CONTENTS

ILLUSTRATIONS

TABLES

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mm	millimeter
cm	centimeter	ms	millisecond
cm^3	cubic centimeter	nL	nanoliter
h	hour	pct	percent
KPa	kilopascals	ppm	part per million
µL	microliter	psig	pound per square inch (gage)
m	meter	s	second
MB	megabyte	V dc	volt, direct current
min	minute	µV dc	microvolt, direct current
mL	milliliter		

A CHROMATOGRAPHIC METHOD FOR RAPID FIELD DETERMINATION OF PARTS-PER-MILLION TO PERCENT LEVEL CARBON DIOXIDE IN NATURAL GAS

By Philip W. Holland[1]

ABSTRACT

This U.S. Bureau of Mines (USBM) report describes a chromatographic method that is used for rapid field determinations of carbon dioxide in natural gas streams at a USBM helium production facility. The method employs a commercially available portable gas chromatograph that is equipped with a 10-m fused-silica capillary column coated with a porous polymer. The instrument operating parameters permit determinations to be performed over a concentration range of 10 ppm to 10 pct with a frequency of 20 samples/h. The speed at which determinations can be performed is an important factor when evaluating efficiency or troubleshooting processes at the helium facility.

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INTRODUCTION

The removal of carbon dioxide from natural gas feedstocks supplied to cryogenically cooled crude helium separation units is essential. If not removed, the carbon dioxide will freeze out and plug the low-temperature regions of the equipment. The carbon dioxide contained in helium-enriched natural gas supplied to USBM crude helium separation units is typically removed by reaction with monoethanolamine in solution with diethylene glycol and a small amount of water. The water vapor in the gas stream is then removed by passing the gas through an adsorbant-filled dryer.

The carbon dioxide content of helium-enriched natural gas, supplied to the USBM's Exell Helium Plant as feed, is determined with either a dispersive-type infrared analyzer or a thermal conductivity detector (TCD) process gas chromatograph equipped with a packed column. These analyzers perform satisfactorily for monitoring the approximately 1 pct carbon dioxide content of the gas; however, they do not have the detection sensitivity or analysis speed required to evaluate or troubleshoot carbon dioxide-removal processes. These instruments are also not suitable for field use since they are not portable.

Seitz (*1*)[2] has described a sensitive method for determining carbon dioxide in helium using a helium ionization detector (HID) chromatograph equipped with dual sample valves and dual packed columns. The elution time for carbon dioxide using this instrument is within 1 min; however, a back-flushing technique must be used to remove slow eluting analytes from the column when the frequency of determination is important. The HID requires a relatively long period of time for baseline recovery when exposed to percent-level analytes; therefore, this type of detector is not suited for determinations of carbon dioxide in natural gas. The HID chromatograph is also not portable.

The method for carbon dioxide determination described in this report utilizes a commercially available, battery-operated TCD gas chromatograph equipped with a fused-silica capillary column coated with a layer of Porapak Q.[3] The operation parameters for the chromatograph were selected to provide carbon dioxide determinations over the concentration range of 10 ppm to 10 pct. The frequency at which determinations of carbon dioxide in natural gas can be performed is about 20/h.

DESCRIPTION OF INSTRUMENTATION

The portable gas chromatograph used in development of the method is a model P200 instrument manufactured by Microsensor Technology, Inc. (MTI), Fremont, CA. The portable gas chromatograph and data system are shown in figure 1.

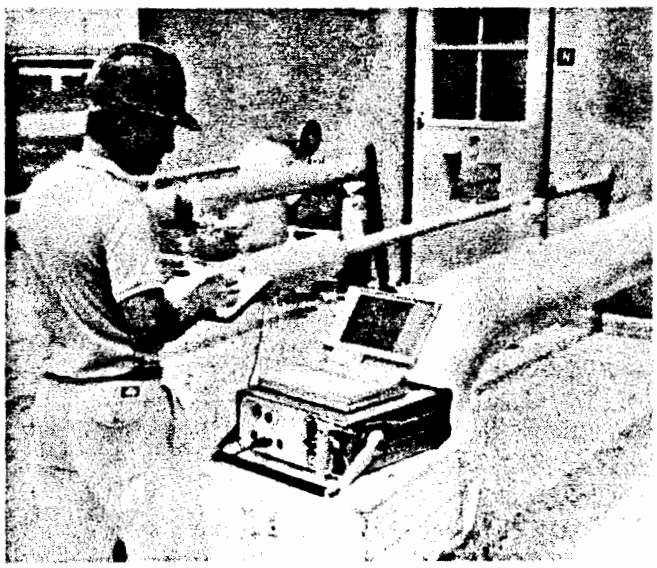

Figure 1.—Portable gas chromatograph and data acquisition system.

