

A Comparison of Current Collection/Sampling Techniques for Waterborne Radon Analysis

James F. Burkhart, University of Colorado at Colorado Springs; Gray, D., United States Environmental Protection Agency, Montgomery Alabama; Martin, R.D., DMA-RADTECH Inc., Allentown, PA; Warrick, B., University of Colorado at Colorado Springs.

ABSTRACT

As the US Radon industry matures, and the USEPA contemplates a Maximum Contaminant Level (MCL) for waterborne radon activity, much concern exists regarding appropriate sampling techniques and their ability to attain reproducible and reliable samples for either the analytical laboratory or in-situ analysis.

The authors have examined eighteen (18) different sampling methodologies, each one using two different types and amounts of scintillant. Sampling variables included:

1. Basin immersion without scintillant.
2. Spigot collection.
3. Various syringe methods.
4. Plastic/Glass collection vehicles.
5. Different types of lids.
6. Two different cocktail types/amounts.

Sampling methods were performed in a geologically stable aquifer with a consistent concentration of approximately 2100 pCi/L.

All environmental sampling was performed by personnel at the University of Colorado at Colorado Springs (UCCS). Sample analysis was performed using liquid scintillation methodology at the USEPA's National Air and Radiation Environmental Laboratory (NAREL), in Montgomery, Alabama, the DMA Analysis Group at DMA-RADTECH, INC. in Allentown, Pennsylvania, and the Radon Measurement Laboratory at UCCS.

In order to eliminate measurement errors generated by different analytical techniques, quality control samples of a known Rn-222 concentration were prepared and analyzed.

INTRODUCTION

Waterborne radon has historically been measured via the Lucas Cell (Lucas 1964) and through liquid scintillation techniques (Prichard and Gesell, 1977). Recent studies have examined, and made recommendations concerning the laboratory techniques (Vitz, 1991) and the water-to-fluor ratios (Lowry, 1991). What has not been decided are the appropriate field sampling techniques which would, on the one hand, allow current analytical technology to be used but, on the other hand, would minimize sample degradation.

Current policies of federal environmental offices and individual state health and environment offices trend toward the use of liquid scintillation technology for analytical purposes (NJDEP Laboratory Certification Program: 1991, USEPA Document 520/5-83-027).

The goal of this paper is neither to discuss nor debate the analytical technologies, but to provide data relevant to a discussion on the merits of the most commonly used sampling techniques and to suggest specific recommendations as to the appropriateness of these sample collection methods.

If indeed the USEPA confirms the waterborne radon Maximum Contaminant Level (MCL) of 300 pCi/L, very careful attention to sampling methodology detail will be necessary to accurately measure environmental samples, especially those samples at or near the MCL.

The objective of this study was to identify which methodologies for the measurement of waterborne radon are the most accurate and reproducible. While it will be shown that the on-site stabilization of the environmental sample with scintillant produces results with the lowest bias and highest radon concentrations (for a given water source), transport of the chemically hazardous material (the scintillant) may not always be permissible in the private sector. For this reason, we discuss alternate collection methods which generate results of reasonable bias (albeit lower reported radon concentrations for the same water source.)

METHOD

Special Precautions

Since the intent of this study is to compare various sampling techniques, it seemed desirable to hold steady any variables which could confound these comparisons. Among these variables is, of course, the possible variation of the radon concentration of the water source during the sampling time. Also, we wanted to be sure that the radon values measured in the lab later were not affected by systematic errors created by the lab handling, transfer and measuring techniques.

The first of these potential problems (the variation of radon levels during sampling) was handled by:

1. Using a relatively deep well (310 feet total depth).
2. Using a well in which the pump was submerged and had sufficient head space (60 feet of water above the pump.)
3. Sampling only after the water holding tank had been completely cleansed of "old" water. We determined that the holding tank was only a fifty gallon tank. We purged the tank for 25 minutes with a flow rate of 10 gallons per minute so that we turned the contents of the tank over approximately 5 times before sampling.
4. The aquifer chosen was in a geological formation known as an extended radon source and not one made up of point sources (The Morrison Formation). Many wells in this part of Colorado, called Black Forest, had been tested and the radon concentration had uniformly been reported around 2000 pCi/l.
5. The sampling experiment was completed two times, once on May 13, 1991 and a second time on May 23, 1991. In both cases, the average radon reported by the labs for the so-called EPA method, in which the water is extracted from a funnel (connected to the spigot) and injected into the scintillant, was essentially identical (2120 +/- 59 pCi/L the first run and 2108 +/- 69 pCi/l the second run.) Both runs used glass vials with foil lined caps.
6. On the first run, on May 13, 1991, methodology #1, the first water sampling of the day (in which the water was extracted from a funnel and injected into a glass vial with a septum top) was repeated at the end of the experiment as methodology #16. The radon concentrations were 1947 +/- 42 pCi/l for method #1 and 2138 +/- 22pCi/l for method #16.

