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A NEW METHOD FOR THE QUANTITATIVE DETERMINATION OF RADON-222 IN NATURAL WATERS

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Introduction:

Several studies in the past have shown radon to be present in many natural waters including mineral springs, hot springs, rivers, lakes, and rainwater (1-4). A compilation of tables of radon concentration in mineral and hot springs all over the world was published by Kuroda in 1953 (1). Most of this radon comes from radium and uranium minerals which the springs flow over. The radon concentration in lakes is from two major souces. One source is dissolved radium and the other is the inflow of high radon concentration groundwaters (4).

Discovered in the early 1900's as an emanation of radium (5), radon is the heaviest of the noble gases and is the only element of that family which has no stable isotopes. As shown below, radon-222 is a decay product of the uranium-238 decay series and has a half-life of 3.823 days.

$$U^{238} \xrightarrow{\alpha} Th^{234} \xrightarrow{\beta-} Pa^{234} \xrightarrow{\beta-} U^{234} \xrightarrow{\alpha} Th^{230}$$

$$Th^{230} \xrightarrow{\alpha} Ra^{226} \xrightarrow{\alpha} Rn^{222}$$

In the past the use of gamma rays from radon's daughters include radiography tests for flawed metal structures and more commonly, radiation treatment of malignant tumors (6). Its presence in uranium mines and the health hazards it poses to workers of those mines have been part of the reason for some of the most recent work on studying radon's activity (7-10).

Since the radon concentration in natural water samples is generally very low, its radioactivity is the basis for any quantitative technique. Some methods are based on the alpha decay of radon-222 (5.846 MeV) or that of its daughter products (6). Previously, two techniques for identifying, detecting, and quantifying radon have been used. The first is the use of an electroscope (6). A sample of water is placed in a container and the radon concentration is allowed to reach equilibrium with the air in the container. The amount of alpha decay of the radon-222 causes a proprtional ionization of air particles. The amount of ionization is then measured as the amount of discharge on the electroscope. This technique is somewhat crude and lends itself to statistical error. Standardization techniques also cause problems.

The second technique is the internal counting method (6). In this method radon is degassed from large volumes of water and absorbed on charcoal beds at liquid nitrogen temperatures. The beds are then heated and the gas is driven into an internal counter to determine its activity. Working with liquid nitrogen temperatures is one drawback of this method. Another disadvantage is the fact that specialized counters must be used.

Using the fact that activity is equal to the number of molecules times a decay constant, the activity of a sample can be compared to that of a known standard to get the concentration of the sample. In the decay of radon-222 transient equilibrium is set up between radon and its daughters. The amount of time it takes to set up this equilibrium can be calculated but that procedure is more complex than is practical for this study. Instead, it can be shown empirically (figure 2) that the equilibrium is set up in about four hours.

Initial experiments aimed at reacting radon gas were the basis for the original belief that radon was inert (11,12). Further attempts to produce reactions with radon resulted in the formation of clathrate compounds (12). These are mixtures in which the gas molecules are surrounded by the crystalline structure of another substance without chemically reacting with it. These clathrate compounds are not considered to be true compounds.

Radon chemistry actually came into being in the early 1960's after studies with xenon would react with PtF_6^- vapor to form $Xe^+PtF_6^-$ (11). This study was followed by the discoveries of XeO_3, $XeOF_4$, and KrF_2 (11). Xenon fluoride was the next breakthrough (13-15). This was made by the cooling of xenon to -195 c and then heating to 400 c while fluorine was added. The mixture was then cooled back to -78 c.

From these experiments it was becoming evident that highly electonegative elements such as oxygen and fluorine could share or completely remove the outer shell electrons from heavier noble gases (11). Furthermore, since radon's first ionization potential is less than that of xenon and krypton, it was felt that radon would react even easier with any compound with which those gases would react (16). The original work with noble gases had been done on xenon because it was not radioactive and would be the most reactive of them except for radon. These predictions were proven correct when radon was shown to react with fluorine to produce radon fluoride (13,16).

