Composition of Natural Gas and Crude Oil Produced From 10 Wells in the Lower Silurian "Clinton" Sandstone, Trumbull County, Ohio

By Robert C. Burruss and Robert T. Ryder

Chapter G.7 of
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[Tables follow figures]

Conversion Factors

Multiply	By	To obtain
	Length	
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
micrometer (µm)	0.000039	inch (in.)
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
	Area	
square mile (mi^2)	2.590	square kilometer (km^2)
	Volume	
cubic foot (ft^3)	0.02832	cubic meter (m^3)
	Velocity	
centimeters per second (cm/sec)	0.3937	inches per second (in./sec)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$°F=(1.8×°C)+32$

Gas is measured in cubic feet using the following terms and abbreviations, which are commonly used in the oil-and-gas industry: standard cubic feet (SCF), million cubic feet (MMCF), and trillion cubic feet (TCF).

The isotopic composition of carbon (carbon 13, ^{13}C) in methane is reported as the deviation (expressed as $\delta^{13}C$) in units of parts per thousand (per mil) relative to the Vienna Peedee belemnite (VPDB) standard.

The isotopic composition of hydrogen (deuterium, ^{2}H) in methane is reported as the deviation (expressed as $\delta^{2}H$) in per mil relative to the Vienna standard mean ocean water (VSMOW).

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By Robert C. Burruss[1] and Robert T. Ryder[1]

Abstract

Natural gases and associated crude oils in the "Clinton" sandstone, Medina Group sandstones, and equivalent Tuscarora Sandstone in the northern Appalachian basin are part of a regional, continuous-type or basin-centered accumulation. The origin of the hydrocarbon charge to regional continuous-type accumulations is poorly understood. We have analyzed the molecular and stable isotopic composition of gases and oils produced from 10 wells in the "Clinton" sandstone in Trumbull County, Ohio, in an initial attempt to identify the characteristics of the accumulated fluids. The analyses show that the fluids have remarkably uniform compositions that are similar to previously published analyses of oils (Cole and others, 1987) and gases (Laughrey and Baldasarre, 1998) in Early Silurian reservoirs elsewhere in Ohio; however, geochemical parameters in the oils and gases suggest that the fluids have experienced higher levels of thermal stress than the present-day burial conditions of the reservoir rocks. The crude oils have an unusual geochemical characteristic: they do not contain detectable levels of sterane and triterpane biomarkers. The origin of these absences is unknown.

Introduction

In the northern Appalachian basin, the "Clinton" sandstone (usage of Ryder, 2000[2]) Medina Group sandstones, and equivalent Tuscarora Sandstone of Early Silurian age are the reservoirs for a regional accumulation of natural gas and oil. A continuous-type (basin-centered) part of this regional accumulation containing an estimated 30 trillion cubic feet (TCF, a standard abbreviation used in the oil and gas industry) of recoverable gas covers an area of 17,000 square miles (mi^2) in a band that stretches from western New York through western Pennsylvania and eastern Ohio to northernmost West Virginia (Ryder and others, 1996). The gas accumulation occurs in rocks of low permeability, usually 0.1 millidarcies (mD) or less, downdip of more permeable, water-saturated rocks. The rocks updip from the continuous-type gas accumulation contain accumulations of oil and gas that have characteristics of both continuous-type (unconventional) and discrete (conventional) accumulations (Ryder, 1998).

In the continuous-type part of the accumulation, individual wells ultimately produce between 50 to 450 million cubic feet (MMCF, an oil and gas industry abbreviation) of natural gas. In addition to gas, many wells produce variable amounts of brine and crude oil. The gas-to-fluid ratio is variable but generally high, on the order of 50,000 to 500,000 standard cubic feet (SCF, an oil and gas industry abbreviation) of gas per barrel of oil or brine. The amount of oil and brine produced affects the economics of individual wells because of the cost incurred to dispose of brine or the value added through the sale of oil. In general, the best gas producers are those wells that produce the least oil and brine.

To better understand the origin of the gas within the "Clinton" sandstone and Medina Group sandstones in the northern Appalachian basin, we are investigating the geochemistry of the gas and the co-produced oil. This report documents 10 oil samples and 3 gas samples from 10 wells producing from "Clinton" sandstone in Trumbull County, Ohio. Future work will focus on samples from both shallower and greater burial depths, allowing study of the range in geochemical properties of the produced hydrocarbons as a function of depth and thermal history of the reservoir rocks.

Previous workers have published analyses of crude oils and natural gases from Silurian reservoirs in the northern Appalachian basin (Barker and Pollock, 1984; Powell and others, 1994; Cole and others, 1987; Jenden and others, 1993; Drozd and Cole, 1994; Laughrey and Baldassare, 1998). Cole and others (1987) suggest that most of the oil in Silurian

[1]U.S. Geological Survey, Reston, Va.

[2]The "Clinton" sandstone in Ohio was miscorrelated by drillers with strata in the type Clinton Group of New York when in fact it is equivalent to the underlying type Medina Group of New York. Although this miscorrelation has caused confusion in nomenclature, the term continues to be used widely in the literature and by the oil and gas industry. Early drillers correctly identified the informal Medina sandstone in Ohio as a partial equivalent of the type Medina Group of New York.

reservoirs in Ohio was generated from marine black shale of Devonian age. Most oil in the Lower Silurian "Clinton" sandstone may have been generated from Middle Ordovician black shale (Drozd and Cole, 1994; Ryder and others, 1998). Molecular and isotopic data on natural gas from Silurian reservoirs in western and central Pennsylvania (Laughrey and Baldassare, 1998) are not as diagnostic of the source sediments for that gas as are the geochemical parameters measured in oil samples. The general conclusion of the work on gases from reservoirs in the "Clinton" sandstone is that they were derived from thermally mature, marine organic matter and that they were probably generated from strata older than Silurian.

Sample Locations

The wells sampled are all within 10 miles (mi) of the southern end of Mosquito Creek Lake, Trumbull County, Ohio, as shown on figure 1. With the exception of two wells sampled for oil in Weathersfield Township, the locations of all samples are within 5 mi of stratigraphic cross section *D–D′* of Keighin (1998) through the "Clinton" sandstone interval. The position of the cross section is shown in figure 1. Selected information on the wells sampled is listed in table 1. Three of the wells in this study were included in a separate report on the potential impact of oil and gas development on water quality in Trumbull County (Barton and others, 1998).

Sampling and Analytical Methods

All oil and gas samples for this study were obtained with the assistance of operating companies' field personnel from the wellhead or from the oil and gas separator of individual wells. Gas was sampled at the pressure-gauge port on the production tubing using evacuated stainless-steel cylinders supplied by Isotech Laboratories, Inc., Champaign, Ill. Oil was sampled, where possible, at the drain for the fluid-level sight glass on the oil and gas separator. The oil is initially saturated with gas at the separator pressure and foams from exsolution of the gas as it exits the sight glass drain. As noted in table 1, two samples could not be obtained this way, and the oil was sampled either from the flow line to the stock tank or from the drain valve at the bottom of the stock tank. The latter sample was relatively heavy oil with some brine.

All samples were analyzed by standard analytical methods. Natural-gas samples were analyzed for molecular composition by gas chromatography and for stable isotopic composition by isotope-ratio mass spectrometry at Isotech Laboratories, Inc. Carbon isotopic composition was determined for methane (C_1), ethane (C_2), and propane (C_3), and hydrogen isotopic composition was determined for methane. Carbon (^{13}C) isotope ratios are reported in standard parts per thousand (per mil) notation relative to the Vienna Peedee belemnite (VPDB) standard, and hydrogen (^{2}H) isotope ratios are reported relative to the Vienna standard mean ocean water (VSMOW) for both gases and oils. Nitrogen (^{15}N) isotope ratios are reported relative to atmospheric nitrogen.

Crude oil samples were analyzed by the U.S. Geological Survey (USGS) in Denver, Colo. The American Petroleum Institute (API) gravity (equivalent to density) of the oil samples was determined gravimetrically using the API standard method. Oils were fractionated by dilution in *n*-heptane to remove asphaltenes. A concentrate of the solution was further fractionated by column chromatography on silica gel by successive elution with heptane, benzene, and benzene-methanol (1:1 volume-to-volume (v/v) concentration ratio) to collect the saturated hydrocarbon, aromatic hydrocarbon, and resin (nitrogen-, sulfur-, oxygen- (NSO-) bearing compounds) fractions, respectively. The carbon stable-isotope composition of an aliquot (a representative sample) of the saturated and aromatic hydrocarbon fractions was determined on a Micromass Optima isotope-ratio mass-spectrometry system.

Gas chromatography of the whole oil and of the saturated and aromatic hydrocarbon fractions was performed with a Hewlett Packard Model 6890 (HP6890) gas chromatograph with a 60 meter (m) × 0.32 millimeter (mm) × 0.25 micrometer (µm) HP-1 fused silica capillary column and a flame ionization detector (FID). The oven was programmed from 50°C to 330°C at 4.5°C per minute and held isothermally at 330°C for 15 minutes with a helium carrier-gas flow rate at 35 centimeters per second (cm/sec). Gas chromatography-mass spectrometry (GCMS) of the saturated hydrocarbon fraction of one oil sample was performed with a HP6890-JEOL GCMate system in selective ion-monitoring mode to identify steranes and terpanes in the fraction.

Results

Natural Gases

The molecular and isotopic compositions of natural gas from three wells are presented in table 2. All three gas samples were rich in methane (about 90 mole percent) with low concentrations of hydrocarbons that have more than three carbon atoms. All samples contained a trace of helium and between 2.5 and 2.8 mole percent nitrogen. The gas compositions of these samples are consistent with those reported for the "Clinton" sandstone in Ohio by the U.S. Bureau of Mines (Moore, 1982).

The carbon isotopic composition of methane, ethane, and propane in all samples is within 1 per mil for all three components. The variation in the hydrogen isotopic composition of methane in the samples is only slightly larger at about 3 per mil. In all three samples, the content of carbon dioxide was so low (0.01 percent or less) that the carbon isotopic composition in the carbon dioxide could not be determined (indicated by "n.a." in table 2).

Crude Oils

Bulk parameters and selected molecular parameters of the crude oil samples are listed in table 3. The API gravity of 9 of the 10 samples was near 40° or greater. The exception, 37° API for the No. 7 Consumer well, was measured on a sample obtained from the stock tank instead of the separator. The oils were uniformly high (86 to 90 weight percent) in saturated hydrocarbons and contained 9 percent or less aromatic hydrocarbons. Carbon isotopic compositions of the saturated and aromatic hydrocarbon fractions showed small ranges of 0.6 per mil and 0.7 per mil, respectively.

Gas chromatograms of the whole oil, the saturated hydrocarbon fraction, and aromatic hydrocarbon fraction for samples from the 10 wells are shown in figures 2*A*, 2*B*, and 2*C*, respectively, through figures 11*A*, 11*B*, and 11*C*. The saturated hydrocarbon gas chromatograms have characteristics similar to those of the "Clinton" sandstone reported by Cole and others (1987). Molecular parameters derived from the gas chromatograms of the saturated hydrocarbon fractions are listed in table 4. In general, all the gas chromatographic data show that these oil samples are remarkably uniform in composition. The whole-oil chromatograms for samples from the No. 1 Wargo, No. 1 Rhine, No. 1 Gowdy, and No. 7 Consumer wells show depletion in the low-carbon number range (lower than *n*-C_{10}), which suggests that the lighter *n*-alkanes were lost by evaporation. The pristine-to-phytane (pr:ph) ratios are given as quotients in table 4 and range from 1.07 to 1.63. The lowest value appears to be an artifact from the software that calculates these properties. This low value is not apparent from the relative peak heights in the gas chromatogram in figure 7*B*; however, two groups of oils apparently can be defined on the basis of the pr:ph ratio, one with pr:ph of about 1.6 and another with pr:ph about 1.3. Whether or not this difference is significant will require analysis of additional samples to identify the full range of variation in this property of oils produced from the "Clinton" sandstone and Medina Group sandstones.

Mass fragmentograms derived from gas chromatography-mass spectrometry (GCMS) studies of crude oil sample 97MCR5 from the No. 1 Baker well are shown in figure 12. The most striking feature of all four fragmentograms is that no ions were detected for the triterpane, sterane, hopane, or aromatized equivalent biomarkers, an indication that this oil has an unusual composition with no detectable biomarkers. All the other oils were examined in a reconnaissance mode, and no biomarkers were detected.

Discussion

The data shown in the tables and the gas chromatograms demonstrate that these gases and oils have a remarkably uniform composition. Two of the oils that show evaporative loss of low-molecular-weight hydrocarbons, from the No. 1 Wargo and No. 7 Consumer wells, were obtained from the flow line to the stock tank or from the stock tank itself. These oils were open to the atmosphere prior to sampling, and evaporative loss is expected. The other oils with evidence of loss of low-molecular-weight compounds, No. 1 Rhine and No. 1 Gowdy, were sampled from the separator and analyzed at the same time as the other samples. Different amounts of evaporative loss from individual samples during analysis are unlikely, and the cause of this aspect of the oils is unknown.

The possible grouping of the oils based on a small distinction in the pristane-to-phytane ratio needs further examination with other geochemical parameters. The fact that the anomalously low pristane-to-phytane ratio in one sample appears to be an artifact of the software that calculates this parameter suggests that small variations in this parameter must be evaluated carefully.

All the oil samples have a slight odd-carbon-number preference (average 1.05, based on the carbon preference index (CPI) reported in table 4). This preference is similar to the odd-carbon-number preference in oil samples from Ordovician reservoirs in Ohio reported by Ryder and others (1998).

The most unusual feature of the oil samples is the absence of common biomarker compounds. The fragmentograms in figure 12 show a baseline response with no detectable compounds that yield ions for terpanes (m/z = 191), steranes and hopanes (m/z = 217), or the aromatized equivalents of these compounds (m/z = 231 and 253, respectively). Normal alkanes are present in the molecular weight range of the biomarkers (C_{21} to C_{35}), demonstrating that no physical fractionation process (such as phase separation) has removed all the compounds in this molecular weight range. Tests were performed on the analytical method to ensure that no problems occurred during sample preparation. As a final test, the sample was sent to another laboratory outside of the U.S. Geological Survey. This laboratory could not detect biomarkers in the oil (J. David King, U.S. Geological Survey, written and oral communications, 1997).

The absence of biomarkers in these oil samples is puzzling. A combination of the following three factors could lead to the development of an oil with no biomarkers: (1) some lower Paleozoic source rocks generate oils with low concentrations of biomarkers, (2) experimental studies demonstrate that most biomarkers are released from the source during the early stages of generation, and (3) biomarkers can be cracked thermally and eliminated from an oil at high levels of thermal maturity. There are, however, no examples documented in the literature.

Conclusions

The 10 oils and 3 natural gases sampled from 10 wells producing from the "Clinton" sandstone in Trumbull County, Ohio, are remarkably uniform in composition. The oils are similar in composition to other Lower Silurian oils from Ohio reported by Cole and others (1987), and the gases are similar

to gases in Lower Silurian reservoirs in Ohio reported by Laughrey and Baldassare (1998). The isotopic composition of the gases and the chemical composition of the oils suggest that they experienced high levels of thermal maturity, possibly greater than those of the present-day burial conditions of the reservoir rocks.

Acknowledgments

Rick Liddle, Lomak Petroleum, Inc., and Loren Smith, Loma Enterprises, Inc., enthusiastically gave permission and made arrangements for us to sample the wells. Assistance with field sampling was kindly and patiently provided by R. Pettanati, Loma Enterprises, Inc., and J. Frederick, Lomak Petroleum, Inc. The opportunity to combine our sampling activities with field work and collaborative research with Gary Barton, Water Resources Division, USGS, was a delightful bonus.

