

**Factors Effecting the Determination of Radon in Groundwater**

**State Laboratory of Hygiene**

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by

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# **1. Introduction and Background**

## **1.1 Purpose and Scope**

In 1991 the U.S. Environmental Protection Agency (EPA) issued a "proposed" analytical method for radon in water (EPA Method 913.0). This method involves injecting a measured amount of sample beneath a liquid-scintillation (LS) cocktail, and then measuring the amount of radon that diffuses into the cocktail (based on the radioactive emissions). The Radiochemistry Unit of the Wisconsin State Laboratory of Hygiene (SLH) was one of a select group of laboratories that participated in a collaborative study of the method, and thus was able to gain experience with this method early on. While using this method to test Wisconsin groundwater samples, the Radiochemistry Unit thought that the chemical characteristics of the water may affect the measured radon concentration through an interaction with the sewer-disposable cocktail recommended by the EPA.

The purpose of this study was to determine the effect of several factors, especially the effect of the chemical composition of the water sample, on the analysis of radon in water by EPA Method 913.0. Various types of water samples (with different chemical compositions) were spiked with known concentrations of radon. These samples were analyzed using EPA method 913.0 and the recovery of the radon determined. Variations from expected recoveries were evaluated with respect to the chemical composition of the water. An attempt was made to identify which factors affected the results and how the method could be modified to overcome these effects.

## **1.2 Status of Radon Regulations**

The EPA is in the process of revising the National Primary Drinking Water Regulations for radionuclides. When this rule becomes final, radon will be regulated, and the new standard is likely to be stringent. Several values have been proposed for the radon standard ranging from 200 to 2,000 picocuries per liter (pCi/L) (Milvy and Cothorn 1990). Although the EPA and many scientific experts agree that any substance that emits ionizing radiation is a carcinogen

(U.S. EPA 1991), the level at which to set the standard is not so clear. The standard must ensure public safety while not creating an undue monetary burden on the public water supplier. Laboratories will have a critical job, since violation of the standard could require expensive water treatment to reduce the radon level in the water. Conversely, the public health may be endangered if the radon determination is biased low.

When the proposed radon standard becomes effective the regulations will apply only to community and non-transient, non-community public water supplies (U.S. EPA 1991). Private water supplies would not fall under the regulation. The EPA's policy for regulating carcinogens in drinking water has always been that the lifetime individual risk should be between  $10^{-4}$  to  $10^{-6}$ . A radon in water level of 200 pCi/L would have a lifetime risk of about  $10^{-4}$ . However, the EPA believes that 300 pCi/L is the lowest radon level that laboratories can successfully measure (U.S. EPA 1991). In addition to all the above mentioned considerations, the EPA also considered available treatment technologies and implementation of the regulations before deciding on 300 pCi/L as the proposed MCL for radon.

Recently, the EPA has stated publicly that the agency is now considering a level as low as 200 pCi/L for the radon MCL. If the MCL is set this low, there will be an even greater challenge for the laboratory to produce an accurate result. The ability of the lab to analyze for radon at low levels is dependent on such factors as (1) time from collection to analysis, (2) instrument background and efficiency, (3) counting time, and (4) an accurate reliable analytical method. Many water systems will be in violation of the MCL set at 200 pCi/L. Also, since radon fluctuates both seasonally and diurnally, the EPA is proposing a more frequent monitoring schedule for radon in water than for other regulated substances.

### **1.3 Health Effects**

The primary health risk from radon is the development of lung cancer from the inhalation of air-borne radon (Milvy and Cothorn 1990). Radon in drinking water can become air-borne during

normal household activities such as using the shower, flushing toilets, or using the washing machine. The direct ingestion of radon in drinking water also has health implications. It is believed that ingestion of radon may lead to other types of cancers of internal organs (Mills 1990). About half of radon's health risks comes from inhalation of radon and about half comes from ingestion of radon (Milvy and Cothorn 1990). It is estimated that up to 100 cancer deaths per year may be avoided by setting the radon MCL between 200 to 500 pCi/L. The EPA considers this to be a substantial public health benefit.

#### **1.4 Occurrence of Radon in Wisconsin Water Supplies**

The SLH has been analyzing public and private water samples for radon since 1986. The data accumulated from September of 1986 to August of 1994 for public water supplies is graphically represented in Figure 1.1. Samples were identified by Public Water System Identification numbers, and system well numbers in an effort to eliminate multiple data points from a single source. If multiple data points existed, the most recent data was used. Data from individual wells from a system was included along with distribution samples. Because of the interest in the compliance violations, the uncertainty value was added to the calculated activity as directed by the EPA. Of the of 1175 samples included in this analysis, 72 percent were over 200 pCi/L, 51 percent were over 300 pCi/L, 8 percent were over 1,000 pCi/L, and 4 percent were below the method detection limit. The data was also categorized by county and is presented in Figure 1.2.

Additionally, county-wide median values were calculated for those counties with greater than three data points. A map of these values can be found in Figure 1.3. Due to population density and sampling priorities, over 40 percent of the samples came from just 12 counties, while five counties had fewer than three data points. Samples with results below detection limit were not included for the calculation of the median, but were included in the count of samples per county. The counties with the highest median radon in municipal supply levels were found in the northern half of the state. However, single values of over 1,000 pCi/L were found throughout the state. The data corresponds well with summarizations of available radon data on a county

