

Determination of ^{222}Rn and ^{226}Ra in Drinking Water by Low-Level Liquid Scintillation Counting—Surveys in Austria and Arizona

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ABSTRACT

One important source to man for both ^{222}Rn and ^{226}Ra is drinking water. ^{226}Ra may be ingested and ^{222}Rn is liberated by household activities; thus adding to the radon concentration already present in indoor air.

Very simple yet specific methods, avoiding any chemical separation, are presented for the determination of both radionuclides, using a commercially available ultra low-level liquid scintillation counter. The lower limit of detection is 40 mBq/L (1.1 pCi/L)—based on 500 min count and 3σ of the background. These methods have been applied for surveys both in Vienna and Arizona, the results of which are presented.

HEALTH HAZARDS OF ^{226}Ra AND ^{222}Rn

Most countries have strict regulations about the maximum permissible concentration (MPC) of ^{226}Ra in drinking water (^{224}Ra is a bone seeker). MPCs range in different countries from 0.11 to 1.85 Bq/L. In Austria it is 0.122 Bq/L.

^{222}Rn is regarded as hazardous, since it is abundant in all indoor air in enhanced concentrations. It emanates from ground or building material, and it is liberated from water by household activities like cooking, washing, toilet flushing, etc. It is estimated¹ that tap water containing 100 kBq/m³ gives off an additional effective dose equivalent to about 0.4 to 0.7 mSv/a from the liberated radon and its daughters. An air change rate of 0.5 changes per hour is assumed. Modern isolation techniques used for energy conservation have altered the air change rate by approximately 0.1 in most cases, enhancing radon concentration in houses. The above mentioned additional dose corresponds to the average additional dose the Austrian population received in the first year after Chernobyl. (Austria was one of the most contaminated European countries outside the U.S.S.R.)

No MPCs for ^{222}Rn are known in any country, but in some countries, for instance Sweden, national health boards give recommendations.² Below 100 Bq/L no restrictions or counter-measures are considered necessary. Between 100 and 1000 Bq/L cases have to be considered individually with regard to other sources of radon and ventilation. If water contains more than 1000 Bq/L it is likely that the concentration of radon daughters in the air exceeds 400 Bq/m³ – which is the action level – and remedial measures should be undertaken.

It is expected that the U.S. Environmental Protection Agency will set recommendation levels for radon in water soon, and they will probably be lower than the Swedish ones at present. In principle, it is possible to apply the recommendation of 4 pCi/L air (0.15 Bq/L), taking the liberation from water into account. Doses from ingestion of radon are negligible compared to the lung doses from inhalation.

Determination of ^{222}Rn and ^{226}Ra in water is therefore of great importance in health physics.

DETERMINATION OF ^{222}Rn AND ^{226}Ra IN WATER

^{222}Ra is highly soluble in toluene and other organic solvents frequently used in cocktails for LSC. Since α -particles are counted with approximately 100% efficiency, LSC is nowadays widely used for measurement of radon.³⁻⁵

One simple method is to mix water with a gel-forming scintillation cocktail and wait about three hours until equilibrium with the daughters is established. Normally ^{222}Rn is present in such high concentrations that any contribution of other naturally occurring radionuclides is negligible. Figure 1 shows the spectrum of an actual water sample, 8 mL of which were mixed with 12 mL of Quickszint 400 (obtained from Zinsser Analytic, Frankfurt). The vial used was a PTFE coated polyethylene vial (from Zinsser). The left peak is the unresolved sum of the peaks of ^{222}Rn (5.49 MeV) and ^{218}Po (6.00 MeV), the right, well-resolved one is due to ^{214}Po (7.69 MeV). The resolution is estimated to be about 300 to 400 keV. The x-axis shows the logarithmic pulse height and not the energy. Efficiency is between 300 and 400%, depending on vial and cocktail. It is determined with a ^{226}Ra standard treated the same way and taking the 100% efficiency of the Ra- α -particles into account.

Another method uses radon extraction from the water phase into a water-immiscible, mineral oil-based scintillation cocktail.⁵ The cocktail employed in this research was PSS-007H from NEN. Ten mL of water is mixed with 10 mL cocktail, shaken vigorously, and counted after about three hours. In this time, equilibrium is established, the sample is cooled, and the phases are separated. The resolution is better (Figure 2) than in the case of the gel-forming cocktail. The efficiency is equally high and is determined with a ^{226}Ra standard. ^{226}Ra is not extracted into the organic phase.

