

S
14,GS:
1P 111



STATE OF ILLINOIS

DEPARTMENT OF REGISTRATION AND EDUCATION

ISOTOPIC IDENTIFICATION OF LEAKAGE GAS
FROM UNDERGROUND STORAGE RESERVOIRS—
A PROGRESS REPORT

Dennis D. Coleman

Wayne F. Meents

Chao-Li Liu

Robert A. Keogh

ILLINOIS PETROLEUM 111

ILLINOIS STATE GEOLOGICAL SURVEY

1977

URBANA, IL 61801

STATE OF ILLINOIS
DEPARTMENT OF REGISTRATION AND EDUCATION

BOARD OF NATURAL RESOURCES AND CONSERVATION

Hon. Joan G. Anderson, Ph.D., Chairperson

Laurence L. Sloss, Ph.D., Geology

H. S. Gutowsky, Ph.D., Chemistry

Robert H. Anderson, B.S., Engineering

Stanley K. Shapiro, Ph.D., Forestry

Thomas Park, Ph.D., Biology

Dean William L. Everitt, E.E., Ph.D., D.Eng.,
University of Illinois

Dean John C. Guyon, Ph.D.,
Southern Illinois University

STATE GEOLOGICAL SURVEY

Jack A. Simon, M.S., Chief

ISOTOPIC IDENTIFICATION OF LEAKAGE GAS FROM UNDERGROUND STORAGE RESERVOIRS— A PROGRESS REPORT

DENNIS D. COLEMAN, WAYNE F. MEENTS, CHAO-LI LIU, and ROBERT A. KEOGH

ABSTRACT

Identifying gas that has leaked from underground storage reservoirs for natural gas can be a difficult problem in areas where bacterially produced methane is common in the ground water. The absence of ethane or heavier hydrocarbons in methane-rich gas is generally interpreted as indicating that the gas was formed by bacteria because methane is the only hydrocarbon produced by bacteria in significant quantities. The data presented in this paper, however, suggest that the presence or absence of hydrocarbons heavier than methane may not be a reliable indicator of gas origin.

Radiocarbon dating of methane can be used to identify bacterially produced gas that was formed from organic materials less than 50,000 years old. This technique, however, requires relatively large samples and cannot distinguish between storage gas and bacterially produced gas from older materials. Determination of the C^{13}/C^{12} ratio of methane is a simpler and more versatile tool for identification of leakage gas. Bacteriogenic methane from Illinois generally has δC^{13} values in the range of -64 to -90 ‰ relative to the Peedee Belemnite (PDB) standard. The 11 samples from pipelines and storage reservoirs that have been analyzed have all had δC^{13} values in the range of -40 to -46 ‰.

Three storage reservoirs have been studied by analyzing samples from the reservoirs and from shallow water wells overlying the reservoirs. At the first reservoir, the δC^{13} value of methane from the storage gas was -46 ‰, whereas the δC^{13} value of methane from overlying water wells was about -76 ‰. Radiocarbon dating confirmed that the gas in the water wells had been formed by bacterial decomposition of materials within the glacial drift.

At the second reservoir, the δC^{13} values of storage-gas samples ranged from -41 to -45 ‰. Samples from water wells ranged from -78 ‰ off the margin of the reservoir to -41 ‰ directly over the reservoir, suggesting an increasing concentration of leakage gas over the reservoir. Although the gas in the reservoir contained approximately 5 percent hydrocarbons heavier than methane, no hydrocarbons heavier than methane were detected in the samples from the water wells.

At the third reservoir studied, leakage gas was being withdrawn from the units overlying the reservoir and reinjected into the reservoir. Samples from several gas wells at various depths had δC^{13} values ranging from about -41 to -43 ‰ and contained from 5 to 7 percent hydrocarbons heavier than methane. A sample from a water well directly over the reservoir had $\delta C^{13} = -60$ ‰ and contained 0.8 percent heavy hydrocarbons. It is estimated that this gas contains from 15 to 40 percent leakage gas and that the remainder is bacterially produced gas.

Although further testing is necessary, isotopic analysis of methane has proven so far to be a reliable technique for differentiating leakage gas from gas produced by bacterial action.

INTRODUCTION

Natural gas is generally believed to be formed by two distinct processes. One process, thermal decomposition of organic material, results from the higher temperatures and pressures caused by deep burial and probably requires millions of years. Gas formed in this way is called petrogenic gas. Commercial gas deposits consist mostly of natural gas of petrogenic origin. The other commonly encountered process of natural gas formation, bacterial decomposition of organic matter, can occur at or near the surface in a relatively short time. Gas formed by this process will be referred to as bacteriogenic gas. Swamp gas or marsh gas is an example of natural gas of bacteriogenic origin. Drift gas, natural gas that occurs in the glacial drift, is commonly formed by bacterial decomposition of buried peats and soils (Coleman, 1976, 1977). Both petrogenic gas and bacteriogenic gas are found dissolved in ground water and as accumulations of free gas.

In Illinois, drift gas occurs in many areas (Meents, 1958, 1960). Most of this gas is probably bacteriogenic, but some of it may be petrogenic gas that has migrated into the glacial drift. Most of the gas that occurs in the bedrock, however, is probably petrogenic even though some of the gas in the upper part of the bedrock is bacteriogenic in origin (Coleman, 1976, 1977).

Besides drift gas and petrogenic gas of local origin, natural gas is piped into the state and is stored in underground reservoirs. This gas is generally of petrogenic origin. Sometimes gas that is stored underground leaks through the caprock of the storage reservoir into the overlying rocks or even all the way to the surface (Buschbach and Bond, 1974). The ability to identify such leakage gas and to distinguish between it and local naturally occurring gas is of both economic and environmental significance. This paper presents some of the preliminary results obtained in the attempt to use isotopic analysis of methane to identify leakage gas.