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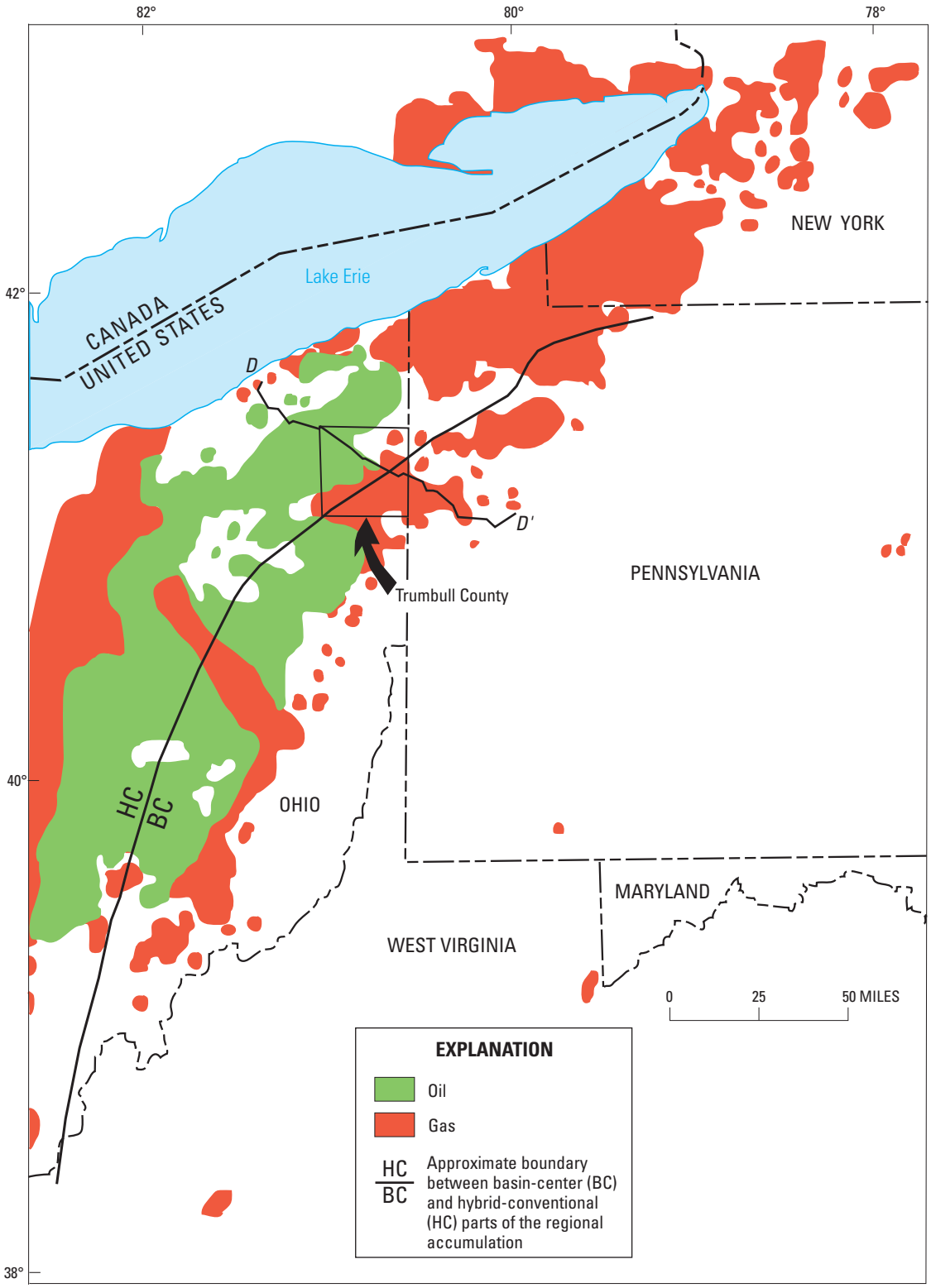
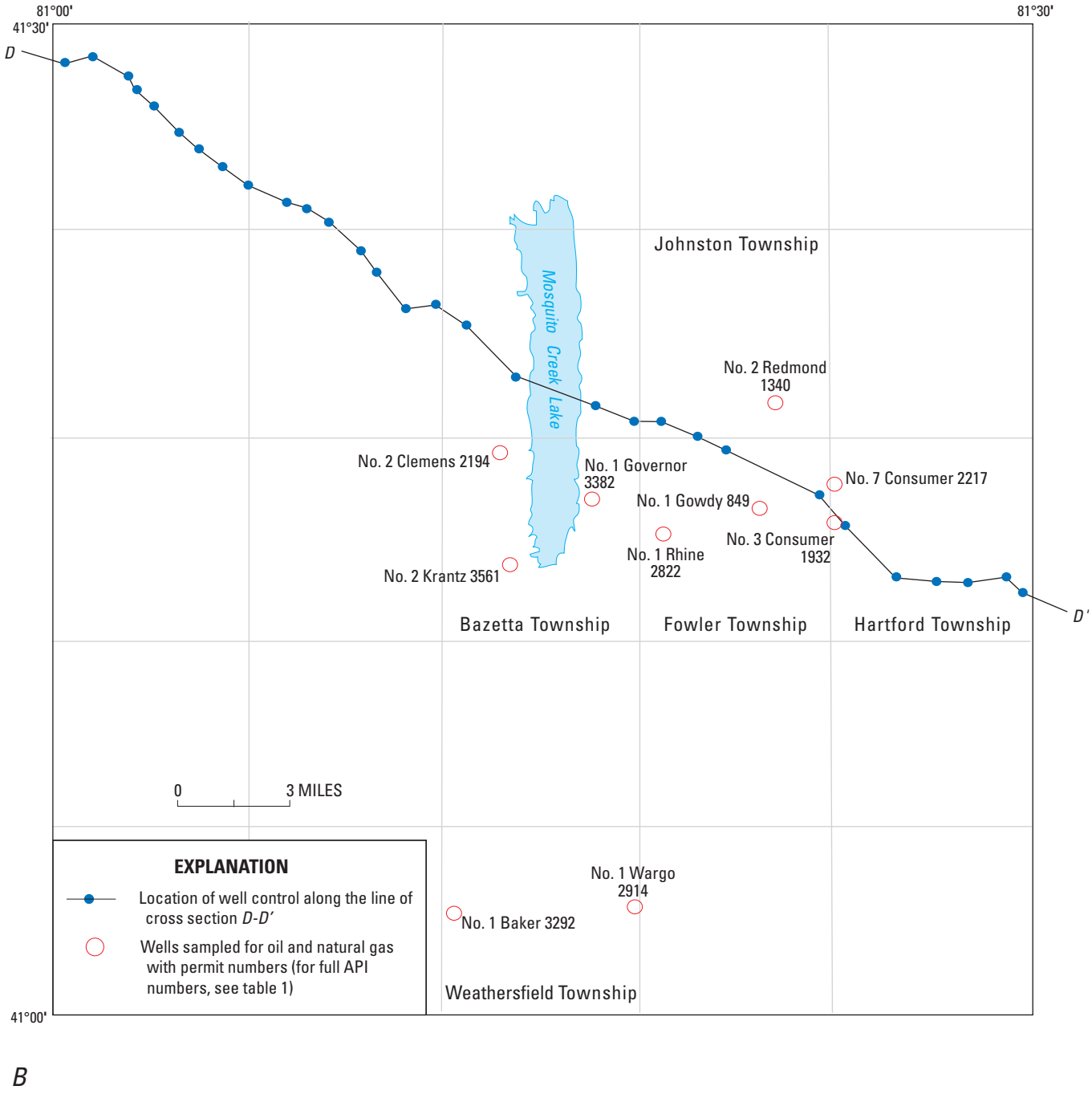
Figures 1–12 and Tables 1–4

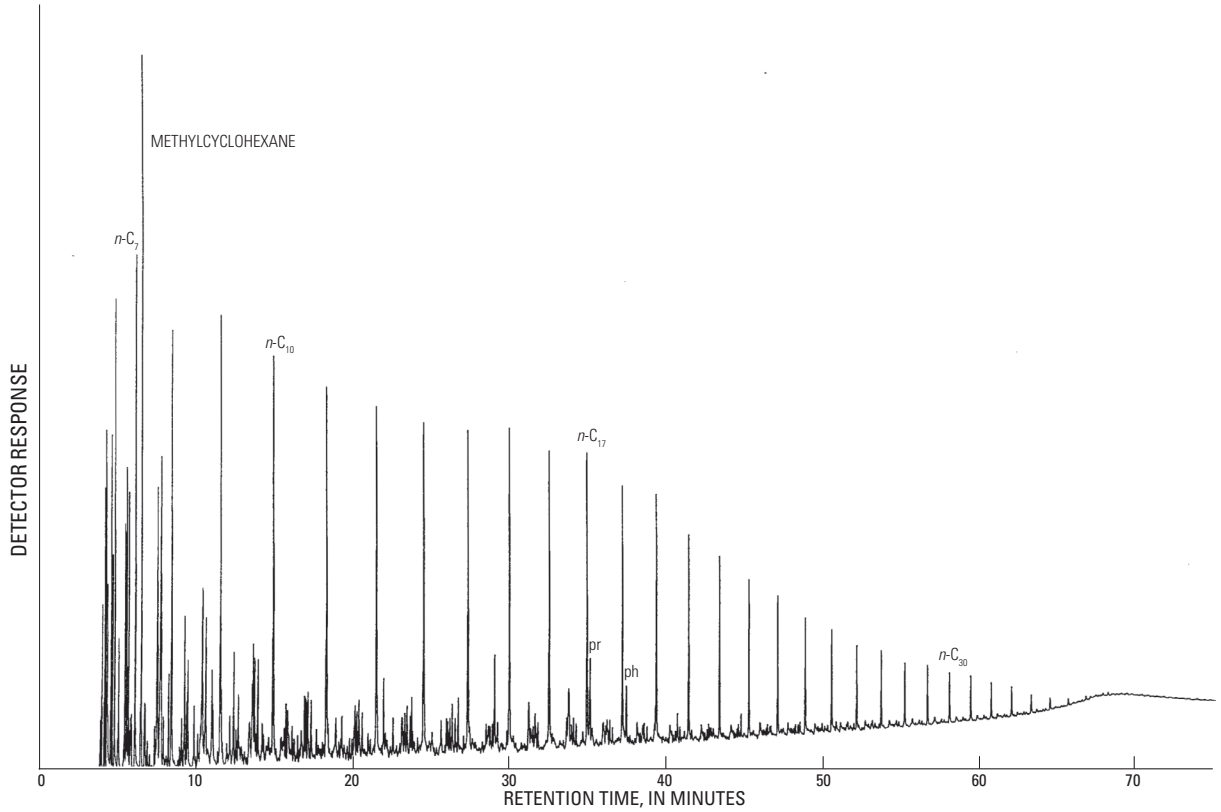

82°
80°
78°
42°
40°
38°
NEW YORK
Lake Erie
CANADA
UNITED STATES
D
D'
PENNSYLVANIA
Trumbull County
OHIO
HC
BC
MARYLAND
WEST VIRGINIA
0
25
50 MILES
EXPLANATION
Oil
Gas
HC
BC
Approximate boundary between basin-center (BC) and hybrid-conventional (HC) parts of the regional accumulation

A

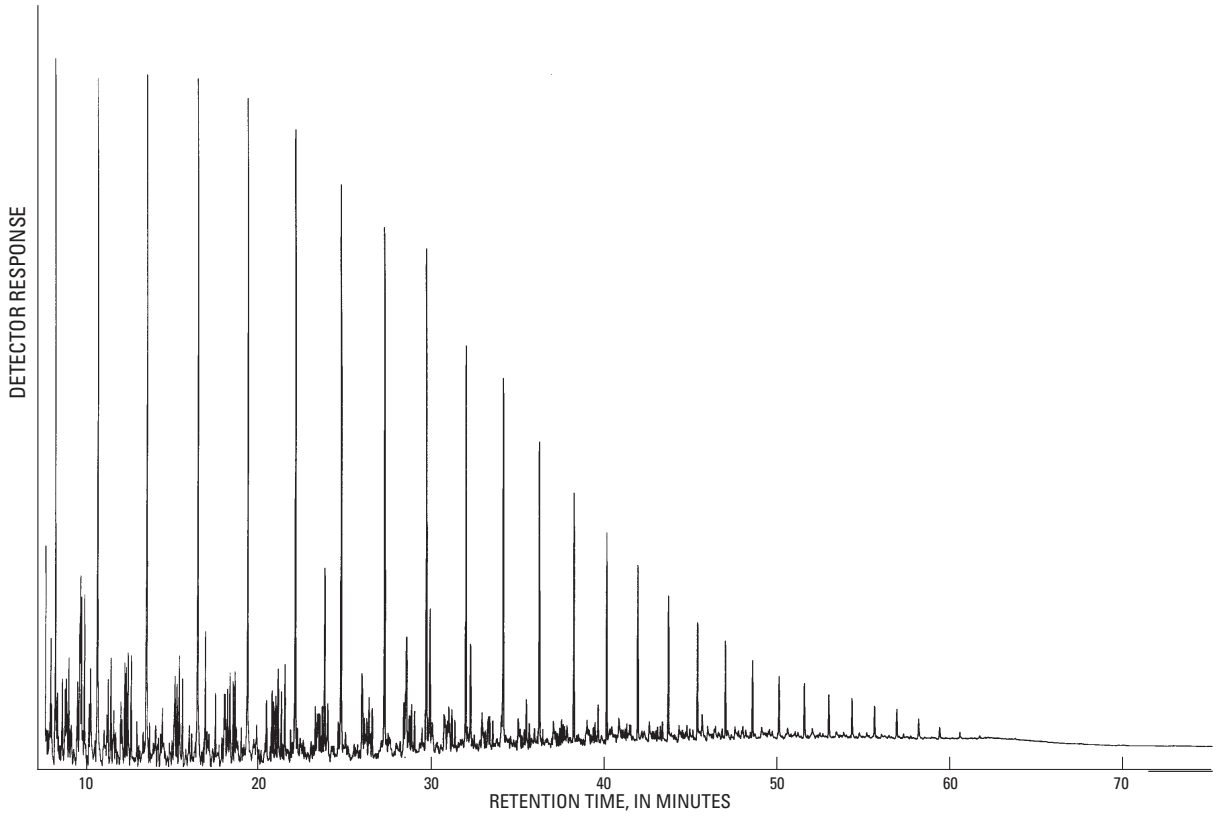


B

Figure 1 (facing page and this page). Maps of the study area. *A*, Map showing distribution of the regional, continuous-type accumulation of gas and oil in the Lower Silurian "Clinton" sandstone, the location of Trumbull County, Ohio, and the regional cross section *D–D'* of Keighin (1998). *B*, Sketch map showing well locations along cross section *D–D'* of Keighin (1998) in Trumbull County, Ohio.


METHYLCYCLOHEXANE
n-C7
n-C10
n-C17
pr
ph
n-C30
DETECTOR RESPONSE
0
10
20
30
40
50
60
70
RETENTION TIME, IN MINUTES

A


DETECTOR RESPONSE
10
20
30
40
50
60
70
RETENTION TIME, IN MINUTES

B

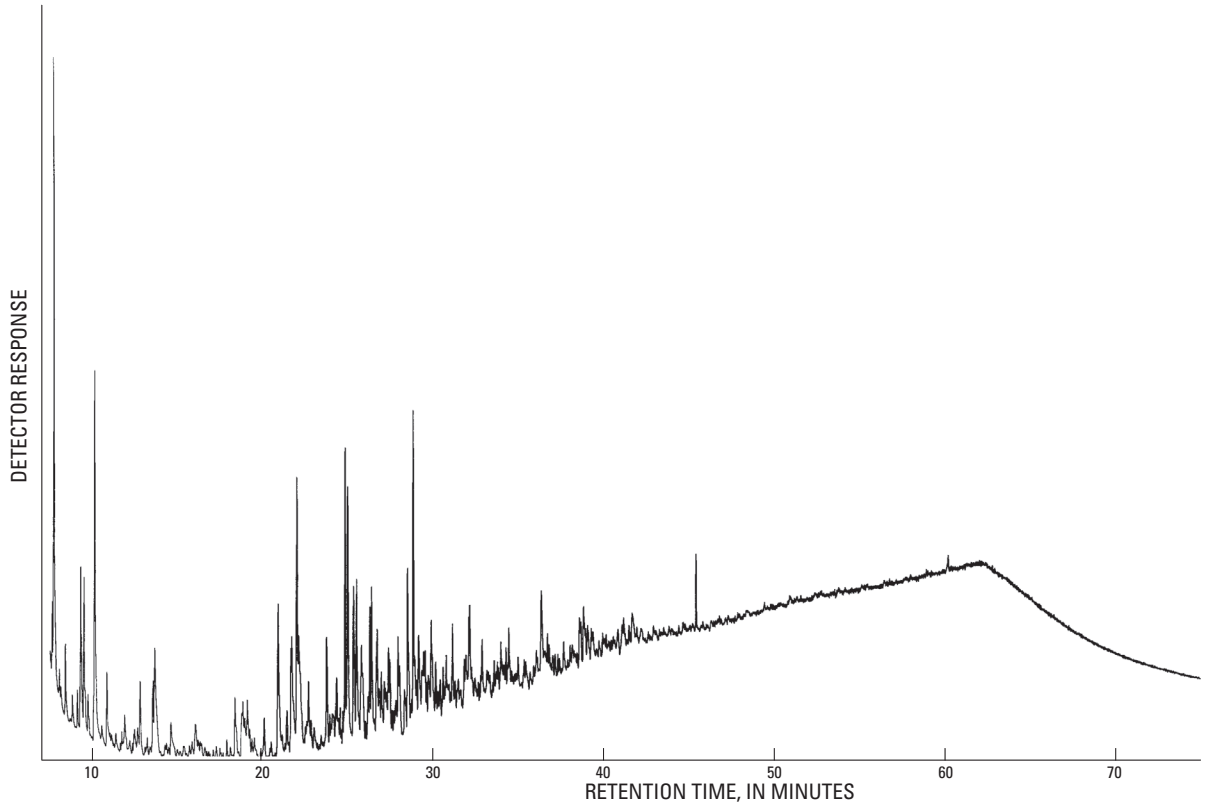
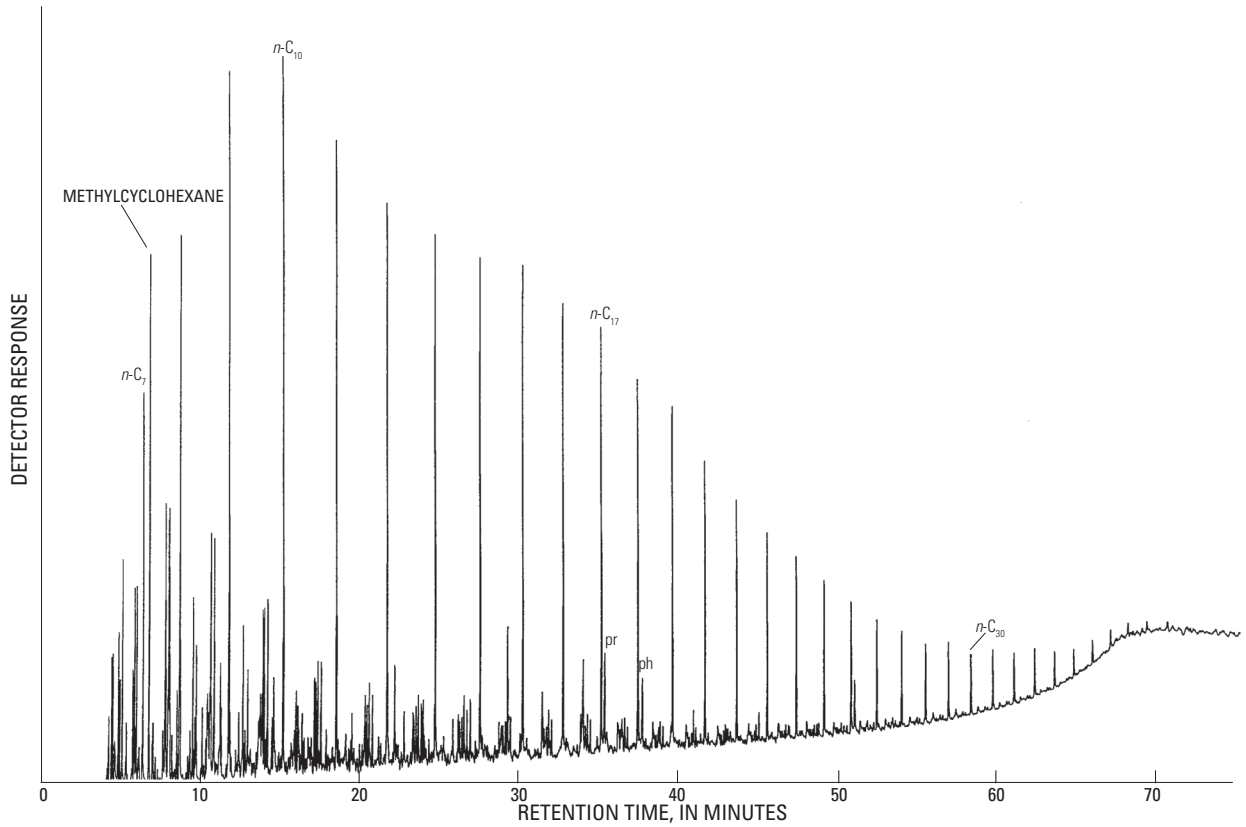


