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Document Name: GPA 2377: Test for Hydrogen Sulfide and Carbon Dioxide in Natural Gas Using Length of Stain Tubes

CFR Section(s): 40 CFR 60.334(h)(1)

Standards Body: Gas Processors Association



Official Incorporator:

THE EXECUTIVE DIRECTOR
OFFICE OF THE FEDERAL REGISTER
WASHINGTON, D.C.

Test for Hydrogen Sulfide and Carbon Dioxide in Natural Gas Using Length of Stain Tubes



*Adopted as a Tentative Standard 1977
Revised and Adopted as a Standard 1984
Revised 1986
Reprinted 1988, 1997, 1998, 1999*

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Test for Hydrogen Sulfide and Carbon Dioxide in Natural Gas Using Length of Stain Tubes

1. SCOPE

1.1 This method covers the determination of hydrogen sulfide in natural gas in the range of 3 ppmv to 5 vol %.

1.2 This method covers the determination of carbon dioxide in natural gas in the range of 0.25 to 10 vol %.

1.3 This method as written is applicable to the determination of hydrogen sulfide and carbon dioxide in hydrocarbons and in air.

2. SUMMARY OF METHOD

2.1 The sample is passed through the detector tube made specifically for the detection of hydrogen sulfide or carbon dioxide by specially prepared chemicals. The hydrogen sulfide or carbon dioxide present in the sample reacts with the chemical to produce a color change. The length of stain (or color change) produced in the detector tube when exposed to a measured volume of sample is directly proportional to the amount of hydrogen sulfide or carbon dioxide present in the sample being tested. A bellows or piston type pump is used to draw a measured volume of sample through the tube at a controlled rate of flow. The length of stain produced is converted to volume by comparison with a calibration scale supplied by the manufacturer with each box of detector tubes. Some tubes have a pre-determined calibration constant which is multiplied by the observed length of stain to arrive at a volume percent concentration in the sample being tested. The apparatus is easily portable and is completely suitable for making spot checks for hydrogen sulfide or carbon dioxide under the field conditions.

3. APPARATUS

3.1 *Piston or Bellows Pump* – The pump is hand-operated and must be capable of drawing a minimum of 100 ml per stroke of sample through the detector tube with an accuracy of ± 2.0 ml.

3.2 *Detector Tube* – Tubes must be made of glass with break-off tips sized to fit the orifice of the pump. The chemical sealed in the tube must be specific for hydrogen sulfide or carbon dioxide and produce a distinct color change when exposed to a sample of gas containing hydrogen sulfide or carbon dioxide. Any substances known to interfere must be listed in instructions accompanying the tubes. A calibration scale or other markings referenced to a scale should be etched directly on the tube to provide for easy interpretation of hydrogen sulfide or carbon dioxide content. Shelf life of the detector tubes must be a minimum of two years when stored according to the manufacturer's recommendations.

3.3 *Gas Sampling Container* – Any container which provides for access of the detector tube into a uniform flow of sample gas at atmospheric pressure and isolated from the surrounding atmosphere.

3.3.1 A suitable container may be devised from a one pint polyethylene bottle. A $\frac{1}{4}$ in OD polyethylene tubing sealed into the bottle and discharging near the bottom provides for flow of sample gas into the bottle. A $\frac{1}{2}$ in hole cut into the cap of the bottle provides both access for the detector tube and a vent for gas flow. (Figure 1.)

Note 1—A one pint polyethylene wash bottle is easily adapted to a suitable sample container.

3.3.2 Mylar gas collection bags are useful as gas sample containers when the supply of sample gas is limited. Mylar bags with a minimum capacity of two liters are an acceptable substitute for the bottle described in 3.3.1.

3.4 *Barometer* – Any barometer equipped with a scale graduated in 1 mm of mercury subdivisions and a range including the expected atmospheric pressure condition at the sampling site.

3.5 *Thermometer* – Standard laboratory thermometer graduated in 1°C subdivisions and including the range of sample temperatures expected during the test.

3.6 *Needle Valve and Tubing* – Any stainless steel needle valve which can be adjusted to control the flow of gas from source pressure into the gas sampling container. Polyethylene or gum rubber tubing may be used to connect the gas sampling container to the needle valve outlet.

Note 2—A pressure regulator may be used to control flow of the sample gas, in lieu of a needle valve.

4. SAMPLING

4.1 Select a sampling point which affords access to a representative sample of the gas to be tested (i.e., a point on the main flow line). Flow line connections should have a centerline tap.

