ORNL-TM-2862

Contract No. W-7405-eng-26

HEALTH PHYSICS DIVISION

FIFTH QUARTERLY PROGRESS REPORT ON THE THEORETICAL EVALUATION OF CONSUMER PRODUCTS FROM NUCLEARLY STIMULATED GAS WELLS

D. G. Jacobs and M. J. Kelly

FEBRUARY 1970

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

FIFTH QUARTERLY PROGRESS REPORT ON THE THEORETICAL EVALUATION OF CONSUMER PRODUCTS FROM NUCLEARLY STIMULATED GAS WELLS

D. G. Jacobs and M. J. Kelly

ABSTRACT

The concentrations of tritium and krypton-85 in the products being removed from the Gasbuggy cavity have been dropping exponentially as a function of the cumulative volume of gas removed from the cavity.[1] The chemical composition of product being removed at the wellhead also shows that mixing with formation fluids is occurring. Tritium appears to be rather uniformly distributed among all hydrogen-bearing components. Analytical requirements for the product from the Rulison cavity are outlined on the basis of these historical radiochemical and chemical data for the products removed from the Gasbuggy cavity.

CONCENTRATION OF TRITIUM AND KRYPTON IN GASBUGGY GAS AS A FUNCTION OF TIME

The concentrations of tritium and krypton-85 in the products being removed from the Gasbuggy cavity have been decreasing with time.[1] When the concentrations are plotted as a function of the cumulative volume of gas removed from the cavity (Fig. 1), it is seen that the drop in concentration follows the curve anticipated for the case in which gas removed from the cavity is replenished by gas from the formation and the gas is well-mixed in the cavity.[2] The equation for the straight lines in Fig. 1 is:

$$C_p = C_o e^{-P/V_o} \tag{1}$$

where

C_o is the concentration of the radionuclide in the cavity gas at the time production starts, corrected for radioactive decay to the date of the detonation (pCi/cm^3),
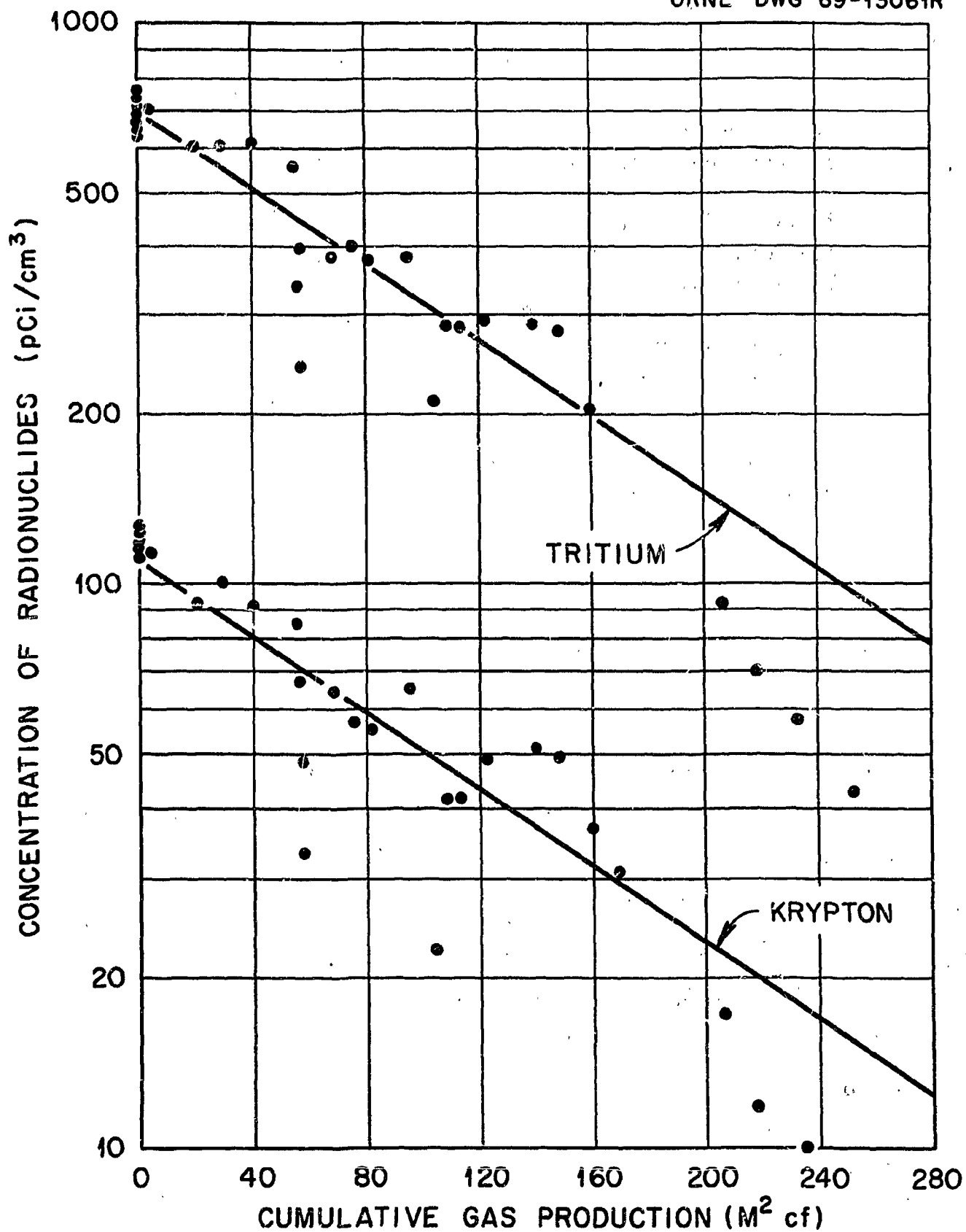
ORNL-DWG 69-13061R