The chromatograph contains two column modules, each having its own solid-state injection system, analytical column, column heater, temperature sensor, and TCD. The chromatograph has its own high-pressure (12,411 KPa or 1,800 psig) carrier gas cylinder, which is regulated internally to supply 552 KPa (80 psig) carrier pressure to the two column modules. Each column module has its own pressure regulator, allowing the column inlet pressure to be independently controlled over the range of 68 to 310 KPa (10 to 45 psig); this corresponds to a carrier flowrate range of about 0.2 to 8 ml/min. The injection systems of the column modules share a common sampling pump that is used to purge the sample loops before injection.

The sample injection system for each column module is fabricated on a 2.54- by 1.90-cm silicon wafer using a silicon micromachining, batch-type process (*2*). Each injection system incorporates two silicon microvalves with internal volumes of 4 nL, an 8-μL-volume sample loop, and etched grooves (microchannels) on the surface of the silicon wafer.

[2]Italic numbers in parentheses refer to items in the list of references at the end of this report.

[3]Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

Injection of the sample is accomplished through microprocessor control. The gas channels and sample loop are purged with 0.2 to 5 ml of sample gas by "pulling" it through the injection system and sample loop with the sampling pump. At the end of the purge sequence, the sample is trapped in the loop by closing the sample inlet valve. The sample is then pressurized with carrier gas to a preset pressure, and the injection valve is opened from 10 to 255 ms, allowing the sample to be "pushed" into the carrier stream. The injection volume can be varied from 0.5 to 7 μL, depending on the time period that the injection valve is open. The injection time period for the described method is either 10 ms for percent-range samples or 255 ms for ppm-range samples.

Miniaturization of the injection system and low-volume interconnecting microchannels allows the use of 1 to 12 m-by 0.1-mm-ID coated capillary columns, 0.32-mm-ID PLOT (porous layer open tubular) columns, and 25-cm-long by 0.5-mm-ID micropacked columns. The length of the column and the type of stationary phase selected are based on the specific determination to be performed. The run time is typically less than 1 min.

The analytical column and reference column are in a planar spiral configuration and are "sandwiched" between copper disks to provide a low mass column "oven" for rapid temperature stabilization. The temperature of each column is controlled independently at an isothermal temperature ranging from 30 to 180° C. The time required to reach the column operating temperature from start-up is about 1 min.

The TCD in each column module is also fabricated by silicon micromachining. The TCD consists of four matched nickel filaments suspended in two channels with a sample and reference filament for each channel. The nickel filaments are deposited on a silicon wafer housed in a ceramic package. The TCD has a volume of 20 nL and a time constant of less than 10 ms; it measures 0.64 cm in length, 0.64 cm in width, and 0.17 cm in height.

The filaments in the detector are fabricated from the same thin film deposition, which results in precise matching. Since silicon is an excellent thermal conductor, the detector exhibits excellent linearity and stability. The linear dynamic range of the detector is reported to be 10^6.

The detector signal is amplified according to a user-selected gain setting of "low," "medium," or "high" that corresponds to detector signal gains of 5, 50, and 500, respectively. The detector amplifiers provide an analog output of 0 to 1 V dc and from 0 to 10 V dc. This output can be supplied to a strip chart recorder or computing integrator.

The chromatography software supplied with the system runs on computers using an MS-DOS operating system. All communications to the chromatograph and data transmissions from the chromatograph are through an RS232 serial interface. The data transmitted from the chromatograph are used by the software for dual-channel chromatogram displaying, data processing, and data storage. The software operates under the MS-Windows (version 3.0 or higher) environment and provides for data processing and reporting as well as complete control and status monitoring of the chromatograph.

The portable computer used as the data station has a random access memory (RAM) of 2 MB. Data files are stored either on the computer's 60-MB hard disk drive or 1.44-MB internal floppy disk drive. The internal nickel/cadmium battery of the portable computer provides 2.5 h of continuous operation before recharging is required.