Acknowledgments

We would like to express our gratitude to the personnel of Northern Illinois Gas Company, Peoples Gas Light and Coke Company, and Natural Gas Pipeline Company of America for allowing us to collect samples from their wells. We

also thank those individual farmers and landowners who gave us permission to collect samples. We would also like to express our appreciation to Dr. T. F. Anderson for allowing us to use the mass spectrometer in his laboratory at the Geology Department, University of Illinois. When this machine was under repair, Dr. Gene Perry of Northern Illinois University graciously allowed us to use the mass spectrometer in his laboratory.

THE ISOTOPIC COMPOSITION OF METHANE

Natural carbon is made up of three different isotopes. One of these isotopes, carbon-14 (C^{14}) or radiocarbon, is formed in the upper atmosphere by reaction of cosmic ray produced neutrons with N^{14} . The C^{14} becomes oxidized to CO_2 and mixes with the rest of the CO_2 in the atmosphere. Because all living things, directly or indirectly, maintain an equilibrium with the atmosphere, they all contain about the same amount (about $1 \times 10^{-10}\%$) of C^{14} relative to total carbon. Radiocarbon, however, is unstable and decays back to N^{14} with a half-life of 5,730 years (Godwin, 1962). When a plant or animal dies, the process of equilibration with the atmosphere ceases, and the C^{14} content gradually decreases. The time that has elapsed since equilibration was discontinued with the atmosphere can be estimated by determining the proportion of C^{14} remaining in a particular organic material. In simple terms, this is the basis for radiocarbon dating. Although the maximum determinable age using radiocarbon is somewhat dependent on the particular equipment used for the C^{14} analysis, it is generally about 40,000 to 50,000 years. In materials older than this, C^{14} is below the limits of detectability.

Because petrogenic gas is formed from materials millions of years old, it contains no detectable radiocarbon. Bacteriogenic gas, however, may have been formed from relatively young materials. Coleman (1977) used radiocarbon dating of methane to verify the origin of some drift gas samples and to study their migrational history. This technique can be used to identify bacteriogenic gas that is less than 50,000 radiocarbon years old. It will not, however, distinguish between petrogenic gas and older bacteriogenic gas. As a tool for identifying leakage gas, therefore, radiocarbon dating can only be used to indicate the presence of young bacteriogenic gas and not to prove the presence of

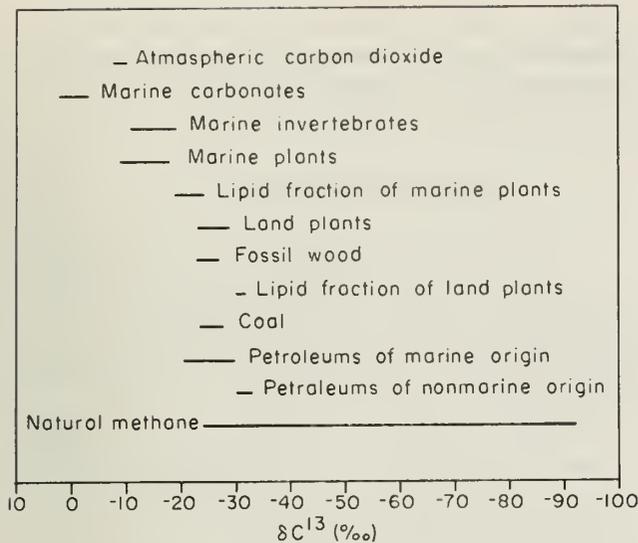


Fig. 1 - Typical carbon-isotopic compositions of some common carbonaceous materials (after Silverman, 1964).

petrogenic gas. Also, radiocarbon dating requires several liters of gas, an amount often difficult to obtain if the gas is in solution in ground water.

The study of the two stable isotopes of carbon, carbon-12 (C^{12}) and carbon-13 (C^{13}), is a more versatile tool for identifying leakage gas. Normal carbon is composed of about 98.9 percent carbon-12 and about 1.1 percent carbon-13 (Nier, 1950). Because of the small but significant difference in mass of the carbon isotopes, the rates at which the isotopic species undergo certain physical and chemical processes are often different. As a consequence, isotopic fractionation (the partial separation of carbon isotopic species) can occur in certain natural processes. The C^{13}/C^{12} ratio in a material such as methane can often be useful in studying its history.

The isotopic composition of carbon (C^{13}/C^{12}) is normally expressed as the per mil (parts per thousand, ‰) difference from a given standard, where that difference is assigned the symbol δC^{13} . These δC^{13} values are related to C^{13}/C^{12} ratios by the following equation:

$$\delta C^{13}_{\text{sample}} = \frac{(C^{13}/C^{12})_{\text{sample}} - (C^{13}/C^{12})_{\text{standard}}}{(C^{13}/C^{12})_{\text{standard}}} \times 1000.$$

For example, a δC^{13} value of -60 ‰ indicates that the material is 60 parts per thousand (or 6 percent) "lighter" than the standard. That is,

the material is enriched in C^{12} by 60 ‰ relative to the standard. Positive values indicate that the sample is "heavier" than the standard or enriched in C^{13} .

Carbon-isotopic compositions are most commonly reported relative to the Peedee Belemnite (PDB) standard used by Craig (1953). This material had a C^{13}/C^{12} ratio similar to that of average marine limestone. All δC^{13} values reported in this study have been calculated relative to PDB. Figure 1 compares the normal range of δC^{13} values for some common carbonaceous materials.