Fig. 1. Concentrations of Tritium and Krypton-85 in Gasbuggy Gas as a Function of the Total Volume of Gas Produced. (The straight line represents the predicted concentrations based on complete mixing of 128 M^2cf of gas in the chimney.)

P is the cumulative production of gas from the wellhead (M^2cf),

V_o is the initial volume of gas in the cavity (M^2cf), and

C_p is the concentration of the radionuclide in the gas at the wellhead after a cumulative production of P. (C_p is in units of pCi/cm^3, corrected for radioactive decay to the day of the detonation.)

When the concentrations are not corrected for radioactive decay, an additional exponential term should be added. The volume of gas in the cavity was assumed to be 128 M^2cf (ref. 3), corrected to normal conditions of 1 atmosphere pressure and 65°F. The most notable deviations from the predicted curve occur after the termination of a period of rapid withdrawal of gas from the cavity. During the period of rapid withdrawal, it would be expected that the formation could not supply gas to the cavity at the rate that it is removed from the wellhead. During such a period of time, the bottom-hole pressure drops and the concentration of radionuclides in the gas being withdrawn falls at a slow rate. When the cavity is given a chance to recover, the bottom-hole pressure increases and the concentration of radionuclides in the cavity gas drops more rapidly due to mixing with uncontaminated gas from the surrounding formation.

If the concentrations are investigated in more detail, it becomes evident that the concentrations drop below those expected for complete mixing. This suggests that a formation near the top of the cavity is supplying formation gas faster than other strata, thus allowing a blanket of low-activity gas to accumulate at the top of the cavity during shut-ins following periods of rapid production.

Based on the radiochemical analyses and flow rate data provided in ref. 1, it is estimated that 1860 curies of tritium were produced in the first 161 M^2cf of gas. This compares favorably with the 1810 curies of tritium one would have predicted would be produced by integration of Eq. (1). For [85]Kr the production in 170 M^2cf of gas amounted to 300 curies compared to the predicted value of 294 curies. Integration of Eq. (1) yields values for the total quantity of tritium and [85]Kr that will be produced during the lifetime of the well of 2525 curies and 400 curies, respectively.

CHEMICAL COMPOSITION OF THE GAS FROM THE GASBUGGY WELL
AND THE DISTRIBUTION OF TRITIUM AMONG COMPONENTS

During the first few days following the detonation, most of the gaseous tritium existed in the cavity as hydrogen gas.[1,3] During the initial few days, the tritium to hydrogen ratio of the hydrogen gas was quite high, on the order of 6×10^9 T.R. (1 T.R. is defined as 1 atom of tritium per 10^{18} atoms of protium.) compared to values of 1.5×10^8 T.R. for methane and 1.3×10^8 T.R. for ethane in the same gas samples.

During production testing of the well, gas removed from the well has been partially replaced by the influx of native, uncontaminated gas from the surrounding formation. The native gas is low in H_2 so that the relative abundance of H_2 in gas being removed at the wellhead has decreased with increased production. The volume percentage of hydrogen in the gas being removed from the chimney has decreased with time, following the same type of curve as the decline of the concentrations of total tritium and krypton in the gas. The same applies for CO_2. The relative abundance of methane and other hydrocarbons has increased during the same production period.