^{226}Ra is usually enriched and isolated chemically. Measurement is frequently done with LSC.⁶⁻⁷ We have been able to develop a method which completely

[A] 0.100 CPM/ch 98.77 min E:\3A\GRUNDW\1\0042401N.001 SP#12
 [B] 0.100 CPM/ch 493.86 min A:\3TRINKW\2-89A\Q11101N.000 SP#12

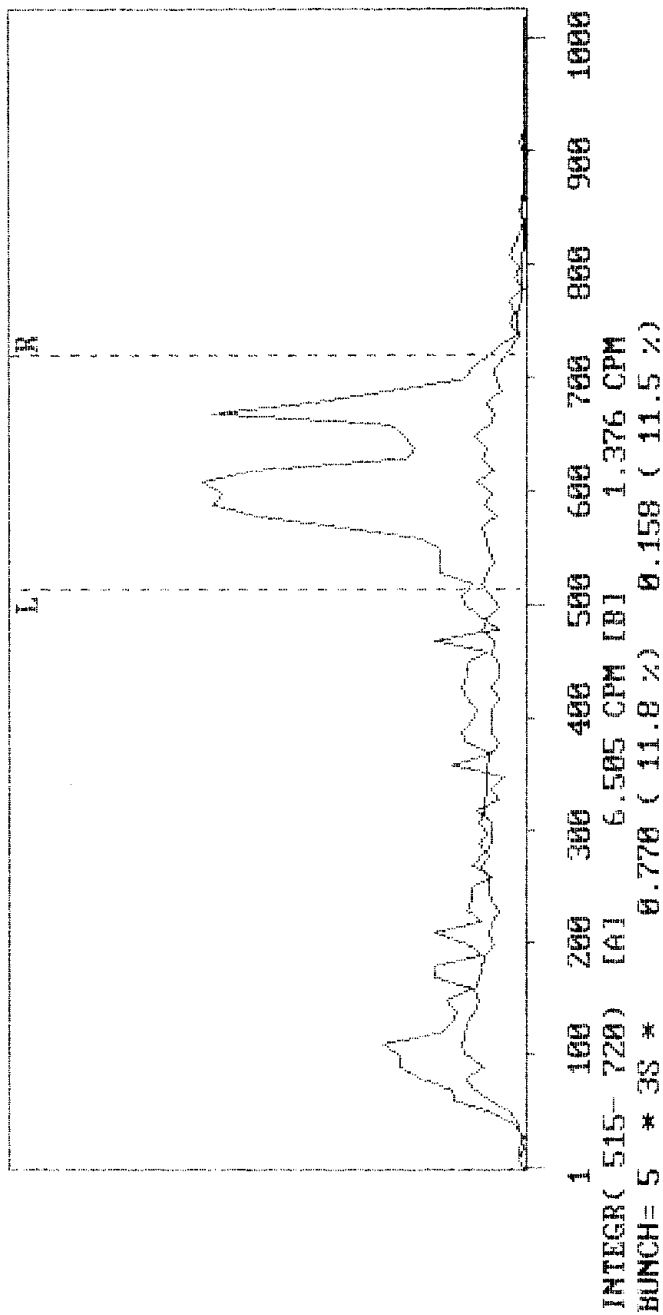


Figure 1. Pulse height spectrum of a water sample containing ^{222}Rn , 8 mL mixed with 12 mL Quick scint 400, and PTFE coated polyethylene vial.