7. On the second run, May 23, 1991, the water extractions for each method were spaced during the sampling time so that any variations in source radon would be averaged over. It happens that this technique allowed us to have confidence in the statistics and the resultant conclusions. As an example of how this sampling technique was employed, consider the following: at time = 0, 3 vials would be filled using method #1, one vial for each of the three labs who were doing the method. At time = 1 minute, 3 vials, using method #2, would be filled. This would continue until all of the methods were finished. Then, we would start on method #1 again, with a second three vials. When all of the methods were finished, we would begin the sequence, a final time, with method #1. Each lab would then receive 3 vials of each method and each of the vials would have been filled at different times during the run. If the radon in the source varied during the run time, that variation would decrease the precision of that methodology. Of course, there was a potential for a great deal of variation. The fact that it did not happen confirmed our hypothesis that, indeed, the source term was more or less constant.

The second problem (systematic errors in the labs) was handled by requiring each lab to treat every vial, regardless of sampling technique, the same. Each lab used its own equipment, scintillant and operating procedures. Also, each vial was identified by a number only. The sampling technique was not revealed to the laboratories or their lab personnel.

Laboratory Equipment

All water samples were measured using liquid scintillation. The USEPA uses a Beckman LS 1801 liquid scintillation counter. DMA uses eight Beckman LS 5000TD liquid scintillation counters, and UCCS uses a singular Beckman LS 100. All labs count for 20 minutes.

The cocktail used by UCCS and the USEPA was Dupont NEN Research Products NEF-957A mineral oil scintillator in 10mL concentrations. DMA used Packard Optiflour-O in 5 mL concentrations. If the water was not already injected into the scintillant (as was proper for some of the methods) all laboratories introduced 10 mL of the environmental sample to their own scintillant.

Sampling Techniques

Eighteen (18) different methodologies were investigated, representing the major sampling techniques currently used in industry. Table 1. represents the sample methodologies used on the first run, May 13, 1991, and includes: sample container type, transfer method, cocktail content and type, sample container closure type, and collection method. Method #16 is a repeat of method #1.

Table 1: various methodologies employed on first run, May 13, 1991

| <u>Method #</u> | <u>Container Type</u> | <u>Cocktail Content/Type</u> | <u>Container Closure Type</u> | <u>Collection Method</u> |
|-----------------|-----------------------|------------------------------|-------------------------------|--------------------------|
| 1 a - f | g | 10 mL/NEN | s | T/Hose & Funnel |
| 1 g - i | g | 5 mL/OFO | s | T/Hose & Funnel |
| 2 a - f | g | 10 mL/NEN | s | T/Pail |
| 2 g - i | g | 5 mL/OFO | s | T/Pail |
| 3 a - f | g | 10 mL/NEN | s | S/Hose & Funnel |
| 3 g - i | g | 5 mL/OFO | s | S/Hose & Funnel |
| 4 a - f | g | 10 mL/NEN | c | T/Hose & Funnel |
| 4 g - i | g | 5 mL/OFO | c | T/Hose & Funnel |
| 5 a - f | g | 10 mL/NEN | f | T/Hose & Funnel |
| 5 g - i | g | 5 mL/OFO | f | T/Hose & Funnel |
| 6 a - i | g | | s | Pail |
| 7 a - i | g | | f | Pail |
| 8 a - i | g | | c | Pail |
| 9 a - i | 8p | | | Hose |
| 10 a - i | 8p | | | Spigot |
| 11 a - i | g | | s | Spigot |
| 12 a - i | g | | f | Spigot |
| 13 a - i | g | | c | Spigot |
| 14 a - i | p | | p | Spigot |
| 15 a - i | p | | p | Pail |
| 16 a - f | g | 10 mL/NEN | s | T/Hose & Funnel |
| 16 g - i | g | 5 mL/OFO | s | T/Hose & Funnel |

KEY

Containers

- g - 25 mL (Fisher) Boro-silicate glass vial
- p - 25 mL Plastic Kimble vial
- 8p - 8 oz Plastic bottles with plastic screw lid

Closures (Caps)

- f - Foil lined lids
- c - Poly cone lids
- s - Septum lids
- p - Plastic caps without lining

Scintillant

- NEN - New England Nuclear (Dupont) Mineral Oil
- OFO - Packard Optiflour - O

Transfer Device

- T - Tygon tubing syringe
- S - Steel needle syringe

Sample Collection Methods from the First Run, May 13, 1991:

Methods 1 a - f were performed using a hose and funnel attached to the spigot. The water was allowed to flow continuously at a non-turbulent rate. A plastic syringe and tygon tubing were used to extract 12 mL. of water from the inverted funnel, the syringe was inverted, the excess 2 mL. expelled, and the remaining 10 mL. of water were then injected under 10 mL. of mineral oil. The septum lid was replaced and the vial quickly shaken. Methods 1 g - i were performed identically to methods 1 a - f except that the cocktail used was 5 mL. of OptiFlour - O.

