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Radon-gas extraction and counting system for analyzing radon and radium in groundwater in seismically active areas

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RADON-GAS EXTRACTION AND COUNTING SYSTEM FOR ANALYZING RADON AND RADIUM IN GROUNDWATER IN SEISMICALLY ACTIVE AREAS

ABSTRACT

A high concentration of radon in groundwater has attracted recent attention as a precursor of seismic activity. We have constructed a system that extracts and counts radon gas from solid, liquid, and gas samples. The radon is extracted in a closed system onto activated charcoal. The desorbed radon is then measured in a phosphored acrylic cell by scintillation counting of gross alpha radiation. The efficiency of the total system (extraction plus counting) is 90 ± 3% or better. Compact design and sturdy construction make the system completely portable and well suited to field operations in remote locations. Results are given for radon and radium in groundwaters in the Livermore area.

INTRODUCTION

Recently, radon has gained attention as a potential precursor phenomenon related to seismic activity. We describe an improved extraction and counting system developed to monitor radon in groundwater along the Greenville Fault, following the seismic events of January 1980.

At that time, existing equipment was inadequate. There were no extraction lines available at the gamma-counting facilities in the Nuclear Chemistry Division. An extraction line and scintillation counter at Hazards Control had been used two years before but had subsequently been dismantled. Furthermore, none of the equipment was suitable for field use. Continuous monitors have been developed for field use, but they are all prototypes, i.e., not commercially available, and typically cost up to $15,000 or more per unit.[1-3] The more economical method to monitor groundwater radon is via discrete sampling, and this is the method we used.

Our system differs from the old Hazards Control system. The latter consisted of a single-pass glass and rubber tubing design, where radon was adsorbed on activated charcoal at dry-ice temperature using helium as a carrier gas. The radon was then desorbed at 400°C and drawn into a glass, zinc sulfide scintillation cell (made by Johnson Laboratories, Baltimore, MD) by a peristaltic pump. This basic design had been copied more or less directly from Lucas.[4] Although the system worked reasonably well in the laboratory, it was not suitable for field use.

Our new system incorporates some very straightforward design changes[5] that greatly improve overall efficiency and result in a more rugged, more easily operated system. It employs stainless-steel tubing, closed-loop gas recirculation, Quick-Connects on the charcoal column and scintillation cell, and components mounted on a pair of aluminum boards. The new counting system uses a commercially available photomultiplier/scaler and low-cost acrylic plastic scintillation cells, which we designed and constructed.

Although developed initially for a specific application, the equipment has a general application in monitoring radon. Radon is a naturally occurring radioactive gas that exists primarily as the longest-lived isotope ^{222}Rn, with a 3.8-day half-life. It is a member of the ^{238}U decay-series and is the immediate daughter of ^{226}Ra, with a half-life of 1620 years. As a noble gas, it is chemically inert and hence offers the ability to act as a tracer for studying many natural processes in geology, geochemistry, hydrology, meteorology, and oceanography. It has also been used in exploration. This report gives examples of these applications, and also presents an historical perspective of the attention given to radon as a potential precursor phenomenon related to seismic activity.

DESCRIPTION OF THE APPARATUS

EXTRACTION BOARD

Figure 1 shows the extraction line. It consists of a closed loop that recycles the carrier gas (helium) through the sample. This process requires a much smaller volume of gas than does a single-pass system.

The carrier gas plus other gases exiting the sample bottle contain CO_2 and water vapor which must be removed before passage of the gases over the charcoal adsorber. For this purpose the line contains an acrylic tube

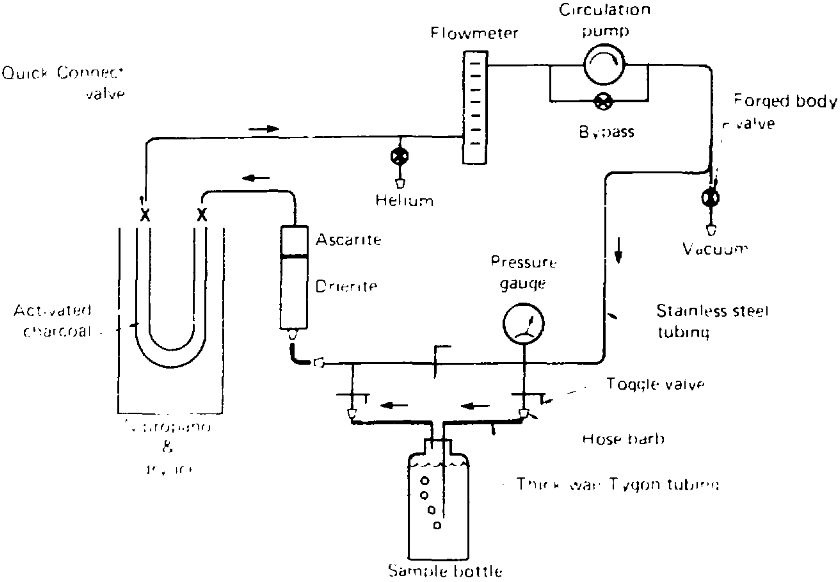

FIG. 1. Schematic of the extraction line used to extract radon from the sample and adsorb it onto activated charcoal.