Raw data on the activity of distillation fractions from the "drip liquid" taken from the Gasbuggy well on February 25, 1969, were reported in the Fourth Quarterly Progress Report.[4] Further examination of some of these samples seemed desirable in an effort to confirm the assumption that tritium had distributed itself over all the hydrocarbons in the well in ratio to the hydrogen atoms per hydrocarbon molecule.

Activity levels were calculated for normal paraffin hydrocarbons (C_nH_{2n+2}) using the tritium concentration in methane projected to February 25, 1969, and assuming a uniform tritium ratio for all species. There was an increase in the expected activity of the liquid paraffins of only 12% in going from n-pentane (b.p. ~ 36°C) to tetradecane (b.p. 253°C). Calculations for selected paraffin isomers, cycloparaffins, and derivatives suggested that they would contain essentially the same activity as the normal paraffins. Only when aromatic hydrocarbons and their derivatives were considered were significant changes noted. The simplest aromatics, benzene, and naphthalene would contain only 63% of

the calculated activity of the n-paraffin having the same boiling temperature. The difference decreases with the addition of methyl groups to the simple aromatics.

Calculated activity levels are compared with measured values in Table 1. With the exception of sample No. 1, which appears low, very good correlation is seen between the measured values and the predicted values. It appears reasonable to assume that the tritium is uniformly distributed over all the hydrocarbons in relation to their hydrogen content.

Realizing that the Gasbuggy liquid samples probably contained many compounds, we selected three for gas chromatography measurements. Sample No. 1, collected from 36 to 104°C, was selected because it appeared to be low in activity. The gas chromatograph results showed fifteen separate peaks, seven over 5% (Table 2). A mixture of aromatic hydrocarbons with paraffins and naphthalenes constitutes a nonideal mixture, and distillation of such a mixture results in concentration of the aromatics in the distillate at temperatures appreciably below their normal boiling point. Hence, we chose peaks likely to belong to the aromatic compounds. If these selections were correct, we would have expected sample No. 1 to contain 85% of the activity of sample No. 8 rather than 67% as shown. Chromatography results from samples No. 8 and No. 16 are also given in Table 2. These show that even for narrow boiling ranges many compounds exist in a sample. Of perhaps more significance is the fact that the major constituents appear to be normal paraffins.

PROJECTED ANALYTICAL REQUIREMENTS FOR EVALUATION OF THE RADIOLOGICAL IMPACT OF POTENTIAL USE OF CONTAMINATED PRODUCTS

In order to make an intensive evaluation of the radiological impact from the hypothetical use of gas from the cavity formed by the Rulison detonation, rather exhaustive chemical and radiochemical analyses will be required. Because of the information obtained from analyses of wellhead product from the Gasbuggy cavity, it may not be necessary to make as many detailed analyses of samples.

Table 1. Tritium Activity in Liquid Hydrocarbons Taken
From the Gasbuggy Well on February 25, 1969[a]

Sample	Boiling Range (^{o}F)	Measured Tritium Concentration ($\mu c/ml$)	n-Paraffin Boiling Point Range	Calculated Tritium Concentration ($\mu c/ml$)
1	97-219	0.094	C_5-C_7	0.129
2	219-275	0.14	C_8	0.134
3	275-325	0.13	C_9	0.135
4	325-349	0.153	C_{10}	0.136
8	390-412	0.14	C_{11}	0.137
13	412-424	0.145	C_{12}	0.138
14	424-439	0.135		
15	439-451	0.13		
16	451-459	0.145		
22	469-473	0.14	C_{13}	0.139

[a]Fractionated samples were supplied by C. R. Bowman, El Paso
Natural Gas Company, El Paso, Texas.

Table 2. Chromatographic Analyses of Drip Liquids
From the Gasbuggy Well on February 25, 1969[a]

Identity of Component[b]	Relative Percentage[c]		
	Sample No. 1 (97-219°F cut)	Sample No. 8 (390-412°F cut)	Sample No. 16 (469-473°F cut)
Hexane	4	---	---
Benzene (?)	16	---	---
Heptane	10	---	---
Methyl cyclo-hexane (?)	20	---	---
Toluene (?)	15	---	---
1:3 dimethyl cyclohexane (?)	7	---	---
Octane	9	---	---
Ethyl benzene	4	---	---
Xylene	6	---	---
Nonane	1.5	---	---
Undecane	---	4	---
Dodecane	---	26	3
Tridecane	---	10	28
Tetradecane	---	5	22
Pendecane	---	1	4
Expected activity level of the mixture ($\mu Ci/ml$)	0.120	0.138	0.139

[a]Fractionated samples were supplied by C. R. Bowman, El Paso Natural Gas Company, El Paso, Texas.