Figure 2 (facing page and this page). Gas chromatograms for sample 97MCR3, No. 1 Governor well, Trumbull County, Ohio. American Petroleum Institute (API) gravity is 40.9°. *A*, Whole-oil gas chromatogram, where *n*-C_x indicates a normal alkane with *x* number of carbons. *B*, Saturated-hydrocarbon-fraction gas chromatogram. *C*, Aromatic-hydrocarbon-fraction gas chromatogram. Abbreviations are as follows: pr, pristine; ph, phytane.


n-C10
METHYLCYCLOHEXANE
n-C7
n-C17
pr
ph
n-C30
DETECTOR RESPONSE
0
10
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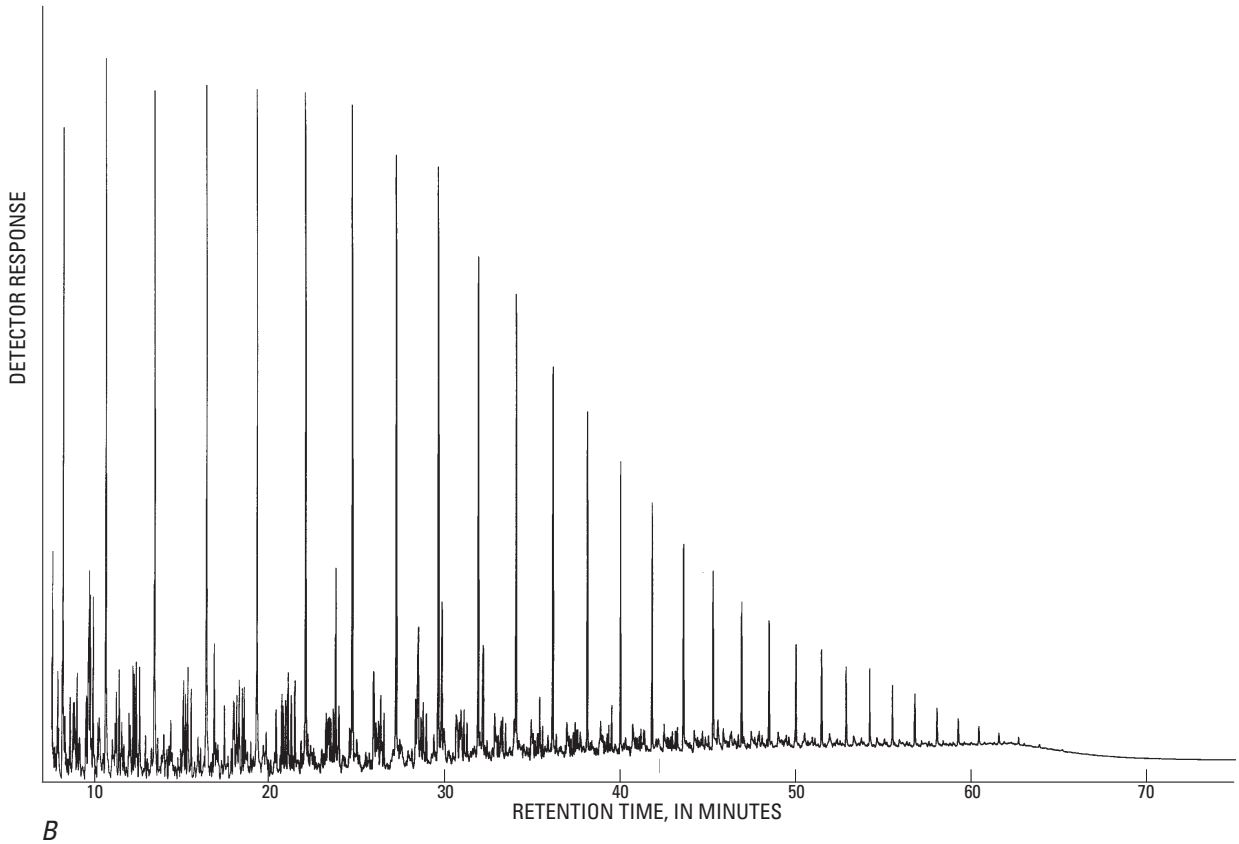
30
40
50
60
70
RETENTION TIME, IN MINUTES

A


DETECTOR RESPONSE
10
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60
70
RETENTION TIME, IN MINUTES

B

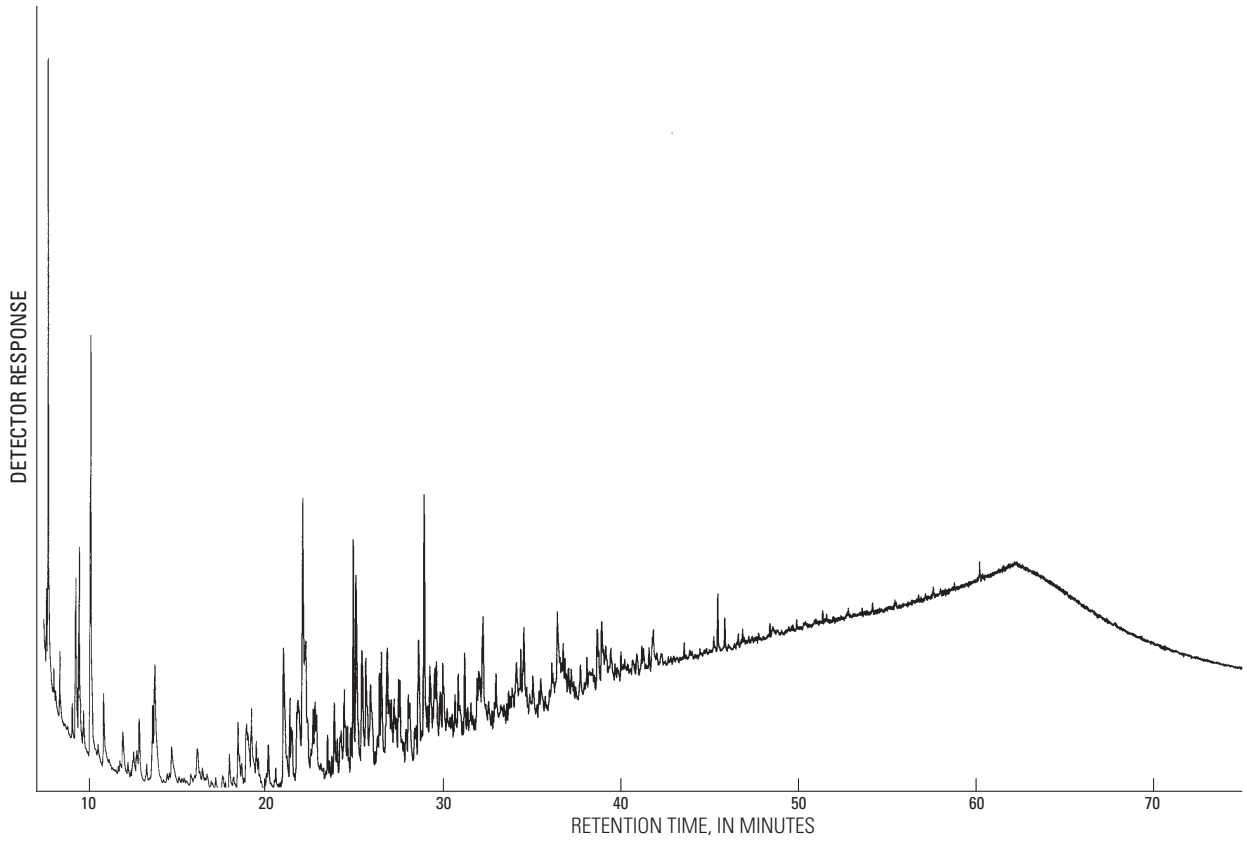
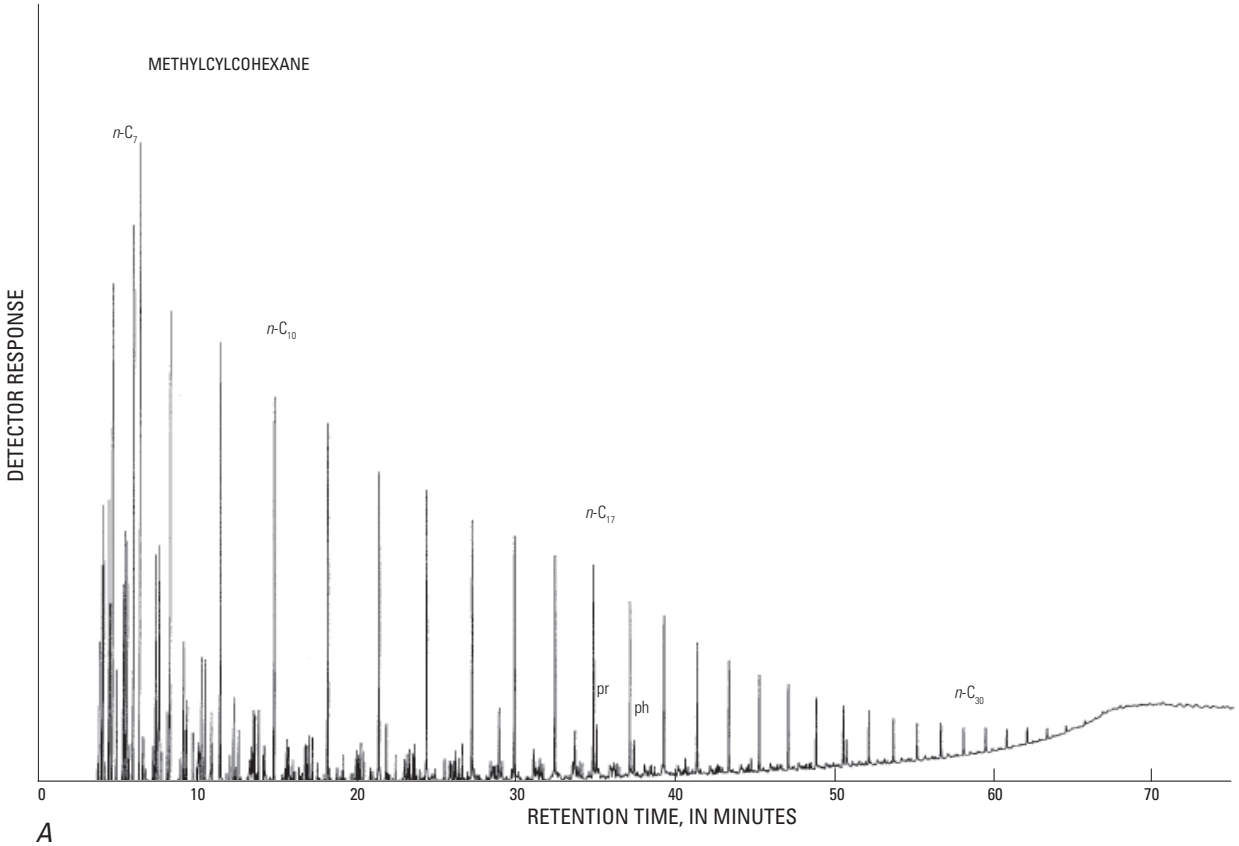
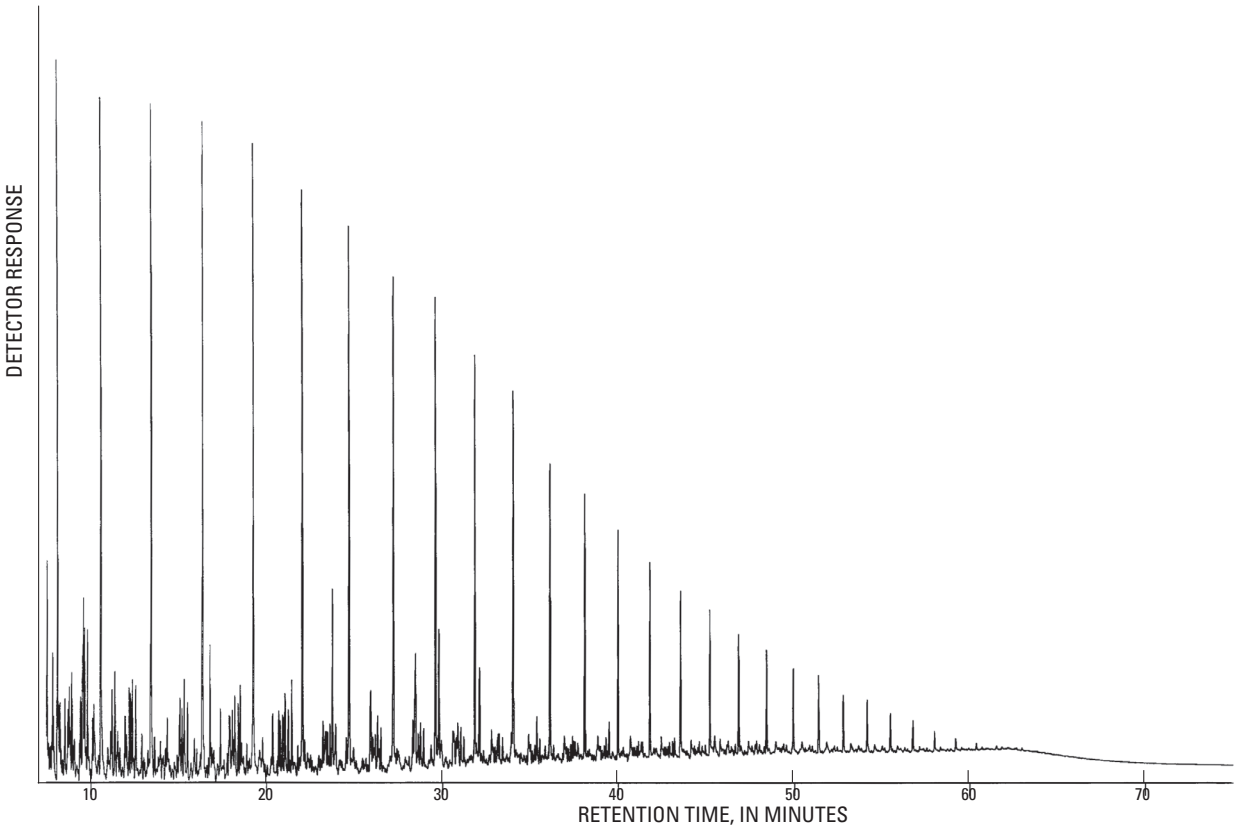


Figure 3 (facing page and this page). Gas chromatograms for sample 97MCR4, No. 1 Wargo well, Trumbull County, Ohio. American Petroleum Institute (API) gravity is 40.5°. *A*, Whole-oil gas chromatogram, where *n*-C_x indicates a normal alkane with *x* number of carbons. *B*, Saturated-hydrocarbon-fraction gas chromatogram. *C*, Aromatic-hydrocarbon-fraction gas chromatogram. Abbreviations are as follows: pr, pristine; ph, phytane.