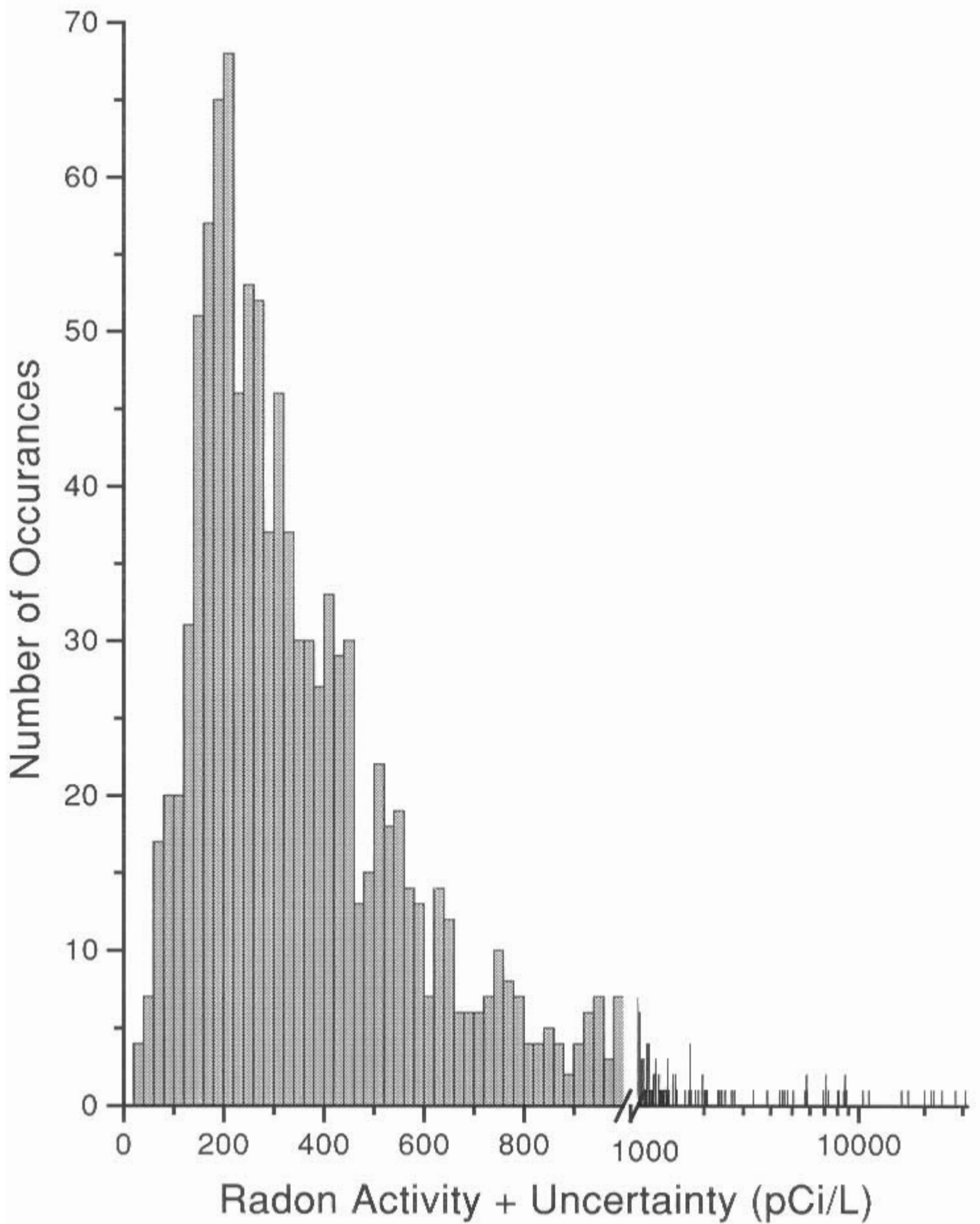


Figure 1.1. Radon in water activities for 1175 Wisconsin public water system samples.

