

0.01% nitrogen by the gas chromatographic method and 0.11% nitrogen by Kjeldahl method. Analysis of this sample after passing through a silicone column for separation on the basis of boiling point showed that there were few differences between the helium carrier gas and the carbon dioxide carrier gas curves when per cent of any area was compared to the total area. This suggests that in this type of sample the nitrogen is distributed rather evenly throughout the mixture. A shale oil gas-oil was analyzed and here some significant differences were noted in

distribution of nitrogen compounds. The data for these are given in Table IV. Further analysis of these data can show important characteristics of mixtures.

Extension of this method to the analysis of sulfur-containing compounds was not successful. A second peak could be obtained for a compound such as thiophene in the desired 4:1 ratio for one or two samples. In later runs only one peak appeared, although the silica gel column still could separate the nitrogen and carbon oxides. Apparently the sulfur oxides reacted with system

components either before or after combination with water.

#### LITERATURE CITED

- (1) Duswalt, A., Brandt, W., *ANAL. CHEM.* **32**, 272-4 (1960).
- (2) Heaton, W. B., Wentworth, J. T., *Ibid.*, **31**, 349-57 (1959).
- (3) Juranek, J., *Chem. listy* **51**, 2280-6 (1957).
- (4) Lake, G. R., *ANAL. CHEM.* **24**, 1806 (1952).
- (5) Sundberg, O. E., Maresh, C., *Ibid.*, **32**, 274-7 (1960).

RECEIVED for review August 1, 1960.  
Accepted December 5, 1960.

# Quantitative Analysis for Carbonyl Sulfide in Natural Gas by Gas-Liquid Chromatography

J. A. SCHOLS

Research and Development Laboratory, Dow Chemical of Canada, Ltd., Sarnia, Ontario

►A quantitative analysis for carbonyl sulfide in natural gas by gas-liquid chromatography has been developed using *N,N*-di-*n*-butylacetamide as a stationary phase. The use of a thermistor-type thermal conductivity detector cell made it possible to determine carbonyl sulfide concentrations ranging from 25 to 1000 p.p.m. with a 10-mv. Varian recorder. The estimated uncertainty was  $\pm 15$  p.p.m. and the time required for an analysis was 6 minutes.

CARBONYL SULFIDE, an impurity in natural gas, presents a problem in the natural gas sweetening process because it reacts irreversibly with some of the commonly used absorbents (8). It also contributes to absorbent losses in the hot carbonate process. In this light, a quick and reliable analysis for traces of carbonyl sulfide in natural gas would be desirable. Volumetric, colorimetric, spectrophotometric, and polarographic methods are available, but interference from other sulfur compounds frequently made the analyses less reliable or more time consuming. Gas-liquid chromatography was considered as a more selective method of analysis requiring less time.

Some polar stationary phases which have been frequently used in gas-liquid chromatography for hydrocarbon analyses were evaluated, but were considered to be inadequate for carbonyl sulfide because of interference from saturated hydrocarbons such as *n*-propane, *n*-butane, and isobutane. The column used by Janak (2) was likewise unsatisfactory for this purpose. Although

Bloch (1) has reported a quantitative analysis for traces of carbonyl sulfide in pyrolysis vapor, *N,N*-di-*n*-butylacetamide as a stationary phase showed better resolution of carbonyl sulfide from the hydrocarbons occurring in natural gas than the column with *n*-propyl sulfone and 2,4-dimethylsulfolane as a partitioning mixture.

#### EXPERIMENTAL

**Reagents.** *N,N* - Di - *n* - butylacetamide, b.p. 113° C. at 9 mm. pressure, Eastman Kodak Co.

Kromat FB, 30- to 60-mesh, Burrell Corp.

Carbonyl sulfide, purity 96% minimum, Matheson Co., Inc.