METHYLCYLCOHEXANE
n-C7
n-C10
n-C17
pr
ph
n-C30
DETECTOR RESPONSE
0
10
20
30
40
50
60
70
RETENTION TIME, IN MINUTES

A


DETECTOR RESPONSE
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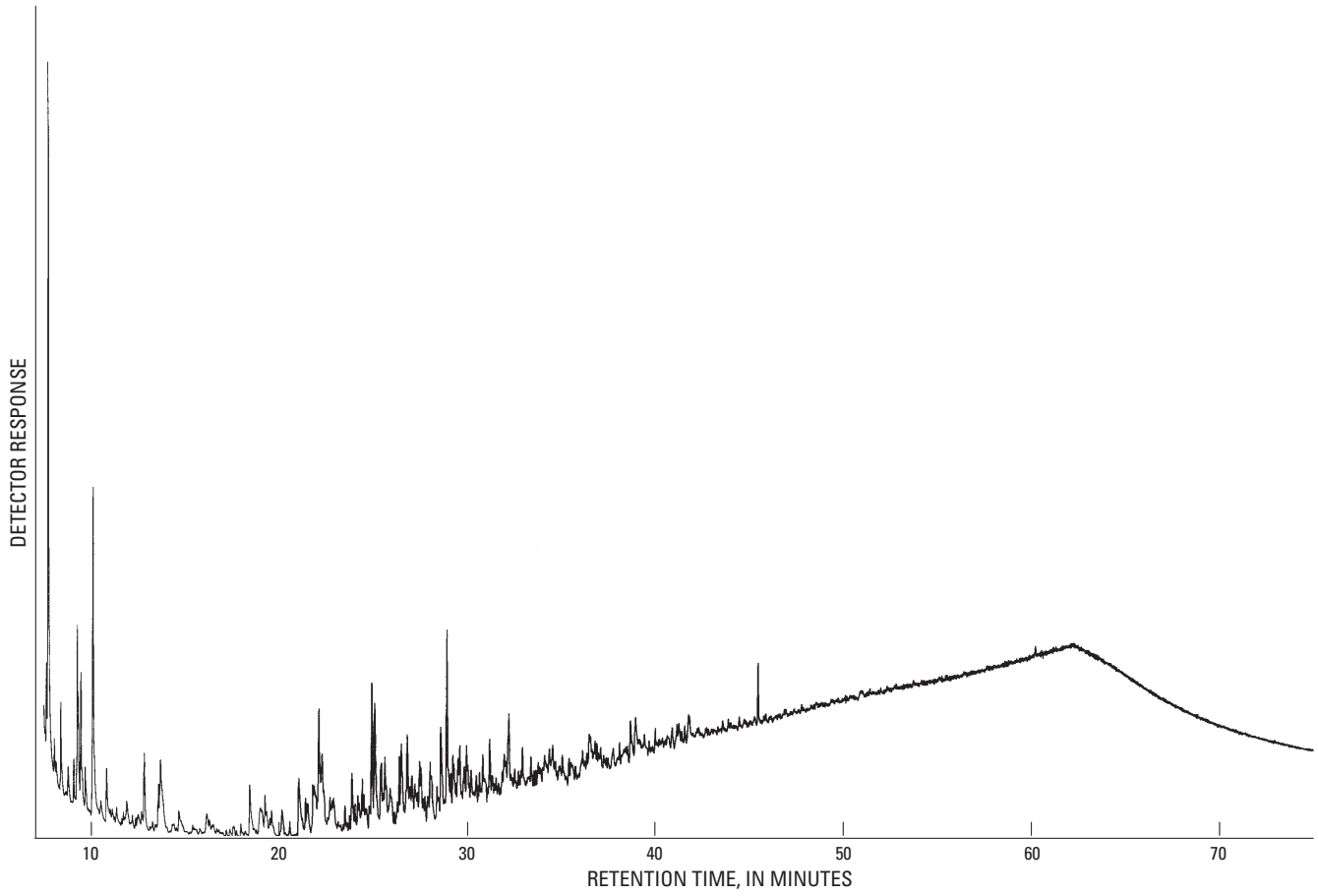
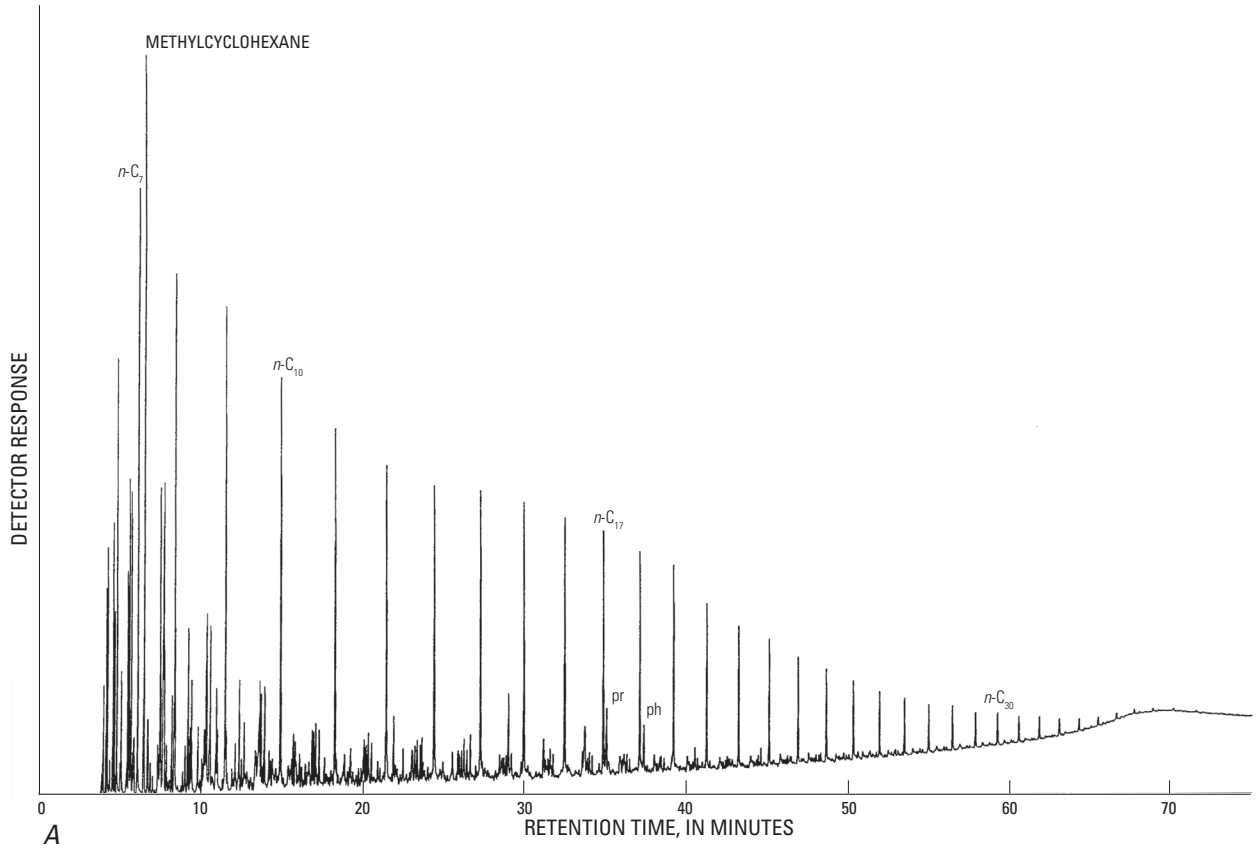
70
RETENTION TIME, IN MINUTES

B

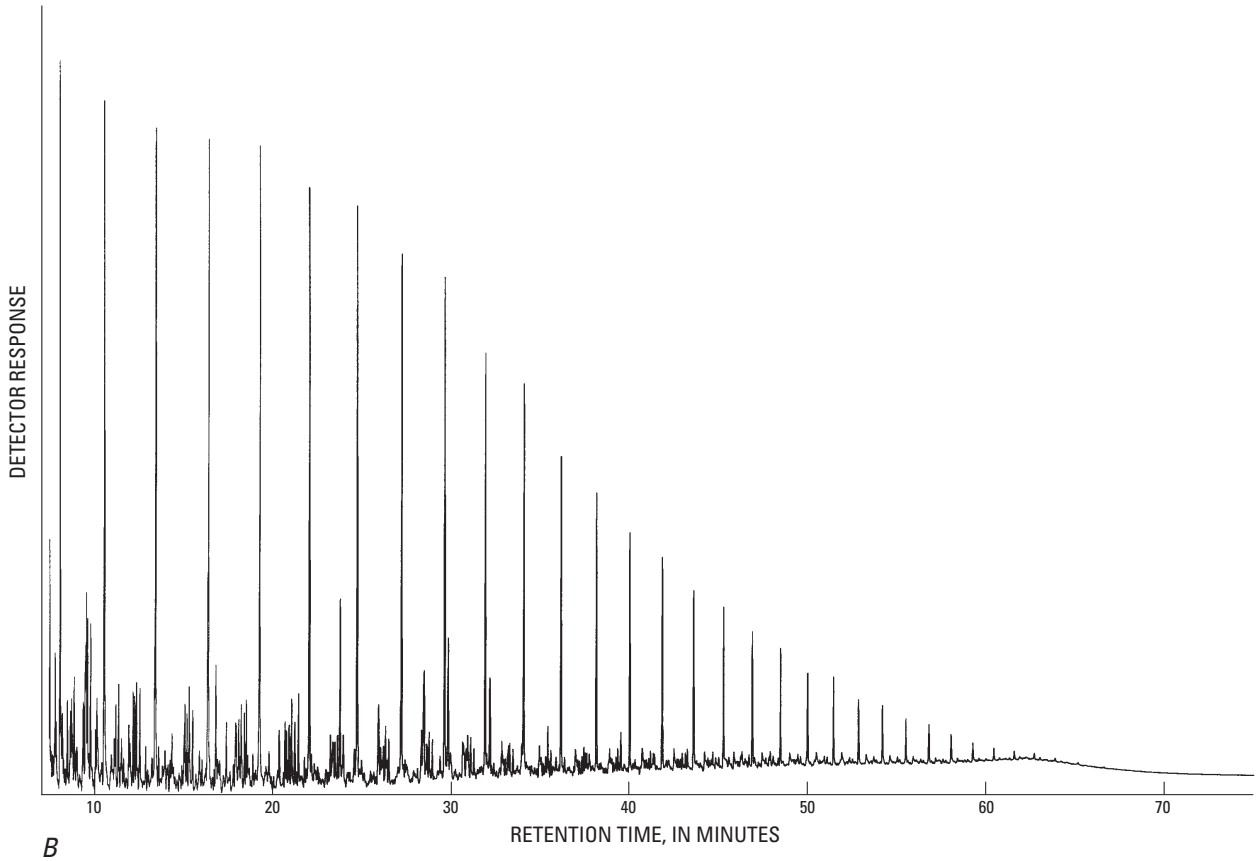


C

Figure 4 (facing page and this page). Gas chromatograms for sample 97MCR5, No. 1 Baker well, Trumbull County, Ohio. American Petroleum Institute (API) gravity is 43.9°. *A*, Whole-oil gas chromatogram, where *n*-C_x indicates a normal alkane with *x* number of carbons. *B*, Saturated-hydrocarbon-fraction gas chromatogram. *C*, Aromatic-hydrocarbon-fraction gas chromatogram. Abbreviations are as follows: pr, pristine; ph, phytane.


METHYLCYCLOHEXANE
n-C7
n-C10
n-C17
pr
ph
n-C30
DETECTOR RESPONSE
0
10
20
30
40
50
60
70
RETENTION TIME, IN MINUTES

A


DETECTOR RESPONSE
10
20
30
40
50
60
70
RETENTION TIME, IN MINUTES

B

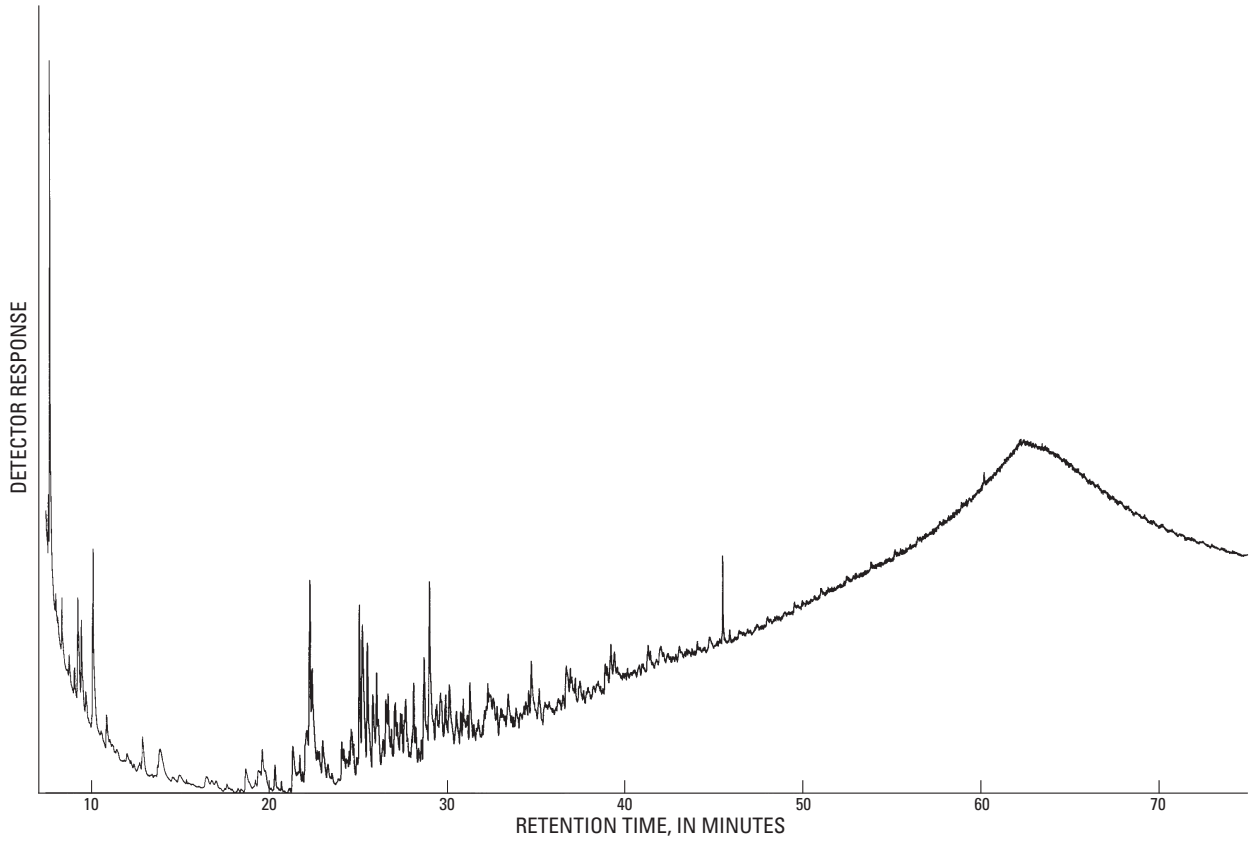
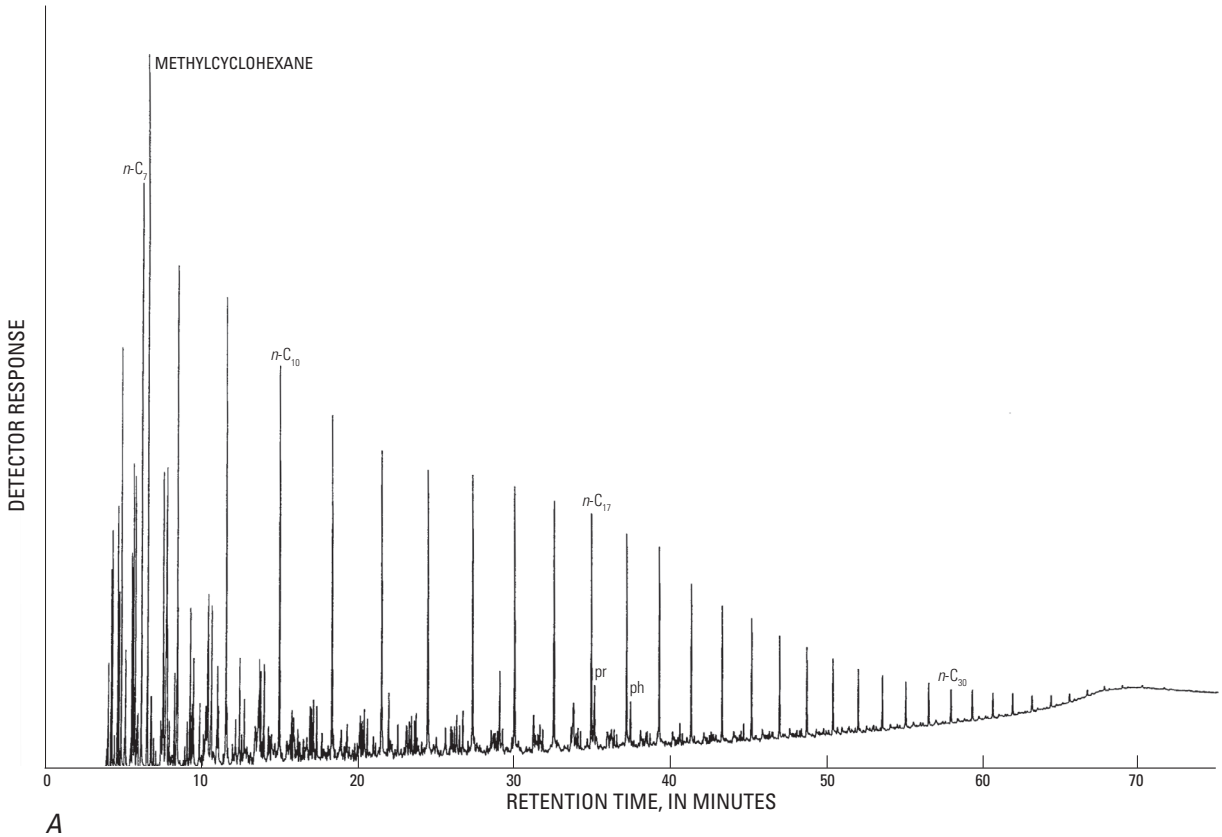
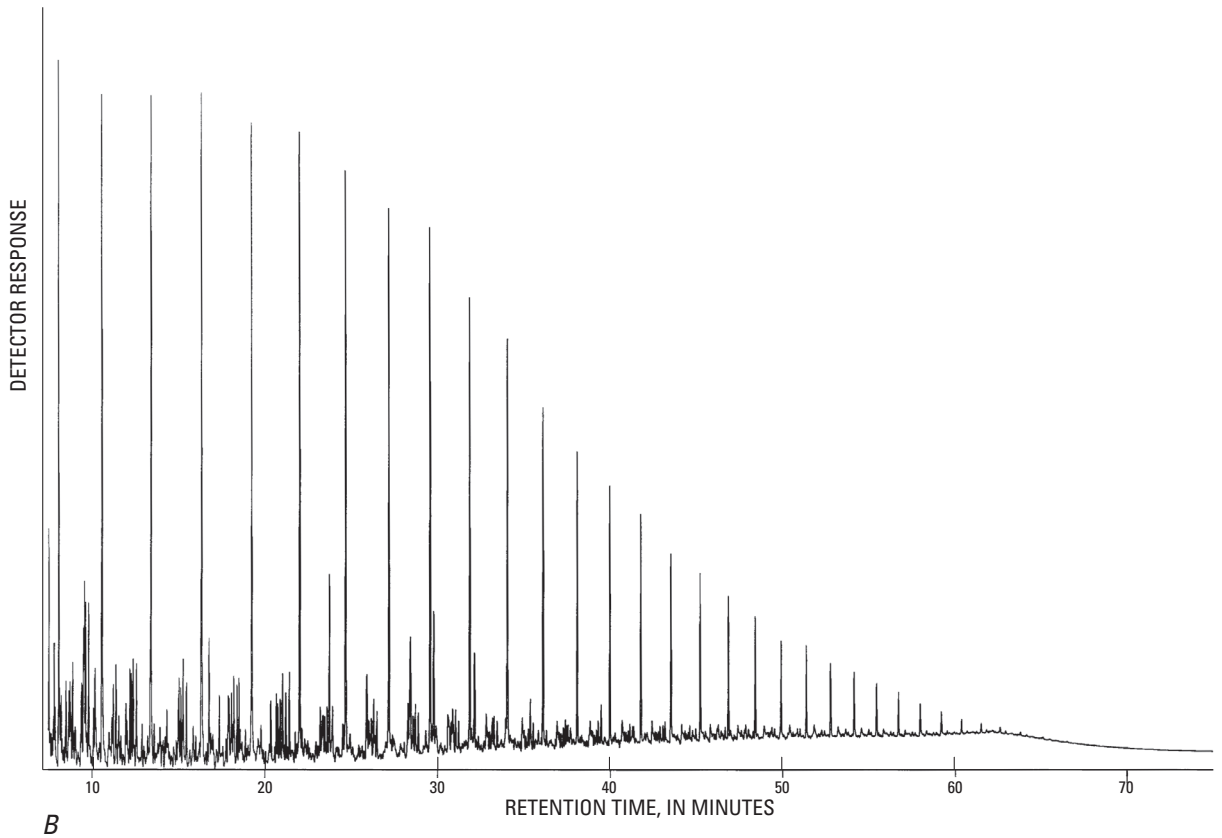