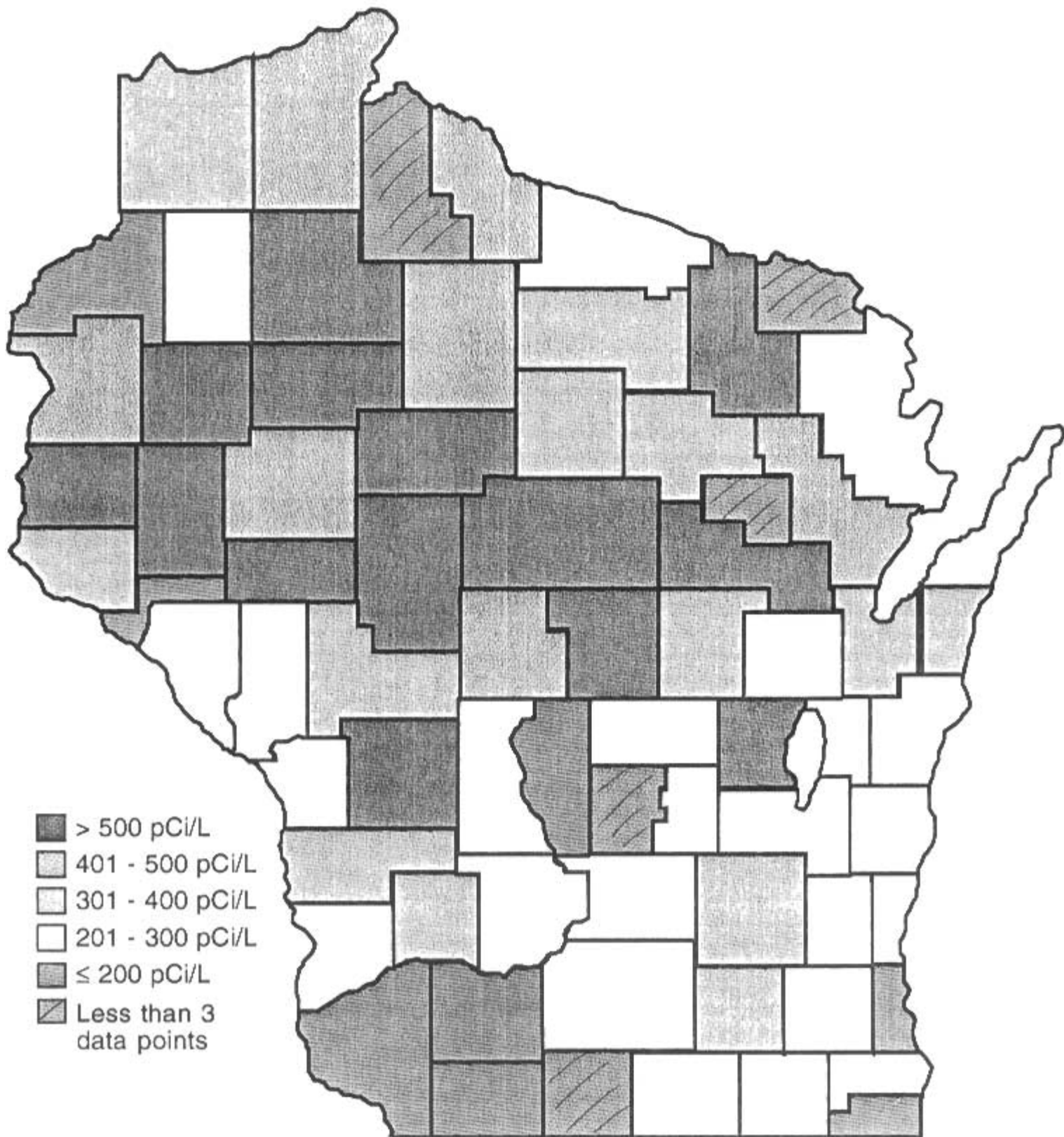


Figure 1.3. Mean Radon Concentration of Municipal Supplies by County

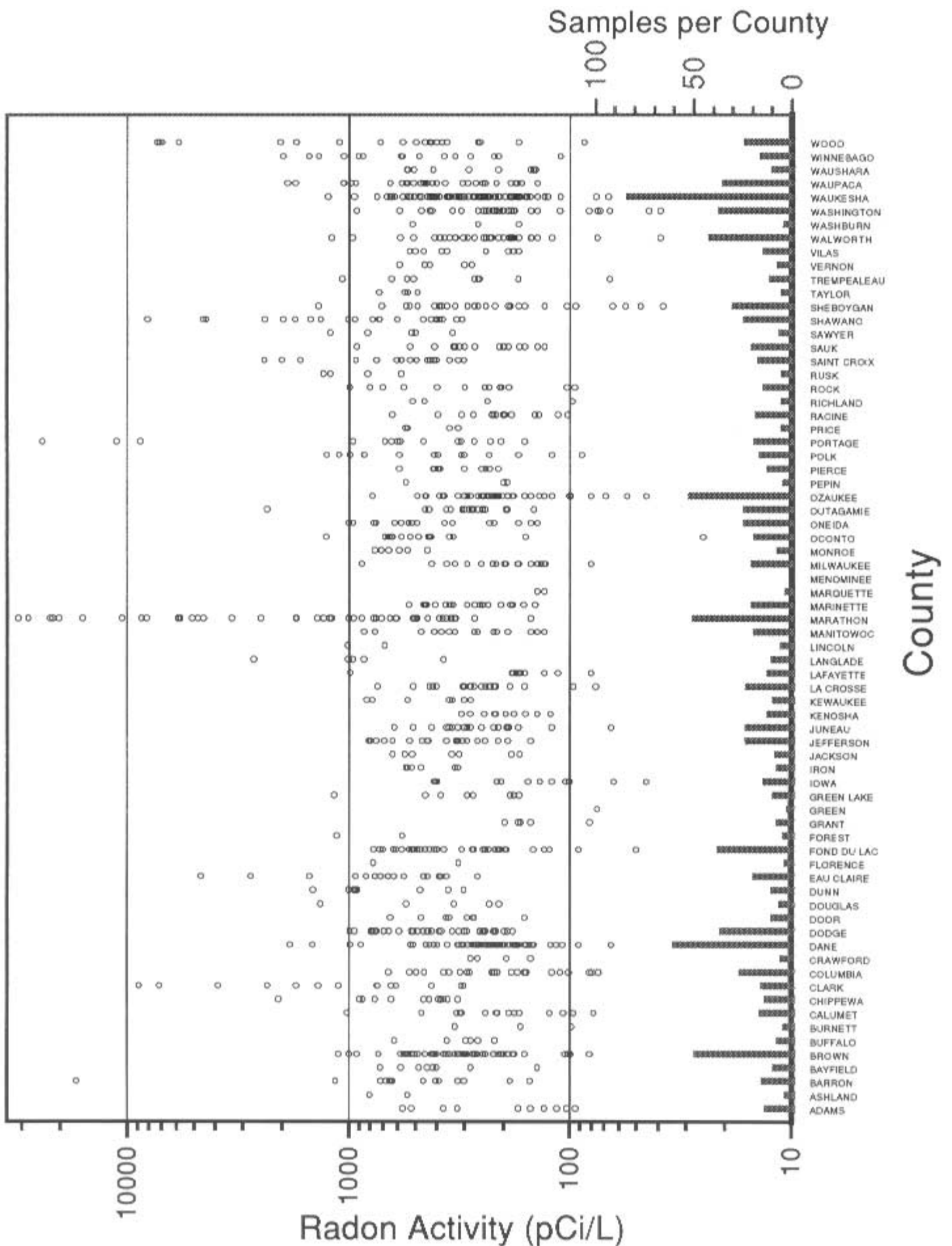


Figure 1.2. Radon in water activity and number of samples from municipal systems tested, by county.

wide basis as shown by Michel and Jordana (1987). Early EPA national surveys to predict occurrence focused mainly on systems that serve more than 1,000 people since this represents 45 percent of the US water usage and therefore, only represents radon levels of larger systems. Other investigators have shown that the highest radon levels occur in the smaller systems. Private and small public supplies tend to draw their water from aquifers that are more likely to have high radon levels. This type of aquifer generally does not yield enough water for large systems. Larger systems often rely on surface waters for their needs and this type of water has been shown to contain little radon.

### **1.5 Chemical and Radiochemical Properties of Radon**

Radon is a chemically inert radioactive gas that occurs naturally. There are three radon isotopes, radon-222, radon-220, and radon-119. These three isotopes all have a radium isotope as its predecessor and each one arises from a different uranium-thorium decay scheme. Radon-222 ( $^{222}\text{Rn}$ ) has a half life of 3.82 days and is the longest lived of the three radon isotopes. The half lives of the remaining isotopes are short, making them inconsequential from a health aspect.

Radon-222 decays through the emission of an alpha particle with an energy of 5.49-MeV (see Figure 1.4). The immediate progeny quickly decay to lead-210 (22 yr half life) and then eventually to the stable isotope, lead-206. Many of radon's progeny also emit alpha particles, and it is with these progeny that most of the potential health effects are produced. Unlike the chemically inert radon atom, the progeny are reactive and, therefore, have properties that allow them to cause considerable damage when inhaled.

Since radon is chemically inert it is more mobile than other non-gaseous naturally occurring radionuclides in aquifers. Its activity is controlled by the amount of radium-226 ( $^{226}\text{Ra}$ ) contained within the aquifer matrix. It can often be found at concentrations that are much greater than that of its parent,  $^{226}\text{Ra}$  (Davis et al. 1987). The concentration of radon that exceeds the radium concentration is referred to as unsupported radon. Uranium-Thorium series isotopes



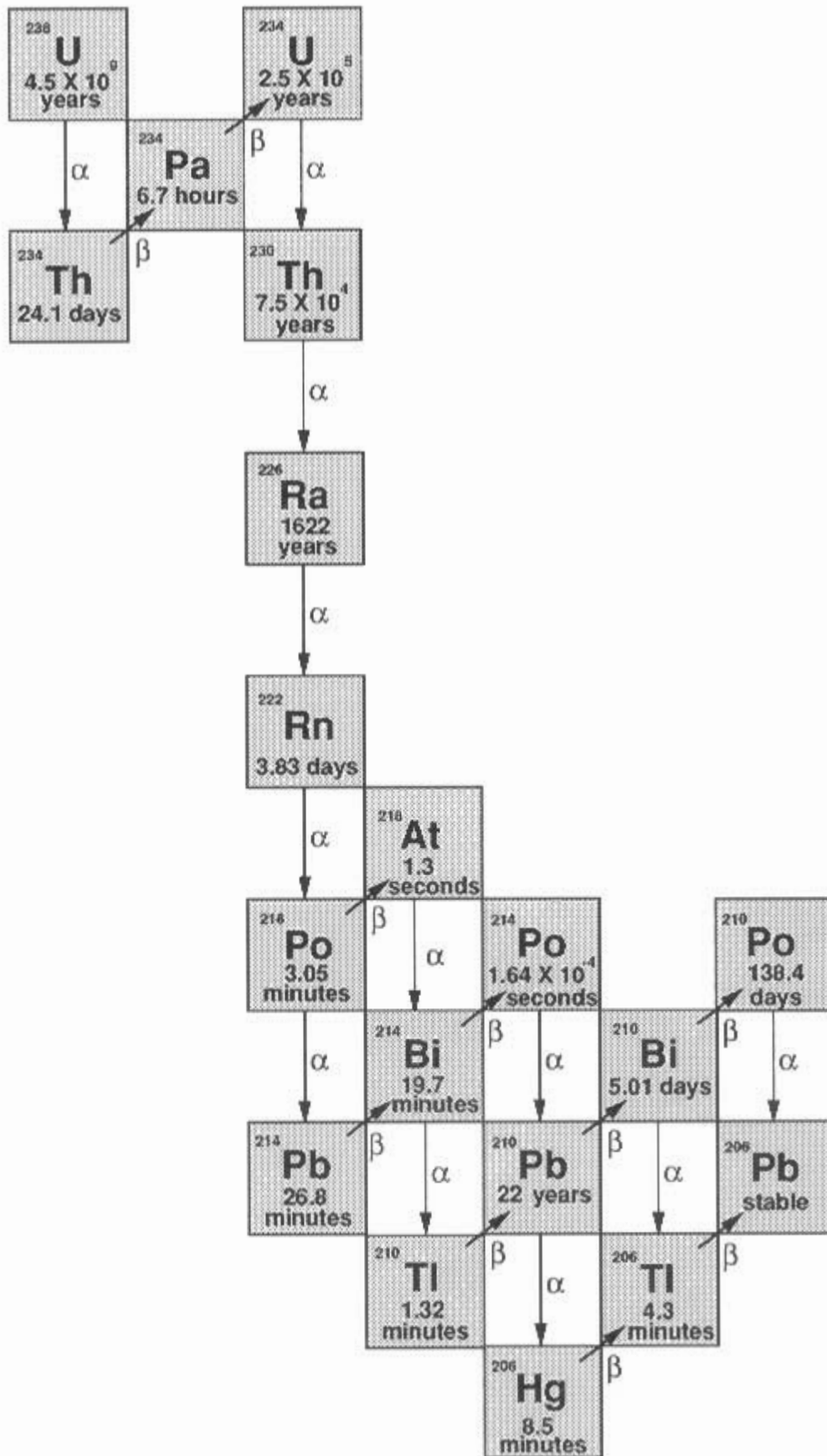


Figure 1.4. Uranium Decay Scheme (Friedlander et al 1964).