**Apparatus.** The apparatus was assembled in this laboratory and is essentially similar to conventional gas chromatographs. The chromatographic column was prepared by packing 12 feet of 1/4-inch O.D. copper tubing with 38 grams of Kromat FB support, coated in the usual way with 30% w./w. of *N,N*-di-*n*-butylacetamide by deposition of the substrate from acetone. The column was operated at 28° C. Helium was used as a carrier gas at a flow rate of 50 ml. per minute, measured at the exit of the detector. Gas samples were introduced with a 5-ml. syringe into the column through a silicone rubber disk or with a 6-way (Wilkens) gas sampling valve. A back-flush valve to reverse the helium flow through the column was also incorporated to permit the rapid removal of components less volatile than carbonyl sulfide. The Gow-Mac thermistor-type thermal conductivity cell (Model AEL 9677) and the column were insulated with glass wool to minimize the

effects of changes in room temperature. The thermistors were connected to a Wheatstone bridge circuit which was powered by a 13 1/2-volt battery. The bridge current was fed into a G-11A Varian recorder having 10-mv. full-scale deflection and a chart speed of 60 inches per hour. The base line drift observed with the Varian recorder was less than 0.1 mv. over a period of 1 hour. During experiments with very low concentrations of carbonyl sulfide, the Wheatstone bridge was connected to a Leeds & Northrup recorder having a range of 1 mv. and a chart speed of 30 inches per hour.

#### RESULTS

The relative retention ratios for carbonyl sulfide and various hydrocarbons obtained with a 12-foot *N,N*-di-*n*-butylacetamide column, taking the retention ratio for *n*-butane (retention time 9 minutes) as unity, are given in Table I. As propylene is the only component in natural gas that could interfere with the carbonyl sulfide peak in the chromatogram, mixtures of propylene and carbonyl sulfide in air were prepared. The samples were made up in a 5-liter round-bottomed flask with a rubber serum cap that contained 45 ml. of glass beads. The amount of carbonyl sulfide calculated to give concentrations varying between 2 and 1000 p.p.m. was introduced into the flask with a syringe. The propylene content in these mixtures varied between 0.1 and 4% v./v. The glass beads were agitated for 2 minutes to ensure a homogeneous gas mixture. The peak heights recorded with a 10-mv. recorder

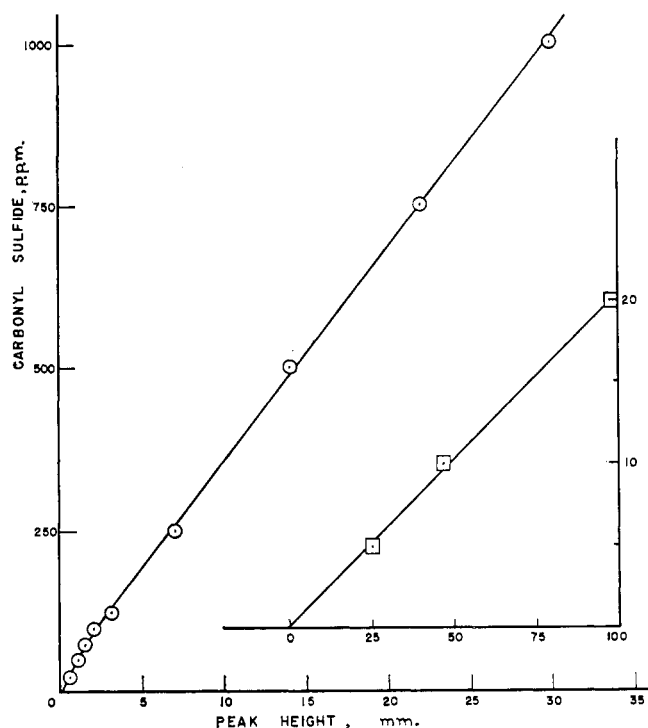


Figure 1. Calibration curves for carbonyl sulfide

○ 10-mv. Varian recorder  
 □ 1-mv. Leeds & Northrup recorder

Table I. Relative Retentions at 28° C. for a 12-Foot *N,N*-Di-*n*-butylacetamide Column