(3/4-in. o.d. × 12 in. long), filled with indicating Drierite (anhydrous $CaSO_4$, 8 mesh, Hammond Co.) and Ascarite (NaOH-coated asbestos, 8-20 mesh, Matheson, Coleman and Bell Co.). The column is connected to the system by two Cajon Ultra-Torr fittings.

The gases then pass through a stainless-steel column (3/8-in. i.d. × 25 in. long) which is formed in a U-shape with approximately 1 in. between sides in order to increase the length of gas passage through a given weight of charcoal. The column is approximately 2/3 full of activated coconut charcoal (6-14 mesh, Fisher Scientific Co.) and plugged with glass wool to hold the charcoal in place. The column is fitted with two Swagelock Quick-Connects with Viton O-rings. To adsorb radon gas, the column is cooled to dry-ice temperature (-78°C) by immersion in a cooling bath made of a slurry of dry ice and n-propanol held in a Dewar flask (3 in. i.d. × 12 in. long).

A circulation pump (Metal Bellows Co.) then returns the carrier gas to the sample bottle. The flow rate is controlled by a bypass valve around the circulation pump circuit and is monitored by a helium-calibrated flowmeter (Fischer-Porter Co.) and a pressure gauge (Matheson Co.). The system is also hooked to a helium source and a vacuum pump.

The system as designed consists primarily of tubing, fittings, and valves made of stainless steel, with the exception of the acrylic drying column and a short section of thick-wall reinforced Tygon tubing. The latter is on one end of the drying column to allow its easy removal. All lines have been kept to a minimum length for compact design. All components (including the circulation pump) are mounted on an aluminum board measuring 21 in. long × 24 in. high which is welded to an 8-in. aluminum base plate.

TRANSFER BOARD

Figure 2 shows the transfer line, a single-pass system for transferring radon from the charcoal to the scintillation cell.

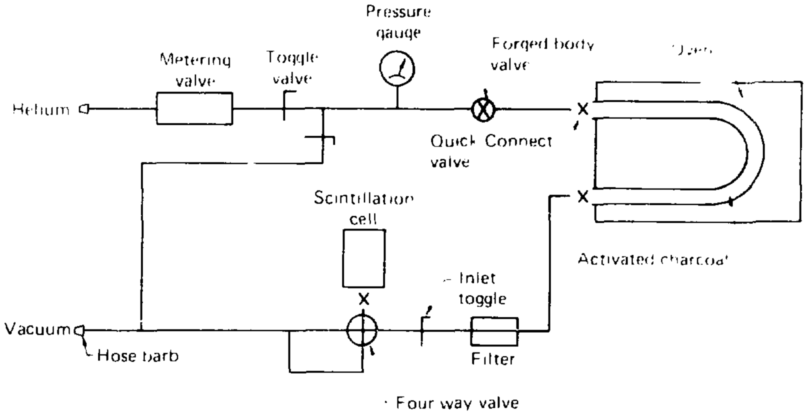

FIG. 2. Schematic of the transfer line used to transfer radon from the activated charcoal column to the scintillation cell.

After the radon is adsorbed on the charcoal column, the U-tube is removed and attached to the transfer line. Here, the column is heated to 500°C in an oven (Type 1400, Thermolyne Co.), desorbing the radon gas. It is slowly flushed into an evacuated scintillation cell using helium gas passed through a metering valve. The radon plus helium carrier are filtered through a 7-µm filter to prevent charcoal dust from entering the scintillation cell. This line is also hooked to a helium source and a vacuum pump and contains a pressure gauge to monitor cell and column evacuation and filling operations.

The transfer line consists entirely of stainless-steel tubing, fittings and valves. All components (with the exception of the furnace) are mounted on an aluminum stand 21 in. [illegible] 17 in. high with a 8-in. aluminum base plate.

SAMPLE CONTAINER

Groundwater samples are taken in 1-liter anodized aluminum bottles (Sigg Co.). The bottles are fitted with a machined brass head which contains two ports. The inlet is connected to a Nyloflow tube extending to the bottom of the bottle and is topped with a bubbler. The outlet brass tube is mounted flush with the base of the brass head, i.e., it does not extend into the bottle at all. The connection between brass head and aluminum bottle is sealed with a Viton O-ring.

The brass tubes on the outside of the head are fitted with 1/4-in.-i.d. thick-wall Tygon tubing and secured by hose clamps. A good seal is made by simply doubling over the Tygon tubing and pinching with a Hoffman [illegible]-type compression screw clamp.

These bottles are lightweight and extremely rugged. Using standard NBS ^{226}Ra solutions as a radon source, we have found them to quantitatively retain radon gas for a month or more after sealing. Moreover, the aluminum bottle itself is inexpensive and commercially available at any backpacking equipment supplier.

SCINTILLATION-COUNTING CELL

Lucas describes a low-level alpha-scintillation cell for radon, made of a Kovar seal and a quartz window.[4] A simplified version of this cell type has been designed of acrylic plastic, which gives comparable efficiency and only a slightly higher background. However, it can be made at a fraction of the cost.

Figure 3 shows a schematic of the scintillation cell. The cell is constructed entirely of acrylic plastic (ultraviolet transmitting) using 2-in.-o.d. pipe and 1/4-in. and 1/2-in. sheet. The nominal internal volume is 100 cc.