are generally chemically bound to the aquifer solids and are only soluble to a limited degree. The diffusion of radon through non-porous material is negligible while its diffusion through porous material is small but measurable (Hall et al. 1987). So the fact that radon may be found at high concentrations may be explained in part by advective transport with ground water and by pressure gradients that are anthropogenically caused.

The concentration of radon in water is not directly effected by such factors as pH, conductivity, redox potential or ionic strength. These parameters only effect the level of supported radon by controlling the solubility of its parent,  $^{226}\text{Ra}$ . The solubility of radon is inversely proportional to temperature. Although radon is soluble in cold water, once the water becomes exposed to air it is released to the air, especially during normal household activities that cause agitation or aeration of the water. Radon has a Henry's Law constant that is similar to some volatile organic compounds (Hiltebrand et al. 1987).

## **2. Materials and Methods**

### **2.1 Procurement of Natural Waters**

The Wisconsin Department of Natural Resources (WDNR) was contacted to provide a list of at least five public water systems that were known to have extreme values for at least one previously measured parameter. The WDNR identified the systems by searching its database of Wisconsin public water supplies and corresponding laboratory test results. Five of the six waters identified by the WDNR were hard waters with high pH, the remaining source was soft and was the least basic of the six sources of water.

### **2.2 Sample Collection**

**2.2.1 Sample Collection for Radon Studies.** Each system was sent a one-quart cubitainer, a mailing carton with address label and a set of collection instructions. The water from these six locations was used in a variety of ways to look at how water quality might effect radon determinations.

**2.2.2 Inorganic Analysis of Natural Waters.** Each system was provided with collection kits as needed to analyze for inorganic analytes. The arrangements and selection of kits was handled by the Inorganic Unit of the SLH. The six water samples were analyzed for a variety of inorganic parameters including metals, pH, conductivity, hardness, sulfate and nitrate to verify previous results. All analyses were performed by the Inorganic Unit of the SLH using EPA approved methods.

### 2.3 Materials

Six different LS cocktails were used in the course of this study. Three were water-immiscible: Opti-Fluor<sup>®</sup> and Ultima Gold<sup>™</sup> F by Packard and Bio-Safe NA<sup>™</sup> from Research Products International (RPI), and three were water-miscible: Beckman Ready Safe<sup>™</sup>, Bio-Safe II<sup>™</sup> from RPI, and RadScint<sup>™</sup> Water made by National Diagnostics. De-ionized water from a MILLI-Q system operated with a specific resistance at 18 Megohm-cm was used for the preparation of standards and dilutions. The <sup>226</sup>Ra standard used was a NIST-traceable solution obtained from the EPA. Bio-Rad AG 50W-X8 Resin in the sodium form was used to prepare the radon generators. The resin is a strongly acidic styrene divinylbenzene ion exchanger with eight percent cross linkage. The mesh was 50-100.

### 2.4 Instruments

**2.4.1 Radon-222 Determination.** All analyses were performed using a Packard Tri-Carb<sup>®</sup> 1500 Liquid Scintillation Analyzer (LSA). Analysis of spectral data was done using in-house programming and Origin<sup>™</sup> graphics and data analysis software by MicroCal Software, Inc.

**2.4.2 Radium-226 Determination.** Radium-226 is determined indirectly by measuring <sup>222</sup>Rn. The radon is transferred to scintillation cells supplied by Rocky Mountain Scientific and counted on Ludlum photomultiplier/scaler systems.

## 2.5 Methods

**2.5.1 General Method of Analysis.** Water samples were analyzed for radon using a suggested modification of EPA Method 913.0 (draft). This method involves introducing 15 mL of water into a glass scintillation vial to which 5 mL of LS cocktail has been added. The sample is shaken and set aside for at least 4 h to allow the radon progeny to equilibrate. After this time, the sample is counted for 50 min on the LSA using a predefined counting window.

**2.5.2 Radon Generators.** The radon generators were prepared by first converting the ion-exchange resin to the sodium form, then measuring approximately 1 g of resin into each of ten 14-mL vials. A known quantity of  $^{226}\text{Ra}$  was then added to the resin along with approximately 10 mL of deionized water. The vials were gently shaken and allowed to sit overnight to facilitate the transfer of radium to the resin beads. Over a 12 to 60 h period of contact, the generators were tested to determine if the radium was completely exchanged onto the resin. Ten mL of the water was removed from each vial and the  $^{226}\text{Ra}$  concentration was determined using a modification of EPA Method 904.1; Determination of Radium-226 in Drinking Water. A summary of the results is found in Table 3.1. The vials were then filled completely with deionized water and capped with teflon-lined septum caps. The vials were allowed to sit for at least 30 days to allow for the complete ingrowth of  $^{222}\text{Rn}$  from the  $^{226}\text{Ra}$ .

**2.5.3 Sample Loading Capacity.** The allowable sample volume for the water-miscible cocktails was determined by adding deionized water, 1 mL at a time, to a known volume of cocktail in a counting vial. The vial was shaken, and observed to determine if a clear, single-phase solution resulted. If the solution remained clear, the process was repeated until a clear solution was no longer produced.

**2.5.4 Determination of Counting Efficiency.** The counting efficiency of each cocktail was determined by adding 1 mL of water, containing a known concentration of radon, to each of three vials containing the cocktail, 1 mL of natural water, and the appropriate amount of

deionized water to yield the proper sample volume. Samples were shaken for 10 s, and allowed to ingrow for at least 4 h before counting. The samples were counted long enough to yield at least 30,000 counts (full-spectrum). The resulting spectra were analyzed to determine the optimum counting region by comparing the efficiency and background values from thousands of different counting windows. These values were plotted, and the optimum counting window was taken from this plot. A summary of the findings can be found in Table 3.2.

**2.5.5 Background Samples.** Background samples were prepared for each of the cocktails using deionized water. Samples prepared with the two-phase cocktails were not shaken. Each was counted for 200 min.