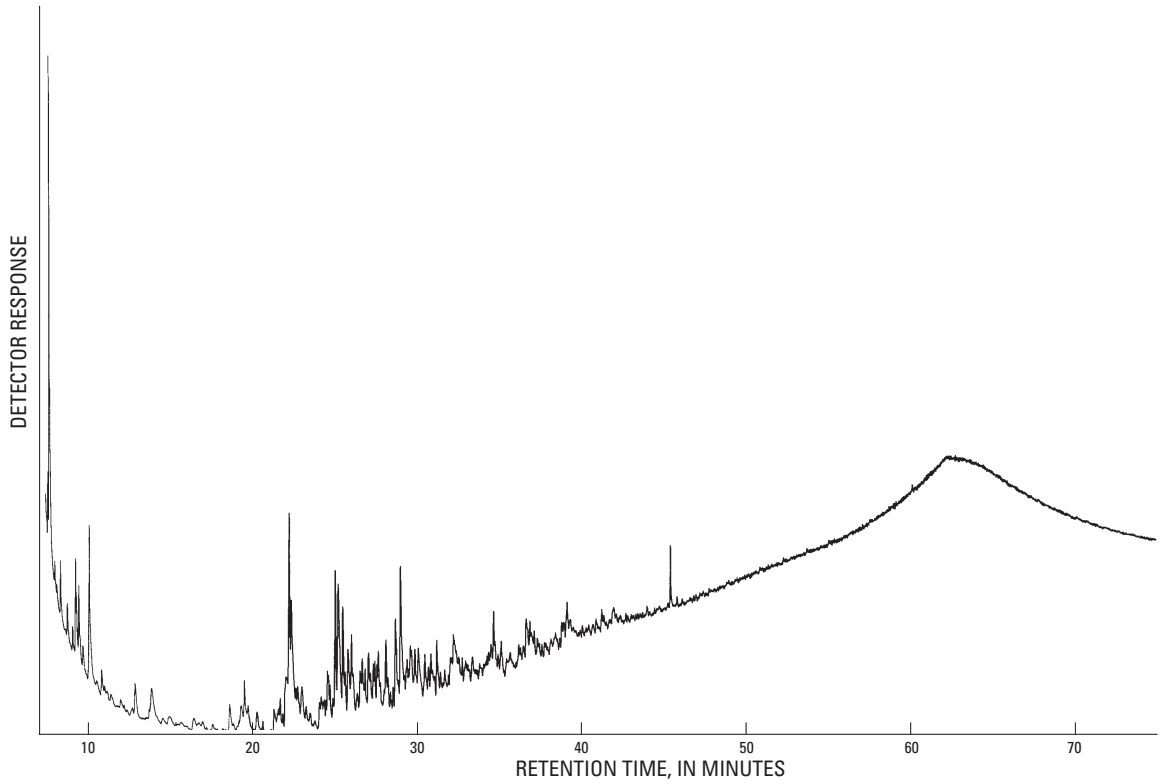
Figure 5 (facing page and this page). Gas chromatograms for sample 97MCR6, No. 2 Clemens well, Trumbull County, Ohio. American Petroleum Institute (API) gravity is 43.5°. *A*, Whole-oil gas chromatogram, where *n*-C_x indicates a normal alkane with *x* number of carbons. *B*, Saturated-hydrocarbon-fraction gas chromatogram. *C*, Aromatic-hydrocarbon-fraction gas chromatogram. Abbreviations are as follows: pr, pristine; ph, phytane.


METHYLCYCLOHEXANE
n-C7
n-C10
n-C17
pr
ph
n-C30
DETECTOR RESPONSE
0
10
20
30
40
50
60
70
RETENTION TIME, IN MINUTES

A

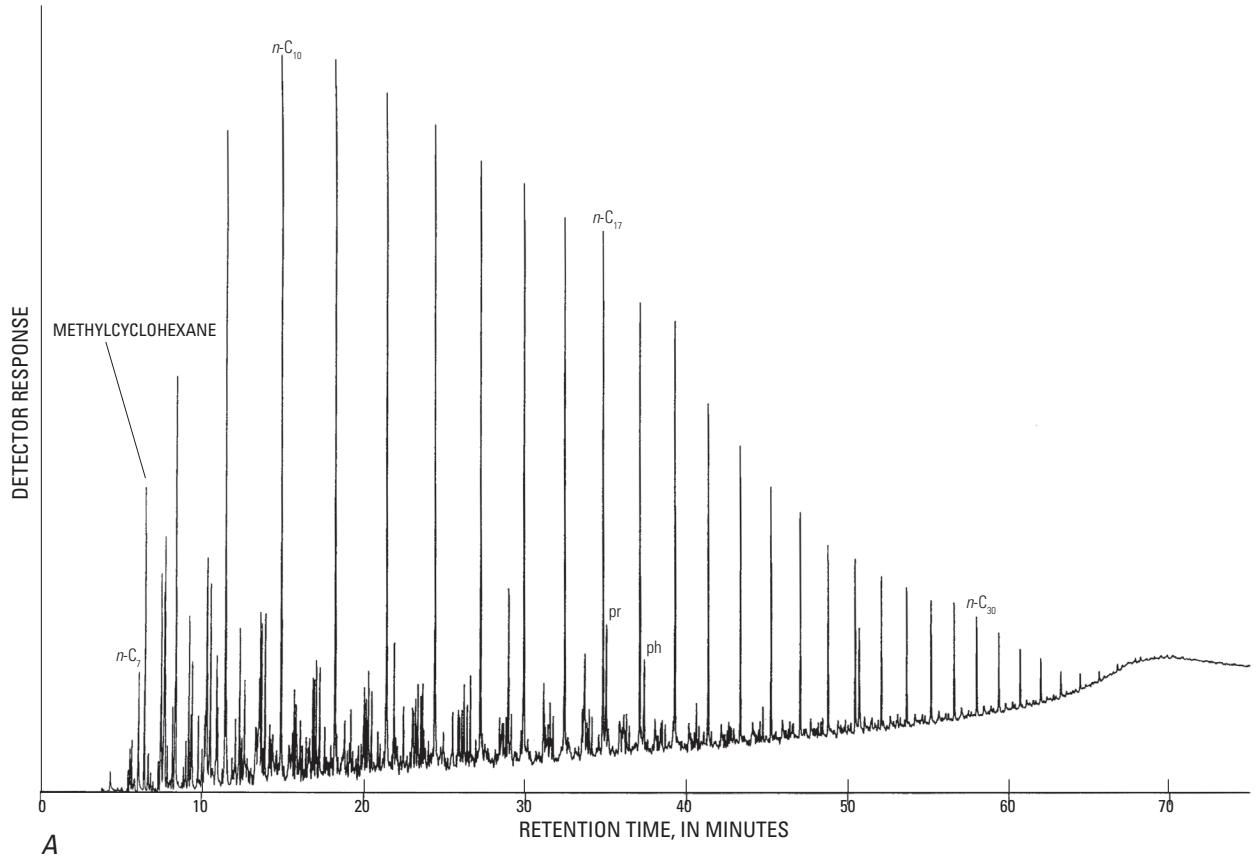

DETECTOR RESPONSE
10
20
30
40
50
60
70
RETENTION TIME, IN MINUTES

B

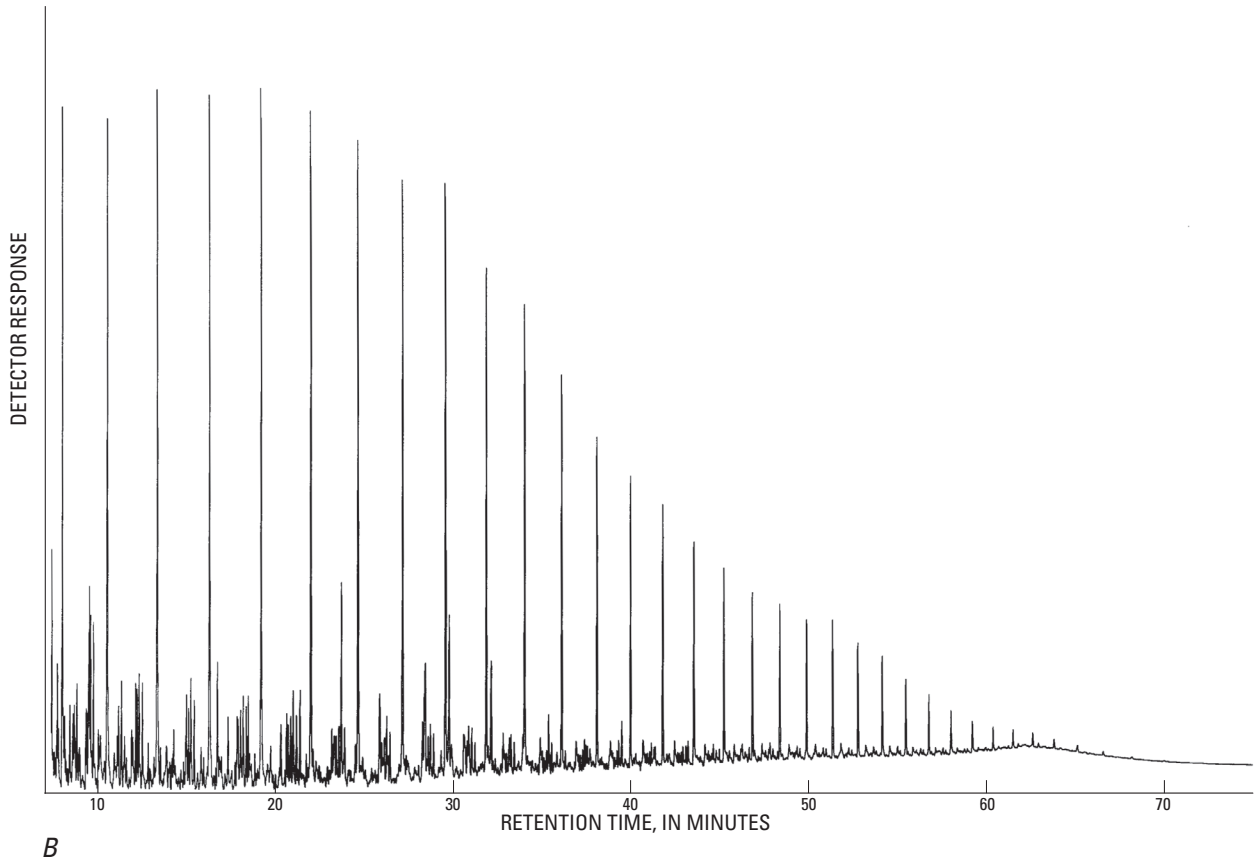


C

Figure 6 (facing page and this page). Gas chromatograms for sample 97MCR7, No. 2 Krantz well, Trumbull County, Ohio. American Petroleum Institute (API) gravity is 43.2°. *A*, Whole-oil gas chromatogram, where *n*-C_x indicates a normal alkane with *x* number of carbons. *B*, Saturated-hydrocarbon-fraction gas chromatogram. *C*, Aromatic-hydrocarbon-fraction gas chromatogram. Abbreviations are as follows: pr, pristine; ph, phytane.


n-C10
n-C17
METHYLCYCLOHEXANE
n-C7
pr
ph
n-C30
DETECTOR RESPONSE
0
10
20
30
40
50
60
70
RETENTION TIME, IN MINUTES

A


DETECTOR RESPONSE
10
20
30
40
50
60
70
RETENTION TIME, IN MINUTES

B

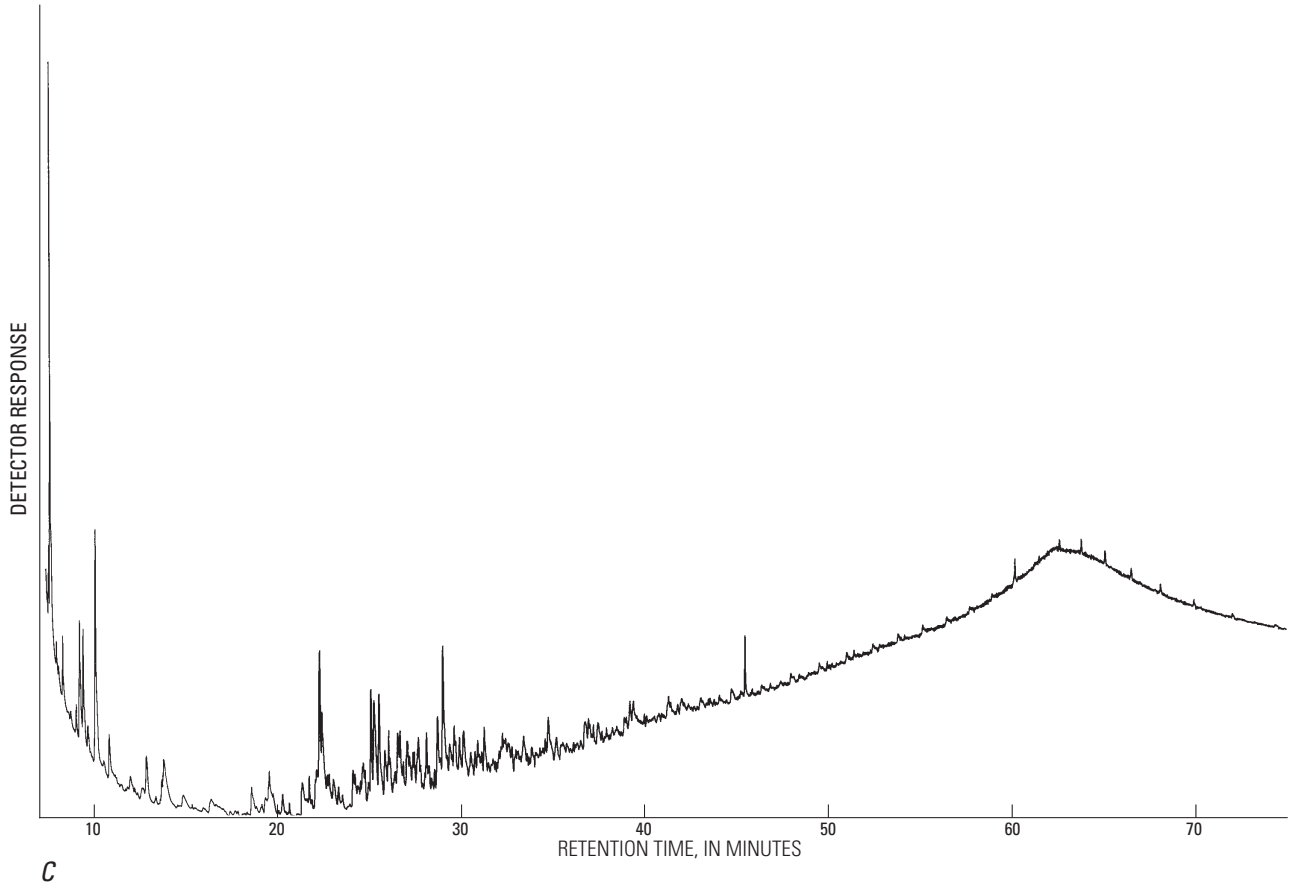
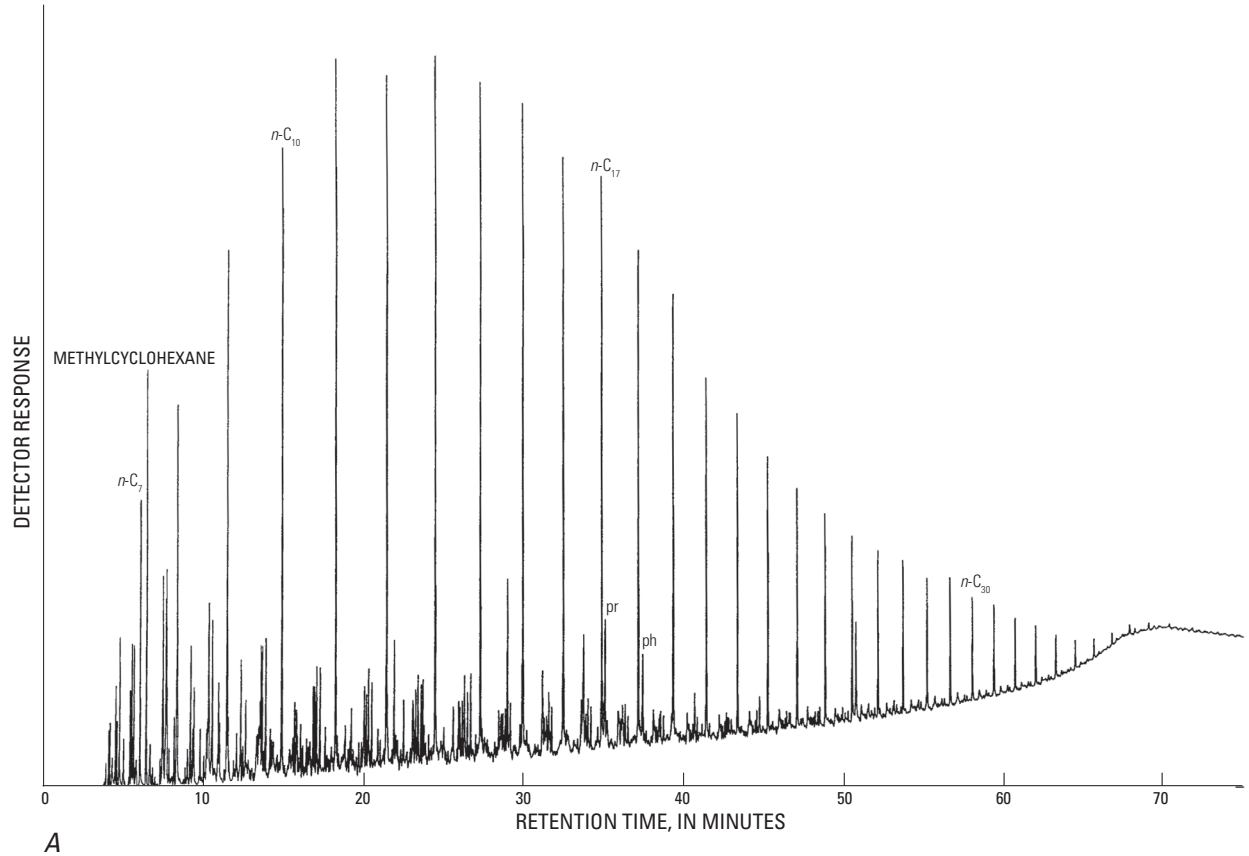
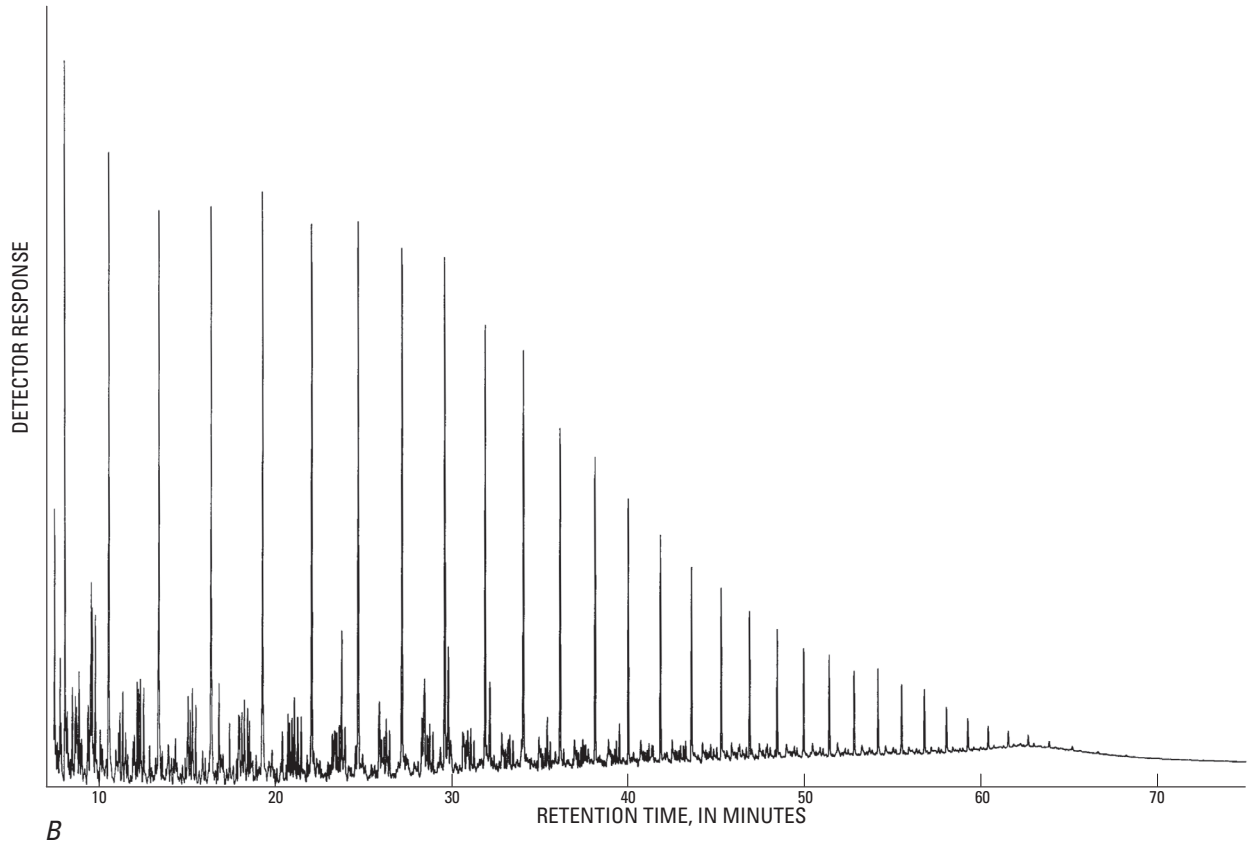