The cell is constructed by first applying a coating of optically transparent crystal grease to all inside surfaces. Then, silver-activated zinc sulfide powder (nickel-poisoned to reduce afterglow, 20-70 μm, Nuclear Enterprises, Inc.) is poured into the cell to totally coat the inside. Excess powder is removed by gently tapping by hand and then blowing with a stream of helium gas. A Swagelock Quick-Connect fitting is epoxied in the neck of the

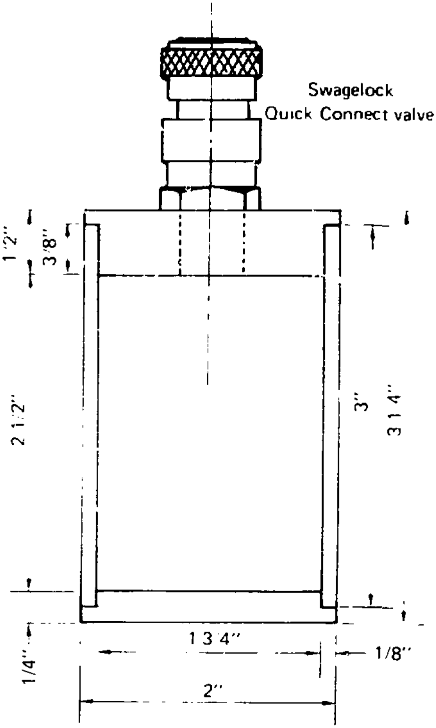

FIG. 3. Schematic of the scintillation-counting cell. The cell is constructed of acrylic plastic.

cell. Finally, the cell is wrapped with aluminum foil and then black electrical tape to make it light-tight. Only the window that rests on the photomultiplier is left uncovered by foil and tape.

COUNTING SYSTEM

During the first month of operation, while the extraction and transfer lines were being debugged and a reliable analytical scheme devised, an old counting system originally used by Hazards Control some years ago was resurrected and used for the radon counting. The counter consisted of a counting chamber, photomultiplier, preamp, amp, scaler, timer and high-voltage power supply. After replacing several components with ones borrowed from Instrument Loan, a usable system evolved. However, it suffered from a spurious noise problem and hence each sample had to be monitored for many short count periods in order to verify a stable count rate. It became obvious very rapidly that another counter would be required. Fortunately, inexpensive commercial counters with this basic design are available and one was acquired for this new system.

The new commercial counter, which has been in use since June 1980, is a two-channel radon counter (DRC-MK6, Applied Techniques Co.). This system consists of two separate counters, each comprised of: counting chamber with cloth hood and PVC cap, RCA 6342A photomultiplier tube, Tennelec 155A preamp, and a power supply and 7-decade counter. These two counters have a common crystal-controlled 7-decade timer. The unit was designed by Bob Lupton of Lamont-Doherty Geological Observatory of Columbia University. Figures 4-5 illustrate the operating characteristics of the photomultipliers and high-voltage power supply. The two-channel counter is compact (17 × 17 × 16 in.) and lightweight (15 lb), and is enclosed in a case with handles. In addition to being completely portable, it may be battery-operated for field use in remote areas.

The principle of operation is as follows. The alpha particles produced from the decay of ^{222}Rn and its daughters ^{218}Po (3.05-min half-life) and ^{214}Po (163.7-μs half-life) produce scintillations in the phosphor coating on the inside of the counting cell. Photons of light are emitted which excite the photocathode of the photomultiplier tube, yielding an electron. For each

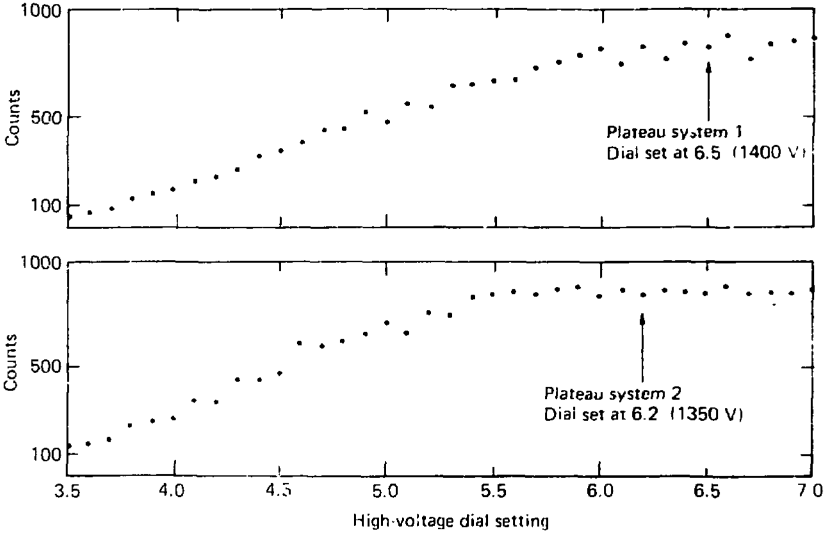

FIG. 4. Operating characteristics of the RCA 6342A photomultiplier tube for systems 1 and 2, showing how operating voltage was set in the plateau region.