**2.5.6 Effect of Water Quality Parameters.** The effect of water quality parameters on the counting efficiency of the particular cocktails was accomplished in the following manner. Varying amounts of the natural water was added to each of four LS vials. Deionized water was added to each of the samples to bring the total volume to 14 mL. Five mL of the cocktail was placed in each of the vials. One mL of deionized water containing a known concentration of radon was then added beneath the cocktail. The samples were immediately capped. After the radon spike was added to all samples, they were shaken for 10 s. After ingrowth the samples were counted and spectra collected. The apparent activity of each sample was calculated using the efficiencies calculated for each of the cocktails, and a percent recovery calculated. A plot of the results can be found in Figure 3.1.

### 3. Results

#### 3.1 Retainment of Radium-226 on Ion Exchange Resin

In Table 3.1, the results of a determination to measure the ability of the resin to retain  $^{226}\text{Ra}$  are shown. The ion exchange resin effectively complexes all radium that was introduced into the radon generators. A 1-mL aliquot of these solutions yielded radon concentrations between

20,000 and 29,000 pCi/L when used for the recovery and efficiency determinations described in Section 2.5. All ten radon generators were checked, and only trace quantities of radium were detected in solution. In a separate analysis, a sample of water taken from one of these radon generators sealed for 91 days also showed only trace amounts of radium.

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<sup>226</sup> Ra in Vial (pCi)	<sup>226</sup> Ra in Solution (pCi)	Percent <sup>226</sup> Ra on Resin
6060	0.44	100
6080	0.16	100
6070	0.36	100
6260	0.61	100
6160	0.52	100
6170	0.24	100
6190	0.78	100
6260	0.49	100
6080	0.73	100
4330	0.22	100

Table 3.1. Retainment of radium-226 on ion exchange resin.

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### 3.2 Liquid Scintillation Cocktails

Table 3.2 compares the counting characteristics of the LS cocktails evaluated in this study. Note the relatively large background and resultingly low Figure-Of-Merit (FOM) for the two single-phase cocktails (FOM and LS counting theory are discussed in Section 4.1).

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LS Cocktail	Counting ROI (keV)	Background (cpm)	Counting Eff. (cpm/pCi)	Figure of Merit
Opti-Fluor <sup>®</sup> O	150 - 750	3.22	6.43	194
Ultima Gold <sup>™</sup> F	150 - 1250	4.08	6.85	173
Bio-Safe NA <sup>™</sup>	140 - 850	4.26	6.23	137
RadScint <sup>™</sup> Water	150 - 700	13.2	7.09	19.1
Ready Safe <sup>™</sup>	150 - 700	11.6	6.97	25.0

Table 3.2. Comparison of counting characteristics of various biodegradable LS cocktails.

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### 3.3 Samples

**3.3.1 Inorganic Analyses.** The sources of the six natural waters used in this study can be found in Table 3.3.

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Source No.	Description
1	Taycheedah C.I. - Well 2
2	Fond du Lac Waterworks - Well 11
3	Benton Waterworks
4	Fond du Lac Waterworks - Well 16
5	North Fond du Lac Waterworks - Well 2
6	Cazenovia Waterworks - Well 2

Table 3.3. Description of natural water sources.

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Table 3.4 shows the results of the inorganic analysis of these waters. As discussed in Section 2.1, these water sources were selected because they represented the extremes of water quality encountered in Wisconsin. Therefore, if water quality was going to have an affect on the radon analysis, it should be apparent with these samples. Through the course of the study it became apparent that additional natural waters from the other extreme should have been chosen and the effects observed. Waters 1-5 had elevated sulfate concentrations and samples 1-4 had elevated levels of barium. Samples 1,5 and 6 contain high iron concentrations.

**3.3.2 Water quality versus radon recovery.** Water from the six sources was diluted with deionized water to varying degrees and then spiked with radon. The percent recovery was used to show if a certain water type would produce biased results. These results are presented in Figure 3.1. Note that only the two most promising cocktails were used in this determination as detailed in Section 4.5.

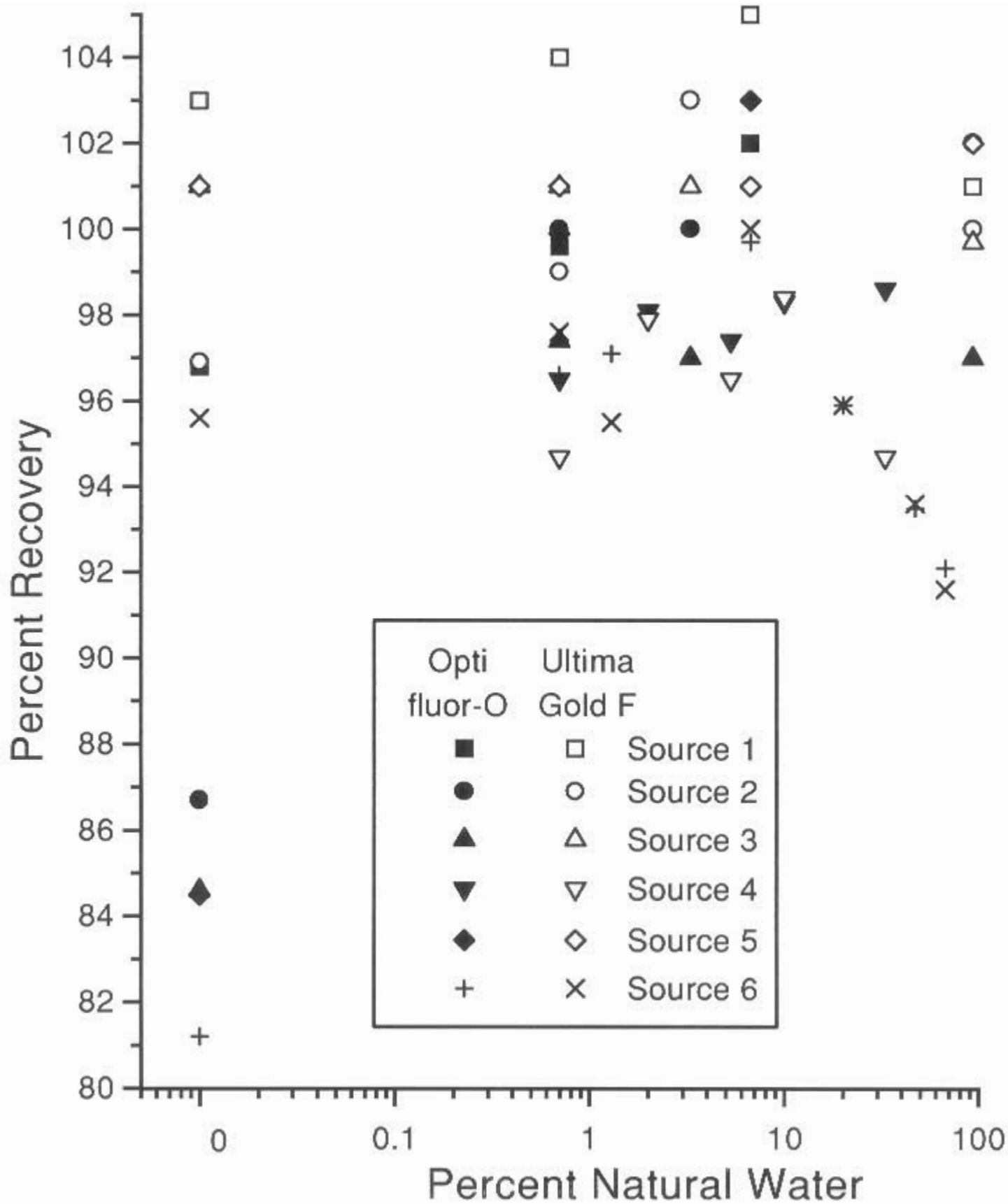


Figure 3.1. Comparison of calculated radon recoveries using two different LS cocktails and various dilutions of six natural waters.