Methods 2 a - f used a plastic pail placed under the spigot. The pail was completely filled, the spigot was placed under the surface of the water, and the flow reduced to a nonturbulent rate. A plastic syringe with tygon tubing was then used to extract 12 mL. of water from the pail. The syringe was inverted and the excess 2 mL. expelled. The remaining 10 mL. of water were then injected under the 10 mL. of mineral oil, the septum lid was replaced, and the vial quickly shaken. Methods 2 g - i were performed in the same manner except 5 mL. of Opti-Flour - O were used.

Methods 3 a - i were performed in the same manner as methods 1 a - i except that samples were drawn through an 18 gauge steel needle instead of the tygon tubing.

Methods 4 a - i were performed in the same manner as methods 1 a - i except poly-cone plastic lids were used in place of septum lids.

As in methods 4 a - i, methods 5 a - i employed the same methodology as number 1 except foil lined lids were used.

Methods 6 a - i used a plastic pail filled from the spigot. The water was allowed to overflow the pail and the flow was reduced to a nonturbulent rate at which time 25 mL. glass vials (bottom down) and septum tops were submerged in the pail and allowed to fill completely. The vials were then carefully sealed and removed from the pail with minimum agitation of the water.

Methods 7 a - i were performed in the same manner as 6 a - i except that foil lined lids were used.

Methods 8 a - i also used the same method as numbers 6 a - i except that poly-cone plastic lids

were used.

In methods 9 a - i, 8 oz. common lab specimen plastic bottles with plastic screw lids were filled with a plastic hose immersed beneath the surface of the water. The lids were replaced, and the vials squeezed lightly to remove any excess air.

Methods 10 a - i were the same as methods 9 a - i except the bottles were filled directly from the spigot.

In methods 11 a - i, 25 mL. glass vials were filled directly from the spigot, and the septum lids replaced to insure that no air bubbles were present.

Methods 12 a - i were performed in the same manner as methods 11 a - i except foil lined lids were used.

Methods 13 a - i also were performed as methods 11 a - i except poly-cone plastic lids were used.

Methods 14 a - i used 25 mL. plastic vials which were filled from the spigot and sealed with plastic caps without linings.

Methods 15 a - i also used 25mL plastic vials and caps. In this method, a pail was filled from the spigot and the water was allowed to overflow at a nonturbulent rate. The vials (bottoms down) and caps were submerged in the pail and the vials were quickly sealed under water with no air bubbles present.

Methods 16 a - i were identical to methods 1 a - i.

Sample Collection Methods from the Second Run, May 23, 1991:

Table 2 shows the 13 methodologies used on the second run, May 23, 1991. Many of these methods are repeats of methods used earlier, but the sampling times were staggered (as explained in the special precautions section above). The new methods were:

Method 2 a-i used a hose and funnel, a hypodermic with a #18 gauge steel needle and the vial was glass with a polycone lid. Method 2 a-f used a mineral oil cocktail while 2 g-i used Optiflour-O.

Method 3 a-i used the same procedure except that foil-lined plastic lids replaced the polycone lids.

Method 10 a and b used the 8 ounce plastic laboratory bottles. These were immersed in a pail and the lids placed on while both the bottle and lid were immersed. Method 10 b deserves special mention because the water was transferred to the scintillant in the lab by piercing the side of the bottle with the #18 gauge steel needle in an attempt to reduce radon loss in the transfer process.

Table 2: Various methodologies employed on second run, May 23, 1991

| <u>Method #</u> | <u>Container Type</u> | <u>Cocktail Content/Type</u> | <u>Container Closure Type</u> | <u>Collection Method</u> |
|-----------------|-----------------------|------------------------------|-------------------------------|--------------------------|
| 1 a - f | g | 10 mL/ NEN | s | S/ Hose & Funnel |
| 1 g - i | g | 5 mL/ OFO | s | S/ Hose & Funnel |
| 2 a - f | g | 10 mL/ NEN | c | S/ Hose & Funnel |
| 2 g - i | g | 5 mL/ OFO | c | S/ Hose & Funnel |
| 3 a - f | g | 10 mL/ NEN | f | S/ Hose & Funnel |
| 3 g - i | g | 5 mL/ OFO | f | S/ Hose & Funnel |
| 4 a - f | g | 10 mL/ NEN | s | T/ Hose & Funnel |
| 4 g - i | g | 5 mL/ OFO | s | T/ Hose & Funnel |
| 5 a - f | g | 10 mL/ NEN | c | T/ Hose & Funnel |
| 5 g - i | g | 5 mL/ OFO | c | T/ Hose & Funnel |
| 6 a - f | g | 10 mL/ NEN | f | T/ Hose & Funnel |
| 6 g - i | g | 5 mL/ OFO | f | T/ Hose & Funnel |
| 7 a - i | g | | s | Pail Immersion |
| 8 a - i | g | | c | Pail Immersion |
| 9 a - i | g | | f | Pail Immersion |
| 10 a - b | 8p | | | Pail Immersion |
| 11 a - i | g | | c | Spigot |
| 12 a - i | g | | f | Spigot |
| 13 a - i | g | | s | Spigot |

KEY

Containers

g - 25 mL (Fisher) Boro-silicate glass vial
8p - 8 oz. Plastic bottle with plastic lids

Scintillant

NEN - New England Nuclear
(Dupont) Mineral Oil
OFO - Packard Optiflour - O

Closures (Caps)

f - Foil lined lids
c - Poly cone lids
s - Septum lids

Transfer Device

T - Tygon tubing syringe
S - Steel needle syringe

RESULTS

The results of the first run are shown in Figure 1 below. Each lab's average radon for each of the 16 methods is graphed separately.