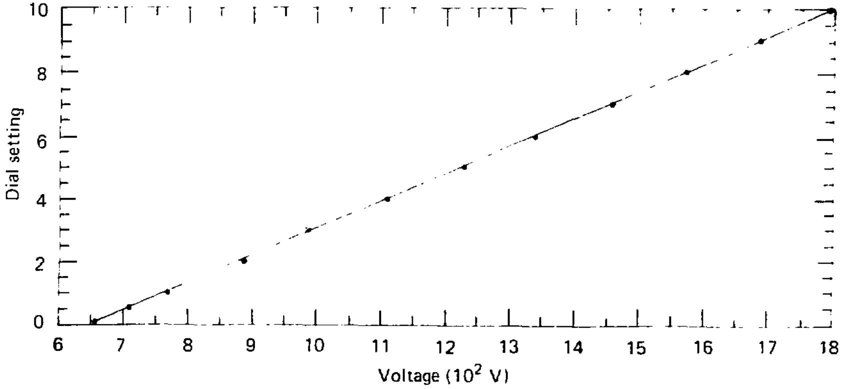

FIG. 5. Calibration line of the high-voltage power supply.

electron given off, approximately six electrons are released from each of the photomultiplier tube's ten dynodes. This electron amplification releases a shower of electrons collected by the anode, and in this way a pulse forms. The preamp amplifies the pulse from the photomultiplier tube anode, and the output is a long-tailed pulse, 0-4 V positive. The counters are set to reject pulses less than 250 mV and they can resolve single pulses up to a counting rate of 10,000 pulses/s.

OPERATION

SAMPLE COLLECTION

Gas samples may be acquired in any appropriate vessel containing an inlet and an outlet to allow circulation of the helium carrier gas. Alternatively, on vessels with only one port, the gas may be expanded into an evacuated extraction board and then circulated. The extraction board contains a sample bypass toggle valve for this purpose. In this case, the extraction efficiency will naturally be somewhat lower.

Liquid samples or solutions resulting from the dissolution of solids may be conveniently acquired and analyzed in the aluminum bottles previously described.

Groundwater samples are collected by drawing the sample into an evacuated sample bottle. At springs, this is accomplished by submerging the Tygon inlet tube. At well sites, a port and valve are installed directly at the well head. Water is passed through a Nalgene bottle which is kept gas-free by introducing the water at the bottom and allowing only a small opening at the top. The water sample is then taken from this bottle in the same manner as for a spring site. Wells are pumped for 20 min prior to sampling to empty the well casing and provide a representative sample.

EXTRACTION PROCESS

The sample bottle, with hose clamps still on, and the U-tube are attached to the board and the line is alternately evacuated and filled with helium three times, in order to flush the system. The toggles to the sample are closed and the hose clamps removed. The U-tube is then cooled for 10 min in the dry-ice bath. The pressure is returned to 1 atm with helium and then the toggles to the sample are opened. The circulation pump is turned on and the flow rate adjusted to 2 l/min, and the stripping process is continued for 30 min.

After stripping, the toggles to the sample are closed and the U-tube is evacuated for 30 s while still cold. The evacuated U-tube is then disconnected from the extraction board.

TRANSFER PROCESS

While the extraction process is taking place, the scintillation cell is attached to the transfer board and flushed three times with helium. It is then evacuated for 30 min. The four-way valve is turned and the inlet toggle closed so as to isolate the cell from the rest of the line. The rest of the line is left open to vacuum.

The U-tube is brought to room temperature and attached to the board and evacuated for 1 min in order to remove air. Little or no radon is lost by evacuating the charcoal at room temperature, provided the evacuation is made through the column outlet. The column outlet is the end of the column through which radon gas exited during the extraction process.

The U-tube is inserted in the preheated oven for 10 min and brought to 500°C. The inlet toggle is opened and the system allowed to stand for an additional 5 min. The radon is slowly backflushed from the U-tube into the scintillation cell with helium carrier passing through the metering valve. During this filling process the flow of helium through the U-tube is reversed from its direction during extraction. Immediately upon filling, the scintillation cell is removed from the transfer board.

After the cell is removed, and while the U-tube is still at 500°C, the charcoal is further flushed with helium for 5 min in order to assure that all radon is desorbed prior to the next sample extraction. The U-tube is then brought to room temperature and reattached to the extraction board. Both boards are flushed three times with helium and evacuated for at least 1 h before running the next sample. Both boards are pressurized to +5 psig with helium overnight to assure they remain gas-tight.

SCINTILLATION COUNTING

The scintillation cells are placed in the counting chamber and remain there for 2-1/2 h prior to counting. This allows the two alpha-emitting Po daughters to grow into transient equilibrium with the Rn in the cell. It also allows the effects of stray light on the scintillation cell to diminish and the cell to stabilize with respect to the negative charge induced by the potential on the photocathode of the photomultiplier tube. Because the counting chambers are covered with a heavy black cloth, no light from the room may strike the photomultiplier. This allows the high voltage to remain on at all times.

The final count is initiated 2-1/2 h after filling the cell. The duration of each final count depends on the sample activity, but is routinely between 30 and 120 min. Recordings of total counts and time elapsed are made periodically over this time interval to verify a stable count rate.

After the final count, the scintillation cells are flushed repeatedly with helium and then evacuated for at least 1 h. The cells are rotated in sequence such that at least one day elapses between removal of the last sample and initiation of the cell background determination prior to the next sample.