Figure 2 shows the isotopic compositions of 49 methane samples from Illinois. The gas wells sampled are not in the immediate vicinity of any storage reservoirs. The wells in bedrock range from 90 to 2,355 feet deep and are completed in rocks ranging in age from Pennsylvanian to Silurian. The samples from these bedrock wells represent petrogenic gas and have δC^{13} compositions ranging from about -45 to -63 ‰. Only 14 of the 24 samples contain detectable quantities (that is, $>.05\%$) of hydrocarbons heavier than methane.

The gas wells in glacial drift that were sampled range in depth from 27 to 324 feet. This gas represents bacteriogenic gas and has a δC^{13} range of from -68 to -90 ‰. Radiocarbon dating has shown that this gas originated from the decay of organic materials in the glacial drift (Coleman, 1977). None of these samples contain detectable quantities of hydrocarbons heavier than methane.

Figure 3 shows the isotopic compositions of 67 samples of methane from freshwater wells

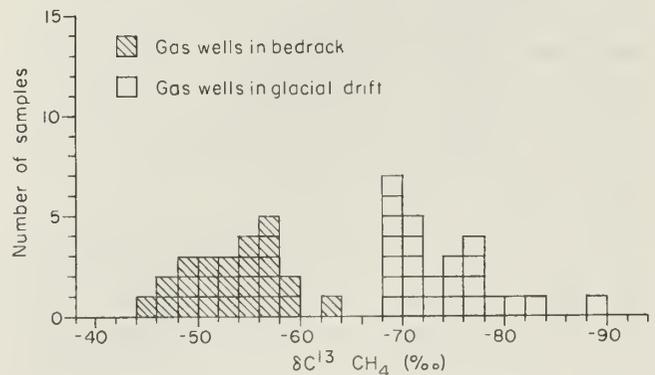


Fig. 2 - Histogram of the carbon-isotopic composition of gas wells in Illinois that are not related to storage reservoirs (includes data from Coleman, 1976).

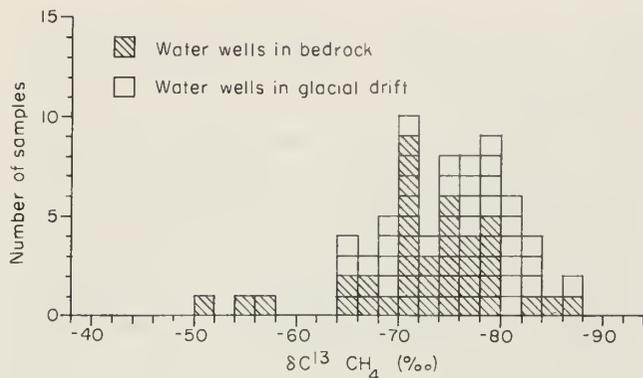


Fig. 3 - Histogram of the carbon-isotopic composition of methane from freshwater wells in Illinois that are not related to storage reservoirs (includes data from Coleman, 1976).

in Illinois. Again, the wells sampled are not near storage reservoirs. The water wells in glacial drift that were sampled range in depth from 65 to 420 feet. The water wells in bedrock range from 55 to 558 feet in depth and penetrate into the bedrock from 4 to 490 feet.

Three of the samples have isotopic compositions heavier than -58 ‰, suggesting that they are of petrogenic origin. The remaining samples, from wells in both glacial drift and bedrock, appear to be bacteriogenic in origin. In fact, some of the samples from wells in bedrock have been shown by radiocarbon dating to be gas that formed in the glacial drift and then migrated into the bedrock with ground water (Coleman, 1976, 1977). None of these samples contain detectable quantities of hydrocarbons heavier than methane.

For the 11 samples of pipeline and reservoir gas piped in from outside of Illinois that have thus far been analyzed (including those samples reported in this study), the range of δC^{13} values encountered is from -40 to -46 ‰. This gas is heavier than all of the bacteriogenic gas samples and heavier than most of the petrogenic samples shown in Figure 2. Most of this gas is piped in from the Texas Panhandle region and the Gulf Coast. Analysis of 39 samples from gas wells in Kansas, Oklahoma, Texas, and New Mexico (Zartman et al., 1961; Wasserburg et al., 1963; and Stahl and Carey, 1975) showed a range in δC^{13} values for methane from -35 to -52 ‰.

Most pipeline and storage gas encountered in Illinois would be expected then to have an isotopic composition much different from bacteriogenic gas and different from most local

petrogenic gas. Isotopic analysis of methane, therefore, provides a possible method for distinguishing between naturally occurring gas and leakage gas from storage reservoirs.

EXPERIMENTAL TECHNIQUES

The techniques used for collecting samples from gas wells are the same as those described by Meents (1958). Samples are collected under pressure in 1.6-liter aviator's oxygen bottles which are heated and evacuated prior to each use.