Intercomparison Data from 5/13/91

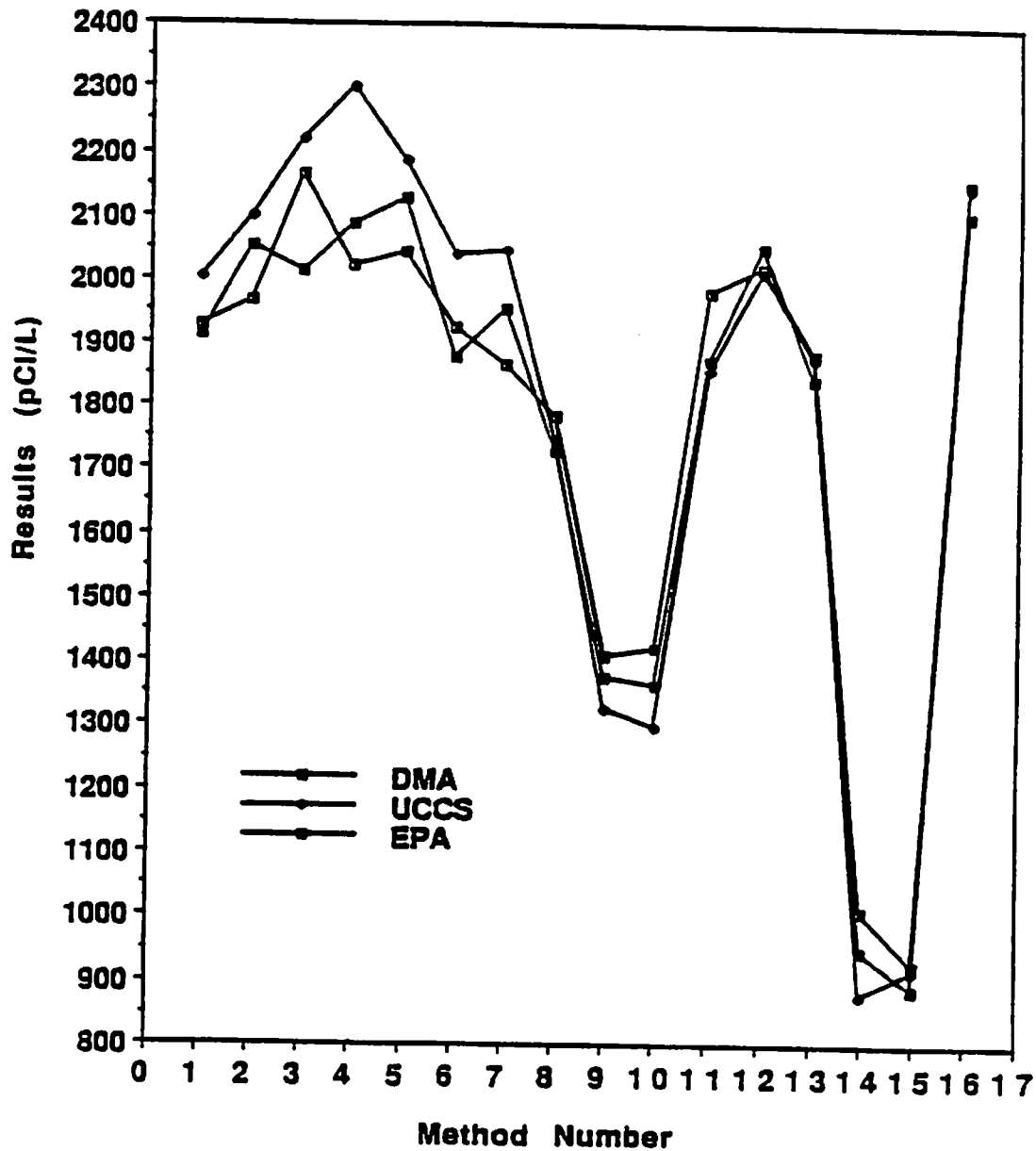


Figure 1. Individual radon averages from each lab from first run, 5/13/91.

As can be seen from Figure 1, all three labs show a surprising consistency in that the individual averages seem to describe the same sort of curve. In order to make some statistical sense of the data, the mean of all three labs was graphed below in figure 2. Error bars shown are 2σ on each side of the mean.