PERFORMANCE CHARACTERISTICS AND EFFICIENCY

We determined the overall system efficiency separately for each scintillation cell by using an NBS standard ^{226}Ra solution as a radon source. Three such standards were made up using distilled water in the same type of aluminum bottles used for groundwater samples. This overall efficiency includes: the extraction efficiency, the transfer efficiency and the counting efficiency. The overall system efficiencies for three scintillation cells are shown as follows:

Cell	Efficiency (%)	
A	88.9 ± 1.7	(n = 4)
B	89.7 ± 2.3	(n = 4)
C	91.3 ± 3.3	(n = 4)

There is no relationship between equilibration time (i.e., length of time between extractions during which the radon grows in toward secular equilibrium) and the derived overall system efficiency. This offers an indication that the sample bottles are quantitatively retaining the radon within them for periods even up to one month.

We determined the extraction efficiency by making two successive 30-min extractions from the same standard solution and comparing the recovered radon activities. It was found that the first 30-min extraction had removed 98.8% of the radon.

The transfer efficiency was determined by sweeping the radon gas desorbed at 500°C from the charcoal column used in a standard extraction into two successive scintillation cells and comparing the recovered radon activities. It was found that the first transfer had swept 99.4% of the radon from the charcoal. Apparently, the bulk of the efficiency loss is due to the counting efficiency of the scintillation cell and counter and not to the extraction or transfer processes.

The cell backgrounds are constantly monitored by filling the cells with helium and counting overnight prior to each sample run. The background is that part of the measured activity due to the counting cell itself, and to a very small degree, to the electronic noise inherent to the photomultiplier tube. It is due to any alpha-particle-emitting substance present in the crystal grease, zinc sulfide, acrylic plastic or other construction materials, or in the counting chamber itself. The cell backgrounds for these counting cells are .35 ± .04 counts per minute (cpm).

There are two types of blanks: a system blank and a bottle blank. The system blank refers to the radon activity contributed by the extraction and transfer boards themselves. The bottle blank refers to the radon activity contributed by the sample bottle. These blanks are due to material containing trace amounts of ^{226}Ra or through which radon can diffuse into the system from the atmosphere.

The system blank was determined by short-circuiting the sample inlet and outlet toggles (there is a bypass toggle for this purpose). It should be noted that the system blank was measured in such a way so as to assess the memory effect of the board. Any radon present in the system is extracted by following, step by step, the normal operational procedure. A standard solution was run first, the board was flushed and evacuated for 1 h and then

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The system blank was determined by short-circuiting the sample inlet and outlet toggles (there is a bypass toggle for this purpose). It should be noted that the system blank was measured in such a way so as to assess the memory effect of the board. Any radon present in the system is extracted by following, step by step, the normal operational procedure. A standard solution was run first, the board was flushed and evacuated for 1 h and then the system blank was determined. This should approximate the effect observed by the second sample run on any particular day. The system blank was found to be approximately 0.14 decays per minute (dpm), which represents about 0.15% of the total standard activity. This percentage is the relative memory effect of the extraction board. A system blank run on an extraction board which had not just been previously used should have considerably less than this activity, possibly as low as 0.05 dpm, which would approximate the contribution to radon activity due to the charcoal alone.[5]

The bottle blank is determined by filling an aluminum bottle with distilled water, flushing the radon out and then measuring the radon that grows in over a 1-month period. After subtracting the cell background and system-blank activity determined above, an additional 0.20 dpm remains, which is the radon activity contributed by the bottle and distilled water.

Table 1 summarizes the performance characteristics for this analytical system.

TABLE 1. Performance characteristics of the radon extraction and counting system. Cell background is expressed as counts per minute (cpm), values for blanks as decays per minute (dpm).

Overall efficiency, %	89-91 (depending on cell)
Extraction efficiency, %	98.8
Transfer efficiency, %	99.4
Cell background, cpm	0.35
System blank, dpm	0.14 or less
Bottle blank, dpm	0.20

CALCULATIONS[5]

1. Calculation of overall efficiency (E)
   a. Calculate cpm_x (counts per minute at time of extraction of ^{222}Rn).

$$cpm_x = \frac{cpm - (bkg + blks)}{e^{-\lambda t_1}}$$

where: cpm = final count rate, commencing 2-1/2 h after filling cell,

bkg = cell background count rate,

blks = count rates of the system blank plus the bottle blank,

$\lambda = .007553\ h^{-1}$,

t_1 = time in hours between end of radon extraction and midpoint of final count.

b. Calculate cpm_o (cpm_x corrected for fraction of equilibrium).

$$cpm_o = \frac{cpm_x}{1 - e^{-\lambda t_2}}$$

where: t_2 = time in hours between flushing.

c. Overall efficiency (E)

$$E = \frac{cpm_o}{q_{std} \times 3}$$

where: q_{std} = activity in decays per minute (dpm) of NBS ^{226}Ra standard.

2. Calculation of the amount of ^{226}Ra in a sample (dpm ^{226}Ra)

a. Flush sample of any ^{222}Rn it contains.

b. Let a second generation of ^{222}Rn grow in.

c. Measure ^{222}Rn.

d. Calculate cpm_x and cpm_o as shown above.

$$dpm\ {}^{226}Ra = \frac{cpm_o}{E \times 3}$$

where: all terms are previously defined.