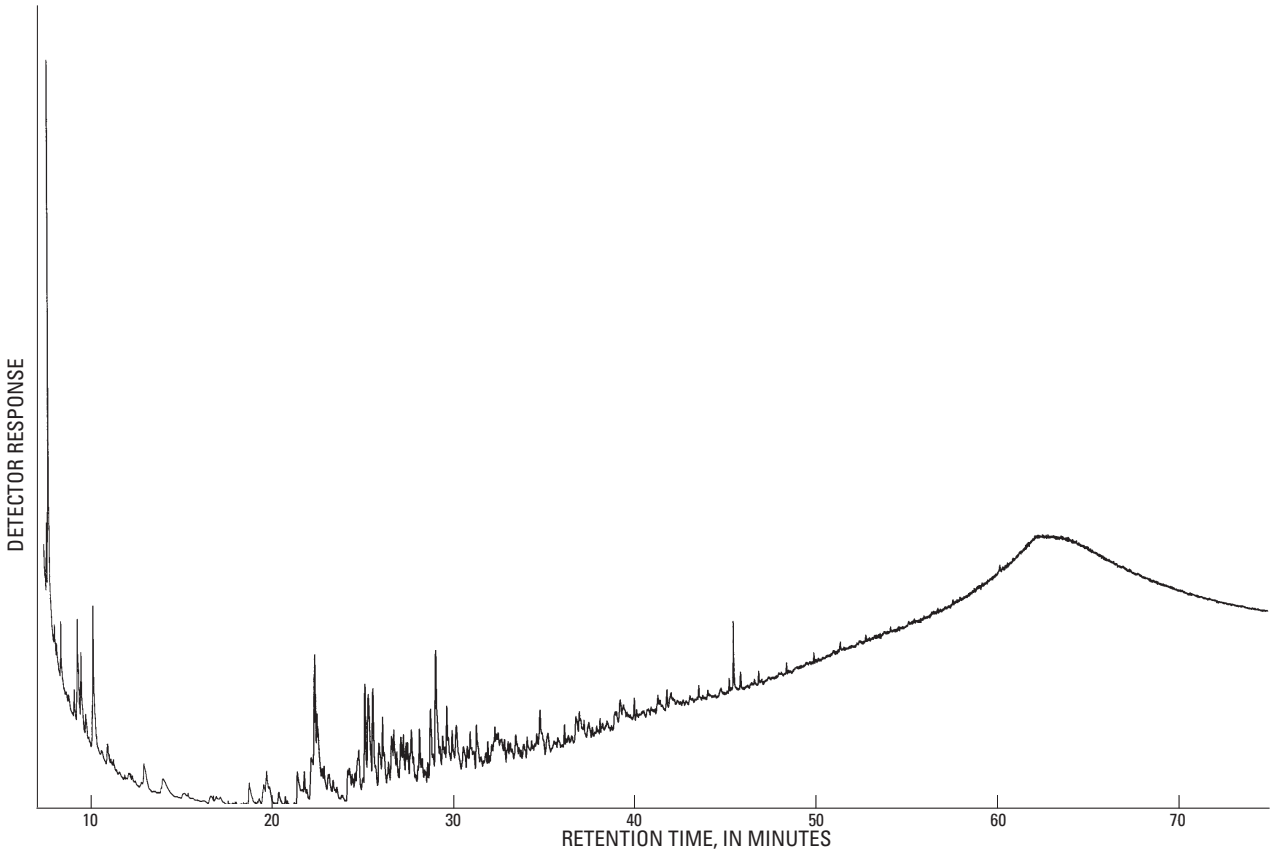
Figure 7 (facing page and this page). Gas chromatograms for sample 97MCR8, No. 1 Rhine well, Trumbull County, Ohio. American Petroleum Institute (API) gravity is 43.1°. *A*, Whole-oil gas chromatogram, where *n*-C_x indicates a normal alkane with *x* number of carbons. *B*, Saturated-hydrocarbon-fraction gas chromatogram. *C*, Aromatic-hydrocarbon-fraction gas chromatogram. Abbreviations are as follows: pr, pristine; ph, phytane.


DETECTOR RESPONSE
METHYLCYCLOHEXANE
n-C7
n-C10
n-C17
pr
ph
n-C30
0
10
20
30
40
50
60
70
RETENTION TIME, IN MINUTES

A

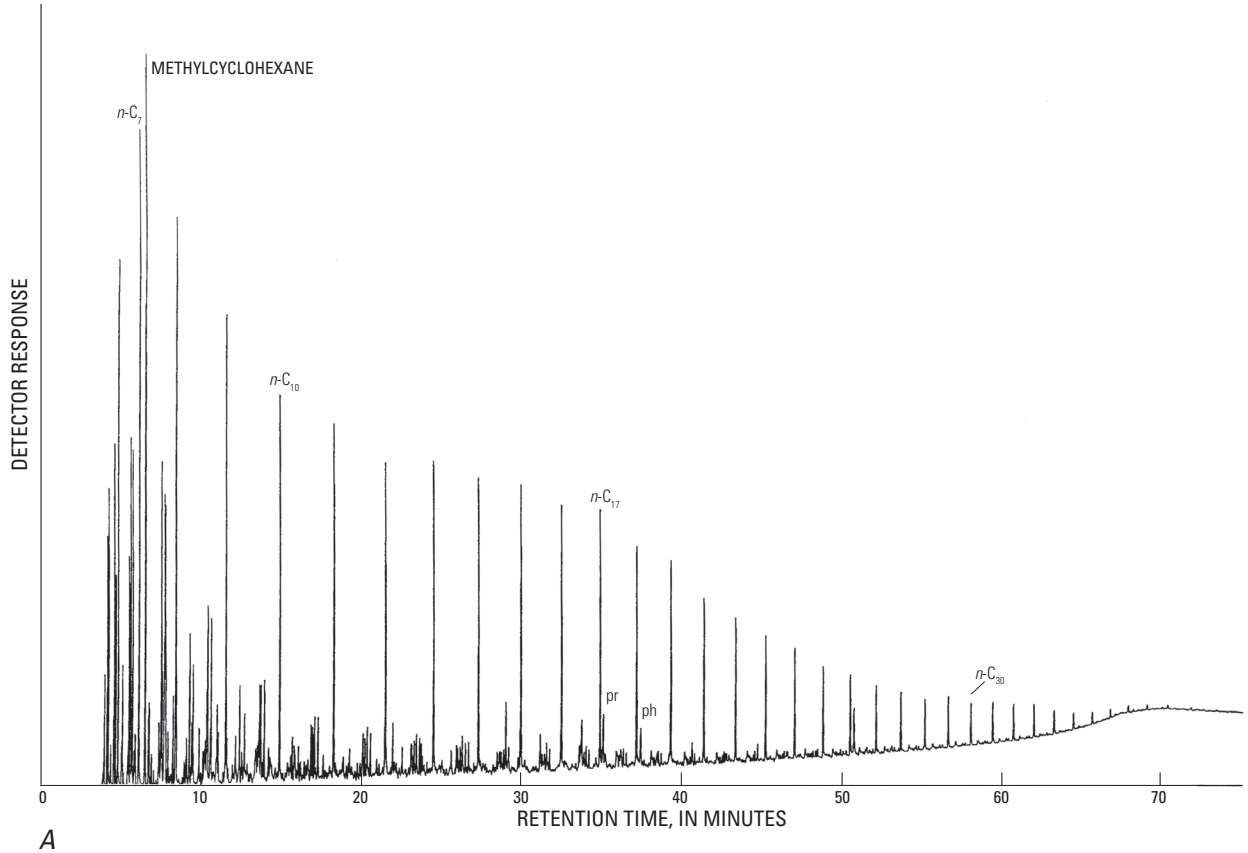

DETECTOR RESPONSE
10
20
30
40
50
60
70
RETENTION TIME, IN MINUTES

B

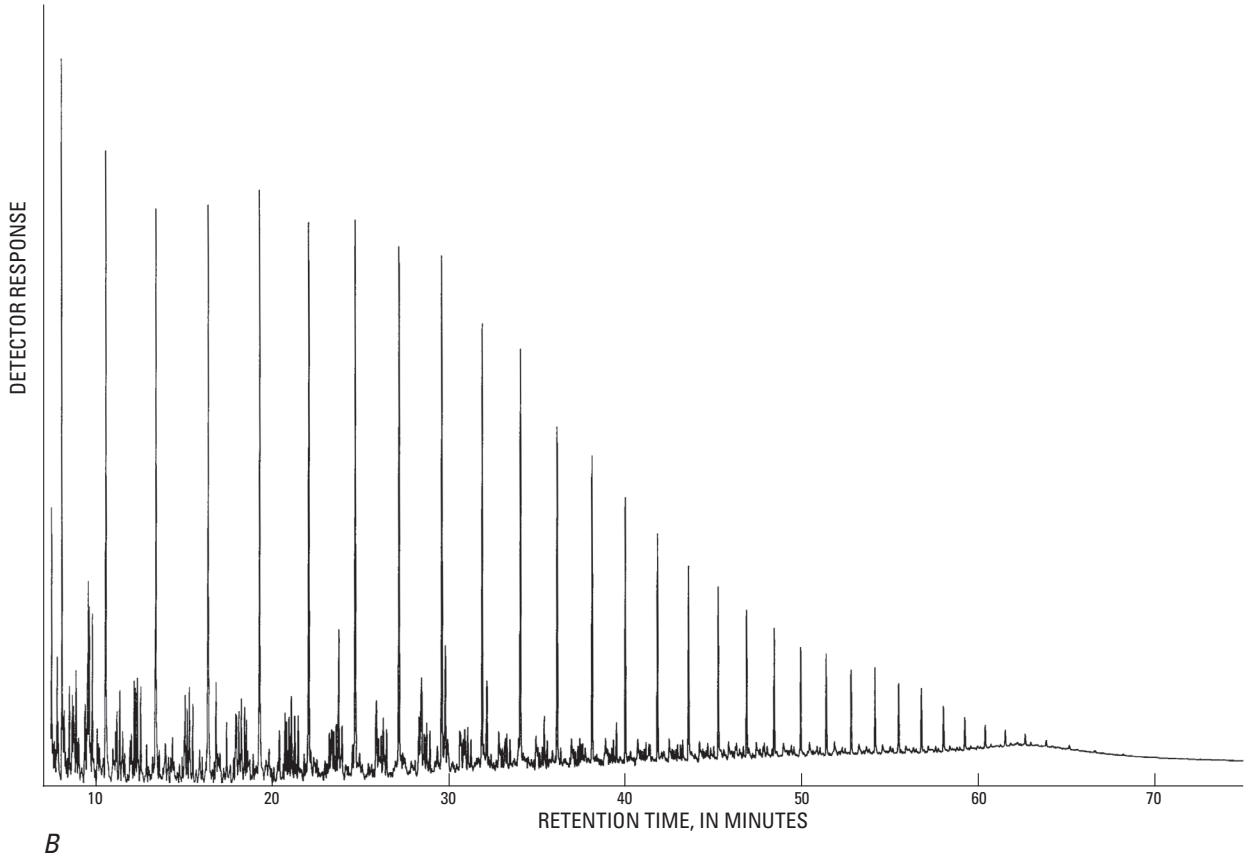


C

Figure 8 (facing page and this page). Gas chromatograms for sample 97MCR9, No. 1 Gowdy well, Trumbull County, Ohio. American Petroleum Institute (API) gravity is 39.7°. *A*, Whole-oil gas chromatogram, where *n*-C_x indicates a normal alkane with *x* number of carbons. *B*, Saturated-hydrocarbon-fraction gas chromatogram. *C*, Aromatic-hydrocarbon-fraction gas chromatogram. Abbreviations are as follows: pr, pristine; ph, phytane.