4.1.1 Open source valve (Valve A), Figure 1, and blow down vigorously to clear foreign materials from source valve and connecting nipple. Close source valve.

4.1.2 Install control valve (Valve B) or pressure regulator on outlet of source valve. Connect outlet of control valve (Valve B) to gas sampling container using shortest length practicable of polyethylene or other suitable tubing.

4.1.3 Open source valve (Valve A) and crack control valve (Valve B) to obtain positive flow of gas through gas sample container venting to atmosphere through tube access and vent (Vent C).

4.1.4 Purge gas sample container until all air is displaced. A minimum purge time of three minutes is recommended.

Note 3—When using collection bags the same procedure is followed except that the deflated bag is attached directly to control valve (Valve B). The bag is filled once, disconnected and deflated. The bag is filled a second time and is then ready for the analysis.

5. PROCEDURE

5.1 Immediately, before each series of measurements, test the pump for tightness by inserting an unopened tube and operating the pump. A loss in vacuum on the pump after 30 seconds indicates a leak.

5.1.1 Select the tube range that includes the expected amount of hydrogen sulfide or carbon dioxide present in the sample. Reading accuracy is improved when the stain extends at

least 50% of the tube length. Consider multiple strokes and/or a lower range tube to achieve this length of stain.

5.1.2 Break off tips and insert outlet end of tube snugly into the pump head. Temperature of tube must remain in the 0 - 40°C range throughout the test period.

5.1.3 Place detector tube well into gas sampling container through the tube access and vent (Vent C).

Note 4—Gas sample container must be completely purged of air and with control valve (Valve B) adjusted to maintain a positive flow of gas leaving the tube access and vent (Vent C) for the duration of the test.

5.1.4 Operate the pump to draw a measured volume of gas through the detector tube. Within limits set by manufacturer's instructions, use multiple strokes to maximize length of stain.

5.1.5 Remove the tube from the pump and immediately read the concentration of hydrogen sulfide or carbon dioxide from graduations on the tube or charts supplied with the tubes. The scale reading even with the end of the stain is the approximate hydrogen sulfide or carbon dioxide concentration. Interpolation can be made between scale readings. If the number of strokes used is different from the number specified by the manufacturer for a particular concentration, a correction must be made as follows:

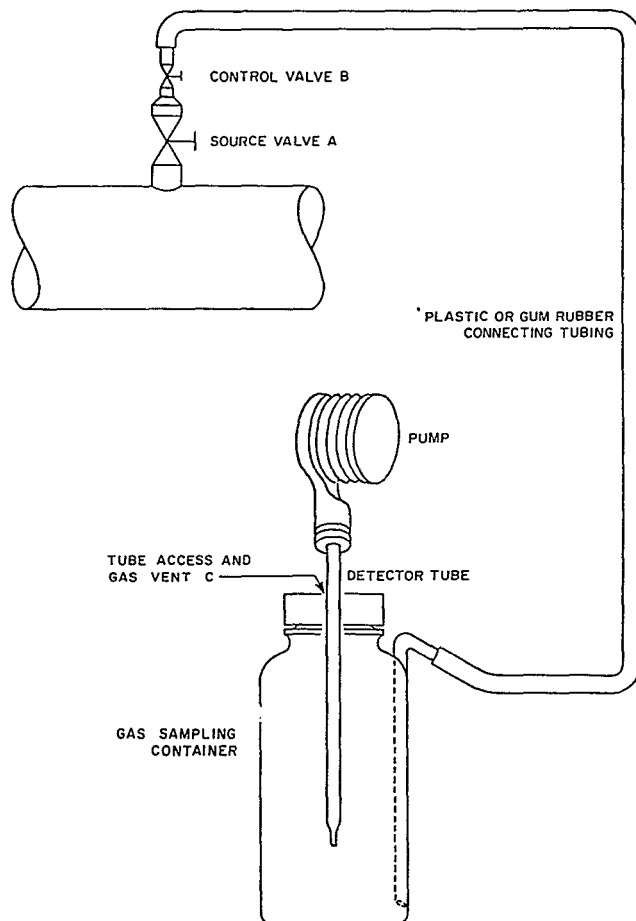


FIG. 1—Sampling manifold to be used with H₂S and CO₂ detector tubes.

$$\text{Corr. H}_2\text{S/CO}_2 \text{ Conc.} = \text{Scale reading} \times \frac{\text{Specified Strokes}}{\text{Actual Strokes}}$$

5.1.6 Record temperature of gas flowing through gas sample container and barometric pressure to provide data for gas volume corrections if required.