Compound	Retention Ratio
Air	0.115
Methane	0.128
Ethane	0.192
Carbon dioxide	0.209
Propane	0.374
Propylene	0.427
Carbonyl sulfide	0.526
Isobutane	0.705
<i>n</i> -Butane	1.00
Isobutene	1.11
1-Butene	1.11
2,2-Dimethylpropane	1.11
2-Butene	1.35
Isopentane	1.55
<i>n</i> -Pentane	2.97

Table II. Interference of Propylene with Carbonyl Sulfide on a 12-Foot *N,N*-Di-*n*-butylacetamide Column

Vol. % of Propylene Present	Minimum Detectable Amt. of Carbonyl Sulfide, P.P.M.
0.5	25
1.0	25
5.0	50
10.0	100

for carbonyl sulfide concentrations between 25 and 1000 p.p.m. are plotted against concentration in Figure 1. A similar plot for concentrations of

Table III. Comparative Analyses of Natural Gas Samples

Sample No.	Carbonyl Sulfide, P.P.M.	
	Mass spectrometry	Gas chromatography
1	110	110
2	90	100
3	100	80
4	700	650

carbonyl sulfide below 25 p.p.m. (1-mv. recorder) is given in Figure 1. These calibrations were carried out with a 5-ml. sample. The amounts of propylene that may be tolerated in natural gas before interference occurs with the neighboring carbonyl sulfide peak are listed in Table II. Various natural gas samples were analyzed for carbonyl sulfide both by the above gas chromatographic technique (10-mv. recorder) and by a modified Type 21-103 Consolidated mass spectrometer; the comparative results are shown in Table III.

#### DISCUSSION

The results of the comparative analyses of various natural gas samples by mass spectrometry and by the present method (Table III) are in good agreement, bearing in mind the estimated uncertainties ( $\pm 30$  and  $\pm 15$

p.p.m., respectively) of the two methods. The present method is subject to interference from propylene (Table II), but the propylene content of natural gas is invariably less than 0.5%. The use of a longer column would permit analysis of carbonyl sulfide in manufactured gases containing higher propylene levels.

Although the exact lifetime of the *N,N*-di-*n*-butylacetamide column has not yet been established, the column was satisfactorily operated for 3 weeks without any appreciable deterioration.

In addition to the high sensitivity achieved, the method is extremely rapid. Furthermore, the present instrumentation can readily be incorporated in a portable unit for field use, owing to the small size of the electrical components and the fact that column and detector block are operated at ambient temperature. Such an instrument is at present under construction.

#### ACKNOWLEDGMENT

The author expresses appreciation to D. M. Young for helpful discussion during the course of this work and to E. O. Camehl, The Dow Chemical Co., Midland, Mich., for carrying out the mass spectrometric analyses.

#### LITERATURE CITED

- (1) Bloch, M. G., paper presented at Second Symposium on Gas Chromatography, Instrument Society of America, June 11, 1959.
- (2) Janak, J., "Vapour Phase Chromatography," D. H. Desty, ed., p. 235, Butterworths, London, 1957.
- (3) Pearce, R. L., Arnold, J. L., Hall, C. K., paper presented at Gas Conditioning Conference, Norman, Okla., March 2-3, 1960.

RECEIVED for review September 20, 1960.  
 Accepted December 5, 1960.

#### Correction

### Chromatographic Estimation of Sugars in Wood Cellulose Hydrolyzates. A Routine Reflectance Method

In this article by J. E. Jeffery, E. V. Partlow, and W. J. Polglase [ANAL. CHEM. 32, 1774 (1960)], on page 1777, Table II, the value for mannan of pulp A by the authors' method should read 0.9 instead of 1.9. On the same page, column 1, lines 25 and 26, the words "with the exception of the mannan of pulp A" should be deleted.