Source No.	1	2	3	4	5	6
Conductivity†	1320	1220	1080	1030	628	282
pH††	7.47	7.39	7.68	7.90	7.85	7.23
Alkalinity*	180	265	328	159	253	90
Arsenic	<12	<12	<12	20	<12	<12
Barium	21.1	39.9	59.7	33.0	42.1	42.1
Beryllium	<0.3	<0.3	0.4	<0.3	1.3	<0.3
Calcium*	159	114	128	109	69.2	25.6
Copper	5	7	<3	5	3	<3
Iron*	0.39	0.17	<0.01	0.10	0.46	1.21
Magnesium*	43.3	63.3	61.2	24.8	31.6	11.9
Manganese	37.9	31.8	21.0	69.5	55.7	355
Potassium*	7.6	4.4	1.8	5.7	3.0	1.1
Sodium*	61.0	47.6	23.2	64.8	14.9	9.46
Vanadium	<2	<2	<2	<2	8	<2
Zinc	<8	8	50	<8	<8	39
Hardness*	580	550	570	380	300	110
Nitrate+Nitrite-N*	<1.00	<1.00	1.08	<1.00	<1.00	2.12
Sulfate*	390	220	240	120	46	11

Units are  $\mu\text{g/L}$  except:

\* =  $\text{mg/L}$

† =  $\mu\text{mhos/cm}$  or  $\text{s/cm}$

†† = SU

Table 3.4. Inorganic Analysis of Natural Water Sources

## 4. Discussion

### 4.1 Scintillation Theory

**4.1.1 General Theory.** Liquid scintillation analysis involves combining the substance containing the radioactivity, in this case water, with a chemical that gives off a single photon of light when it interacts with the energy of a radioactive particle. This chemical scintillator is combined with a solvent solution to form the LS cocktail. As the alpha or beta particle travels through the solution it interacts with some of the light emitting molecules. Since higher energy particles travel farther through the solution, more photons are produced by higher energy particles. The light given off is analyzed by the electronics of the LSA, that keeps track of the

number of radioactive particles detected in each of 4000 discrete energy ranges (Packard 1987). This forms a distinctive spectrum of the radioactivity found in the sample. Since radioactive nuclides give off particles of specific energies, the quantity of a particular nuclide in the sample can be determined by examining a specific portion of this energy spectrum. In LS analysis this portion of the spectrum is referred to as the counting window. The counting window is set to yield the highest number of counts from the nuclide(s) of interest while keeping the background counts to a minimum. This interrelationship between sample count rate and background count rate is known as the Figure-of-Merit (FOM) (Packard 1987). Generally, a larger FOM yields a lower limit of detection. Optimum counting windows are normally set when determining the counting efficiency for a particular analysis.

**4.1.2 Quenching.** If something interferes with the number of photons detected by the LSA, the energy of an individual radioactive particle will be underestimated. This alters the shape of the sample spectrum by shifting these counts to lower energies. This effect, known as quenching, has a variety of causes. Of particular interest is optical quenching; photons are absorbed or scattered by the medium before they can be detected (Packard 1987). Quenching can cause a significant number of counts to be shifted out of the preset counting window, resulting in a lower count rate and therefore a lower apparent activity. An example of quenching on a radon in water spectrum can be seen in Figure 4.1. The quench of a sample is an integral factor in the counting efficiency of a sample. Therefore, for accurate results, the quench of the samples must be as close as possible to the quench of the method calibration samples.

**4.1.3 Types of Cocktails.** There are two types of cocktails that can be used for radon in water analysis. These are water miscible (single-phase) and water immiscible (two-phase). Single phase cocktails yield the highest absolute counting efficiency for radon in water analysis. This is due primarily to the large light emitting surface area presented to the photon detectors (nearly the entire height of the vial). Unfortunately a larger surface area also leads to higher background count rates. The most limiting factor in the use of single-phase cocktails is the sample loading

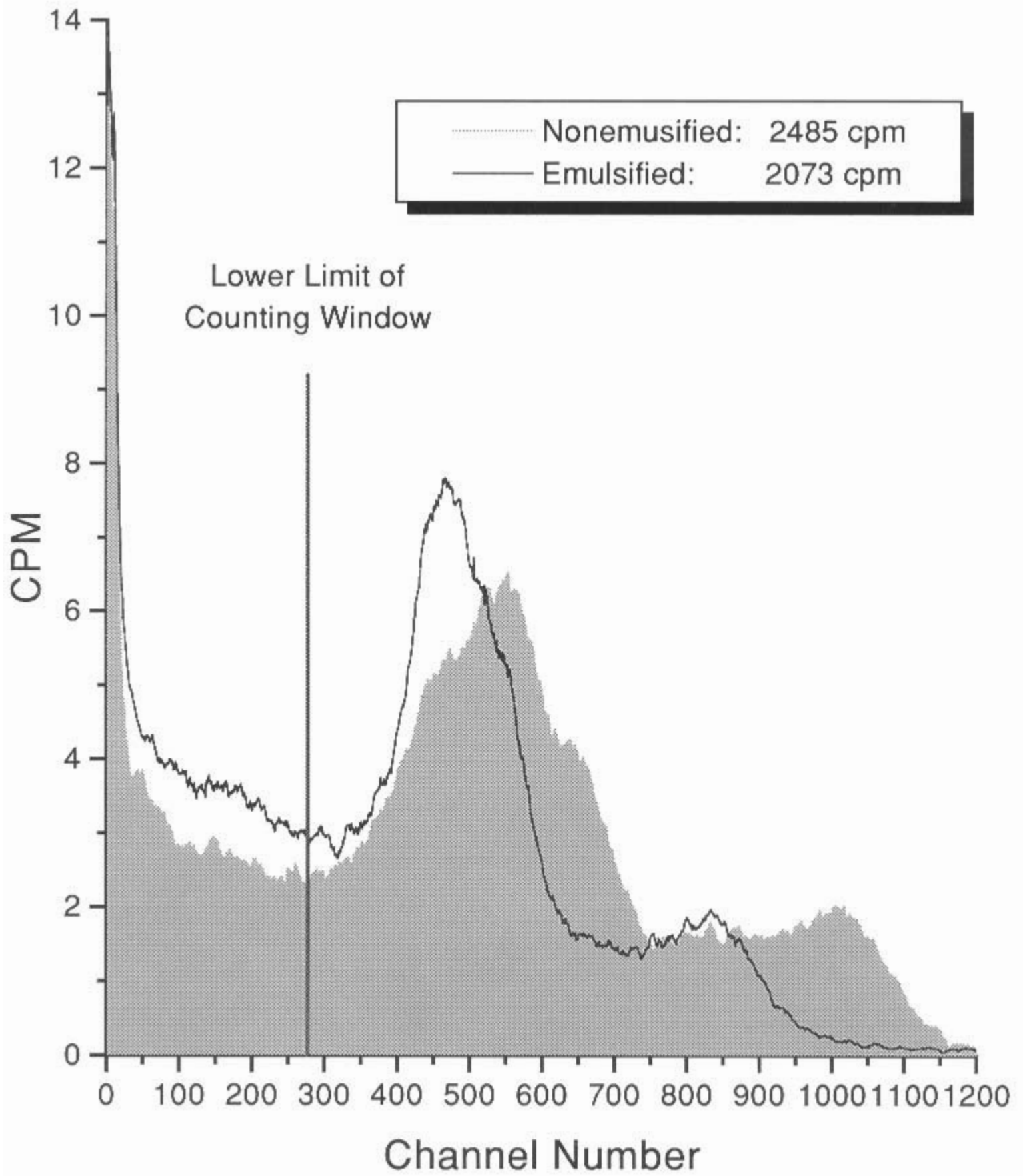


Figure 4.1. Comparison of emulsified and nonemulsified radon standard samples.

capacity. This is the amount of water that can be mixed with the cocktail and still produce a clear solution.