The next advance came in the early 1970's at Argonne National Laboratory. There it was shown that bromine trifluoride and several other halogen fluorides along with some halogen fluoride-metal fluoride complexes could oxidize radon (8). It was suggested that the bromine trifluoride reaction,

$$Rn + BrF_3\text{-------}\ RnF_2 + BrF$$
$$RnF_2 + BrF_3\text{-------}\ RnF^+ + BrF_4^-$$
$$RnF^+ + BrF_3\text{-------}\ Rn^{+2} + BrF_4^-$$

could be used for the decontamination of air in uranium mines but it was hoped that a less dangerous compound might be found.

Further studies with halogen fluoride-metal fluoride complexes showed radon capable of reacting with $ClF_2^+SbF_6^-$, $BrF_2^+SbF_6^-$, $BrF_2^+BiF_6^-$, and $IF_6^+SbF_6^-$ (11). After studies had shown xenon and krypton (9) would react with some fluoronitrogen and dioxygenyl compounds it was shown that the more reactive radon would form stable compounds in reactions with dioxygenyl hexafluoroantimonate and hexafluoroiodine hexafluoroantimonate (9,10). Though the exact products of these reactions have not been analyzed it is assumed that they are analagous to the reactions with xenon and krypton. The reaction believed to occur is

$$Rn + 2\ O_2^+SbF_6^-\text{-------}\ RnF^+Sb_2F_{11}^- + 2\ O_2$$

It has been shown that dioxygenyl hexafluoroantimonate powder or pellets can be used to remove practically all (99+ %) radon from air samples containing up to 10^{-7} Ci/L (10). Stein also has shown an inverse relationship between percent radon unreacted and the square root of the contact time (10). Decreased temperatures have also shown to lower reactivity (10). Tests with water and its vapor, CO, CH_4, SO_2, NO_2, and NO have all produced reactions with $O_2^+SbF_6^-$ (17). Stein suggests that the reaction of radon with $O_2^+SbF_6^-$ is preferable to that of bromine trifluoride because $O_2^+SbF_6^-$ is a solid powder which can be stored in Pyrex or fluorinated plastic containers. It is also more efficient so smaller quantities can be used (9,10).

Stein showed the usefulness for the reaction of radon and $O_2^+SbF_6^-$ for the removal of radon from air (9,10). The purpose of this study is to apply a similar technique to remove radon from natural waters. It would seem possible to degas a solution with radon in it. Then pass the gas through a drying tube and into a container with $O_2^+SbF_6^-$. The activity could be measured using the gamma emissions of radon's daughter products, B-214 and Pb-214.

$$\mathrm{Rn}^{222}\xrightarrow[3.823d]{\alpha}\mathrm{Po}^{218}\xrightarrow[3.05m]{\alpha}\mathrm{Pb}^{214}\underset{\begin{array}{l}=.352\text{ MeV}\\ .295\\ .777\\ .053\end{array}}{\xrightarrow[26.8m]{\beta-}}\mathrm{Bi}^{214}\underset{\begin{array}{l}=.609\text{ MeV}\\ 1.764\\ .063\\ .191\end{array}}{\xrightarrow[19.8m]{\beta-,\alpha}}$$

Figure 1 shows a gamma spectra with the Pb-214 and Bi-214 peaks labeled. Radon could react with $O_2^+SbF_6^-$ to form a compound that can be transferred in the reaction vessel. This would give the advantage of being able ot use conventional counters instead of the internal counters mentioned previously. The remainder of this paper will be involved with the description, discussion, and analysis of the experiments directed at developing such a technique.

Experimental:

All chemicals used were reagent grade chemicals. Thirty grams of $O_2^+SbF_6^-$ were purchased from Atomergic Chemicals Corporation of Plainview, New York. Gamma emissions were measured on the 5.5 mm NaI (Tl) crystal of a 256-D multichannel analyzer made by The Nucleus Incorporated. The multichannel analyzer was standardized using the .667 MeV gamma emission of cesium-137. The analyzer was also equipped with region of interest (ROI) capability which gave the total activity over a set region thus eliminating the need to record data channel by channel. Emissions were measured over channels 23-70 to encompass the two main peaks of lead-214 and bismuth-214 gamma emission (.35 MeV and .61 MeV respectively) with the region of interest counter.