6. CALCULATIONS

6.1 Gas volume corrections may be desirable to improve precision of results. The effect of temperature is usually negligible; however, the barometric pressure becomes significant at altitudes above 2,000'. Correction for barometric pressure is done as follows:

$$\text{Corr. Volume \%} = \text{Vol \% (read from tube)} \times \frac{760 \text{ mm Hg}}{\text{Baro. Press. mm Hg}}$$

6.2 Check with manufacturer if it becomes necessary to test at gas temperatures outside the 0 - 40°C range.

7. PRECISION

7.1 The following criteria should be used for judging the acceptability of hydrogen sulfide or carbon dioxide concentration when determined using a "length of stain" detector tube. (95% confidence limit)

7.1.1 *Repeatability*—Duplicate results by the same operator should be considered suspect if they differ by more than the following amounts:

Component	Range of Sample Conc.	Repeatability
H ₂ S	3 - 120 ppmv	10% of amount found
H ₂ S	0.05 - 5 vol %	5% of amount found
CO ₂	0.25 - 10 vol %	2% of amount found

7.1.2 *Reproducibility*—The results submitted by each of two laboratories should be considered suspect if the two results differ by more than the following amounts:

Component	Range of Sample Conc.	Reproducibility
H ₂ S	3 - 120 ppmv	12% of amount found
H ₂ S	0.05 - 5 vol %	7% of amount found
CO ₂	0.25 - 10 vol %	5% of amount found

7.1.3 *Accuracy*—The expected error in measurement of the two commercial tubes (Dräger & Gastec) based on all of Work Group studies is as follows:

Tube Model	Comp.	Sample Conc.	Mean Value	Actual Mean Value	No. of Meas.	% Error
Dräger	H ₂ S	35 ppmv	30 ± 1	35	39	15
Dräger	H ₂ S	481 ppmv	455 ± 33	481	12	7
Dräger	H ₂ S	0.49 Vol%	0.57 ± 0.1	0.49	12	13
Dräger	H ₂ S	5.23 Vol%	4.62 ± 0.4	5.23	12	12
Dräger	CO ₂	0.25 Vol%	0.27 ± 0.02	0.25	12	8
Dräger	CO ₂	4.99 Vol%	5.07 ± 0.2	4.99	12	2
Dräger	CO ₂	10.00 Vol%	9.31 ± 0.8	10.00	12	7
Gastec	H ₂ S	35 ppmv	32 ± 1	35	65	9
Gastec	H ₂ S	481 ppmv	460 ± 10	481	24	4
Gastec	H ₂ S	0.49 Vol%	0.56 ± 0.04	0.49	24	14
Gastec	H ₂ S	5.23 Vol%	5.26 ± 0.3	5.23	24	1
Gastec	CO ₂	0.25 Vol%	0.24 ± 0.04	0.25	24	4
Gastec	CO ₂	4.99 Vol%	4.76 ± 0.2	4.99	24	5
Gastec	CO ₂	10.00 Vol%	9.61 ± 0.4	10.00	24	4

Note 5—Precision limits shown above were obtained from raw data generated by 10 to 13 laboratories involved in cooperative testing of eight separate samples. Computations on the raw data were made using ASTM Bulletin RR D-2-1007, "Manual on Determining Precision Data for ASTM Methods on Petroleum Products and Lubricants." The cooperative tests were completed prior to finalizing the method write-up.

Note 6—Cooperative test results indicate a major source of error to be in the variance in response from lot number to lot number of tubes as supplied by the manufacturer. The fidelity of a given lot number of tubes can be

verified by calibrating one or more tubes using a gas with a known concentration of hydrogen sulfide or carbon dioxide. The cooperative test results are shown in Tables I, II and III.

Note 7—Precision data on high levels of hydrogen sulfide and carbon dioxide were obtained from raw data generated by six laboratories in the cooperative testing of six blends of known concentration. All six laboratories used identical tube lot numbers for testing. The cooperative test results are shown in Table IV.