[A] 7.000 CPM/Ch 29.71 min A:\TRINK\RN\14\0034391N.001 SP#12

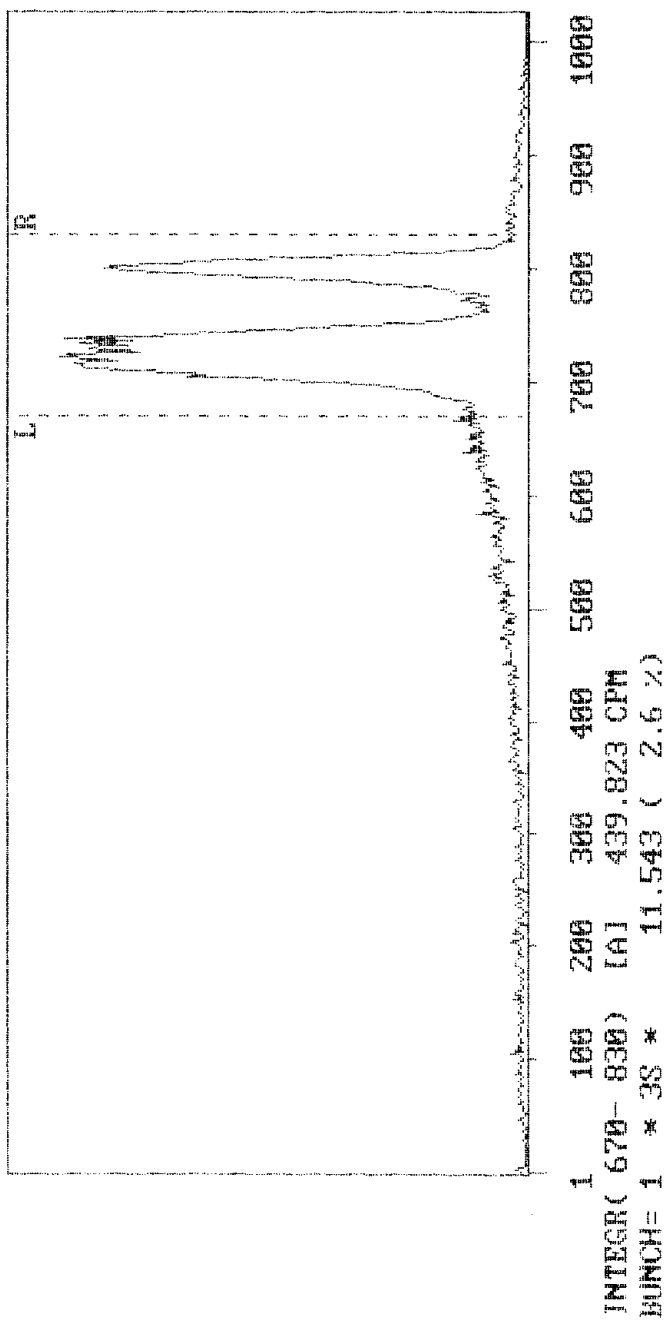


Figure 2. Pulse height spectrum of a water sample containing ^{222}Rn , radon extracted from 10 mL water into 10 mL of NEN cocktail, and PTFE coated polyethylene vial.

avoids the chemical isolation by using the ultra low-level LS counter "Quantulus" (Pharmacia—Wallac, Turku, Finland). This instrument exhibits extremely low background due to heavy passive and active shielding consisting of an anticoincidence unit based on a liquid scintillator. Moreover activity of the selected construction material is very low. Pulse height spectra are recorded automatically and can be used for control of possible interferences. Tests with standards of ^{226}Ra showed that the above mentioned methods for ^{222}Rn (simple mixing of water with the above mentioned cocktails) were well applicable for ^{226}Ra and they gave a lower limit of detection of about 37 to 48 mBq/L (1.0 to 1.3 pCi/L) (based on 3σ of the background and 500 min counting time), which is well below the maximum permissible concentration in Austria of 0.122 Bq/L (3.3 pCi/L).

The mixture of water with the gel-forming cocktail is not recommended for ^{226}Ra , since in such low concentration ranges heavy interferences from other naturally occurring radionuclides, especially ^{40}K , may occur. Quench effects from the water may also cause heavy interference. The extraction with the mineral oil-based cocktail, however, is specific for ^{226}Ra . After ingrowth of ^{222}Rn from ^{226}Ra (or decay of excess and unsupported ^{222}Rn) only ^{222}Rn in equilibrium with ^{226}Ra is extracted. ^{220}Rn and ^{219}Rn would not interfere because each has a very short half-life.

In practice, water was analyzed for ^{222}Rn immediately after it received the sample by the mineral oil cocktail method. Then it was stored for the appropriate time to allow for decay of unsupported ^{222}Rn . The same sample was then measured again for ^{226}Ra , thus the manual labor involved for determination of both radionuclides was simply the pipetting of 10 mL of sample and 10 mL of the cocktail—not to forget the shaking. For ^{222}Rn the measurement time is usually 60 min. For ^{226}Ra 500 min is was chosen, which means automatic determination of three samples per day, also during weekends and holidays. The high costs of our instruments have been compensated for by long time savings of personnel and labor.

RESULTS

The afore described methods were applied for surveillance purposes in Austria, and the method for ^{222}Rn has been used to survey risk area in Carefree/Cave Creek Basin in Arizona.

In Carefree, 26 wells were tested. The frequency of the concentrations found can be seen in Figure 3. Eleven wells (42%) show concentrations above the 100 Bq/L, which the Swedish authorities regard as the concentration below which no countermeasures need to be considered. They result in an additional effective dose equivalent of 0.4 to 0.7 mSv/a, which is much higher than the impact of nuclear power plants on people living in the surrounding area.