A 0.54×10^6 Ci/5ml radium-226 standard solution was purchased from Amersham. It was diluted to yield solutions of 2.4×10^5 dpm/L, 2.4×10^4 dpm/L, 2.4×10^3 dpm/L, 12,000 dpm/L, 2400 dpm/L, 1200 dpm/L, 240 dpm/L.

In order to develop the technique, original experiments used pitchblend as a source of high-level radon. Later, after some refinements were made, the radium standards were used. Soda lime and cobalt-silica gel were used as drying reagents in earlier experiments and ALCOA alumina beads were used in later trials. The set up used for capture of radon involved degassing a solution containing radon by using compressed air. The compressed air entered through a tube into a two liter bottle with one liter of solution and then the air stream was passed into a drying tube which contained one of the drying reagents mentioned above. The drying tube was connected to the reaction vessel which contained .1 mm glass beads coated with $O_2^+SbF_6^-$. Figure 3 shows the complete experimental apparatus. Most solutions were degassed for fifteen minutes at about 150 cm^3/min. However, the flow rate was not measured for each experiment. The flow rate was measured by catching bubbles from the gas inlet tube in an inverted graduated cylinder and measuring the amount of time required to displace a given amount of water.

The dominant portion of experiments involved developing a cartridge which would 1) not react with $O_2^+SbF_6^-$ 2) allow for capture of the radon as it passed through and 3) provide maximum counting geometry. $O_2^+SbF_6^-$ was coated on glass beads which were then funneled into the cartridges. Plastic Finn pipette tips, teflon tubing, copper tubing, 5 ml Pyrex pipettes, and 10 and 25 ml Pyrex volumetric flasks with added sidearms were all experimented with. The Finn tips were used in the form they were purchased. The coated glass beads were placed in the cartridge and it was stoppered with glass wool. Teflon tubing was cut into 5 cm segments to make cartridges which could be filled like the Finn tips. The copper was used in 15 cm segments. It was filled with coated glass beads and then after degassing had taken place, the tubing was coiled to improve counting geometry. 5 ml pipettes were prepared for use by cutting off the ends to leave only the enlarged portion of the pipette to serve as the reaction vessel. Each Pyrex volumetric flask had a glass sidearm welded to it to allow the gas to flow through.

Other experiments used tandem cartridges in order to determine if the first cartridge was collecting all of the radon. Also an experiment was performed where one cartridge was used for fifteen minutes and was then replaced by a second cartridge in order to determine whether or not the degassing time was long enough to remove all radon from the solution. The possibility of cartridge reuse composed another segment of experimentation. Cartridges were used once and were then reused after the activity had returned to approximately zero.

One spring sample was degassed to determine radon concentration. Water was collected from a spring near Bismark, Arkansas into a five gallon bottle. The bottle was filled completely and then stoppered. Upon returning to the laboratory the volume of water in the bottle was adjusted to ten liters. The sample was then degassed in the same manner as the standards had been.

Results and Discussion:

As was mentioned above the first expaeriment involved the use of pitchblend as a high-level radon souce in order to determine if radon could be captured by this method. When the activity of the compound in the cartridge was measured prominent peaks at .35 MeV and .61 MeV were seen. These peaks correspond to the energies of the gamma emissions of lead-214 and bismuth-214 respectively. Using the beginning of the .35 MeV peak and the end of the .61 MeV peak it was decided that the region of interest should be set from .23 MeV to .70 MeV. A plot af activity versus time showed that equillibrium was set up between radon and its daughter products in about four hours (see figure 2).

Experiments with the reaction vessels made of different materials and different shapes allowed the determination of the container best suited for quantifying radon. Plastic Finn tips and Teflon tubing both proved to react with the $O_2^+SbF_6^-$. Copper tubing was shown to be impractical because not enough reagent could be placed in the tube due to the tight fit of the glass beads coated with $O_2SbF_6^-$. Also the copper tubing could not be twisted into a shape that would produce good counting geometry. Pyrex pipettes and volumetric flasks showed the ability to hold sufficient amounts of reagent and not react with it. Though the 5 ml pipettes were effective at capturing radon, Their counting geometry was not as good as that of the 10 ml volumetric flask. The 10 ml volumetric did not have as good geometry as the 25 ml flask. Oviously, the larger the counting surface of the cartridge that faces the crystal the better the counting geometry.