Average of Three Labs from 5/13/91

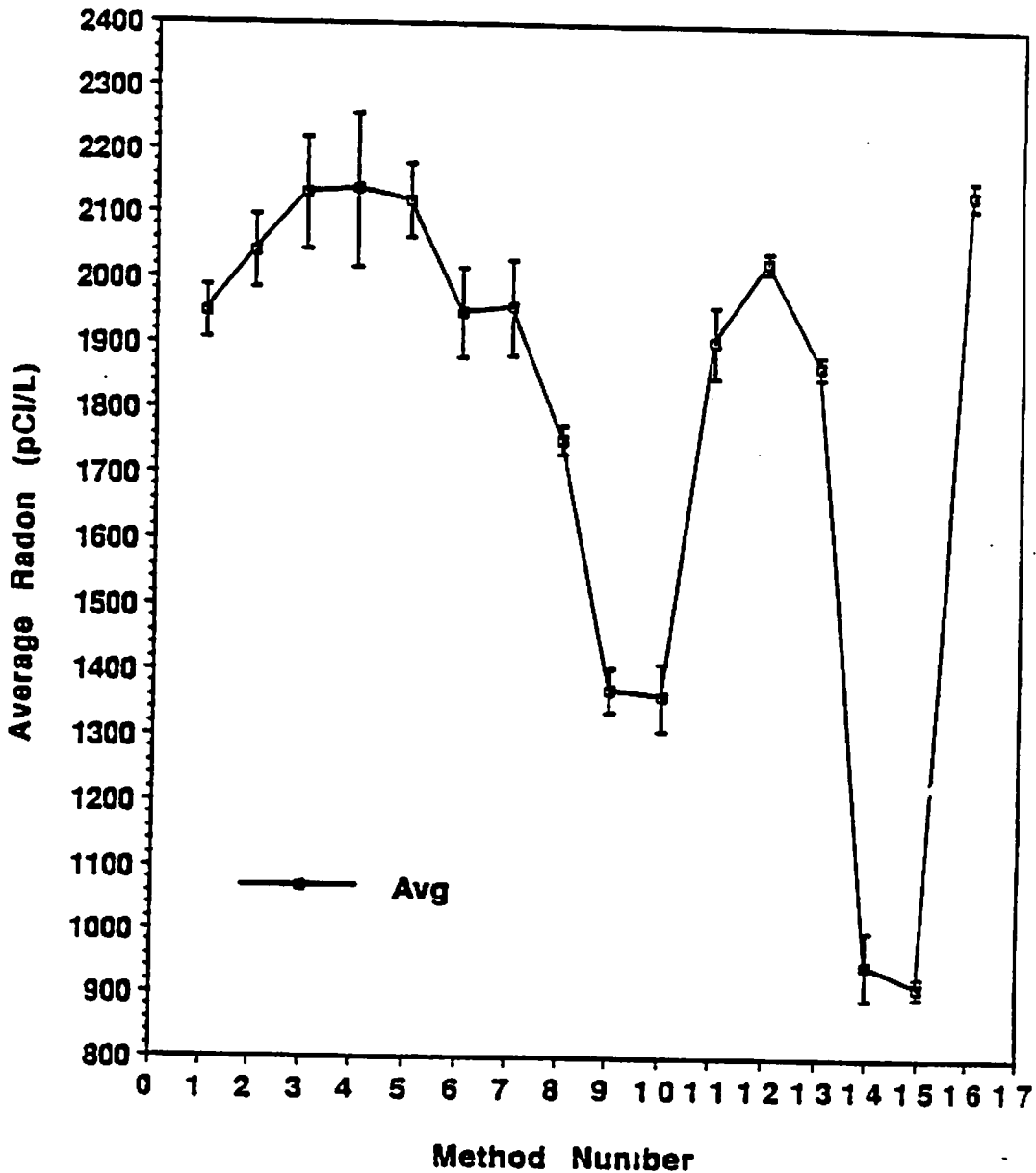


Figure 2. Average of three labs from first run, 5/13/91.

Figure 2 allows us to make no distinction between methods 1 through 7, 11 through 13 and 16.

although it would appear that the immersion methods (methods 6, 7 and 8) do not do as well as do the methods which extract the water from the funnel or bucket for immediate injection into the scintillant (methods 2-5). Also, filling the vial directly from the spigot appears to not give as high an average radon concentration as do methods 2-5. Clearly, methods 9 and 10, filling 8 ounce plastic bottles either with a plastic tube attached to the spigot or directly from the spigot itself for later transfer to the scintillant in the lab, give very poor results. Methods 14 and 15, filling the 25 ml Kimble plastic vials either from a spigot or immersion in a pail for later transfer to the scintillant, give the worse results.

Method 16, which is a repeat of method 1, would indicate that the radon concentration at the end of the test period was near the radon concentration at the beginning of the test period.

Two unanswered questions remained, however. (1) Was the increase in reported radon concentrations during the period in which the first three measurements were taken a real increase in the actual radon in the water (caused, for example, by an incomplete flushing of the holding tank) or were we looking at small variations caused by the different methodologies? (2) Were the fluctuations in radon concentrations during the test period the result of the effectiveness of the different methodologies or was the radon concentration of the water actually changing that much over the few minutes we tested?