TABLE I
Length of Stain Method for Determination of H₂S in Natural Gas

Reproducibility of Laboratories
Samples Mean/Laboratory

	Lab Fid Gas 9 ppm	Lab Fid Gas 98 ppm	Lab Permeation Tube-44 ppm	Ecospan 88 ppm	Ecospan 18 ppm	Fid Gas 35 ppm	Fid Gas 93 ppm
Lab A	—	100	54	91	15	29	95
Lab B	—	101	42	89	13	28	—
Lab C	11	118	53	—	—	31	93
Lab E	9	—	47	34	14	—	—
Lab F	9	98	48	—	14	—	—
Lab G	—	—	43	79	21	29	93
Lab I	10	110	45	—	—	28	—
Lao J	9	91	43	86	10	29	100
Lab K	9	95	39	80	12	—	—
Lab P	7	98	—	86	9	38	101
Lab S	—	—	—	—	—	30	93
No. of Labs Participating ...	7	8	9	7	8	8	6
ppm H ₂ S Mean	9	101	46	85	13.5	30	96
% Error	0	3.1	4.5	3.4	25	14	3.2
Std. Deviation	1.2	8.7	5	4.4	3.6	3	3.7
Probable Error of Mean	.31	2.06	1.13	1.12	.87	.78	1.02
Probable Error	.81	5.83	3.38	2.96	2.5	2.2	2.50
Std. Deviation from Mean	.46	3.05	1.7	1.66	1.2	1.2	1.51
Std. Deviation for 95% Confidence Level	1.1	7.2	3.8	4.07	3.0	2.5	3.9

TABLE II
GPA Sulfur Analysis Work Group H₂S Data, May 11-June 7, 1976

Gas Source	PPM H ₂ S	% Error	Experimental Data—Detector Tubes		
			No. Determinations	PPM H ₂ S (Ave.)	
Ecospan	18	22%	38	14±5	o = 1.4
Ecospan	88	6%	36	83±8	o = 2.2
Permeation Tubes	44	5%	73	46±8	o = 1.6
Field Gas	9±1*	11%	83	10±3	o = 0.55
Field Gas	98±8*	5%	73	103±13	o = 2.53
Shamburger Lake Plant Inlet	35±3*	11%	124	31±4	o = 0.79
Sun-Lateral = 2	221±15	2%	36	226±13	o = 4.75
Sun M. T. Cole = 21	93±7	9%	39	101±6	o = 2.2

o (Standard Deviation for 95% Confidence Unit)

* Precision reflects repeatability of CdSO₄ method according to GPA Standard 2265.

+ H₂S concentration was apparently continuously increasing during 4-5 hour period of CdSO₄ gas sampling. Determinations by detector tubes occurred near end of CdSO₄ method sampling and instrumental determinations even later.

TABLE III
Detector Tube H₂S Measurements by Tube Lot Numbers - June 7-8, 1976

Dräger 5/b Ch29801 5-60 ppm Range								Average
Lot No.....	157091	1050184	1050185	1050186	1056371	1052101	255761	
No. Measurements.....	5	8	4	12	3	4	3	39
PPM H ₂ S	32±1	30±1	29±1	29±2	28±0	29±1	31±1	30±1
% Error	9%	14%	17%	17%	20%	17%	11%	17%

Gastec 4LL 0-60 ppm Range								Average
Lot No.....	51215	30710	30912	40113	40809	60116	50217	50913
No. Measurements.....	19	13	6	9	6	4	4	4
PPM H ₂ S	30±2	28±2	38±1	36±1	36±1	28±1	27±1	30±1
% Error	14%	20%	9%	3%	3%	20%	23%	14%

Field Gas Source

Shamburger Lake Plant Inlet-35 PPM

TABLE IV
GPA Analysis Work Group Data, July 29, 1985

	H ₂ S	H ₂ S	H ₂ S	CO ₂	CO ₂	CO ₂
Blend No.	1	2	3	1	2	3
Nominal Blended Value (Vol %)	0.05	0.50	5.0	0.25	5.0	10.0
Laboratory	ppm	Vol %	Vol %	Vol %	Vol %	Vol %
A	460	0.585	5.27	0.237	4.73	9.78
B	472	0.583	5.35	0.248	4.82	9.75
D	448	0.542	5.63	0.250	4.63	8.98
E	458	0.552	4.78	0.230	4.87	9.93
F	473	0.620	4.87	0.250	5.22	9.45
G	437	0.540	4.38	0.286	4.93	9.17
Mean Value	458	0.570	5.05	0.250	4.87	9.51
Blended Value	481*	0.490*	5.23*	0.250**	4.99**	10.00**
Repeatability#	DT 18	0.03	0.16	0.01	0.05	0.32
Reproducibility##	DT 30	0.05	0.38	0.03	0.21	0.34
Repeatability#	GT 11	0.07	0.16	0.01	0.08	0.14
Reproducibility##	GT 14	0.07	0.38	0.01	0.13	0.44

* Measured by Iodometric Titration

** Measured by Gas Chromatography

Precision within Laboratories

Precision between Laboratories

