat in an oven or muffle furnace at 400°C for 15 to 30 minutes. Do not heat volumetric ware. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Thorough rinsing with acetone and pesticide-quality hexane may be substituted for the heating. After drying and cooling, seal and store glassware in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high-purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

- 3.2** Carbon disulfide may be a direct interferent in wastewaters. This method includes procedures to purge CS₂ from the wastewater prior to acid hydrolysis of the sample. A vortex evaporator is used for CS₂ removal.

- 3.3** Additional matrix interferences may be caused by contaminants that are coextracted from the sample and from other CS₂ generating compounds. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the sample.

4. SAFETY

- 4.1** The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis.

Additional references to laboratory safety are available and have been identified³⁻⁵ for the information of the analyst.

- 4.2 Nabam (ethylene bis (dithiocarbamate)) has been identified as having substantial evidence of carcinogenicity and should be handled according to OSHA regulations.

5. APPARATUS AND MATERIALS

- 5.1 Sampling equipment, for discrete or composite sampling.

5.1.1 Sample containers: 40-mL screw-cap vials (Pierce No. 13075 or equivalent): each equipped with a polytetrafluoroethylene (PTFE)-faced silicone septum (Pierce No. 12722 or equivalent). Prior to use, wash vials and septa with detergent and rinse with tap and distilled water. Allow the vials and septa to air dry at room temperature, place in a 105°C oven for 1 hour, then remove and allow to cool in an area known to be free of organics.

5.1.2 Automatic sampler (optional): Must incorporate glass sample containers for the collection of a minimum of 250 mL. Sample containers must be kept refrigerated at 4°C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow-proportional composites.

- 5.2 Glassware

5.2.1 Centrifuge tube: 15- mL, conical, with PTFE-lined screw-cap.

5.2.2 Volumetric flask: 250-mL with glass stopper.

5.2.3 Bottles: 100- to 20-mL capacity with PTFE-lined screw-caps.

- 5.3 Vortex Evaporator: Buchler 3-2200, equipped with sample block to hold 36 15-mL conical-bottom centrifuge tubes and appropriate vacuum cover.

- 5.4 Water bath: Heated, capable of temperature control ($\pm 2^\circ\text{C}$). The bath should be used in a hood.

- 5.5 Balance: Analytical, capable of accurately weighing to the nearest 0.0001 g.

- 5.6 Gas chromatograph: Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

5.6.1 Column: 180 cm by 2 mm ID glass, packed with 0.1% SP-1000 on Carbopack C (80/100 mesh) or equivalent. This column was used to develop the method

performance statements in Section 14. Alternative columns may be used in accordance with the provisions described in Section 11.1.

5.6.2 Detector: Hall detector operated in the sulfur mode. This detector has proven effective in the analysis of wastewaters for the compounds listed in the scope and was used to develop the method performance statements in Section 14.

6. REAGENTS

6.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the MDL of each parameter of interest.

6.2 Hexane: Distilled-in-glass quality or equivalent.

6.3 Sulfuric acid, 12N: Slowly add 100 mL concentrated sulfuric acid to 200 mL reagent water.

6.4 Sodium phosphate, tribasic, dodeca-hydrate: Baker reagent grade or equivalent.

6.5 Tribasic sodium phosphate, 0.1M: Dissolve 38 g of tribasic sodium phosphate in reagent water and dilute to 1000 mL with reagent water.

6.6 Stannous chloride: $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, ACS grade.

6.7 Stannous chloride reagent: Dissolve 1.5 g stannous chloride in 100 mL 12N sulfuric acid. Prepare fresh daily.

6.8 Sodium chloride: Heated at 45°C for 8 hours.

6.9 Stock standard solutions (0.1 $\mu\text{g}/\mu\text{L}$): Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

6.9.1 Prepare dithiocarbamate spiking solutions by accurately weighing about 0.025 g of pure material. Dissolve the material in 0.1M Na_3PO_4 and dilute to volume in a 250-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

6.9.2 (0.1 $\mu\text{g}/\mu\text{L}$) Prepare CS_2 stock standard solution by adding 7.9 μL of CS_2 to hexane and diluting to volume in a 100-mL volumetric flask.