Samples from water wells are collected by water displacement. A one-quart mason jar is immersed in a pail of water and then inverted. A hose is connected to the water system and, after allowing the water to run for several minutes, the flow rate is adjusted to about 3 gallons per minute. A copper U-tube $3/4$ inch in diameter attached to the end of the hose is then inserted in the inverted jar as shown in Figure 4. Because of the decrease in pressure as the water flows out of the tube, gas comes out of solution and collects in the jar, gradually displacing the water. When enough gas is collected, the U-tube is removed and a lid is placed on the jar while it is still underwater. Although the amount of sample collected varies with the amount of gas in the water, some water is always left in the jar to form a liquid seal. The

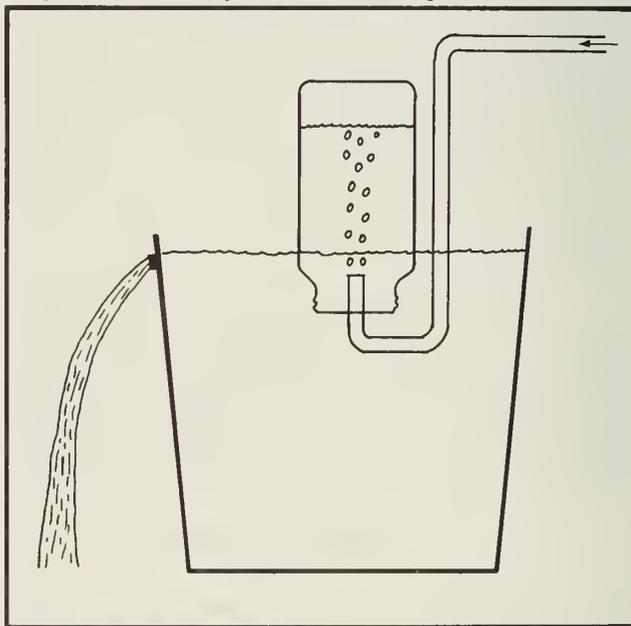


Fig. 4 - Water-displacement technique for collecting gas samples from water wells (Coleman, 1976).

jars are transported and stored inverted to maintain this seal. In the laboratory, the still-inverted jar is again submerged in water and the lid removed and replaced with a specially designed aluminum lid fitted with a rubber gasket and a brass valve. Splits for analysis are then taken through this valve. The detailed procedures by which these splits are taken are described by Coleman (1976).

After separation and combustion of methane as described by Coleman (1976), isotope ratio determinations are made on a Nuclide Model 6-60-RMS mass spectrometer at the University of Illinois Department of Geology. This mass spectrometer is a 6-inch, 60-degree sector instrument with a double collector.

Chemical analyses of the samples are performed on a Perkin Elmer Model 154 gas chromatograph. A 15-foot column filled with molecular sieve 5A and operated at ambient temperature is used in the analysis of CH₄, N₂, and O₂. Concentrations of CO₂ and hydrocarbons lighter than C₅ are determined using a 30-foot silicon oil (200/500) column operated at 90°C. Gas concentrations are reported as volume percent.

RESULTS AND DISCUSSION

Isotopic analysis of methane for identifying leakage gas from underground storage areas has been attempted in three localities chosen to represent leakage of varying degrees. To compare isotopic analysis with conventional techniques for identifying leakage gas, the results of the hydrocarbon analyses are also reported. The data are tabulated in Table 1.

Crescent City Project

The Crescent City Project, located between Crescent City and Watseka, Illinois, is operated by Northern Illinois Gas Company. Storage is in the St. Peter Sandstone and the trap is an asymmetrical anticline (Buschbach and Bond, 1974). One gas well and two water wells in the shallow bedrock were sampled in this area. Their locations are given in Figure 5 which shows the structure on the St. Peter Sandstone.

Figure 6 is an idealized cross section from A to A' on Figure 5. The numbers represent

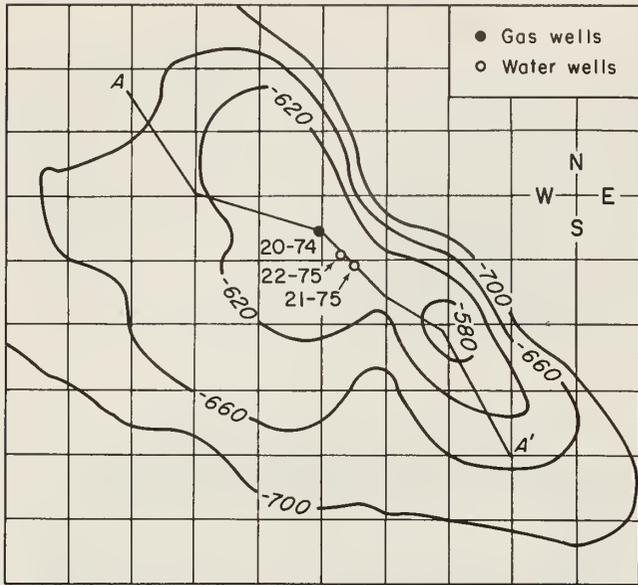
TABLE 1 - WELL DESCRIPTIONS AND ANALYTICAL RESULTS

Sample number	Type of well	Depth in feet	Material	CH ₄ (%)	C ₂ H ₆ (%)	C ₃ H ₈ (%)	C ₄ H ₁₀ (%)	ΣC _n > ₄ (%)	δC ¹³ (‰)
Crescent City Reservoir Area									
21-75	water	225	Silurian ls	100	nd†	nd	nd	nd	-75.2
22-75	water	193	Silurian ls	100	nd	nd	nd	nd	-75.8
20-74	gas	1,399	St. Peter SS	94.7	2.6	.4	.1	2.2	-46.1
Manlove Reservoir Area									
2-75	water	162	glacial drift	100	nd	nd	nd	nd	-77.9
12-76	water	284	glacial drift	100	nd	nd	nd	nd	-76.0
96-75	water	286	glacial drift	100	nd	nd	nd	nd	-55.4
5-75	water	205	glacial drift	100	nd	nd	nd	nd	-41.1
28-75	gas	1,554	St. Peter SS	94.9	3.9	.9	.3	nd	-40.9
10-76	gas	*	Mt. Simon SS	95.1	2.2	.4	.2	2.1	-44.8
11-76	gas	4,142	Mt. Simon SS	94.1	2.9	.5	.2	2.3	-41.1
Herscher Reservoir Area									
19-76	water	112	Ft. Atkinson (Divine)LS	99.2	.7	.1	nd	nd	-60.1
18-76	gas	705	St. Peter SS	94.4	2.9	.5	.2	2.1	-40.7
17-76	gas	905	Prairie du Chien Group	95.2	2.6	.4	.1	1.7	-41.6
16-76	gas	1,774	Galesville SS	93.2	2.5	.4	.1	3.8	-42.8
15-76	gas	2,568	Mt. Simon SS	94.2	2.8	.5	.2	2.3	-41.8
14-76	gas	2,665	Mt. Simon SS	92.8	3.3	.5	.2	3.2	-42.2
13-76	gas	‡	Galena (Trenton) Group	94.1	3.0	.5	.2	2.2	-41.9