Concerning ^{222}Rn in Austria, the results from a risk area in the northeastern part of the country are presented. After a nationwide survey, work was con-

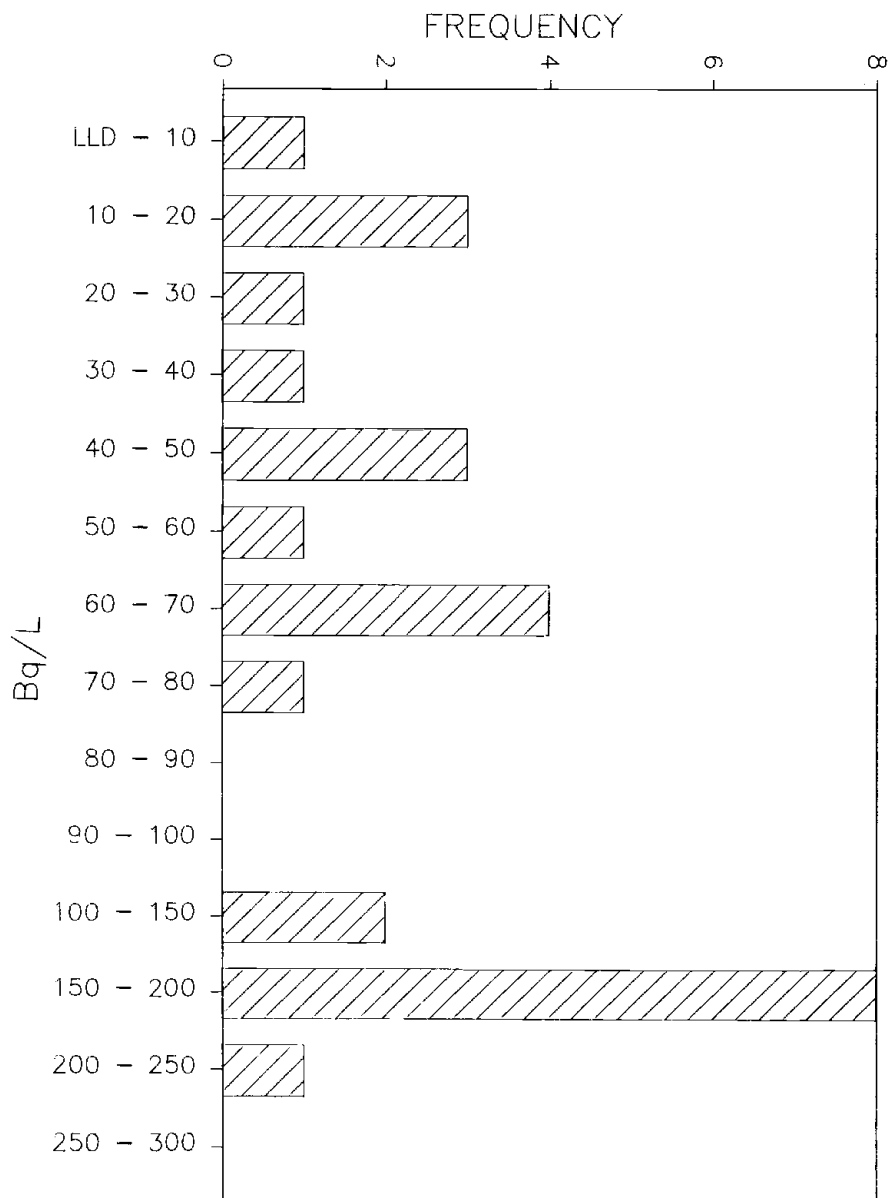


Figure 3. Distribution of concentrations of ^{222}Rn in water, Carefree/Cave Creek Basin, Arizona.