Experiments using cartridges in tandem produced conflicting results. When done with 5 ml pipettes the second cartridge had no activity. However, the second cartridge had significant amounts of activity when the 25 ml volumetric flasks were used for a similar experiment.

The experiment in which two cartridges were used for two successive fifteen minute degassing periods on the same standard solution showed no activity in the second cartridge. This showed that all the radon was removed from the solution in the first fifteen minutes.

Since radon decays with a half-life of 3.8 days, within a 25 to 35 day period only an insignificant amount should remain in the cartridge. Also very little of the reagent is used up by the reaction with radon. There is significantly more $O_2^+SbF_6^-$ reacted by exposure to moisture in the air than by reaction with radon. Noting these facts, two experiments were designed to determine the capbility of reuing cartridges.

In each case there was a decrease in the activity of the second degassing as compared to the first. This could be due to a variation in the gas flow rate. The effects in that type of variation will be discussed later. The important reult of these experiments is that the ability to reuse the cartridges was confirmed.

Conclusion:

The counting geometry of the flat bottom of a volumetric flask is definitely the best of the cartridges studied and it is difficult to see how that could be improved. Table 1 summarizes the results of the several experiments using different cartridges.

Stein had shown the capability of detecting 2.74 counts/min-pCi (10). Sample #1 of the 25 ml volumetric flasks in this study produced 16.13 counts/min-pCi. Sample #2 showed 30.13 counts/min-pCi. Assuming the second sample is correct and only 50 counts/min can be detected accurately, then a detection limit of 1.7 pCi exists for a 1 liter sample. Sample sizes sould be enlarged to 10 liters so that as little as .17 pCi/L could be detected.

An appreciable amount of activity, 747 counts/min, was detected in the spring sample. Once again assuming that the 30.13 count/min-pCi result for sample #2 is correct, a radon concentration of 1.2 uCi/L can be calculated. This value is in the range of those reported by Kuroda (1) for mineral springs in Arkansas. Figure 4 shows the gamma spectra for the spring water sample. Peaks at .38 MeV and .63 MeV confirm the presence of radon.

As was mentioned above, the two samples using 25 ml volumetrics for cartridges and 2.54×10^5 dpm/L standards, showed a large difference in activity. Sample #1 had an activity of 1849 counts/min at equilibrium while sample #2 had 3447 counts/min. This difference of a factor of two is too large to be explained by statistical considerations. Instead, there must be some variable which has not been determined at this point. One possibility for that variable could be variability of flow rate since there was no measurement of that factor in each experiment. Stein's work had shown an inverse relation between radon reacted and contact time (10). Since flow rate is one of the factors effecting contact time an increase in flow rate would cause a decrease in the amount of radon which is reacted in the cartridge. If this relation is non-linear and the change of flow rate is in a part of the curve which has a steep slope, a small change in flow rate would result in a large change in the percent radon captured as it flows through the cartridge. Unfortunately, since the second volumetric was the last sample degassed, this variable was discovered at a point when time would not permit a chance to test this theory.

This study has shown that radon-222 can be removed from water then collected by reaction with $O_2^+SbF_6^-$. This method should be preferable to methods previously used because the reaction can take place at room temperature using small amounts of reagent, and the activity can be measured directly from the reaction vessel using commonly available counters. However, the reagent must be handled in a dry box in order to avoid contact with water vapor. The cost of $O_2^+SbF_6^-$ is another disadvantage. If the problem of variable results can be corrected by flow rate adjustment this method could be used for determining radon concentration in springs, rivers, and lakes. There is also the possibility that this method could be used to demonstrate advective movement in reservoirs.