†Not detectable (that is, <.05 percent).

*This sample was from a pipeline feeding injection gas to several wells.

‡This sample was from a collection line servicing several wells in the Galena (Trenton) Group.



Contours on St. Peter Sandstone
Interval 40 feet

0 1 2 Miles

Fig. 5 - Location of wells sampled at the Crescent City Project (modified from a map prepared by Northern Illinois Gas Company).

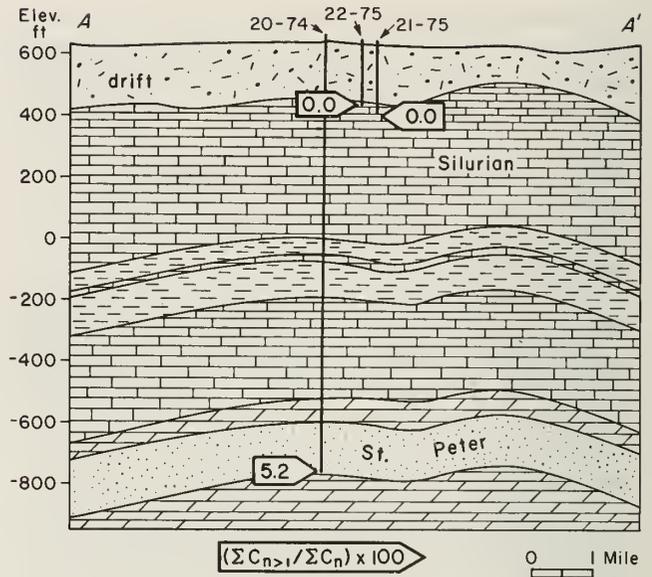


Fig. 6 - Idealized cross section through the Crescent City reservoir showing the percentage of heavy hydrocarbons in samples from the wells indicated (after a cross section prepared by Northern Illinois Gas Company).

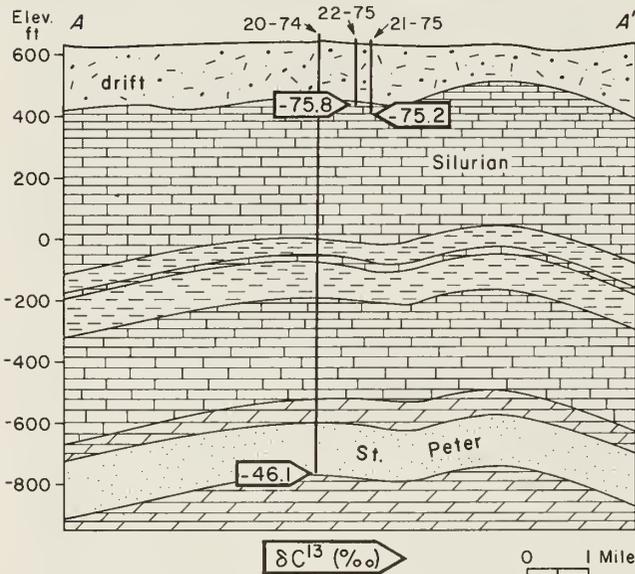
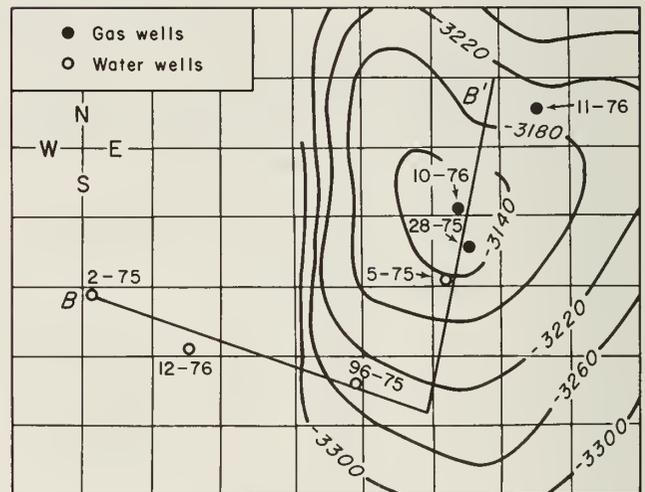


Fig. 7 - Isotopic composition of methane in samples from the Crescent City Project.