Two-phase cocktails work by extracting the radon from the water into the immiscible layer containing the chemical scintillator. The primary advantage to this method is the ability to use a larger sample volume. The disadvantage is that since most of the vial contains water, the light producing area is only about 25 percent of the vial height. This leads to a lower absolute efficiency, but also lower background count rate. This gives the two-phase cocktails a desirable, larger FOM for radon in water analysis.

## 4.2 Radon Generators

The preparation of a radon standard is not a simple matter. Ideally, a standard used for method quality control should mimic the actual samples being tested as closely as possible, and should be able to be run as a sample. Preparing a solution of  $^{226}\text{Ra}$ , sealing and allowing for ingrowth provides a standard with equal concentrations of  $^{226}\text{Ra}$  and  $^{222}\text{Rn}$ . This is not the case with natural water samples, where the  $^{222}\text{Rn}$  activity can be many orders of magnitude above the  $^{226}\text{Ra}$  concentration. In addition, the use of this type of standard on a regular basis would greatly increase the volume of radioactive waste to be disposed. The EPA suggests the preparation of this type of sample as a quality control check source, where three identical standards are counted at the beginning, middle and end of each run of samples. This type of standard is fine for monitoring instrument stability, but it provides no information on the method itself. Complexing of the  $^{226}\text{Ra}$  on the ion-exchange resin provides a virtually permanent source of radium-free radon-rich water, without adding to the radioactive waste generated by the laboratory. A series of these standards with varying concentrations can be used to provide a check on method accuracy and range with every run. The primary disadvantage of this method is the possibility of losing some of the thousands of resin beads containing the radium. A method of securing the resin to the vial is a future concern of the investigators.

In the past, investigators have used a radium-selective resin produced by Dow Chemical Company to research radium and its progeny. This resin had an extreme affinity for radium, so much so that its production was halted because of concerns over waste disposal problems. In this study, the resin selected retains the radium adequately and has the advantage of removability. The radium can be removed from the resin if necessary using a basic EDTA solution (West 1992).

#### **4.3. Problems caps and vials**

One option considered to circumvent the emulsification problem (see Section 4.4) was to allow the radon in the water samples to diffuse into the cocktail without shaking. Although recoveries of 96 percent were achieved with this method, an elution time of almost 2 days made this procedure impractical. The time for complete transfer from the water to the cocktail was determined by repeatedly counting the vials at specific intervals. When the activity reached a plateau, the transfer was complete. During these investigations it was noted that some of samples appeared to be losing radon. Figure 4.2 shows the difference between vials with and without leaks. On closer examination of these vials, slight deformities of the vial or cap were detected. Although all vials and caps were inspected before use, these seemingly insignificant flaws were not detected. The supplier (RPI) was notified. Coincidentally, subsequent shipments of caps have been of higher quality. A different type of cap has been ordered for testing.

#### **4.4 Variations between Different LS Cocktails**

As a part of this study the best LS cocktail for radon in water analysis was sought. The search was limited to biodegradable cocktails because of a request by the University of Wisconsin-Madison Safety Department to use these cocktails whenever possible. Representatives from various companies were asked to provide their best biodegradable cocktail for radon in water analysis. Although EPA method 913.0 calls for a water immiscible scintillation cocktail, three of the cocktails received were water miscible. This demonstrates just one difficulty for labs just

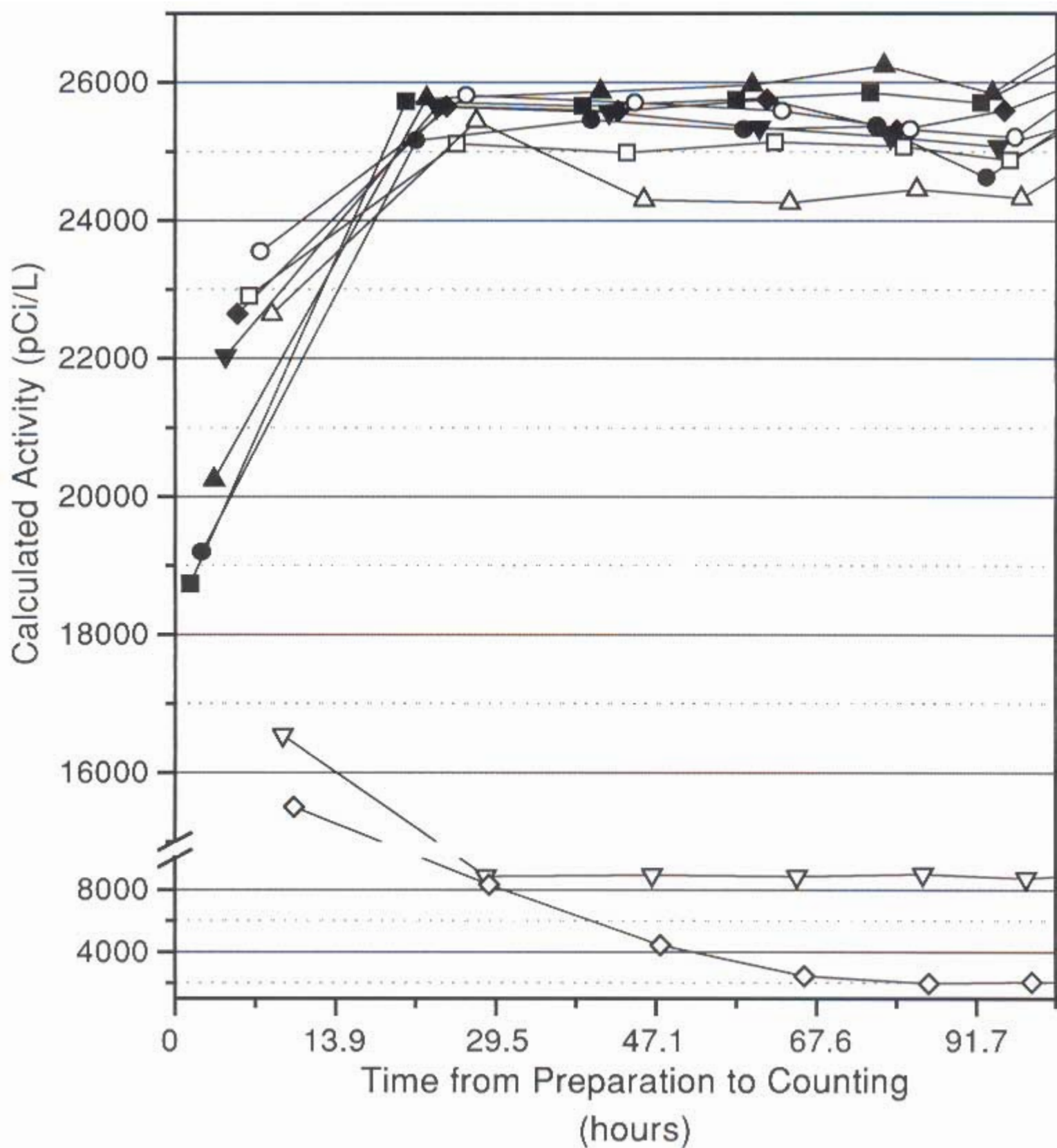


Figure 4.2. Comparison of calculated activities for a series of vials prepared from a single standard. The vials were not shaken, and were repeatedly counted.