3. Calculation of the amount of excess ^{222}Rn in groundwater (^{226}Ra unsupported)

a. Calculate cpm_x as shown above.

b. Determine dpm_x (total ^{222}Rn at time of first extraction).

$$dpm_x = \frac{cpm_x}{E \times 3}$$

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where: cpm = final count rate, commencing 2-1/2 h after filling cell,

bkg = cell background count rate,

blks = count rates of the system blank plus the bottle blank,

λ = .007553 h^{-1},

t_1 = time in hours between end of radon extraction and midpoint of final count.

b. Calculate cpm_o (cpm_x corrected for fraction of equilibrium).

$$cpm_o = \frac{cpm_x}{1 - e^{-\lambda t_2}}$$

where: t_2 = time in hours between flushing.

c. Overall efficiency (E)

$$E = \frac{cpm_o}{q_{std} \times 3}$$

where: q_{std} = activity in decays per minute (dpm) of NBS ^{226}Ra standard.

2. Calculation of the amount of ^{226}Ra in a sample (dpm ^{226}Ra)

a. Flush sample of any ^{222}Rn it contains.

b. Let a second generation of ^{222}Rn grow in.

c. Measure ^{222}Rn.

d. Calculate cpm_x and cpm_o as shown above.

$$\text{dpm } ^{226}\text{Ra} = \frac{cpm_o}{E \times 3}$$

where: all terms are previously defined.

3. Calculation of the amount of excess ^{222}Rn in groundwater (^{226}Ra unsupported)

a. Calculate cpm_x as shown above.

b. Determine dpm_x (total ^{222}Rn at time of first extraction).

$$dpm_x = \frac{cpm_x}{E \times 3}$$

where: all terms are previously defined.

[illegible]. Determine dpm ^{226}Ra as shown previously.

[illegible]. Determine dpm$_y$ (excess ^{222}Rn at time of sample collection).

$$dpm_y = \frac{dpm_x - dpm\ ^{226}Ra}{e^{-\lambda t_3}}$$

where: t_3 = time in hours between [illegible] and [illegible] during first extraction.

MEASUREMENTS OF GROUNDWATER RADON IN THE LIVERMORE AREA

HISTORICAL PERSPECTIVE OF RADON MEASUREMENTS IN EARTHQUAKE PREDICTION

The development of reliable methods for predicting earthquakes is one of the most urgent problems of seismology. One approach to this problem has been to study various phenomena which reflect changes in the stress state of rocks in regions of potential seismic centers.

It has been observed that various fluid-phase constituents seem to reflect changes in the stress state of rocks preceding and accompanying earthquakes. The Russians observed anomalies in the groundwater content of: radon (^{222}Rn), radium (^{226}Ra), uranium activity ratio ($^{234}U/^{238}U$), and helium associated with the magnitude 5.3 Tashkent event (1966) and the magnitude 5.2 Georgia event (1973).[6-9] The Chinese successfully predicted the large, magnitude 7.3 Haicheng event (1975) in part through the observation of groundwater radon anomalies.[10] The Japanese observed precursory changes in groundwater radon concentration prior to the magnitude 7.0 Izu-Oshima-Kiukai event (1978).[11] A radon increase was observed in an Icelandic thermal well prior to an earthquake.[12] In this country, short-term changes in radon emanation, induced apparently by seismic activity, have been observed in a geothermal reservoir during periods of steady geothermal fluid production.[13] A large radon increase occurred prior to the magnitude 4.8 Big Bear Lake earthquake swarm.[12]

These precursory effects apparently occur before many, and perhaps all, shallow earthquakes. Rock dilatancy (inelastic volumetric increase prior to failure) is accompanied by the formation and propagation of cracks. Water flows from nearby pores and cracks into the newly formed cracks. This dilatancy model contains some interesting features.[14] It requires that the duration of the dilatancy anomaly be a function of the size of the earthquake that follows it. Also, it provides two potential mechanisms to explain the observed radon increases precursory to earthquakes. The first, increase in surface area in the dilatant region, is an unlikely explanation of elevated radon content of well water due to the distance to the source (6-12 km) and the short half-life of radon. The second mechanism, increased fluid flow in the dilatant zone, may suggest that, simply by continuity, the large-scale acceleration of fluid flow is transmitted upward to the surface layers sampled by wells and springs. In this way the loss of radon by radioactive decay decreases, contributing to the observed higher concentrations. It has also been suggested that the fault gouge zone is mechanically compliant and strain changes may concentrate in the fault zone over long distances.[15] This may provide yet another mechanism for enhancing the local source function.[16] Despite the fact that this field of study is relatively new, it is of such importance that perhaps as many as a dozen groups are now working on various hydrological and geochemical studies directed at earthquake prediction.[17-20]