Contours on Mt. Simon Sandstone
Interval 40 feet

0 1 2 Miles

Fig. 8 - Location of wells sampled near the Manlove Project. Sample 10-76 was actually from a pipeline feeding injection gas to several wells in the area. For diagrammatic purposes, only one well is shown. (This figure is modified from a map prepared by Peoples Gas Light and Coke Company.)

the percentages of hydrocarbons heavier than methane in the samples. The two samples from the shallow water wells (22-75 and 21-75) contain no heavy hydrocarbons, whereas the sample from the reservoir (20-74) contains 5.2 percent heavy hydrocarbons. Because bacteriogenic gas does not contain heavy hydrocarbons in significant quantities, these data would normally be interpreted as indicating that the gas in the water wells was formed by bacteria and is unrelated to that in the reservoir. This interpretation is verified by the isotopic data presented in Figure 7. The methane from the water wells has an isotopic composition typical of bacteriogenic methane, whereas that in the reservoir has a composition typical of pipeline gas. Coleman (1977) has shown that the methane from one of these water wells was actually formed in the glacial drift and then carried into the bedrock with ground water.

Chemical and isotopic analyses both support the conclusion that the gas in the water wells sampled at the Crescent City Project is of bacteriogenic origin and is unrelated to the gas in the storage reservoir.

Manlove Project

The Manlove Storage Reservoir in west-central Champaign County is operated by Peoples Gas Light and Coke Company. Storage was originally attempted in 1961 in a domal structure in the St. Peter Sandstone. However, storage in this unit was discontinued when migration of gas upward into the glacial drift was discovered (Buschbach and Bond, 1974). Gas is now stored in the Mt. Simon Sandstone.

Seven samples of gas were collected from wells over or near the Manlove Reservoir. The location of these wells relative to the storage area is shown in Figure 8. Three of the samples are storage gas, and four are from shallow water wells in the area.

The results of the chemical analyses of the samples are shown in Figure 9, an idealized cross section through the area. Again, the percentage of hydrocarbons heavier than methane is given. None of the samples from water wells were found to contain heavier hydrocarbons. It would normally be concluded from this information that the gas in the water wells is of bacteriogenic origin and is unrelated to the storage reservoir.

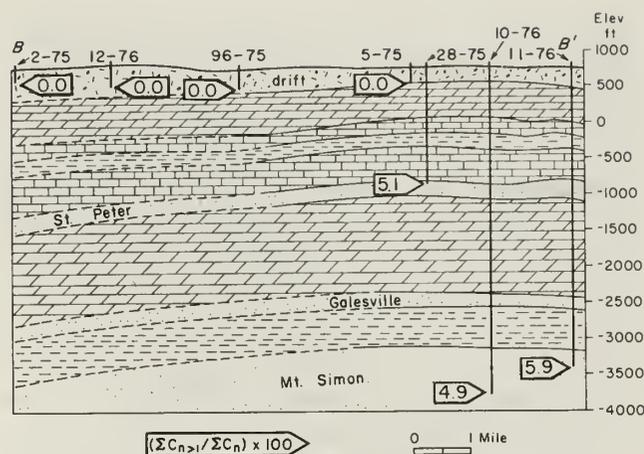


Fig. 9 - Idealized cross section through the Manlove Project showing the concentrations of hydrocarbons heavier than methane (modified from a cross section prepared by Peoples Gas Light and Coke Company).

The results of the isotopic analyses shown in Figure 10, however, present a different picture. The methane samples from the two water wells in the western part of the region (2-75 and 12-76) off the margin of the reservoir area have isotopic compositions typical of bacterially produced drift gas. The methane from water well 5-75, however, has the same isotopic composition as the gas in the St. Peter Sandstone. Because methane of this isotopic composition is not known to occur naturally in Illinois, it is concluded that this gas has migrated upward. It is probably part of the gas that was injected in the St. Peter Sandstone in 1961.

Well 96-75 in Figure 10 contains gas that has an isotopic composition intermediate between that of the drift gas in the western water wells and that of the leakage gas in the eastern water well. This gas is probably a mixture of gas from these two sources.

The most noteworthy point about these samples is that although the leakage gas in the water wells has not undergone any significant change in isotopic composition, the chemical composition has changed considerably. Although it cannot be said with certainty at this time what happened to the heavier hydrocarbons that were originally present in the gas, it appears that some mechanism of chemical fractionation (that is, a change in the chemical composition) has resulted in complete removal of the heavier hydrocarbons as the gas migrated upward from the St. Peter Sandstone to the surface.

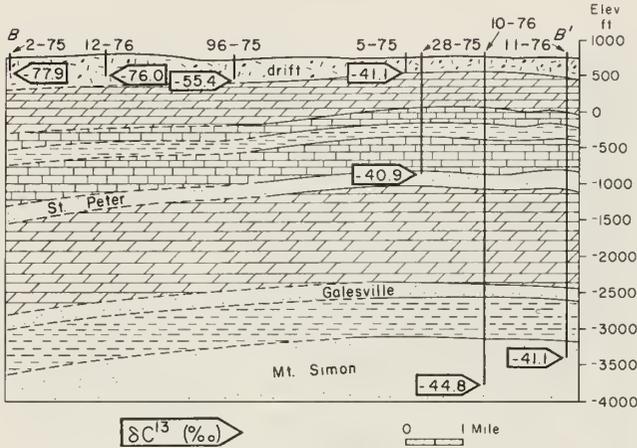


Fig. 10 - Isotopic composition of samples from near the Manlove Project.