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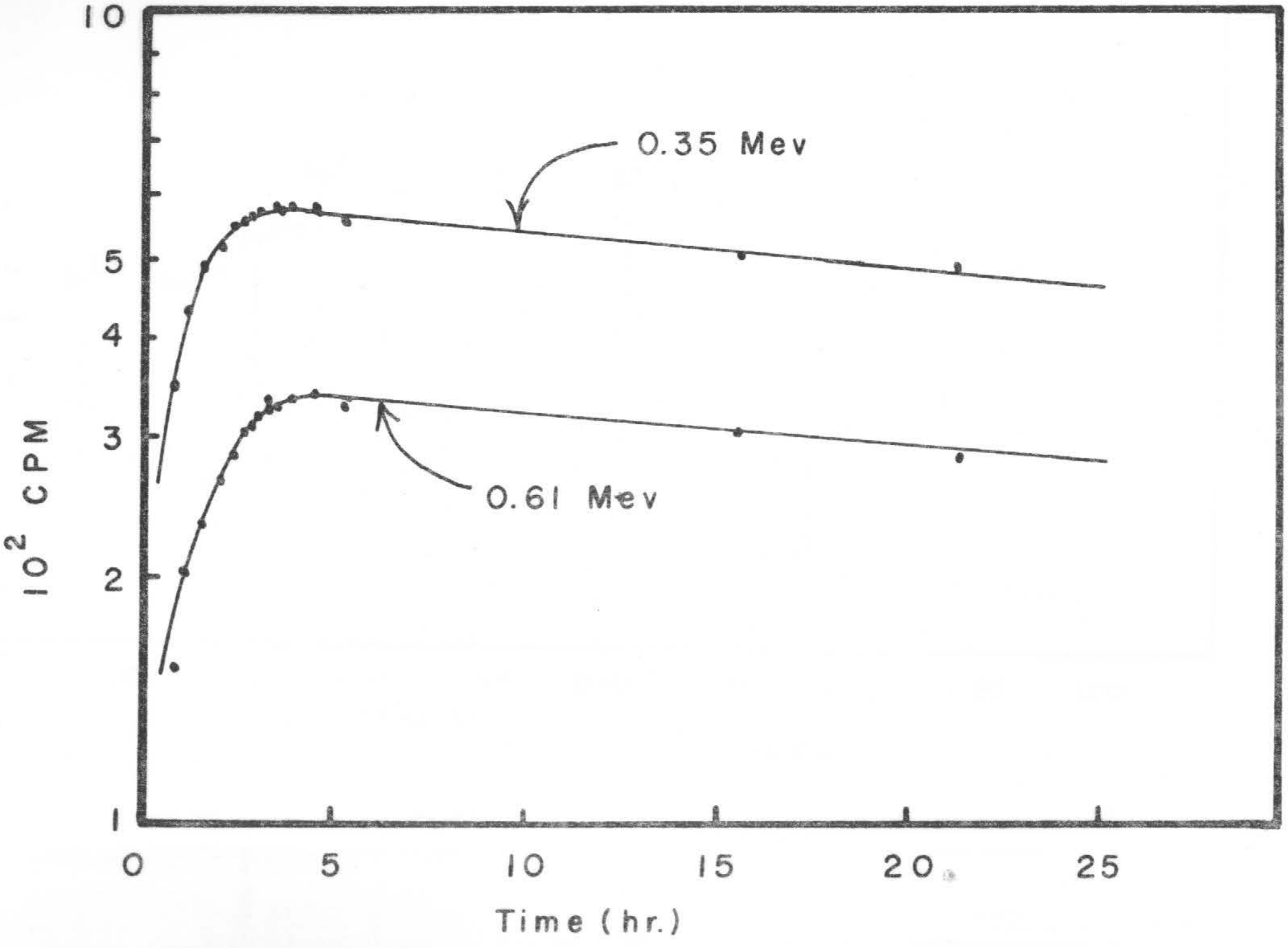
TABLE 1

Radon Source	Cartridge	cpm	cpm/pCi
pitchblend	Finn tips	508.2 ± 8.8	----------
radium-226 2.54×10^5 dpm	5 ml pipette	220.18 ± 3.3	1.93
radium-226 2.54×10^5 dpm	10 ml volumetric flask	394.2 ± 3.9	3.46
radium-226 2.54×10^5 dpm	25 ml volumetric flask #1	1850 ± 9.6	16.13
radium-226 2.54×10^5	25 ml volumetric flask #2	3447 ± 13.9	30.13
spring water	25 ml volumetric flask	360.1 ± 4.2	30.13*

For the purposes of determing the concentration of the spring water it is assumed that it has the same cpm/pCi as the second 2.54×10^5 don standard in the 25 ml volumetric.