ANALYTICAL PROCEDURES

A chromatograph equipped with a 10-m by 0.32-mm-ID Porapak Q PLOT column was used for the described method. The Porapak Q column is capable of separating nitrogen, methane, carbon dioxide, ethane, propane, acetylene, and ethylene. Before its initial use, the column was conditioned at 180° C for 1 h with the carrier gas flow adjusted to 4 cm^3/min.

INSTRUMENT OPERATION PARAMETERS

The chromatograph operation parameters for performing carbon dioxide determinations are shown in table 1.

With the exception of the column inlet pressure, all of the set points are transferred to the chromatograph by the software. The column inlet pressure is set manually by adjusting the column pressure regulator located at the rear panel of the chromatograph. A column inlet pressure of 211.7 KPa (30.7 psig) was selected to provide a carrier flow rate of about 4 cm^3/min.

Table 1.—Operation parameters for performing carbon dioxide determinations

Column temperature . . .	60° C
Column inlet pressure . .	211.7 KPa (30.7 psig)
Detector output setting . .	medium (gain of 50)
Sample injection time . . .	10 or 255 ms
Sampling time	10 s
Run time	45 s

A column oven temperature of 60° C was chosen to provide adequate separation while minimizing drain on the chromatograph's 12-V dc lead/acid storage battery. At this column temperature, the storage battery provides an operation time of about 6 h. The elution time for carbon dioxide using the selected carrier flow rate and column temperature is about 33 s.

A detector output setting of "medium" (gain of 50) was used to provide adequate sensitivity for carbon dioxide determinations from the 10-ppm to 10-pct range. Selection of a single detector output setting allows the same peak-slope sensitivity setting to be used over the entire concentration range. The requirement for greater sensitivity at low ppm carbon dioxide levels was achieved by changing the sample injection time from 10 ms to 255 ms. The change in sample injection time increases the volume of sample admitted to the column from about 0.5 μL to 6 μL.

A sampling time of 10 s was selected. This is the period of time that the sample pump operates to purge the injection system and sample loop before injection occurs. A sampling time longer than 10 s should be avoided since operation of the pump rapidly drains electrical power from the storage battery.

The run time for the method was selected to be 45 s, which is 10 s after the elution of the carbon dioxide peak. Although the time to complete a carbon dioxide determination is 45 s, an additional 2 min is allowed to ensure that all other components of the natural gas sample have eluted from the column before the next determination is performed.

INTEGRATION PARAMETERS

The peak slope and fine slope sensitivities and peak width are programmed into the software as timed events. For integration of the carbon dioxide peaks, the slope and fine slope sensitivities were selected to be 50 and 30 μV dc/s, respectively. These values were selected based on the "medium" detector output setting that is used. An integration peak width (width at base) value of 4 s is used to provide proper integration of peaks when determining carbon dioxide from the ppm to percent range. To speed up the integration processing time and to conserve data storage space on the computer's hard disk, signal integration is inhibited during the first 20 s of the run.

DISCUSSION OF ANALYTICAL RESULTS

LINEARITY STUDY

The linearity for carbon dioxide over the concentration ranges of 10 to 1,000 ppm and 0.1 to 10 pct was demonstrated by comparing a series of weighed standards (*3-4*) containing carbon dioxide in helium. The calculated carbon dioxide contents of the weighed standards used to make comparisons over the two ranges are given in table 2.

Table 2.—Carbon dioxide contents of weighed standards

PPM-range standards		Percent-range standards	
Standard	CO_2 content, ppm	Standard	CO_2 content, pct
1	9.960 ± 0.003	1	0.09761 ± 0.00001
2	33.990 ± 0.010	2	0.9997 ± 0.0001
3	100.190 ± 0.010	3	3.4427 ± 0.0004
4	652.4 ± 0.2	4	7.3807 ± 0.0008
5	976.1 ± 0.1	5	10.7286 ± 0.0003

Linear regression plots of the peak areas versus the carbon dioxide contents for the 10- to 1,000-ppm range standards and the 0.1- to 10-pct range standards are shown in figures 2 and 3, respectively. The calculated correlation coefficients (R^2 values) for two curves are 0.999959 and 0.999992, respectively.

The sample injection time was the only chromatograph operation parameter changed for the two comparison studies. For the standards that contained from 9.96 to 976.1 ppm carbon dioxide, the sample injection time was set to 255 ms; and for standards that contained 0.1 pct carbon dioxide and greater, the sample injection time was set to 10 ms.