METHYLCYCLOHEXANE
n-C7
n-C10
n-C17
pr
ph
n-C30
DETECTOR RESPONSE
0
10
20
30
40
50
60
70
RETENTION TIME, IN MINUTES

A


DETECTOR RESPONSE
10
20
30
40
50
60
70
RETENTION TIME, IN MINUTES

B

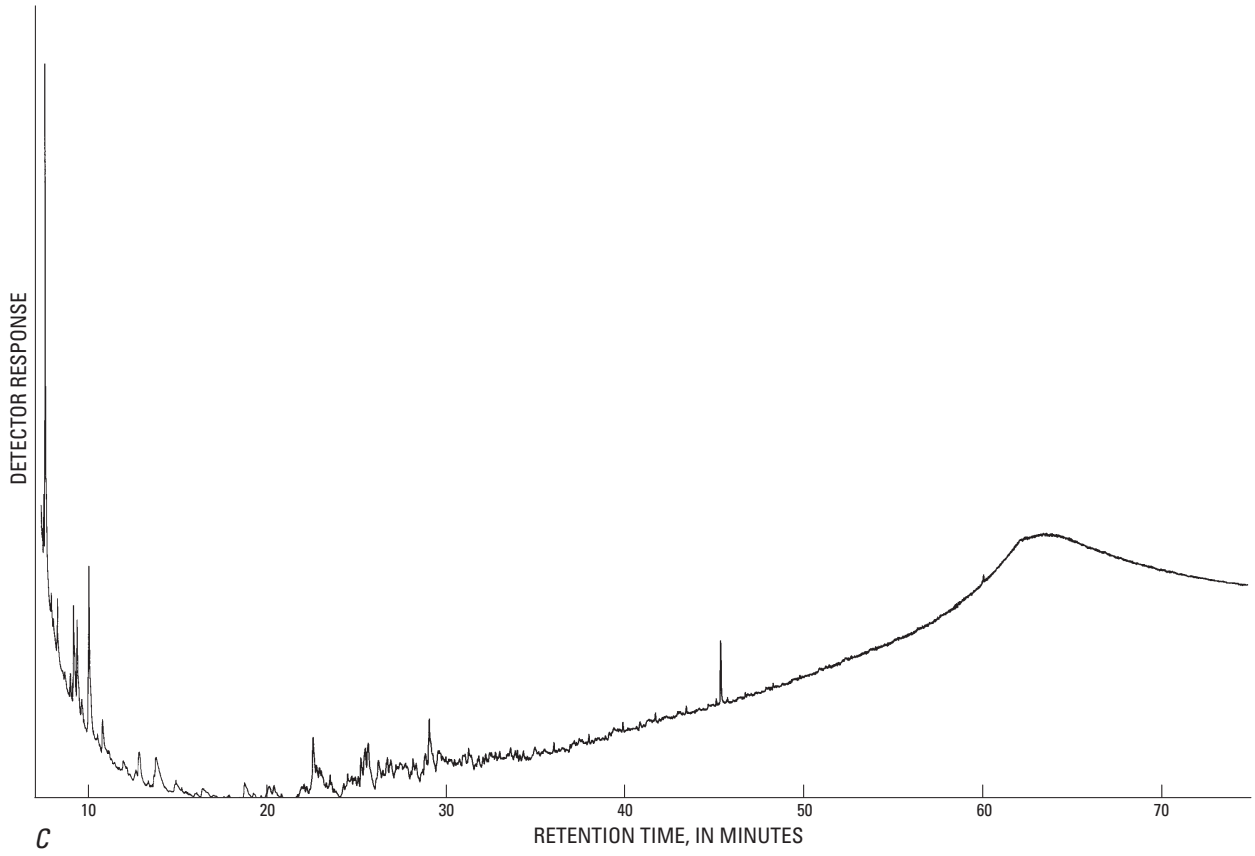
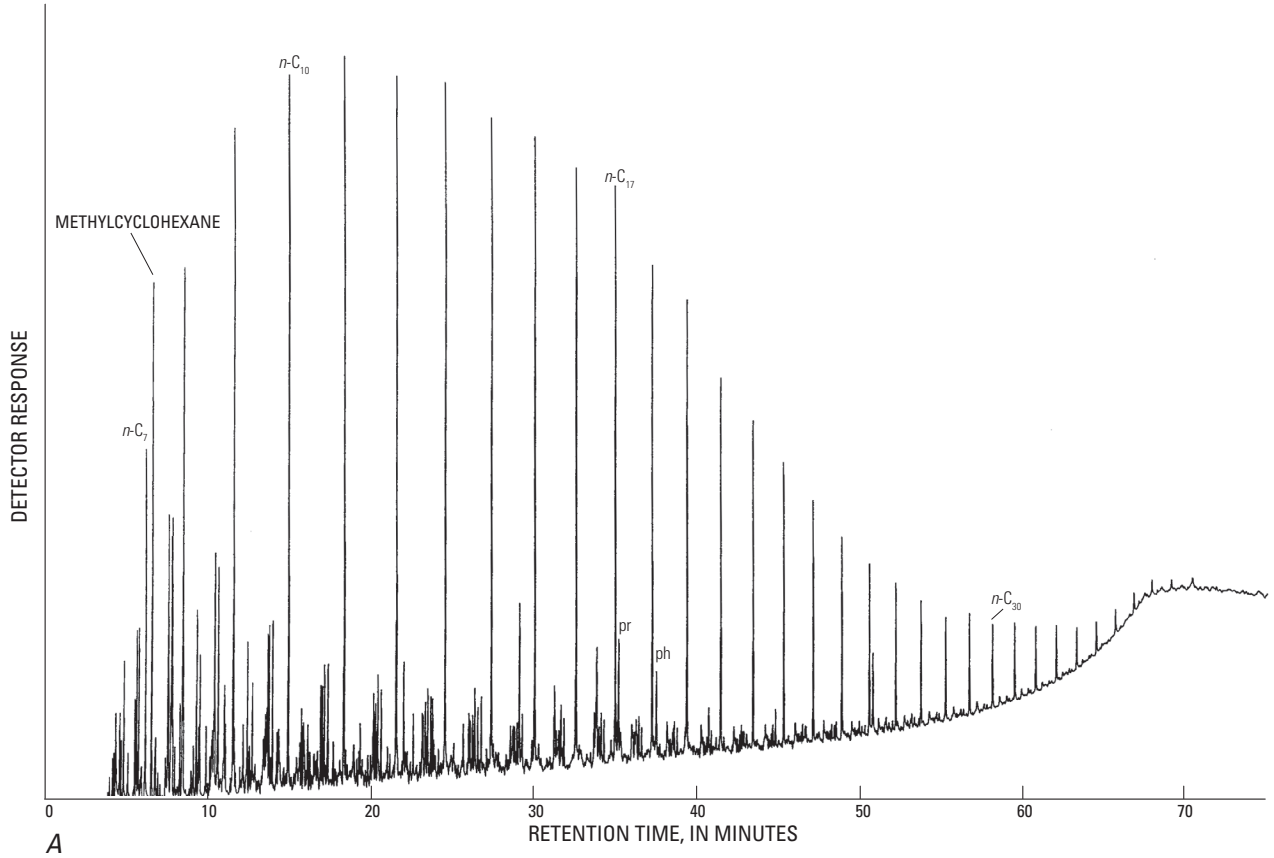
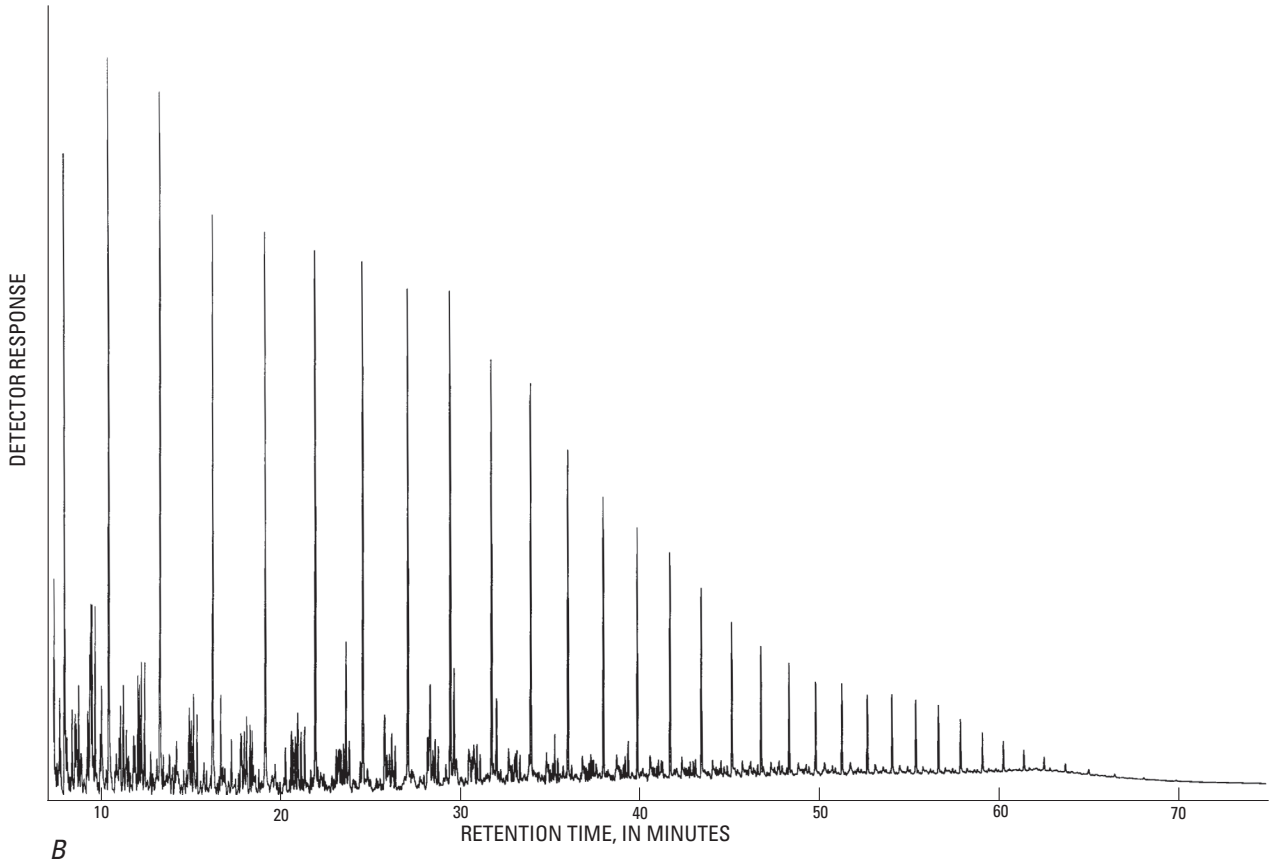


Figure 9 (facing page and this page). Gas chromatograms for sample 97MCR10, No. 2 Redmond well, Trumbull County, Ohio. American Petroleum Institute (API) gravity is 44.3°. *A*, Whole-oil gas chromatogram, where *n*-C_x indicates a normal alkane with *x* number of carbons. *B*, Saturated-hydrocarbon-fraction gas chromatogram. *C*, Aromatic-hydrocarbon-fraction gas chromatogram. Abbreviations are as follows: pr, pristine; ph, phytane.


n-C10
n-C17
METHYLCYCLOHEXANE
n-C7
pr
ph
n-C30
DETECTOR RESPONSE
0
10
20
30
40
50
60
70
RETENTION TIME, IN MINUTES

A


DETECTOR RESPONSE
10
20
30
40
50
60
70
RETENTION TIME, IN MINUTES

B

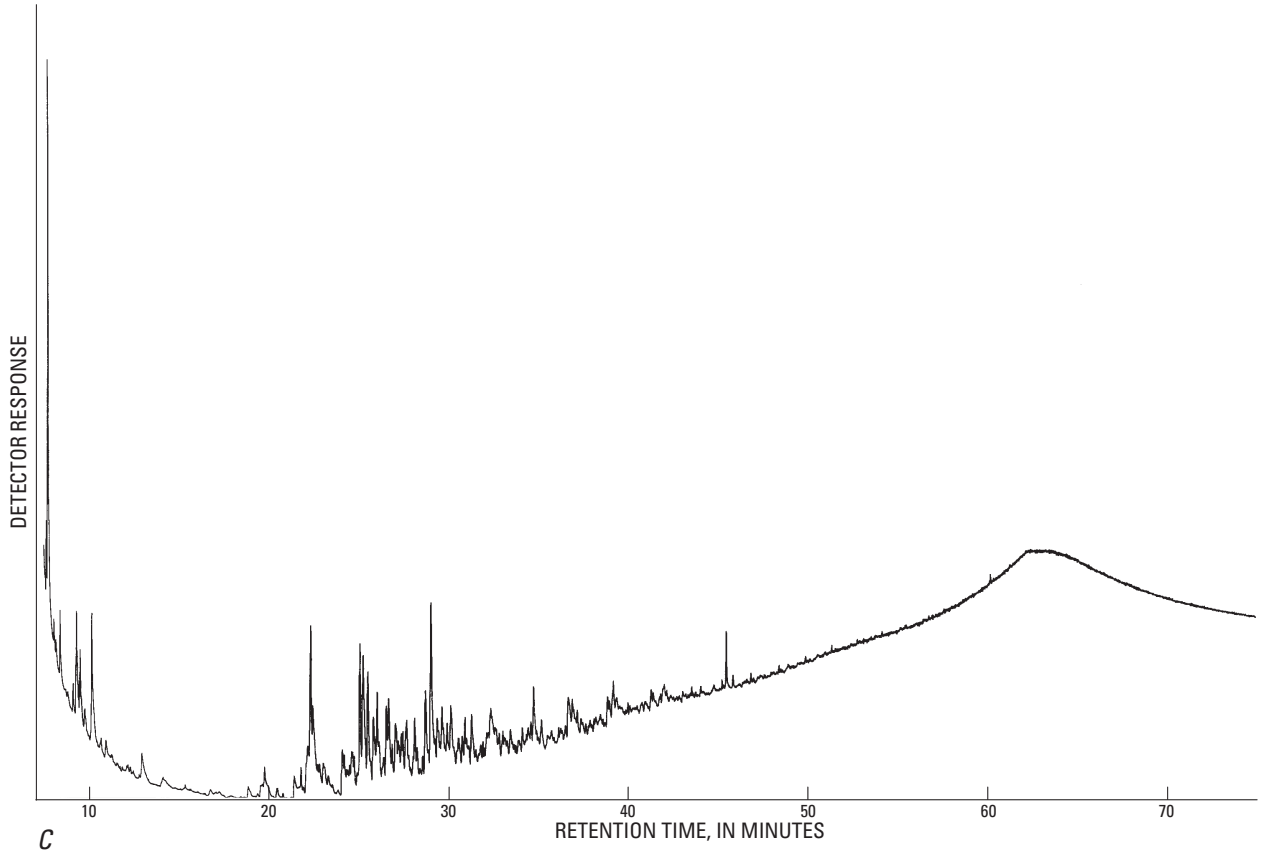
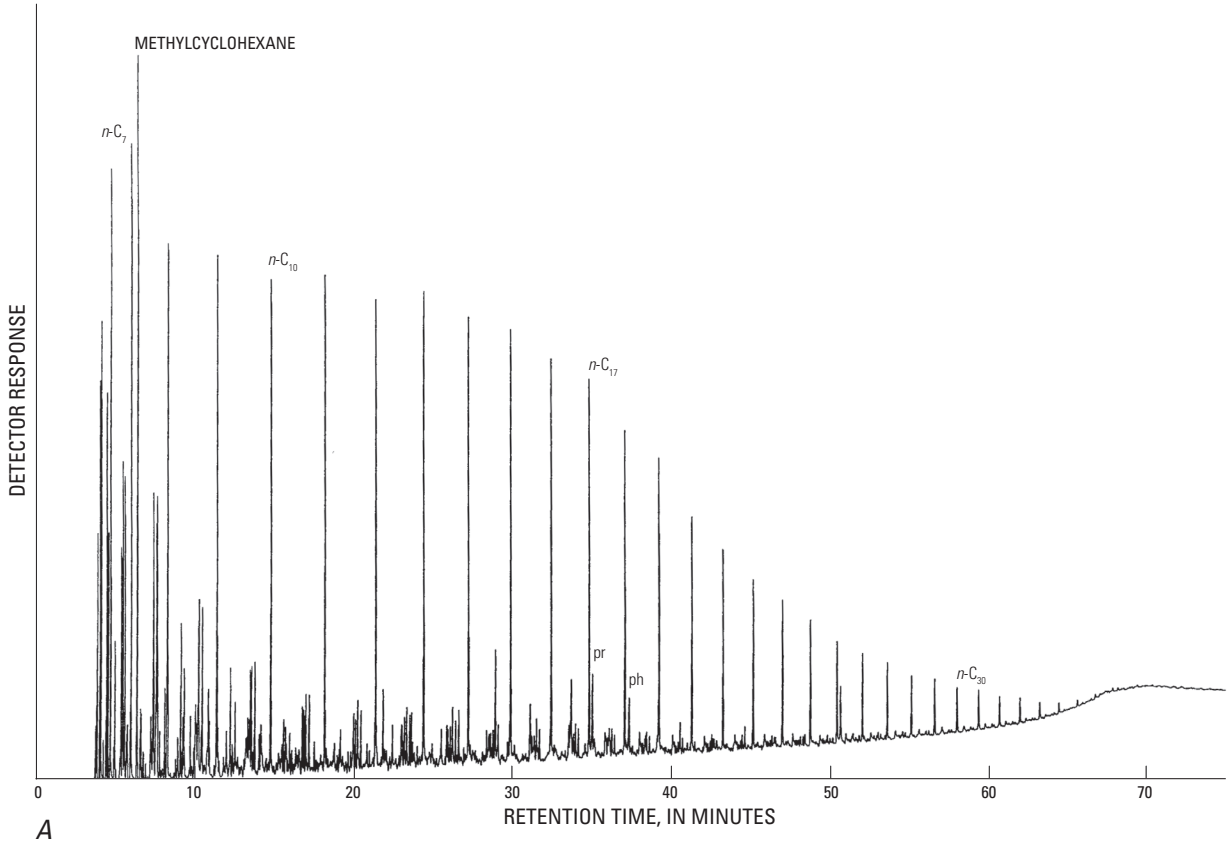
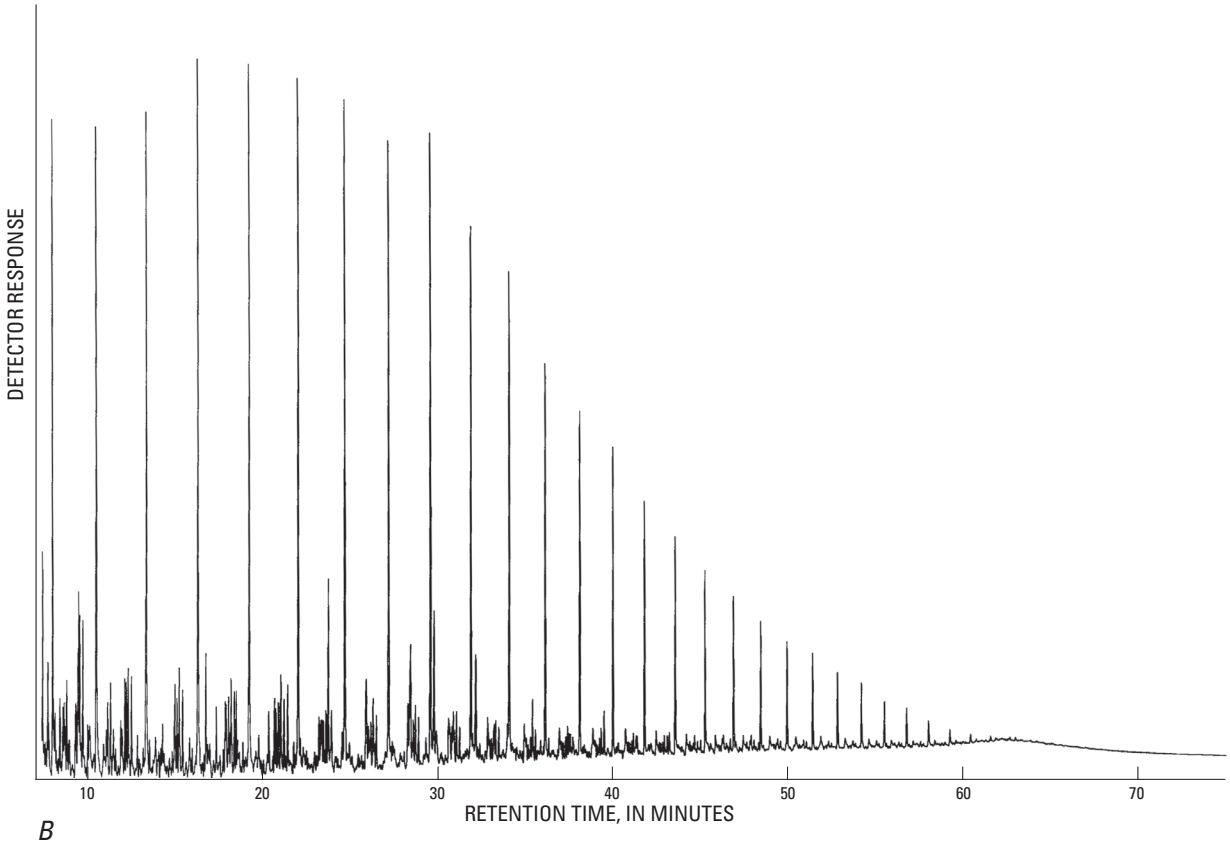


Figure 10 (facing page and this page). Gas chromatograms for sample 97MCR11, No. 7 Consumer well, Trumbull County, Ohio. American Petroleum Institute (API) gravity is 37.3°. *A*, Whole-oil gas chromatogram, where *n*-C_x indicates a normal alkane with *x* number of carbons. *B*, Saturated-hydrocarbon-fraction gas chromatogram. *C*, Aromatic-hydrocarbon-fraction gas chromatogram. Abbreviations are as follows: pr, pristine; ph, phytane.