6.9.3 Transfer the stock standard solutions into PTFE-sealed screw-cap bottles. Store at 4°C. Frequently check standard solutions for signs of degradation or evaporation.

6.9.4 Stock standard solutions must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

7. CALIBRATION

- 7.1 Use ziram as the standard for total dithiocarbamates when a mixture of dithiocarbamates is likely to be present. Use the specific dithiocarbamate as a standard when only one pesticide is present and its identity has been established.
- 7.2 Establish gas chromatographic operating parameters equivalent to those indicated in Table 1. The gas chromatographic system can be calibrated using the external standard technique (Section 7.3).
- 7.3 External standard calibration procedure.
- 7.3.1 Prepare calibration standards at a minimum of three concentration levels by adding volumes of the CS₂ stock standard to a volumetric flask and diluting to volume with hexane. One of the external standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the range of concentrations expected in the sample concentrates or should define the working range of the detector.
- 7.3.2 Using injections of 1 to 5 µL of each calibration standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for CS₂. Alternatively, the ratio of the response to the mass injected, defined as the calibration factor (CF), can be calculated at each standard concentration. If the relative standard deviation of the calibration factor is less than 10% over the working range, the average calibration factor can be used in place of a calibration curve.
- 7.3.3 The working calibration curve or calibration factor must be verified on each working shift by the measurement of one or more calibration standards. If the response for CS₂ varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared.
- 7.4 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate the absence of interferences from the reagents.

8. QUALITY CONTROL

- 8.1 Each laboratory using 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 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.
- 8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

- 8.1.2** In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Section 8.2.
- 8.1.3** The laboratory must spike and analyze a minimum of 10% of all samples to monitor continuing laboratory performance. This procedure is described in Section 8.4.
- 8.2** To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.
- 8.2.1** Select a representative spike concentration for each compound to be measured.
- 8.2.2** Add a known amount of an individual dithiocarbamate standard to a minimum of four 5-mL aliquots of 0.1M tribasic sodium phosphate. A representative wastewater may be used in place of the reagent water, but one or more additional aliquots must be analyzed to determine background levels, and the spike level must exceed twice the background level for the test to be valid. Analyze the aliquots according to the method beginning in Section 10.
- 8.2.3** Calculate the average percent recovery (R), and the standard deviation of the percent recovery (s), for the results. Wastewater background corrections must be made before R and s calculations are performed.
- 8.2.4** Using the appropriate data from Table 2, determine the recovery and single-operator precision expected for the method, and compare these results to the values measured in Section 8.2.3. If the data are not comparable, the analyst must review potential problem areas and repeat the test.
- 8.3** The analyst must calculate method performance criteria and define the performance of the laboratory for each spike concentration and parameter being measured.
- 8.3.1** Calculate upper and lower control limits for method performance as follows:

$$\text{Upper Control Limit (UCL)} = R + 3s$$

$$\text{Lower Control Limit (LCL)} = R - 3s$$

where R and s are calculated as in Section 8.2.3. The UCL and LCL can be used to construct control charts⁶ that are useful in observing trends in performance.

- 8.3.2** The laboratory must develop and maintain separate accuracy statements of laboratory performance for wastewater samples. An accuracy statement for the method is defined as $R \pm s$. The accuracy statement should be developed by the analysis of four aliquots of wastewater as described in Section 8.2.2, followed by the calculation of R and s. Alternatively, the analyst may use four wastewater data points gathered through the requirement for continuing quality control in Section 8.4. The accuracy statements should be updated regularly.⁶