REPEATABILITY STUDY

The repeatability of the method at the 10-ppm and 1-pct carbon dioxide levels was demonstrated by performing 10 successive injections of natural gas samples. The injections were performed at the frequency of every 3 min. Weighed standards containing 100.19 ± 0.01 ppm and 3.4427 ± 0.0004 pct carbon dioxide in helium were used to perform a two-level calibration of the chromatograph prior to beginning each run sequence. The results are given in table 3.

A chromatogram of a natural gas sample containing about 1 pct carbon dioxide is shown in figure 4.

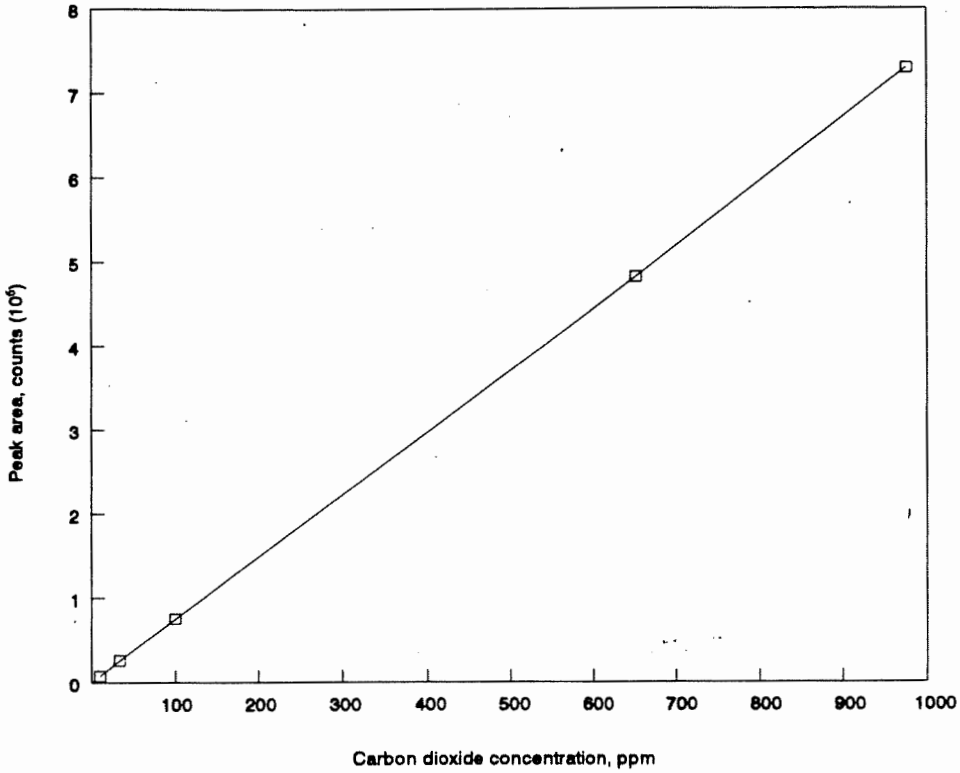

Figure 2.—Linear regression plot of peak area versus carbon dioxide concentration over 10- to 1,000-ppm range.