Herscher Project

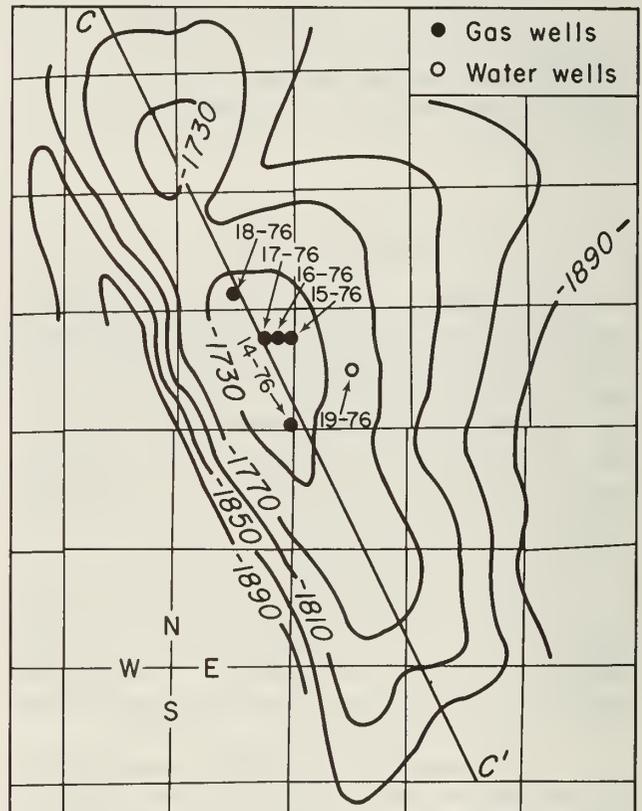
The Herscher Project in western Kankakee County is operated by Natural Gas Pipeline Company of America. In this field, gas is injected into both the Galesville Sandstone and the Mt. Simon Sandstone. No leakage of gas from the Mt. Simon Sandstone has been observed (Buschbach and Bond, 1974); however, leakage from the Galesville Sandstone does occur. To keep this gas from reaching the surface, gas is withdrawn from the units overlying the Galesville Sandstone and reinjected into the deeper units.

The locations of the seven wells sampled from this area are shown in Figure 11. Six of the samples are from gas wells in the different stratigraphic units, and one is from a shallow water well directly over the reservoir. The percentage of hydrocarbons heavier than methane present in the samples is shown in the cross section in Figure 12. In the samples from gas wells, this value ranges from 4.8 to 7.2 percent. Although there are variations, there do not appear to be any consistent trends, and at least part of the variation may be due to differences in the composition of the injected gas.

The sample from the water well (19-76) contains only 0.8 percent heavier hydrocarbons. If this gas is entirely leakage gas, there has been a significant chemical fractionation in the later part of the migration. No such fractionation is observed, however, as the gas migrates up through the lower units. If this gas is a mixture of leakage gas and naturally occurring bacteriogenic gas, it may be primarily bacteriogenic gas. If the fraction that is leakage gas contains heavier hydrocarbons in the same proportions

observed in the gas wells, leakage gas makes up only about 11 to 17 percent of the total. The value should be higher than this if some chemical fractionation has occurred.

The isotopic data obtained are shown in Figure 13. Although there are variations in the samples from gas wells, no consistent trends are apparent. The sample from the water well (19-76) is considerably lighter and, as the chemical data imply, appears to be mostly bacteriogenic gas mixed with some petrogenic storage gas that has leaked upward. Using the range in the isotopic composition of bacteriogenic gas shown in Figures 2 and 3 and the range observed for the storage gas, this gas is calculated to be between 15 and 65 percent leakage gas. The chemical data suggest that the actual value is in the low end of this range. A value between 15 and 40 percent is most likely.



Contours on Mt. Simon Sandstone Interval 40 feet

0 1 2 Miles

Fig. 11 - Location of wells sampled at the Herscher Project (modified from a map prepared by Natural Gas Pipeline Company of America).

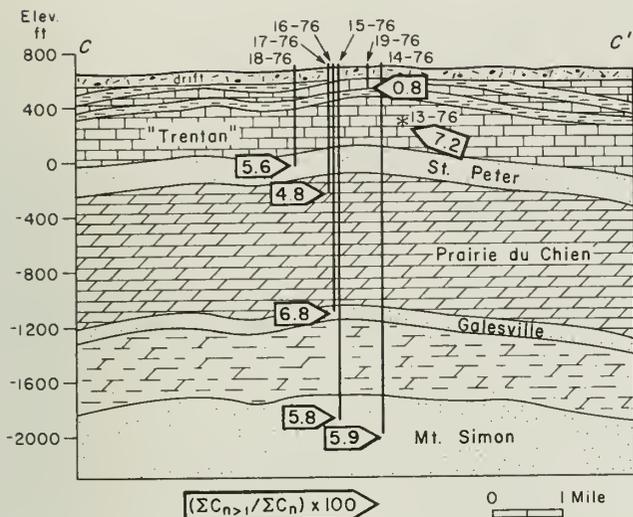


Fig. 12 - Idealized cross section through the Herscher Storage Reservoir showing the percentage of hydrocarbons heavier than methane present in the samples collected. Sample 13-76 was from a collection line servicing several wells in the unit. This cross section was constructed from contour maps prepared by Natural Gas Pipeline Company of America and a sketch in Katz and Coats (1968).