starting a radon analysis program. Reliance on a supplier's assumed expertise could cause unnecessary delays. These cocktails were included in this study to demonstrate why a water immiscible cocktail is preferred. The first step in the evaluation of the cocktails was to determine the allowable sample volume. For the three water-immiscible cocktails, 15-mL sample and 5-mL cocktail were used as was recommended by the EPA for the May 1992 collaborative study. For the water-miscible cocktails the allowable sample volume was determined as described in Section 2.5.3 The three water miscible cocktails were found to have allowable sample volumes of 3 mL, 5 mL and 6 mL in a 20-mL LS vial. Since sample size of 3 mL was considered too small to be practical, BioSafe II was eliminated from further consideration. The two remaining water miscible cocktails were eventually removed from consideration because of their low FOM values and relatively small sample volume. Of the water immiscible cocktails, Bio-Safe NA was found to be unacceptable because it formed a variable three-phase sample with all waters tested. Of the two remaining cocktails, Ultima Gold F had a slightly higher efficiency, but Opti-Fluor O had a higher FOM. Therefore, given the same sample size, Opti-Fluor O would yield a lower detection limit. The advantage of Ultima Gold F is that it does not form an emulsion even with pure deionized water. This makes the determination of efficiency, and percent recovery less complicated. The only disadvantage of this cocktail is cost. At twice the cost of Opti-Fluor O, it must be determined if this convenience is worth the price. The emulsification that occurs with Opti-Fluor O when combining it with pure deionized water can be overcome by adding about 0.1 mL of 2M HCl. Thereby making it the cocktail of choice.

#### **4.5 Natural Waters Spiked with Radon**

A primary goal of this project was to determine if there were any water quality factors that might cause interferences with the procedure. The six natural water sources were spiked with radon and the percent recovery was determined. All six water sources and the various dilutions of these waters yielded acceptable percent recoveries. However, deionized water spiked with radon had much lower percent recoveries. Significant emulsification occurred when deionized water

was used (see Figure 4.3). Although varying degrees of minor emulsification have been observed in samples previously analyzed in the laboratory, none of the natural waters collected for this study produced any emulsification when analyzed using Opti-Fluor O. It became apparent throughout the course of this study that extremely soft natural waters would have been a better choice for observations of partial emulsification. However, the final outcome of the study would be identical. Emulsification to any degree will decrease the efficiency of the LS cocktail. Elimination of the potential for emulsification can be easily accomplished by the addition of one drop of 2N HCL. Recoveries for all natural water and the various dilutions were acceptable using both cocktails tested. The emulsification of Opti-Fluor O occurred only with pure deionized water. The addition of even small amounts of the natural water eliminated the emulsification. The Ultima Gold F did not emulsify even with deionized water. Recovery values for deionized water using Opti-Fluor O were considerably lower than those found using Ultima Gold F. This was because of the extreme emulsification that occurred with this mix. One deionized water sample using Opti-Fluor O cocktail did not emulsify. Although the reason for this behavior is not clear, previous results suggest that a small amount of some unknown contaminant could be the cause.

## 5. Conclusion

The effect of water quality parameters on the measured value of  $^{222}\text{Rn}$  was insignificant provided the degree of emulsification of the efficiency standard is similar to that of the natural waters. If the efficiency sample is prepared as directed in method 913.0 using deionized water and Opti-Fluor O is the chosen cocktail, there is the possibility of a positive bias. The determined efficiency will not adequately reflect the actual sample efficiency. To ensure that a similar quench (i.e. emulsification) is obtained in all samples, the addition of a small amount (approximately 0.1 mL) of 2M HCl to a 15 mL water sample is recommended.

The State Laboratory of Hygiene Radiochemistry Unit will continue to use Packard



Opti-Fluor O LS cocktail for the analysis of radon in water. We will continue to search for a more reliable LS vial cap and recommend that laboratories randomly check sample vials for leaks by repeatedly counting a vial. Additionally, the long term stability of the radon generators should be evaluated so that a replacement date can be set.

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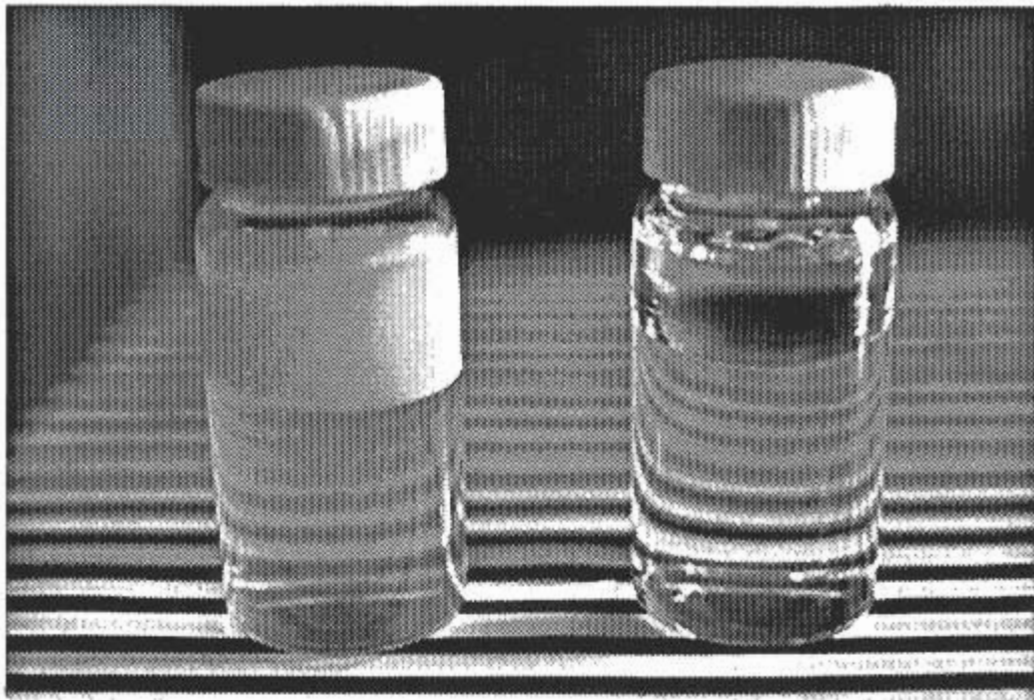


Figure 4.3. Comparison of emulsified and non-emulsified samples.

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