Figure 1



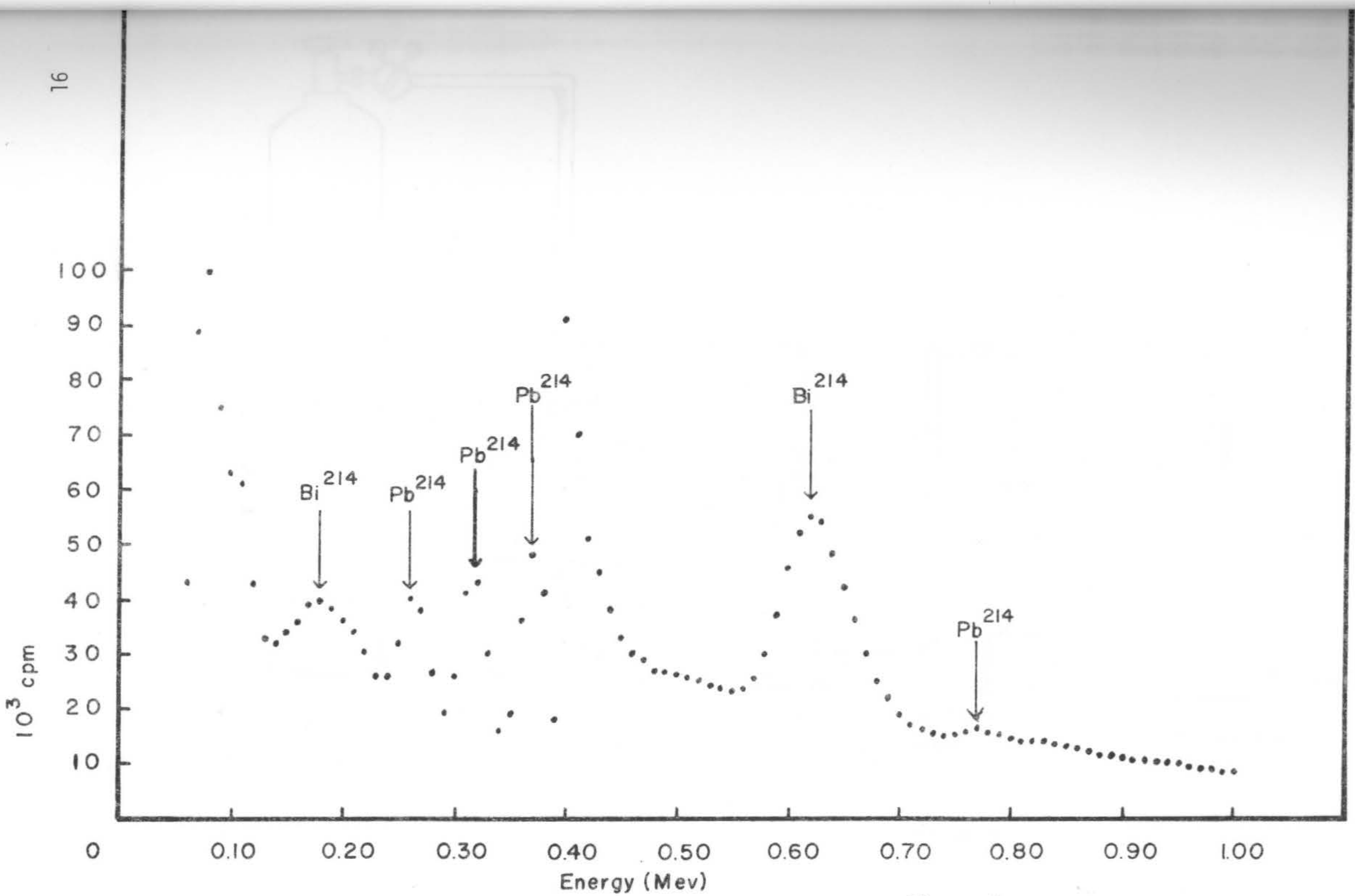

100
90
80
70
60
50
40
30
20
10
10^3 cpm
0
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
Energy (Mev)
Bi^{214}
Pb^{214}
Pb^{214}
Pb^{214}
Bi^{214}
Pb^{214}