- 8.4** The laboratory is required to collect in duplicate a portion of their samples to monitor spike recoveries. The frequency of spiked sample analysis must be at least 10% of all samples or one sample per month, whichever is greater. One aliquot of the sample must be spiked and analyzed as described in Section 8.2. If the recovery for a particular compound does not fall within the control limits for method performance, the results reported for that compound in all samples processed as part of the same set must be qualified as described in Section 12.3. The laboratory should monitor the frequency of data so qualified to ensure that it remains at or below 5%.
- 8.5** Before processing any samples, the analyst should demonstrate through the analysis of a 5-mL aliquot of 0.1M tribasic sodium phosphate that all glassware and reagent interferences are under control. Each time a set of samples is extracted or there is a change in reagents, a laboratory reagent blank should be processed as a safeguard against laboratory contamination.
- 8.6** It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

9. *SAMPLE COLLECTION, PRESERVATION, AND HANDLING*

- 9.1** Grab samples must be collected in glass containers. Conventional sampling practices⁷ should be followed; however, the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of plastic and other potential sources of contamination.
- 9.2** The samples must be iced or refrigerated at 4°C from the time of collection until extraction.
- 9.3** Add 15.2 g of tribasic sodium phosphate per 40 mL of sample to the sample to adjust pH to 12 to 13 at time of collection.

10. *SAMPLE CLEANUP AND EXTRACTION*

- 10.1** Place 5 mL of sample in a 15-mL conical centrifuge tube.
- 10.2** Add 0.75 g of NaCl and shake tube to dissolve salt.
- 10.3** Add 2 mL of MTBE and process in a vortex evaporator for 10 minutes with the temperature at 30°C, a vacuum of 30 inches Hg, and the vortex speed control set at 4.5.
- 10.4** Repeat step in Section 10.3 twice.

- 10.5 Add 0.75 mL of hexane and 2.5 mL of SnCl₂ reagent to the aqueous layer. Cap tube tightly and invert in a water bath at 50°C for 30 minutes.
- 10.6 Remove tube from water bath and let cool inverted to room temperature.
- 10.7 Shake tube for 1 minute without venting. Analyze the hexane layer by GC with a Hall detector in the sulfur mode. If CS₂ levels are outside of the GC calibration range, the sample can be diluted a known amount with hexane and reanalyzed.

11. GAS CHROMATOGRAPHY

- 11.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are estimated retention time and MDLs that can be achieved by this method. An example of the chromatography achieved from Column 1 is shown in Figure 1. Other packed columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met. Capillary (open-tubular) columns may also be used if the relative standard deviations of responses for replicate injections are demonstrated to be less than 6% and the requirements of Section 8.2 are met.
- 11.2 Calibrate the gas chromatographic system daily as described in Section 7.
- 11.3 Inject 1 to 5 µL of the sample extract using the solvent flush technique.⁸ Record the volume injected to the nearest 0.05 µL, and the resulting peak sizes in area or peak height units. An automated system that consistently injects a constant volume of extract may also be used.
- 11.4 The width of the retention-time window used to make identifications should be based upon measurements of actual retention-time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.
- 11.5 If the response for the peak exceeds the working range of the system, dilute the extract with hexane and reanalyze.
- 11.6 If the measurement of the peak response is prevented by the presence of interferences, further cleanup is required.

12. CALCULATIONS

- 12.1 Determine the concentration of carbon disulfide in the sample.
 - 12.1.1 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor in Section 7.2.2. The concentration of dithiocarbamate in the sample can be calculated as follows:

Equation 1

$$\text{Concentration, } \mu\text{g/L} = \frac{(A) (V_i) (M_c)}{(V_t) (V_s) (76) (C)}$$

where

A = Amount of CS_2 injected, in ng

V_i = Volume of extract injected, in $\mu\text{g/L}$

V_t = Volume of total extract, in μL

V_s = Volume of water extracted, in mL

M_c = Molecular weight of dithiocarbamate

C = Theoretical number of moles of CS_2 formed per mole of dithioabamate

12.2 Determine the concentration of total dithiocarbamates in the sample as ziram. When a specific dithiocarbamate is being measured, quantitate in terms of the selected pesticide.

12.3 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

12.4 For samples processed as part of a set where the laboratory spiked sample recovery falls outside of the control limits in Section 8.3, data for the affected compounds must be labeled as suspect.