We also decided to retest methodology 9 and 10, using the large plastic bottles, only we would immerse the 8 ounce bottles in a basin and (in one case) extract the water through the side of the plastic bottle with a needle and syringe instead of opening the top of the bottle. As will be seen later, the plastic bottle performed poorly regardless of how they were filled or how the water was extracted from them in the lab.

The second run occurred on May 23, 1991 at the same location. In order to reduce the uncertainty we had concerning the possible radon fluctuations during the testing period, each method was employed at three different time periods with only three samples (one for each lab) being taken each time. Later, each lab was given three samples of each method, but each one would have been taken at a different time, with the other methods interspersed between them. Any radon fluctuation in the water would then show up by biasing many different methods. Such a bias would be seen as a decrease in precision (because of the wide spread of data points for any one method).

Figure 3 shows the individual average radon concentrations reported by each lab. Not shown on Figure 3 is the radon measured for method 10 a and b, which was the retest of the 8 ounce plastic bottles. This is not shown because only one lab (UCCS) did the retest. Method 10a, where the water was extracted through the open top of the bottle and injected into the scintillant, gave a radon concentration of 1427 +/- 204 pCi/L and Method 10b, in which the water was extracted through the side of the plastic bottle measured 1342 +/- 203 pCi/L. Thus, using plastic bottles of this type for collection vehicles leads to poor results, regardless of how the bottle is filled or how the water is transferred to the scintillant later in the lab.

Intercomparison Data from 5/23/91

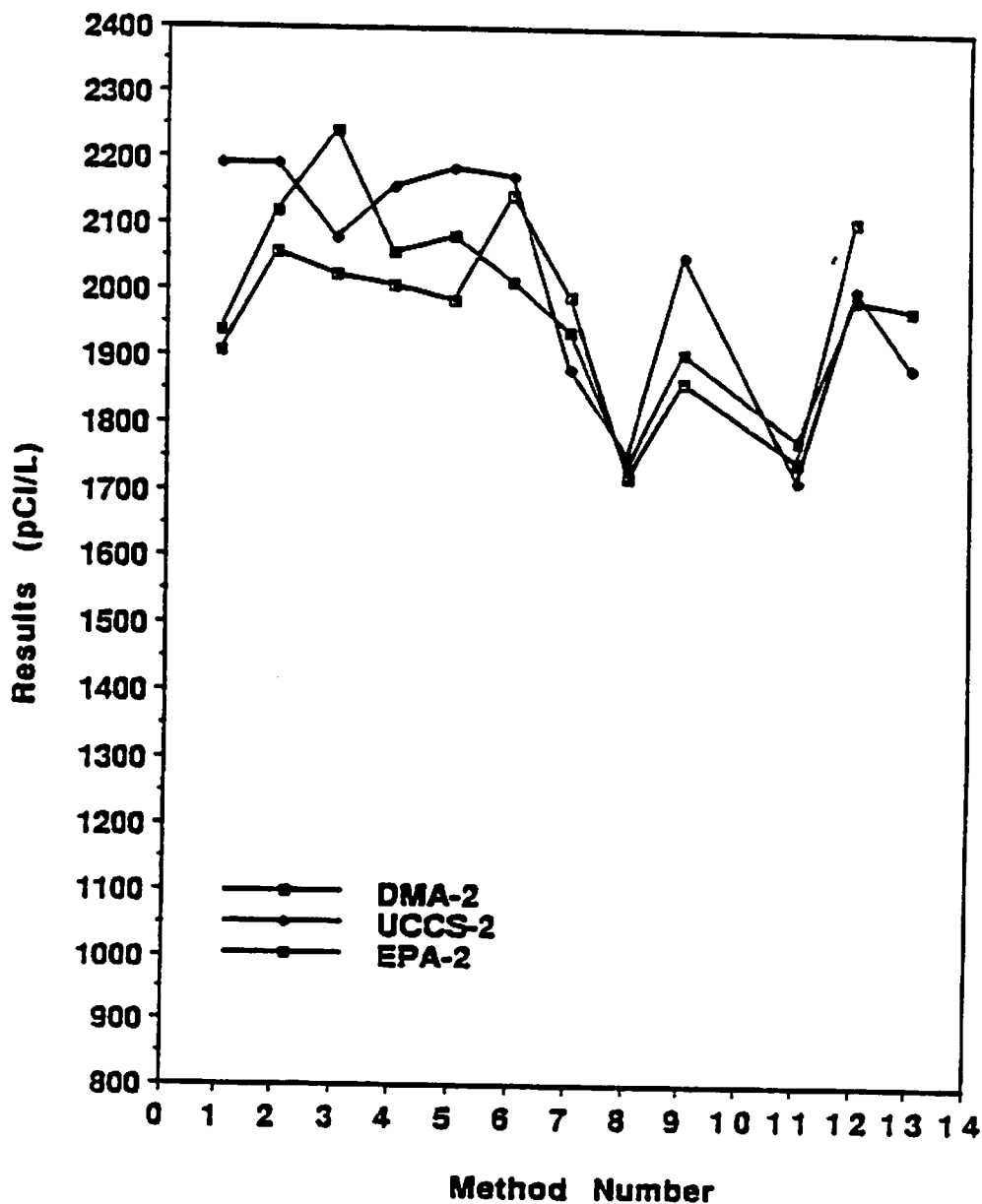


Figure 3. Individual radon averages from each lab from second run, 5/23/91.