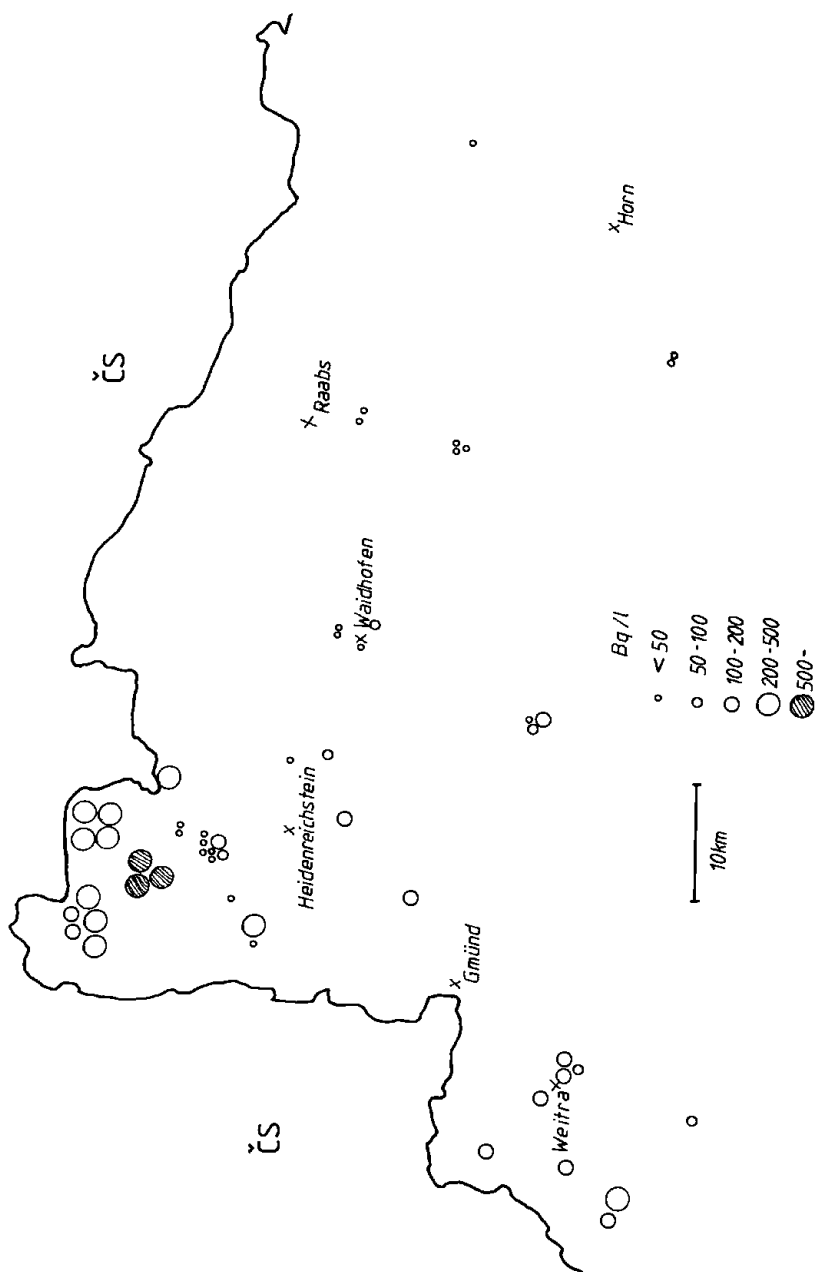


Figure 4. Geographical distribution of ^{222}Rn in water in a risk area in northeastern Austria.

centrated on an area where the ground consists partly of granite and partly of metamorphicum (mostly from sediments). The regional distribution of ^{222}Rn concentrations in household water is shown in Figure 4. Clearly, small areas with extreme concentrations can be distinguished from areas with rather high concentrations. The former ones coincide well with granite areas and the latter ones with metamorphicum.

In spite of the extreme values for ^{222}Rn , even in the risk area, only a few samples exceeded the lower limit of detection of 40 mBq/L for ^{226}Ra . By far, the highest value observed was 490 mBq/L, followed by 180 mBq/L.

CONCLUSIONS

The simple methods for both ^{222}Rn and ^{226}Ra determination have made it possible to survey a large number of samples within a short time. The results show that both Arizona and Austria have risk areas for high ^{222}Rn concentrations in water, and analysis has to be extended to other risk areas. The concentrations found are significant health concerns, and after limits are defined, countermeasures have to be undertaken.

Regarding the instrumentation, it is attempted to test the α - β -discrimination unit of "Quantulus" thoroughly for its application in ^{226}Ra determination. Since the background for α emitters can be reduced practically to zero, it is expected that a much lower LLD for ^{226}Ra can be achieved. Careful investigations of vials and cocktails will be necessary.

ACKNOWLEDGEMENT

The authors thank Christian Tschapka and Jeffrey Brown for performance of measurements and evaluation of data used in this chapter, Robert Mecl, Franz Oesterreicher, Kurt Hierath (water department of the Federal Institute), and Oswald Ruttner (BBSUA, Vienna) for collecting and providing most of the Austrian water samples.

The research in Arizona was financially supported by the Arizona Department of Environmental Quality, which is gratefully acknowledged.

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