13. METHOD PERFORMANCE

13.1 The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.⁹ The MDL concentrations listed in Table 1 were obtained using spiked reagent water samples.¹

13.2 This method has been tested for linearity of recovery from spiked reagent water and has been demonstrated to be applicable over the concentration range from 10 to 1000 $\mu\text{g/L}$.

13.3 In a single laboratory, Battelle Columbus Laboratories, using spiked wastewater samples, the average recoveries of the parameters listed in Section 1.1 presented in Table 2 were obtained. Seven replicates of the wastewater were spiked and analyzed. The standard deviation of the percent recovery is also included in Table 2.¹

References

1. "Determination of Pesticides and Priority Pollutants in Industrial and Municipal Wastewaters," EPA Contract Report 68-03-1760, Work Assignment 4 (in preparation).
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4. "OSHA Safety and Health Standards, General Industry" (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976).
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8. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," *Journal of the Association of Official Analytical Chemists*, 48, 1037 (1965).
9. Glaser, J.A. et al. "Trace Analysis for Wastewaters", *Environmental Science and Technology*, 15, 1426 (1981).

Table 1. Chromatographic Conditions and Method Detection Limits

<i>Parameter</i>	<i>Retention Time (min)¹</i>	<i>MDL (µg/L)</i>
Amobam	1.3	1.1
Busan 40	1.3	4.4
Busan 85	1.3	1.3
EXD	1.3	5.2
Ferbam	1.3	2.9
KN Methyl	1.3	2.7
Metham	1.3	3.1
Nabam	1.3	1.6
Nabonate	1.3	0.9
Na DMDTC	1.3	2.8
Thiram	1.3	2.2
Zineb	1.3	4.1
Ziram	1.3	4.6

¹ Retention time of CS₂ under the following conditions: Carbopack C (80/100 mesh) coated with 0.1% Sp-1000 packed in a glass column 180 cm long by 2 mm ID with helium carrier gas at a flow rate of 25 mL/min. Column temperature held at 7°C for 3 minutes, programmed at 20°C/min to 120°C, and then held at 120°C for 5 minutes. Column effluent is vented from the Hall detector after elution of CS₂ from the column. Injector temperature and detector temperatures are 200°C. The Hall detector is operated in the sulfur mode following manufacturer's specifications.

Table 2. Single-Laboratory Accuracy and Precision

<i>Parameter</i>	<i>Sample Type^a</i>	<i>Background (µg/L)</i>	<i>Spike (µg/L)</i>	<i>Mean Recovery (%)</i>	<i>Standard Deviation</i>	<i>Number of Replicates</i>
Amobam	1	4.6	50	90	7.8	7
	1	4.6	500	93	8.7	7
Busan 40	1	6.6	50	110	7.2	7
	1	6.6	500	100	6.1	7
Busan 85	1	5.9	50	110	5.5	7
	1	5.9	500	100	2.0	7
EXD	1	4.5	50	71	7.5	7
	1	4.5	500	76	2.4	7
Ferbam	1	5.2	50	94	4.8	7
	1	5.2	500	110	1.8	7
KN Methyl	1	5.4	50	90	6.1	7
	1	5.4	500	89	2.5	7
Methan	1	6.2	50	110	5.2	7
	1	6.2	500	84	5.9	7
Nabam	1	4.8	50	62	6.6	7
	1	4.8	500	65	13	7
Nabonate	1	6.1	50	66	11	7
	1	6.1	500	56	12	7
Na DMDTC	1	5.4	50	110	2.5	7
	1	5.4	500	110	4.2	7
Thiram	1	4.5	50	89	2.9	7
	1	4.5	500	82	3.4	7
Zineb	1	5.2	50	87	3.4	7
	1	5.2	500	86	9.4	7
Ziram	1	5.7	50	100	12	7
	1	5.7	500	95	19	7

(a) 1 = Wastewater from a manufacturer of a dithiocarbamate diluted 1000:1 with Columbus POTW secondary effluent.