Figure 4 gives the average radon concentration found by combining all of the three labs data. The 2 σ error bars are shown.

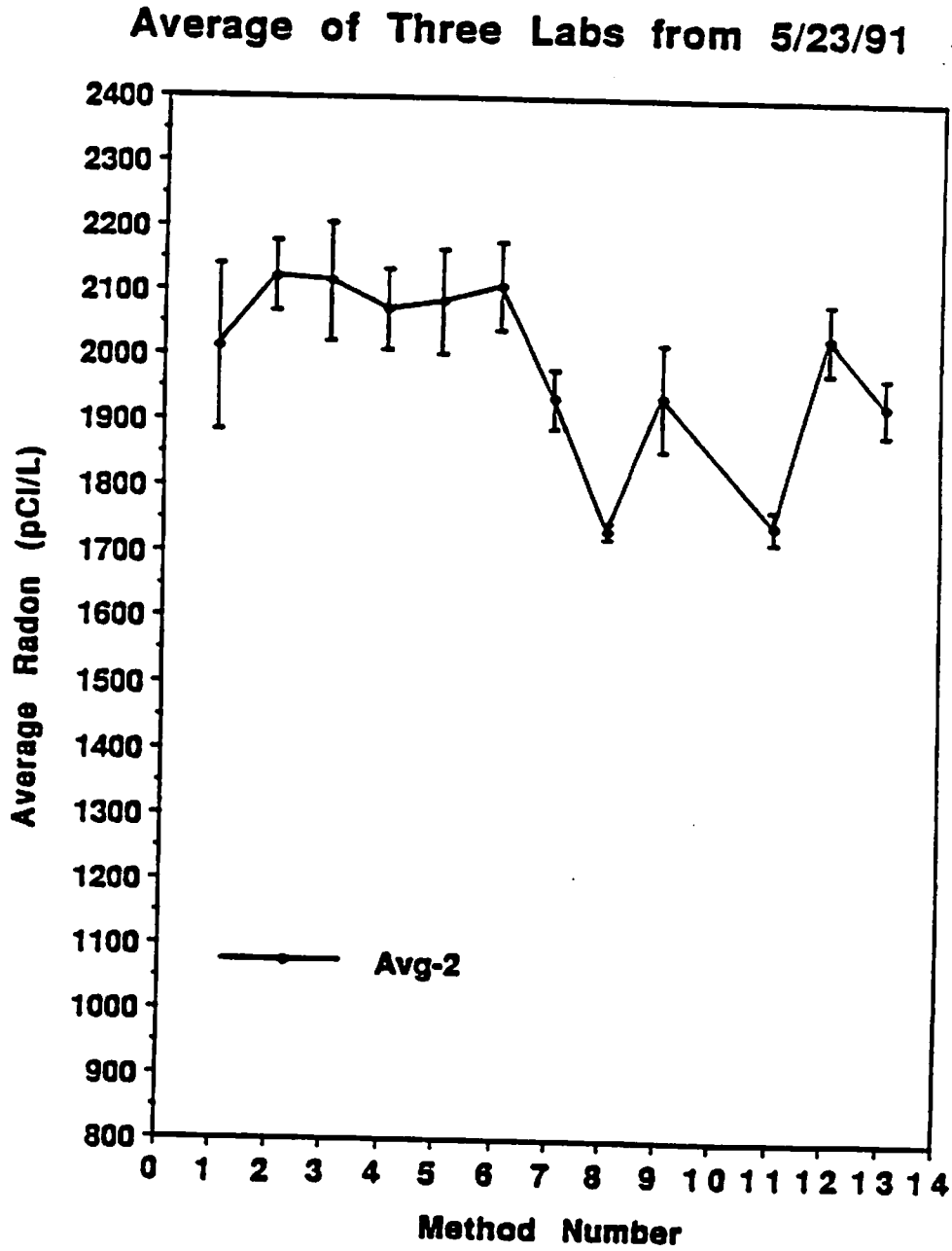


Figure 4. Average of three labs from second run, 5/23/91

For some of these data points, the spread in data is less than the distance between the points and one might infer that the differences in reported radon concentrations are now indeed showing a difference in the effectiveness of the methodologies.

In order to make such inferences, Student-t tests were performed comparing the various methodologies to method 2, the so-called EPA method. This method performed well in both runs in that it gave consistently high results with a good precision. The Student-t distribution tests the significance of the difference between two sample means when the number of samples are small. Making the assumption that the two samples being compared come from populations that can be approximated closely with a normal distribution and the assumption that these two populations have equal standard deviations, the criterion which we use to test the hypothesis that the average of each of the following methodologies is less than the average of the EPA methodology will be set at the 97.5 % confidence level requiring a t value of 2.365 or higher (for 9-2, or 7 degrees of freedom.)