[b]Question marks in parentheses denote peaks for which identification is not certain.

[c]Additional intermediate peaks were obtained so that the summation of relative percentages does not equal 100%.

In spite of the fact that no evidence was obtained for the presence of nongaseous radionuclides in Gasbuggy gas,[5,6] it is necessary for a complete analysis of the radiological impact from the hypothetical use of gas from the Rulison cavity to establish detection limits for these nongaseous radionuclides. The detection limits obtained for these radionuclides in the gas from the Gasbuggy cavity could all be considered satisfactory except for ^{90}Sr. The detection limit of 1.4×10^{-3} pCi/cc obtained for the Gasbuggy gas would give rise to a 50-year dose commitment to the bone of about 250 mrem if the gas were used for nonvented home heating[2,6] (6000-degree days per year and a home dilution factor of 110 for 80-degree days of heating per day) with no pipeline dilution with uncontaminated gas. Thus ^{90}Sr could contribute a significant dose commitment if it were present in the gas in a concentration approaching this detection limit. We believe that a more sensitive analytical technique should be used to establish a lower detection limit in the gas from the Rulison cavity.

In the establishment of the detection limits of the nongaseous radionuclides, it is suggested that gamma scans be made of any filters used and that acid washes of filters and sample containers should be subjected to radiochemical analyses of beta emitters. Only a few samples need to be assayed for these radionuclides, perhaps on the order of three to five.

Unfortunately, it will not be possible to make an adequate analysis of short-lived gaseous radionuclides because of the long shut-in period of the Rulison cavity before radiochemical analyses are begun. These short-lived radionuclides, such as ^{37}Ar, ^{39}Ar, ^{133}Xe, ^{131}Xe, and ^{131}I, do not contribute significantly to the total radiological impact from the hypothetical use of the gas, because they would have decayed before gas production commences. Smith[5] has pointed out that the analysis of chimney gas for ^{131}I could be used to set reasonable upper limits for a number of semivolatile radionuclides. Radon-222, a daughter of ^{226}Ra, is present in natural gas in concentrations ranging from 0.0002 pCi/cc to 0.16 pCi/cc (ref. 7). Utilization of natural gas with these levels of ^{222}Rn for nonvented home heating for 6000-degree days per year could lead to a 50-year dose commitment to the lung of 0.004 to 3 mrem.

Although the radiation dose from ^{222}Rn appears to be small, it seems advisable to establish its concentration in gas being removed from the wellhead, since this dose establishes the practical lower limit of radiation dose that could be expected.

The tentative production testing schedule for the Rulison cavity includes an initial 3-week period of intermittent high volume testing. This is to be followed by a 2-month production testing period when the flows will be noncontinuous at a rate similar to that anticipated for actual production of such wells. Finally, there will be a long-term period, 6 to 8 months, during which time the production rate is expected to decline due to loss of downhole pressure. An outline of the sampling program we recommend is shown in Table 3.

Tritium and Krypton

Tritium and krypton-85 were the major radionuclides of concern in gas from the Gasbuggy cavity. Krypton was found only in the gaseous phase, but tritium was distributed throughout all hydrogen containing constituents. Because these radionuclides are likely to be the major contributors to the dose equivalents associated with use of the product gas, they should be monitored continuously. For routine monitoring an analysis of this total content in all components is sufficient.

In addition to the continuous monitoring, samples should be taken from the wellhead periodically and analyzed for total tritium and ^{85}Kr under laboratory conditions in order to confirm the monitor values. In this case it would seem advisable to oxidize all forms of tritium to tritiated water and to determine the total hydrogen as well as total tritium in the sample. On the basis of the concentration history of ^{3}H and ^{85}Kr in the Gasbuggy cavity, it would appear that these check samples should be taken at about every 20 million cubic feet of gas production during a period of rather steady flow of the well. During the initial production testing period, samples should be taken every day that gas is released from the wellhead. During the second phase the sampling frequency could be reduced to weekly intervals and in the final phase to an interval of about 3 weeks to a month. Part of these samples should also be allocated for a complete mass spectrometer analysis for hydrocarbon species.