RADON LEVELS IN LIVERMORE GROUNDWATER

Following the January 1980 earthquakes, we constructed the radon/radium system and performed a search to identify potential sample points. Wells were selected for a number of reasons, including: proximity to the Greenville and/or Las Positas Faults, well-use (pumping) pattern, ability to access line at well head (to acquire representative water for gas analysis), well not located in valley-fill alluvium, and some anomalous behavior associated with the January events. Since May 1980, four wells have been routinely monitored for radon (^{222}Rn), radium (^{226}Ra), and uranium isotopes (^{234}U and ^{238}U). The wells being monitored are briefly described in the Appendix. To the author's knowledge at this time, no other workers are monitoring potential earthquake precursors in this area. Dr. C. Y. King (U.S.G.S., Menlo Park) has been monitoring soil gas radon on the Calaveras Fault near the Calaveras Reservoir, and this is the nearest point to us on his sampling network.[21]

Based on the work of Scholz et al.[14] it was known from the empirical relationship between duration time of various precursory phenomena and earthquake magnitude that a semi-monthly sample interval would suffice to identify events greater than magnitude 4 to 4.5, assuming a detectable signal is actually generated. Hence, samples were taken, in the manner previously described, twice a month, and analyzed after delays of 3 to 5 days, depending on their activity. This delay allows the radon activity to decrease to levels at which no dead-time correction is necessary.

The results for radon and radium are presented in Table 2 and Fig. 6. Although two samples were taken at each site prior to 6/27/80 (on 5/30/80 and 6/13/80) they were counted on the old counter, which proved to be rather unstable, and so are not included here. In the figures, the mean value (solid line) and the standard deviation in the mean (broken lines) have been identified; the arrow indicates the date (8/24/80) of the magnitude 3.9 event, with an epicenter on the Valle Fault located approximately on the southern end of Del Valle Reservoir, some 12 miles south of Livermore.

The radon data range from 650 to 4000 dpm/kg between the four sites. However, the values at each site are relatively stable, with a standard deviation in mean value of some 3 or 4% over the 3-month period. The differences between sites reflect not only differences in source function (parent uranium distribution) but also differences in mean residence time and flow rates in the immediate vicinity of each well. Both well BF and BF are reducing in nature; i.e., they contain obvious amounts of dissolved H_2S, and upon exposure to oxygen in the atmosphere they precipitate [illegible].

The radium analyses confirm the fact that radon is being injected directly from rock to groundwater. Since the radium values are only from 0.02% to 0.4% of the corresponding radon values, the radon is not radium-supported. This fact simplifies the excess radon calculation by making it less critically dependent upon time delay in analyses, at least for delays on the order of a few radon half-lives. However, the low radium values also imply that, unless larger samples are taken, the radium content cannot be monitored as a potential precursor. The 20-liter flint glass bottles used for surface-seawater radium analyses may be adequate for this purpose.[5]

TABLE 2. Radon and radium content of groundwater in four wells in the Livermore area. Samples were taken at semi-monthly intervals from June to September 1980. Concentrations are expressed as decays per minute per kilogram (dpm/kg).

Well	Date	Radon concentration (dpm/kg)	Radium (dpm/kg)
BP	6/27	764.3	
	7/11	762.9	
	7/25	772.4	
	8/14	699.9	
	8/29	733.0	≤ 0.21
	9/12	699.9	
		Mean: 738.7 ± 32.9 (4.4%)	
BR	6/27	638.2	
	7/11	649.0	
	7/25	637.4	
	8/14	688.6	
	8/29	641.2	3.10
	9/12	641.2	
		Mean: 649.3 ± 19.7 (3.0%)	
TG	6/27	1529.2	
	7/11	1381.0	
	7/25	1460.7	
	8/14	1495.8	
	8/29	1539.6	0.44
	9/12	1529.1	
		Mean: 1489.2 ± 60.4 (4.1%)	
KD	6/27	3908.0	
	7/11	3762.8	0.28
	7/25	4051.5	
	8/14	3922.7	
	8/29	4114.1	0.59
	9/12	3836.2	
		Mean: 3932.6 ± 131.1 (3.3%)	

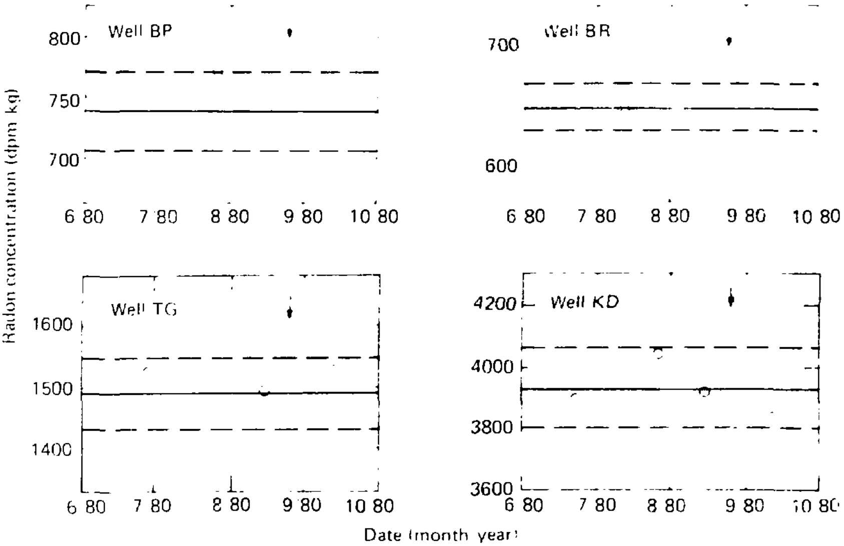

FIG. 6. Radon concentrations in water from four sample wells in the Livermore area. Arrows indicate the date, August 24, 1980, of a seismic event of magnitude 3.9. There is an association between the seismic event and radon concentration. Radon concentration is expressed as decays per minute per kilogram (dpm/kg). Solid lines represent mean concentration; broken lines represent standard deviation in the mean.