1) There is no difference among the various hose and funnel methods, regardless of the type of lid used on the vial or whether a steel needle or tygon tubing is used. Thus, methods 1 through 6 give similar results. For example when comparing method 1 to the EPA method (method 2), a t value of 1.389 was calculated.

2) Immersing the vial into a pail and filling with water for later transfer into the scintillant is not as good a method as method #2 (at the 97.5% confidence level). For example, a t value of 3.21 was calculated for method 7 (where the glass vial has a septum lid), a t value of 11.79 was calculated for method 8 (where the glass vial has a poly-cone lid) and a t value of 3.21 was found for the foil lined lid of method 9. Of the three lids used in the immersion method, the poly-cone lid performed noticeably worse and the foil lined cap noticeably better than the average of the three.

3) Although methods 11 and 13, which are filling the glass vial from the spigot using a poly-cone lid and a septum lid respectively, are not as good as method 2 (with t values of 10.75 and 4.05), filling from the spigot into a vial which is then covered by a foil lid works as well as does method 2 (with a t value of 1.98.)

Although the t distribution test was never performed on the data from run 1 (because of our questions concerning its accuracy), it can now be seen that these conclusions using the Student-t distribution are confirmed qualitatively by examining Figure 2.

INVESTIGATIVE CONCLUSIONS

The following conclusions were derived as a result of this investigation, and are listed in order of importance:

No difference was observed in the results of the waterborne radon assay when the collection of the environmental sample was made by either the funnel or the basin method in those collection vehicles which contained the liquid scintillant stabilizing fluid.

Using the USEPA hose and funnel method and a stabilizing scintillant, no differences were observed when injecting the environmental sample under the fluid using various closure types (Poly-cone lid, septum lid, foil lined lid).

Using the USEPA hose and funnel method, no difference was observed when injecting the sample under the scintillant fluid using either a steel 18 gauge needle or a flexible tygon tubing substitute secured to the luer tip of the syringe.

Using statistical t tests, the immersion methodologies without scintillant resulted in slightly lower results than the USEPA funnel method with injection under the scintillant.

In collection procedures where no scintillant was used, the investigators found a small difference between the samples using the septum lid and the foil lined plastic lid. The investigators found significant radon concentration losses when environmental samples were capped with poly-cone lids. The radon is believed to have diffused into the head-space occupied by the cone.

In comparison with the USEPA hose and funnel method, the spigot methodology produced noticeably lower results except when in combination with a glass vial and foil lined cap.

If no scintillant is added to the collection vehicle, under no circumstances is the poly vial with the poly-cone lid or the standard 8oz collection vial appropriate for maintaining environmental sample integrity.

No appreciable difference between the spigot and the immersion methods were found, except that significant radon concentration losses were determined when implemented in concert with poly-cone lids or plastic vials.

SOME PRACTICAL CONCLUSIONS

The investigators believe that stringent rules for sample collection and preparation need to be understood and enforced by those involved in radionuclide analysis, but that latitudes must be available for the experienced technician.

Clearly the most reproducible and consistent method for acquiring an environmental waterborne radon sample is to quickly introduce the sample to a stabilizing scintillant. This technique is impractical for the commercial radon testing industry because the Federal Consumer Product Safety Commission forbids the distribution of potentially hazardous chemicals to the general public. Those chemicals are: toluenes, mineral oils, flours, and other long-chain alcoholbenzenes used in commercially available scintillation cocktails. Although some latitude is given to universities and the USEPA, the commercial sector would be prohibited from its use.

The use of plastic vehicles is inappropriate as the radon is hydrophobic, and therefore is attracted to the first matrix layer of the high-density-poly-ethelene (HDPE) vial and to the head space occupied by the poly-cone.

Therefore, in light of these restraints and constraints on the commercial industry, the investigators recommend that the most practical collection method (that is, when the scintillant cannot be sent to the collection site) may be:

The use of a basin, submerging the vial and cap to assure no air entrainment in concert with a glass vial and either a septum lid or a foil lined cap.

The use of a hose and funnel method with the same collection devices and closure method as above.

REFERENCES

- Lowry, J.D. Measuring Low Radon Levels in Drinking Water Supplies. Research and Technology 149-153: 1991.
- Lucas, H.F. A fast and accurate survey technique for both radon-222 and radium-226.
In: Adams, J.A.S., and Lowder, W.M. The natural radiation environment; Chicago, IL:
University of Chicago Press: 1964:315-329.
- NJDEP Laboratory Certification Program: 1991, USEPA Document 520/5-83-027.
- Prichard, H.M. and Gesell, T.F. Rapid measurements of Rn-222 concentrations in water with a commercial liquid scintillation counter. Health Phys. 33:577-581: 1977.
- Vitz, E. Toward a Standard Method for Determining Waterborne Radon. Health Phys. 60:817-829: 1991.