METHYLCYCLOHEXANE
n-C7
n-C10
n-C17
pr
ph
n-C30
DETECTOR RESPONSE
0
10
20
30
40
50
60
70
RETENTION TIME, IN MINUTES

A


DETECTOR RESPONSE
10
20
30
40
50
60
70
RETENTION TIME, IN MINUTES

B

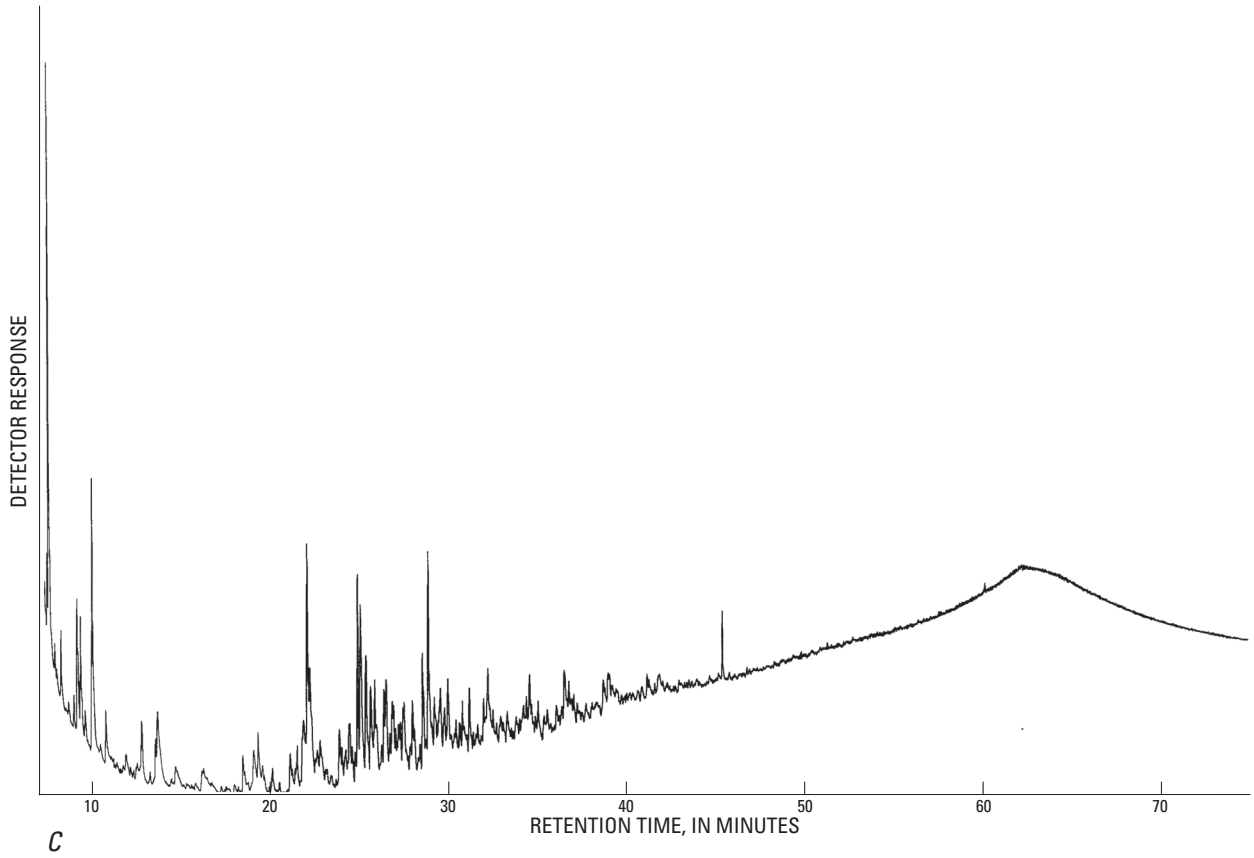


Figure 11 (facing page and this page). Gas chromatograms for sample 97MCR12, No. 3 Consumer well, Trumbull County, Ohio. American Petroleum Institute (API) gravity is 42.6°. *A*, Whole-oil gas chromatogram, where *n*-C_x indicates a normal alkane with *x* number of carbons. *B*, Saturated-hydrocarbon-fraction gas chromatogram. *C*, Aromatic-hydrocarbon-fraction gas chromatogram. Abbreviations are as follows: pr, pristine; ph, phytane.

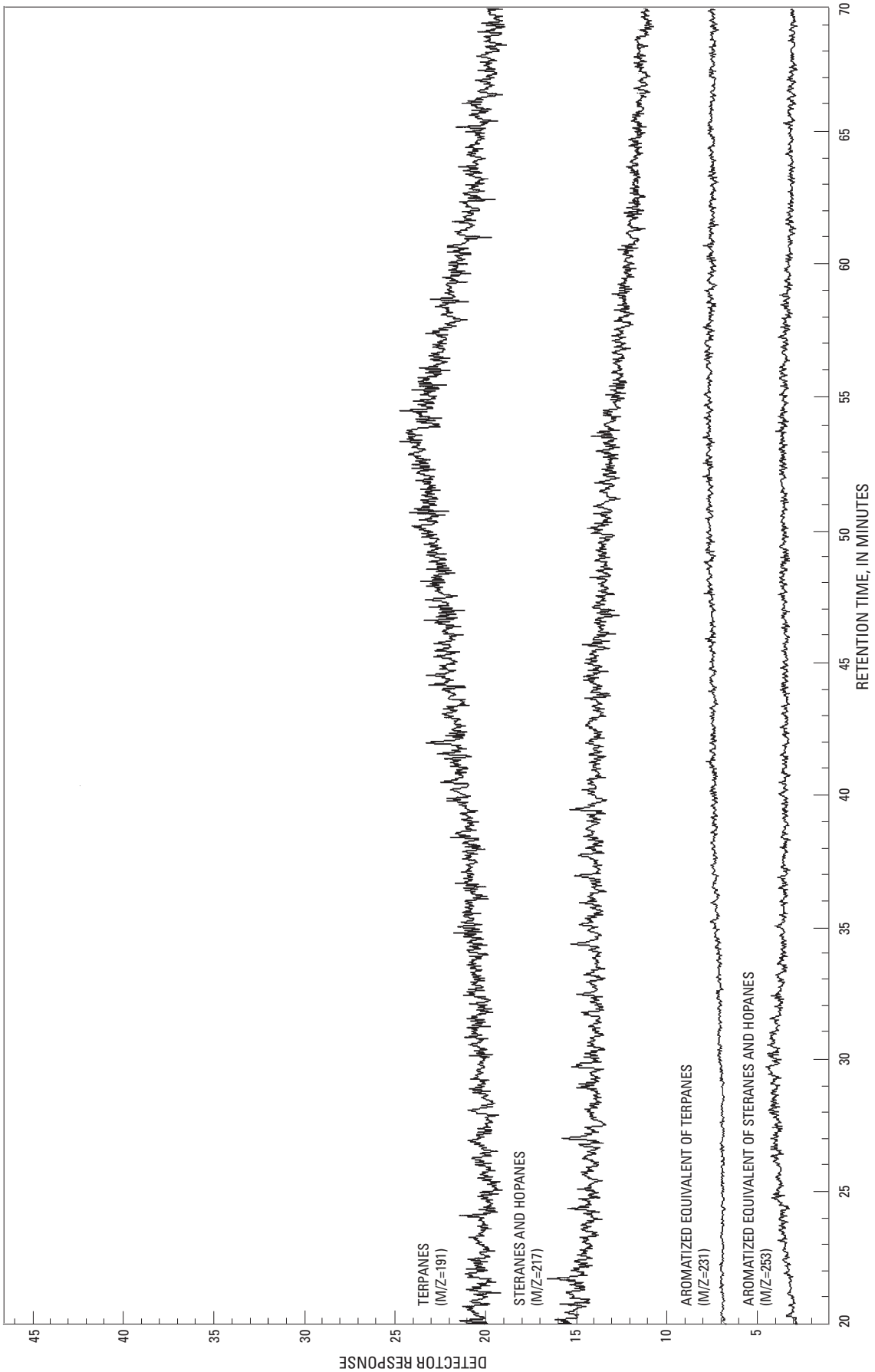


Figure 12. Mass fragmentograms for biomarkers in sample 97MCR5, No. 1 Baker well. *m/z*, mass to charge ratio. *m/z*=191, terpanes; *m/z*=217, steranes and hopanes; *m/z*=231 and *m/z*=253, aromatized equivalents of these compounds, respectively.

Table 1. Wells sampled for gas and oil in Trumbull County, Ohio.

[Abbreviations are as follows: API, American Petroleum Institute; Inc., Incorporated; ft, feet. Note: API number is a unique identification number assigned to each oil and gas well. The rightmost four or five digits are the well permit number used to identify wells in figure 1*B*]

U.S. Geological Survey sample identification number	Well name	Operator	API number	Ohio township	Producing formation	Perforation depth		Total depth (ft)	Sample type	Oil sample point
						Top (ft)	Bottom (ft)			
97MCR3	No. 1 Governor	Loma Enterprises, Inc.	34–155–23382	Bazetta	"Clinton" sandstone	4,372	4,432	4,602	Gas, oil	Sight glass
97MCR4	No. 1 Wargo	Loma Enterprises, Inc.	34–155–22914	Weathersfield	"Clinton" sandstone	4,746	4,786	5,006	Oil	Flow line
97MCR5	No. 1 Baker	Loma Enterprises, Inc.	34–155–23292	Weathersfield	"Clinton" sandstone	4,612	4,686	4,825	Oil	Sight glass
97MCR6	No. 2 Clemens	Lomak Petroleum, Inc.	34–155–22194	Bazetta	"Clinton" sandstone	4,252	4,318	4,472	Gas, oil	Sight glass
97MCR7	No. 2 Krantz	Lomak Petroleum, Inc.	34–155–23561	Bazetta	"Clinton" sandstone	4,356	4,397	4,600	Gas, oil	Sight glass
97MCR8	No. 1 Rhine	Lomak Petroleum, Inc.	34–155–22822	Fowler	"Clinton" sandstone	4,560	4,620	4,821	Oil	Sight glass
97MCR9	No. 1 Gowdy	Lomak Petroleum, Inc.	34–155–20849	Fowler	"Clinton" sandstone	4,627	4,677	4,854	Oil	Sight glass
97MCR10	No. 2 Redmond	Lomak Petroleum, Inc.	34–155–21340	Johnston	"Clinton" sandstone	4,450	4,496	4,685	Oil	Sight glass
97MCR11	No. 7 Consumer	Lomak Petroleum, Inc.	34–155–22217	Hartford	"Clinton" sandstone	4,545	4,599	4,767	Oil	Stock tank
97MCR12	No. 3 Consumer	Lomak Petroleum, Inc.	34–155–21932	Hartford	"Clinton" sandstone	4,600	4,628	4,798	Oil	Sight glass

Table 2. Molecular and isotopic composition of gas samples.

[Abbreviations are as follows: n.d., not detected; n.a., not analyzed; +, C_6 and higher hydrocarbon numbers]

U.S. Geological Survey sample identification number	97MCR7	97MCR3	97MCR6
Well name	No. 2 Krantz	No. 1 Governor	No. 2 Clemens
Molecular analysis, in mole percent			
Methane	89.34	90.33	90.64
Ethane	5.11	4.64	4.48
Ethylene	n.d.	n.d.	n.d.
Propane	1.65	1.47	1.32
iso-Butane	0.22	0.2	0.18
n-Butane	0.4	0.38	0.31
iso-Pentane	0.11	0.11	0.085
n-Pentane	0.11	0.13	0.096
Hexane+	0.12	0.14	0.12
Helium	0.091	0.089	0.099
Hydrogen	0.0013	0.0024	n.d.
Argon	n.d.	n.d.	n.d.
Oxygen	n.d.	n.d.	n.d.
Nitrogen	2.84	2.5	2.67
Carbon dioxide	0.01	0.01	n.d.
Isotopic analysis, per mil			
Methane, $\delta^{13}C$	–37.49	–37.20	–37.40
Hydrogen (deuterium), $\delta^{2}H$	–168.5	–166.6	–165.7
Ethane, $\delta^{13}C$	–35.29	–34.88	–34.67
Propane, $\delta^{13}C$	–30.94	–30.58	–30.40
Carbon dioxide, $\delta^{13}C$	n.a.	n.a.	n.a.

Table 3. Properties of whole crude oil and crude oil fractions.

[Abbreviations are as follows: API, American Petroleum Institute]

U.S. Geological Survey sample identification number	Well name	API gravity (degrees)	Petroleum fractions (weight percent)				Isotopic composition (per mil)	
			Saturated hydrocarbons	Aromatic hydrocarbons	Nitrogen-, sulfur-, and oxygen-bearing organics	Asphaltenes	Saturated hydrocarbons ($\delta^{13}C$)	Aromatic hydrocarbons ($\delta^{13}C$)
97MCR3	No. 1 Governor	40.9	86.7	8.6	3.2	1.6	–29.80	–28.96
97MCR4	No. 1 Wargo	40.5	89.2	7.2	2.4	1.3	–29.73	–28.68
97MCR5	No. 1 Baker	43.9	90.5	6.3	2.2	1.0	–29.76	–28.90
97MCR6	No. 2 Clemens	43.5	87.3	8.5	3.4	0.8	–29.61	–29.08
97MCR7	No. 2 Krantz	42.2	89.3	7.6	1.8	1.3	–29.66	–28.86
97MCR8	No. 1 Rhine	43.1	85.7	9.2	3.8	1.3	–29.50	–28.92
97MCR9	No. 1 Gowdy	39.7	88.9	7.7	2.7	0.7	–29.71	–29.19
97MCR10	No. 2 Redmond	44.3	88.8	7.8	2.5	0.9	–30.05	–29.23
97MCR11	No. 7 Consumer	37.3	90.9	6.8	2.3	0.9	–29.76	–28.55
97MCR12	No. 3 Consumer	42.6	89.4	7.0	2.4	1.1	–29.59	–28.87

Table 4. Properties of the saturated hydrocarbon fraction of the crude oils.

[Abbreviations are as follows: pr, pristane; ph, phytane. The condensate index (defined by Lewan and Buchardt, 1989) was calculated as the percent of n-C_{11} in n-C_{10} to n-C_{30}]

U.S. Geological Survey sample identification number	Well name	Saturated hydrocarbon characteristics					
		pr:ph	pr/n-C_{17}	ph/n-C_{18}	Carbon preference index	n-alkanes (percent)	Condensate index
97MCR3	No. 1 Governor	1.57	0.41	0.33	1.09	37.50	9.64
97MCR4	No. 1 Wargo	1.61	0.38	0.29	1.06	39.65	8.08
97MCR5	No. 1 Baker	1.63	0.41	0.32	1.04	38.03	9.30
97MCR6	No. 2 Clemens	1.63	0.40	0.31	1.04	38.89	8.93
97MCR7	No. 2 Krantz	1.35	0.38	0.33	1.04	39.64	8.41
97MCR8	No. 1 Rhine	1.07	0.32	0.33	1.01	42.41	8.44
97MCR9	No. 1 Gowdy	1.27	0.34	0.31	1.03	43.10	7.44
97MCR10	No. 2 Redmond	1.32	0.33	0.30	1.04	40.53	7.97
97MCR11	No. 7 Consumer	1.24	0.32	0.30	1.06	41.12	9.05
97MCR12	No. 3 Consumer	1.58	0.34	0.27	1.08	41.58	7.84