Of primary interest in a study of this nature is the temporal variation in radon at each site and the relationship, if any, between these variations and seismicity. For the data presented here the observed radon concentration at each site remains just within plus or minus two standard deviations of the mean value. Hence, no single observation may be considered statistically anomalous in the simplest sense. In many cases documented to date, long term (seasonal?) cycling is noted in the radon content of groundwaters,[12] and so an observation period of only three months is clearly inadequate to establish the "normal" variation to be expected at these sites. Long-term monitoring is required to identify these cycles, if they exist here, and then they may be easily filtered from the data.

Even considering all these caveats, it is most interesting that there is a hint of some association with the only significant seismic event occurring during this 3-month interval. Three of the four sites display some slight change in radon content in samples taken from one to six weeks before the event. The most noteworthy case is that of Well BR. There is a marked increase (although just at the two-sigma level) in the radon content of the sample taken 10 days before the event. This site is in solid bedrock (the Tertiary Cierbo Fm) and is actually a spring, so there are no problems with well-use patterns. The other two sites (Wells BP and TG) display some slight decrease in radon from one to three samplings prior to the event, although certainly no statistical significance can be attached to these variations. Precursory radon decreases in groundwaters have been observed previously, and it has been suggested that the direction of change is related to the seismic quadrant (compression or dilation).[22] The event occurred on the Valle Fault which is subparallel to the Greenville, Tesla, and Ortigalita Faults, although some 6 or more mi to the west and not directly linked to them.[23] This rather weak association with the Greenville Fault may cause the poor correlation.

CONCLUSIONS

A complete system has been constructed to isolate and measure radon gas from solid, liquid, and gas samples. The system has been calibrated using NBS standards, and consistently maintains a total efficiency (extraction plus counting) of 90 ± 3% or better. The compact design and sturdy construction make the whole system portable and suitable for field operations in remote areas.

The system has been used to monitor groundwater radon and radium in the Livermore area. Preliminary results suggest the potential of this approach in monitoring changes in the stress state of rocks in the area. The use of groundwater radon as a potential earthquake precursor is but one of many important ways that radon measurements have been applied in the geological sciences. Some other ways include:

- Determination of recharge temperatures for hydrothermal systems.[24]

- Determination of transport times, fracture permeability, porosity, flow characteristics, and volumes of geothermal reservoirs.[25]
- Determination of gas exchange rates between surface waters and the atmosphere.[26]
- Determination of mixing rates and circulation patterns in surface waters.[27]
- Determination of mixing rates and circulation patterns in the atmosphere.[28,29]
- Determination of the age of groundwaters via He/Rn ratios.[30]
- Exploration for new geothermal resources and delineation of reservoirs.[31]
- Exploration for new uranium ore bodies and delineation of their size and extent.[32]
- Determination of the location of faults covered by thin alluvial cover or which are otherwise masked.[33]

The system described in this report may be used to address these and many other types of problems in the geological sciences where measurements of radon and radium are required.

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APPENDIX

FOUR SAMPLE WELLS IN THE LIVERMORE AREA

1. Well BP

Location is on Morgan Territory Road in 1S/2E-31. The well is situated on the Marsh Creek (Diablo) Fault, approximately 1/2 mi east of U.S.G.S. seismometer CMO. It was drilled to 150 ft in 1963 and is entirely in bedrock (mainly sandstone, Cretaceous Shasta Fm). The well is pumped daily for domestic use. Water quality and flow rate were affected by the January 24, 1980 event.

2. Well BR

Location is off N. Vasco Road in 2S/2E-22, approximately 1 mi east of LLNL station CL03. It is situated within the Greenville Fault system, approximately 1/4 mi west of enechelon cracking across N. Vasco Rd. resulting from the January 24, 1980 event. This well is 100 ft deep and is artesian; it was actually drilled over an existing spring. It is entirely within bedrock, mostly conglomerate (Tertiary Cierbo Fm). The well is pumped daily for domestic and livestock use. Water quality and flow rate were affected by the January 24, 1980 event.

3. Well TG

Location is off Patterson Pass Road in 3S/3E-7, near LLNL station P1GS. The well is situated within the Greenville Fault system at the intersection with the Las Positas Fault, and within the Livermore syncline at a point adjacent to the Livermore oil field (older Quaternary alluvium at surface, Tertiary Cierbo Fm at depth). It was drilled to 130 ft in 1951. The water is used for watering stock and is pumped daily. A high boron content makes it unfit for human consumption. The holding tank contained oily residue, apparently pumped from the well immediately after the January 24, 1980 event.

4. Well KD

Location is on Cross Road in 3S/3E-17. The well is situated within the Greenville Fault system on a short faulted segment transverse to the Greenville Fault trend, but subparallel to the Las Positas Fault (older Quaternary alluvium at surface, Livermore Fm gravels at depth). The well is 240 ft deep and the well pipe was broken during the January 24, 1980 event.