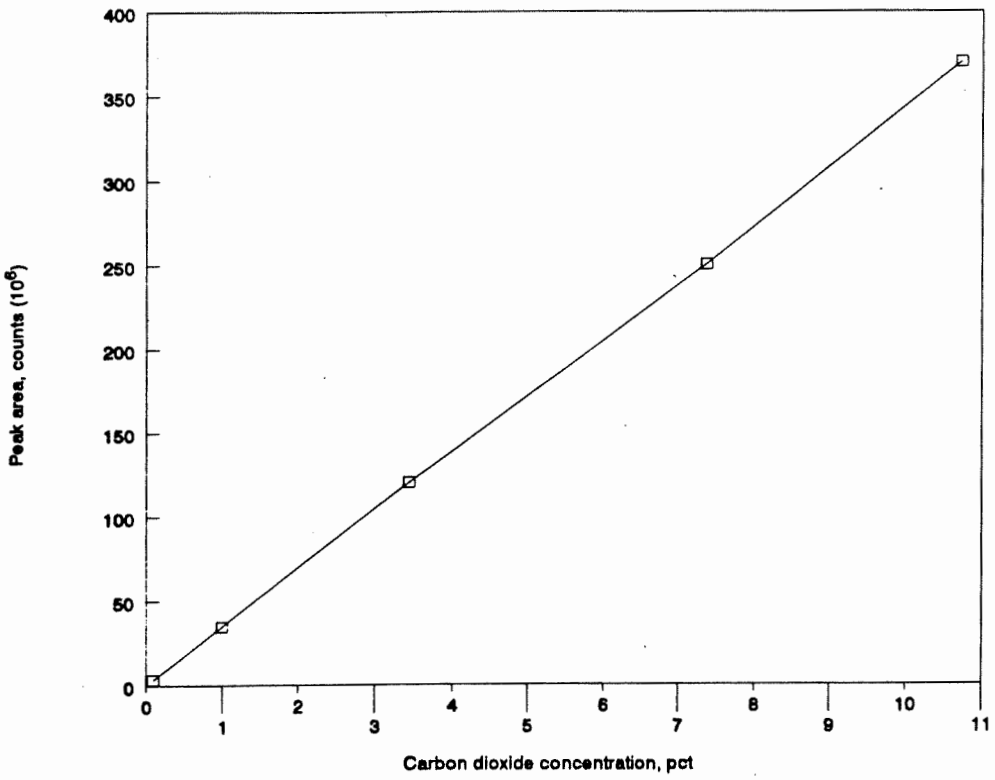

Figure 3.—Linear regression plot of peak area versus carbon dioxide concentration over 0.1- to 10-pct range.

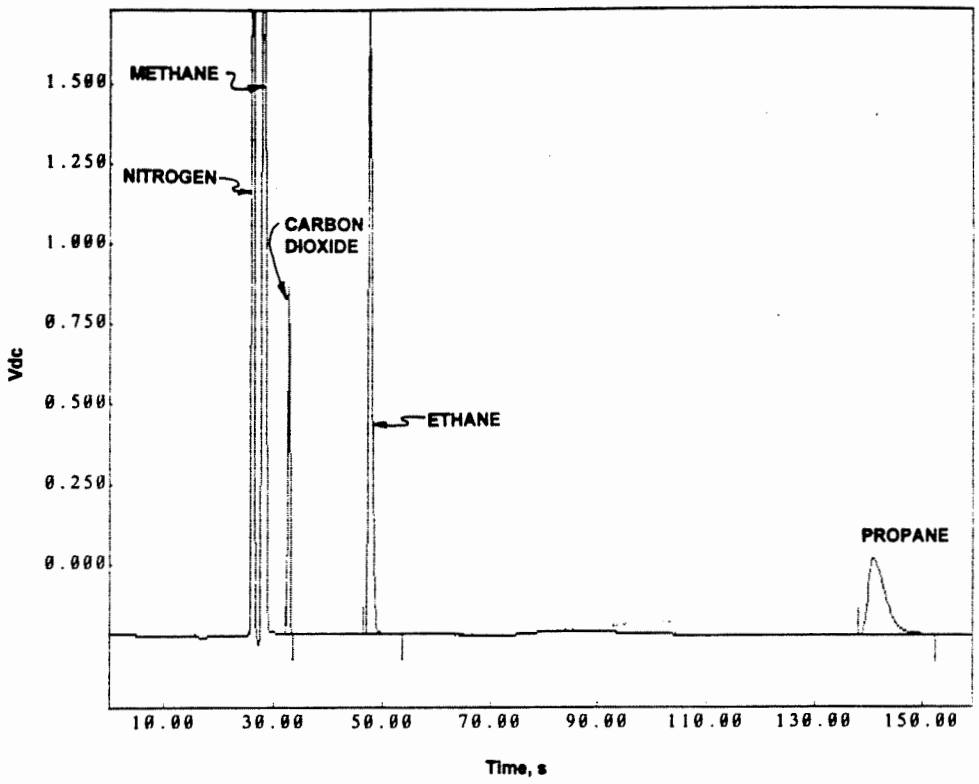

Figure 4.—Chromatogram of natural gas sample containing about 1 pct carbon dioxide.

Table 3.—Repeatability of analytical method

10 determinations of 10 ppm carbon dioxide in natural gas	10 determinations of 1 pct carbon dioxide in natural gas
9.69 ppm	1.302 pct
10.22	1.298
9.65	1.302
10.28	1.299
9.67	1.297
9.88	1.298
10.69	1.297
9.64	1.298
10.55	1.299
10.15	1.299
Mean = 10.04 ppm	Mean = 1.299 pct
SD = ±0.39 ppm	SD = ±0.002 pct

SD = standard deviation for 10 determinations.