Figure 2

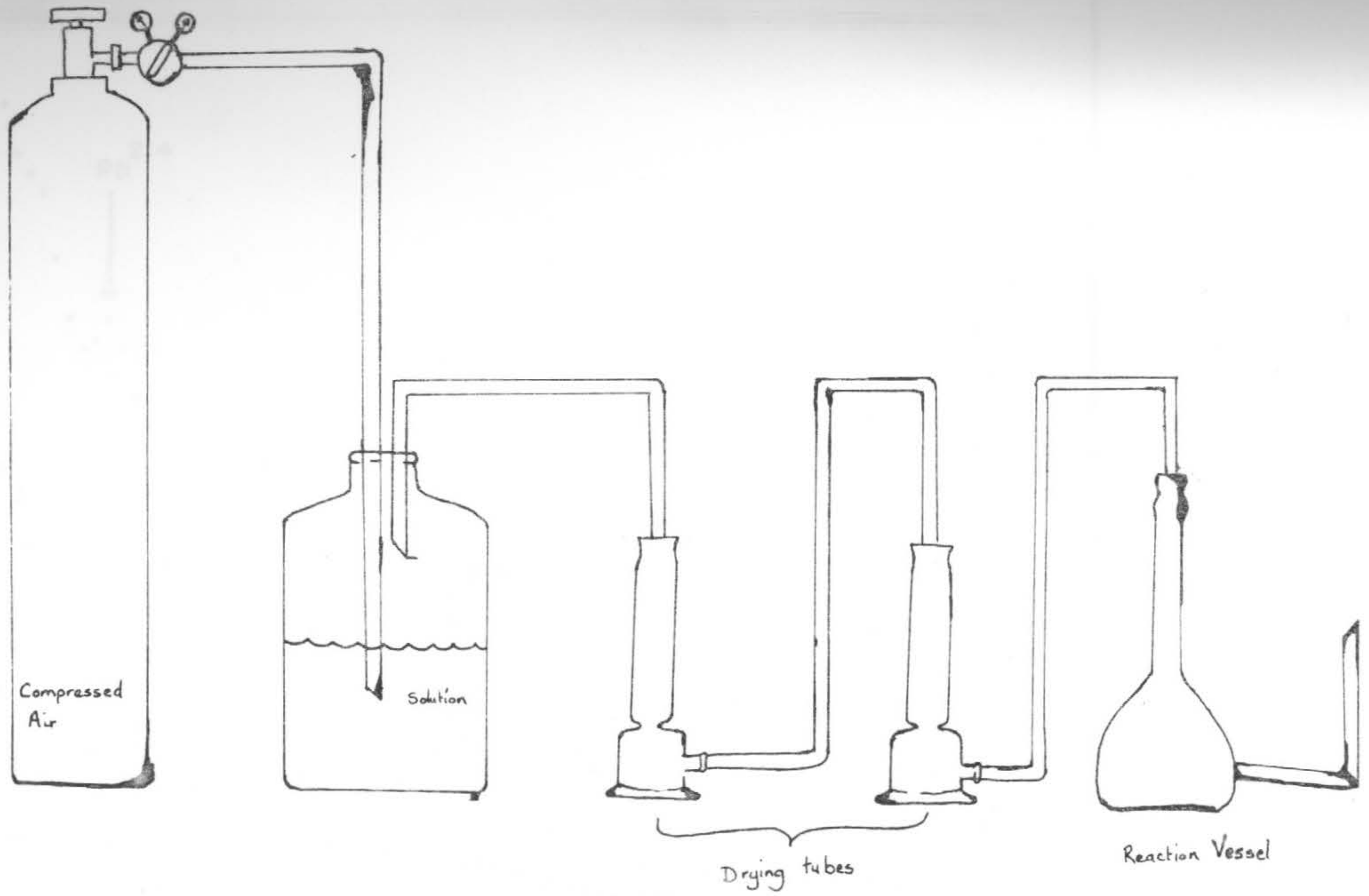


Figure 3

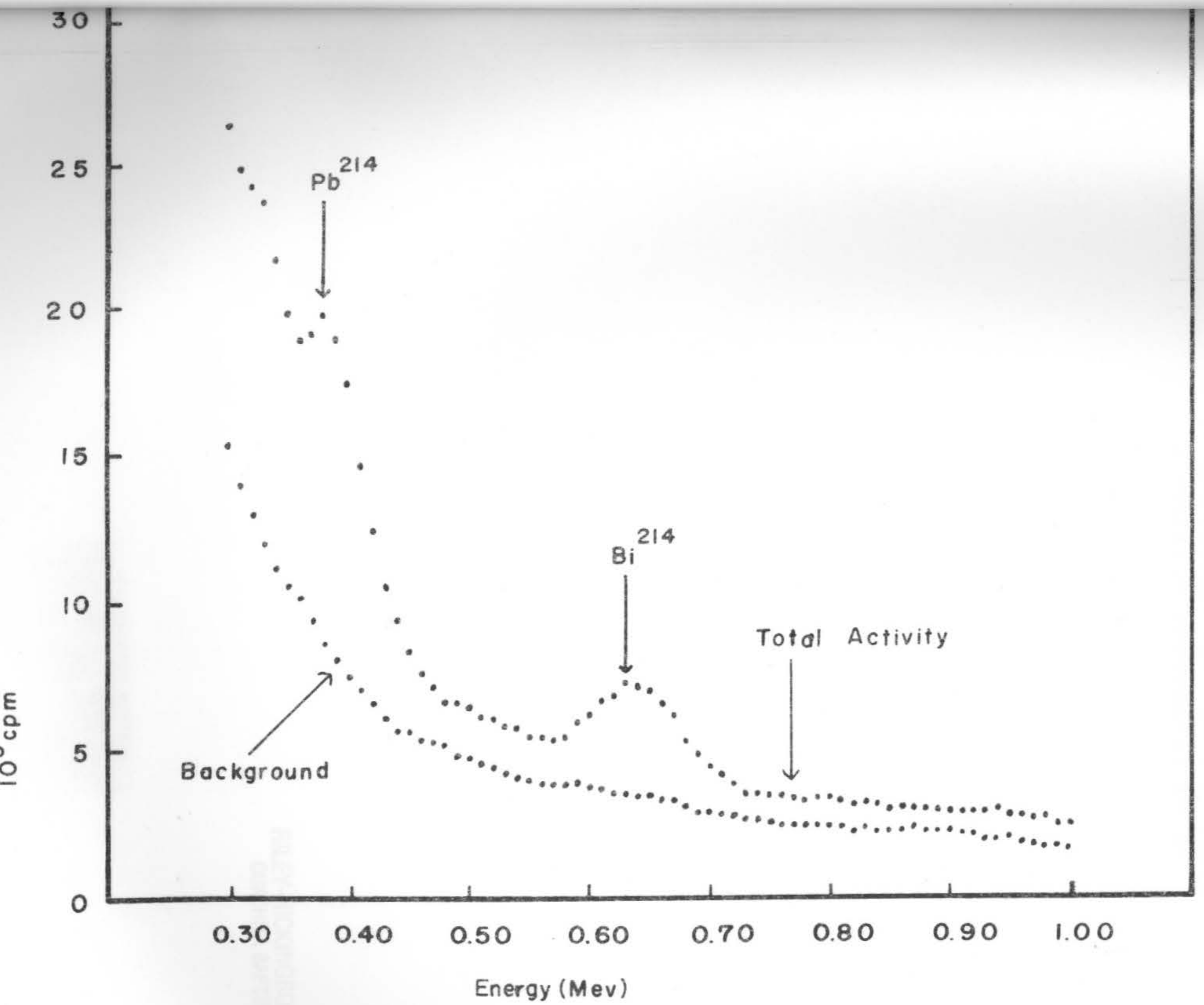

30
25
20
15
10
5
0
10^3cpm
Pb^{214}
Bi^{214}
Total Activity
Background
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
Energy (Mev)

Figure 4