Table 3. Recommended Sampling and Analysis Schedule for Gas from the Rulison Cavity

Radionuclide	Type of Sample	Frequency of Sampling Time	Production Volumes (M^2cf of gas)	Analysis Performed	Remarks
^{3}H and ^{85}Kr [a]	Gas	Daily	20	Total ^{3}H and ^{85}Kr	During first 3 weeks of high-volume production testing.
^{3}H and ^{85}Kr	Gas	Weekly	20	Total ^{3}H and ^{85}Kr	During second period (2 months) of production testing.
^{3}H and ^{85}Kr	Gas	Semimonthly to monthly	20	Total ^{3}H and ^{85}Kr	During 6- to 8-month production testing period.
	Gas		50	Mass spectrometer	Analysis of chemical composition (hydrocarbons).
^{3}H	Gas		50	Chromatographic separation of hydrocarbons	Analysis of each component for ^{3}H.
^{14}C	Gas		50	Total ^{14}C in CO_2 and hydrocarbons	CO_2 and hydrocarbons separated chromatographically.
^{222}Rn	Gas		50	Total ^{222}Rn	
^{90}Sr	Solid particulates in gas			Total ^{90}Sr	Three to five samples from acid washes of filters and sampling equipment.
Other β and α emitters	Solid particulates in gas			Total β and α scans	Three to five samples from acid washes of filters and sampling equipment.
^{3}H	Liquid		50[b]	Total ^{3}H	Both H_2O and liquid hydrocarbons.
	Liquid		50[b]	Mass spectrometer and total hydrogen content	Hydrocarbons only.

[a] Continuous monitoring of gas stream for these radionuclides in addition to laboratory analyses.

[b] Additional samples to be taken during periods of unusually high production of liquid at the wellhead.

There is still some question regarding the distribution of tritium between the hydrogen-containing components. As a result it will be necessary to make a breakdown analysis of the tritium content of each hydrogen-containing species. Such analyses are expensive and time consuming and should be held to as low a number as practicable. It is suggested that such analyses need be performed each 50 million cubic feet of gas production and that the samples be collected during a period of rather constant flow conditions. Carbon-14 analysis should also be performed for the CO_2 separated from the gas sample.

Liquid Samples

Liquids are produced during the production of most gas wells. At the Gasbuggy well the analysis of water for tritium indicated that the water obtained from samples at the wellhead is often quite diluted with nontritiated formation water.[1] During a period of continued flow the water is more nearly representative of the cavity water, but it is not possible to dismiss the effect of dilution. However, it is suggested that liquids being produced at the wellhead, both water and hydrocarbons, be analyzed for tritium. In the case of hydrocarbon liquids it would be of further help if the total hydrogen content of the sample were also assayed and if the sample were subjected to chromatographic analysis for major constituents. Liquid samples should be taken for analysis on an interval of about 50 million cubic feet of gas production. In addition, samples should be collected whenever there is an unusually high production of liquid product.

REFERENCES

1. C. F. Smith, Jr., Project Gasbuggy Gas Quality Analysis and Evaluation Program Tabulation of Radiochemical and Chemical Analytical Results, UCRL-50635 (April 22, 1969).

2. D. G. Jacobs, P. S. Rohwer, and K. E. Cowser, Third Quarterly Progress Report on the Theoretical Safety Evaluation of Consumer Products from Project Gasbuggy, ORNL-TM-2657 (July 1969).

3. C. F. Smith and F. F. Momyer, Gas Quality Investigation Program Status Report for Project Gasbuggy, UCRL-71314, Revision 1 (Sept. 18, 1968).

4. D. G. Jacobs and M. J. Kelly, Fourth Quarterly Progress Report on the Theoretical Evaluation of Consumer Products from Project Gasbuggy, ORNL-TM-2721 (Oct. 1969).

5. C. F. Smith, Jr., Nongaseous Radioisotopes--Project Gasbuggy Chimney Gas, UCRL-50634 (April 7, 1969).

6. C. F. Smith, Non-gaseous Radioisotopes Project Gasbuggy Chimney Gas, January 15, 1969, an attachment to a letter from G. H. Higgins, Lawrence Radiation Laboratory, to S. V. Kaye, Oak Ridge National Laboratory, February 24, 1969.

7. L. A. Bunce and F. W. Sattler, "Radon-222 in Natural Gas," Radiological Health Data and Reports 7(8), 441-444 (Aug. 1966).