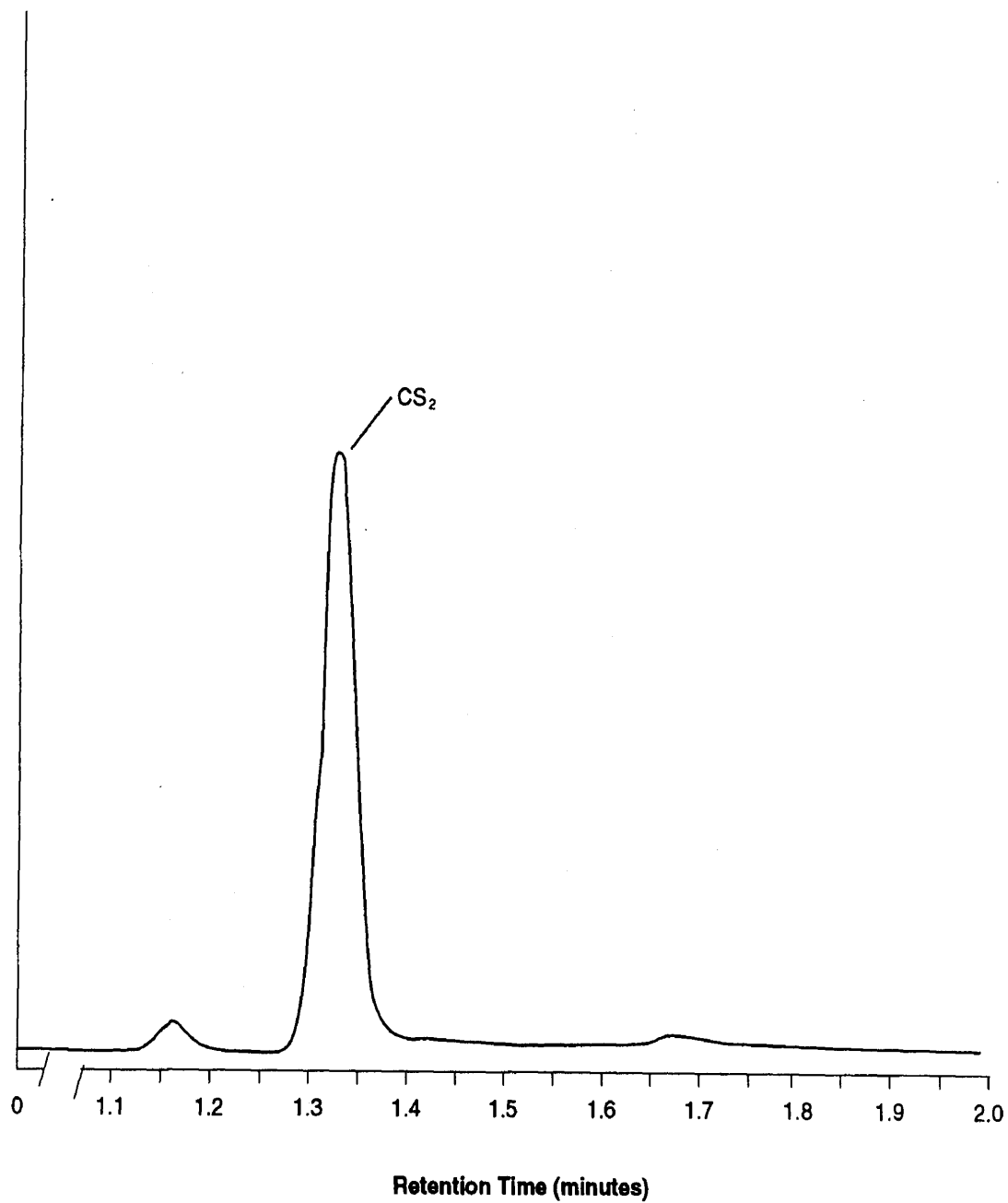


Figure 1. GC-HALL Chromatogram of 0.1 ng of CS