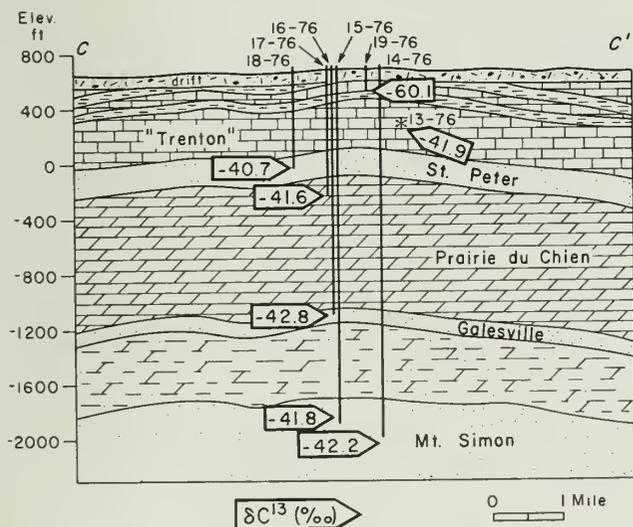


Fig. 13 - Isotopic composition of samples from the Herscher Project.

Prior to analysis, it was anticipated that this gas was entirely leakage gas. The results, therefore, suggest that the recycling procedure being used at the Herscher Project is quite successful in limiting the amount of gas that enters the shallow ground water. The amount of leakage gas in the aquifer is probably less than the amount of gas derived by bacterial action in the shales directly above and below the aquifer and/or in the overlying glacial drift.

PRELIMINARY CONCLUSIONS

The data presented in this preliminary report suggest that in areas where bacteriogenic methane occurs in the near-surface ground water, isotopic analysis of methane can be used to distinguish this gas from gas that has leaked from underground storage reservoirs. Bacteriogenic methane generally has a δC^{13} value in the range of -64 to -90 ‰, whereas the pipeline and reservoir gases analyzed thus far have all had δC^{13} values in the range of -40 to -46 ‰.

Although determining the concentration of hydrocarbons heavier than methane may still be useful in identifying leakage gas, the data from one of the reservoirs studied suggest that chemical fractionation of the gas as it migrates can, under some circumstances, result in essentially complete removal of the heavier hydrocarbons without significantly affecting the isotopic composition of the methane. Therefore, isotopic analysis of methane is probably a more reliable technique, although further study is needed to verify these findings.

In some cases, it may also be possible to estimate the proportions of leakage gas and bacteriogenic gas in a given aquifer. This can best be done by using both chemical and isotopic data.

PLANS FOR CONTINUED RESEARCH

The conclusions reached in this progress report are based on a limited number of samples. The Illinois State Geological Survey is working to increase the number of samples analyzed and to expand this type of study to other storage areas. Additional samples of naturally occurring gas will also be analyzed to more thoroughly characterize the isotopic composition of this gas.

Although this study has dealt only with identification of leakage gas from underground storage reservoirs, isotopic analysis should be similarly useful for identification of leakage from pipelines. It is also possible that isotopic analysis could be used to distinguish pipeline or storage gas from naturally occurring petrogenic gas; however, the difference in compositions here is much smaller. Research in these areas is planned.

The production of synthetic natural gas is also becoming a significant source of pipeline gas. A study is planned to determine if this gas can be readily distinguished from the naturally occurring forms.

Also in progress are laboratory studies to determine the relative isotopic and chemical changes that occur as natural gas migrates through or out of rocks.

REFERENCES

- Buschbach, T. C., and D. C. Bond, 1974, Underground storage of natural gas in Illinois—1973: Illinois State Geological Survey Illinois Petroleum 101, 71 p.
- Coleman, D. D., 1976, Isotopic characterization of Illinois natural gas: Dissertation, University of Illinois, 175 p.
- Coleman, D. D., 1977, The origin of drift-gas deposits as determined by radiocarbon dating of methane, *in* Berger, R., and H. E. Suess, eds., Proceedings of the Ninth International Radiocarbon Conference: Los Angeles and San Diego, June 20-26, 1976, in press.
- Craig, H., 1953, The geochemistry of the stable carbon isotopes: *Geochimica et Cosmochimica Acta*, v. 3, p. 53-92.
- Godwin, H., 1962, Half-life of radiocarbon: *Nature*, v. 195, p. 984.
- Katz, D. L., and K. H. Coats, 1968, Underground storage of fluids: Ann Arbor, MI, Ulrich's Books, Inc., 575 p.
- Meents, W. F., 1958, Tiskilwa drift-gas area, Bureau and Putnam Counties, Illinois: Illinois State Geological Survey Circular 253, 15 p.
- Meents, W. F., 1960, Glacial-drift gas in Illinois: Illinois State Geological Survey Circular 292, 58 p.
- Nier, A. O., 1950, A redetermination of the relative abundances of the isotopes of carbon, nitrogen, oxygen, argon, and potassium: *Physical Review*, v. 77, p. 789.
- Silverman, S. R., 1964, Investigations of petroleum origin and evolution mechanisms by carbon isotope studies, *in* Isotopic and Cosmic Chemistry: Craig, H., S. L. Miller, and G. J. Wasserburg, eds., Amsterdam, North Holland Press, p. 92-102.
- Stahl, W. J., and B. D. Carey, 1975, Hydrogen and carbon isotope data of Texan natural gases and the relations to the maturity of their source bed material: Geological Society of America Abstract with Programs, v. 7, no. 7, p. 1281.
- Wasserburg, G. J., E. Mazor, and R. E. Zartman, 1963, Isotopic and chemical composition of some terrestrial natural gases, *in* Earth Science and Meteoritics: Geiss, J., and E. D. Goldberg, eds., Amsterdam, North Holland Publishing Co., p. 219-240.
- Zartman, R. E., G. J. Wasserburg, and J. H. Reynolds, 1961, Helium, argon, and carbon in some natural gases: *Journal of Geophysical Research*, v. 66, no. 1, p. 277-306.

Illinois State Geological Survey Illinois Petroleum 111
10 p., 13 figs., 1 table, 2,200 cop., 1977
Urbana, Illinois 61801