ON-SITE STUDY

On-site determinations of carbon dioxide in a helium-enriched natural gas process stream were performed at the USBM's Exell Helium Plant. The stream passes through a carbon dioxide removal system and subsequently through one of a pair of gas dryers. The intent of the study was to monitor the carbon dioxide content of the gas stream, after completing a specific valve-switching sequence which places a regenerated dryer in service, while removing the spent dryer for regeneration.

Before beginning the study, the chromatograph was calibrated using a certified standard containing 187±2 ppm carbon dioxide in helium. The chromatograph's operation parameters were set as listed in table 1. A sample injection time of 255 ms was selected to ensure adequate sensitivity for the expected low-ppm carbon dioxide content in the gas stream.

A plot of the stream's carbon dioxide content versus time (time "zero" = valve-switching time) is shown in figure 5. The carbon dioxide concentration in the stream was initially determined at a point downstream from the gas dryers and found to be 13 ppm. Determinations were then performed at this point every 3 min for a 36-min period after completion of the valve-switching sequence. The switching sequence required about 2 s to complete. The stream was sampled through a metering valve that was adjusted to allow a flow of 200 cm^3/min to pass through the chromatograph's inlet system.

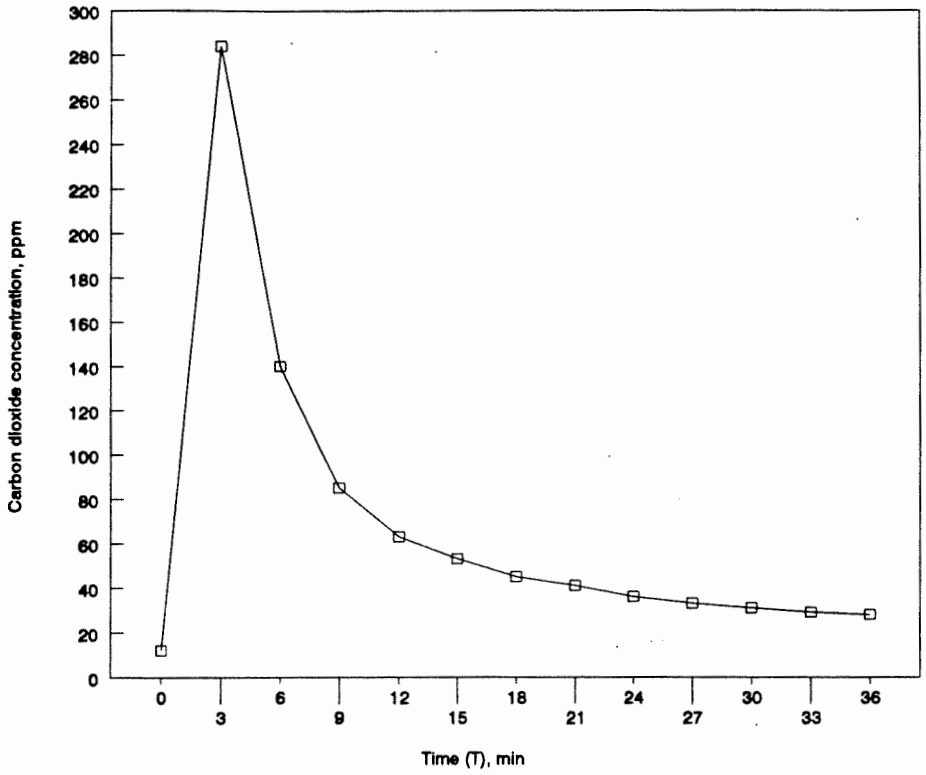

Figure 5.—Plot of carbon dioxide content versus time.

CONCLUSIONS

This chromatographic method provides for rapid field determinations of carbon dioxide in natural gas. The range of the method is from 10 ppm to 10 pct carbon dioxide. Owing to the miniaturization of the chromatographic system and the relatively short PLOT capillary column (10 m in length) employed for separation, determinations can be performed accurately and repeatably at a rate of every 3 min. The method has been used successfully for on-site determinations of a rapidly changing carbon dioxide content in a natural gas process stream.

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U.S. Department of the Interior
Mission Statement

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Cover Photo: A U.S. Bureau of Mines geologist collects field data to calculate the Coal Mine Roof Rating (CMRR). (Photo: David K. Ingram, Pittsburgh Research Center, U.S. Bureau of Mines)