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TECHNICAL INFORMATION

Radon Progeny Exposure Measurement Using Lead-210

RADON PROGENY EXPOSURE MEASUREMENT USING LEAD-210

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FOREWORD

The lead-210 Project was conceived and initiated by Aaron L. Bond, Chief, Occupational Health, Radiation Protection and Air Quality Control Division of the New Mexico Environmental Improvement Agency, in 1968. The project was aimed at the development and interpretation of liquid scintillation counting methods for the analysis of Lead-210 in uranium mine atmospheres. Work on the project was begun over a year before I started by another investigator.

My involvement with the study began in June, 1971, several months after the resignation of the previous project investigator. At the time he left he had reached the conclusion that there were anomalously high levels of Pb-210, both in mine air and the ambient air of the state. These results were anomalous, since the concentrations believed to have been found were very much higher than expected or previously reported in the literature. The ambient air levels determined from approximately 20 samples taken from every section of the state appeared to be near the MPC for Pb-210. The conclusions he was prepared to adopt were that Pb-210 cannot be used as a dosimeter, and further, that there may be a serious problem of high levels of Pb-210 in the New Mexico atmosphere.

These preliminary findings are being cited here to provide a context for this report; they were not subsequently verified by my own investigations. My task at the outset was clearly not simply to take up the work where it had left off. There were too many unresolved questions concerning the puzzling data obtained by a novel technique to accept it or the procedures which had been developed to obtain it. There had to be a reason why no previous investigator had reported as high levels of Pb-210 in the ambient air as were apparently being measured by the liquid scintillation technique. Of the several possible reasons considered, the one which had the most weight was the possibility that a serious error had been made in the calibration of the instrument and the techniques of sample preparation. It should be noted here that there was no doubt that Pb-210 could be measured by liquid scintillation techniques. That has been conclusively demonstrated by two respected radio-chemists in 1968. The difficult work yet to be accomplished was then first, to resolve the perplexities produced by the initial work on the project, and then second, if successful, to develop an application of liquid scintillation counting of Pb-210 to environmental samples containing large amounts of aerosols such as dust and carbon-black.

Given the context of the project outlined above, it was decided to make a fresh start, begin with the instrument calibration problem, and work from there. The investigation has taken the following course:

A. Instrument calibration, being the foundation for all the subsequent work, was repeated with considerable care. A certified Pb-210 standard was purchased, and it was soon found that the standard previously used for calibration purposes had been mislabeled. This would account for the apparent high concentrations of Pb-210 thought to have been observed since the efficiency of the instrument was thought to be quite low.

B. A natural outgrowth of the calibration process, which involved the separation of Pb-210 from its daughters Bi-210 and Po-210, was a possible solution to the problem of counting Pb-210 attached to interfering aerosols. The technique which proved successful was to employ a solvent extraction technique to completely separate Pb-210 away from the sample matrix for counting. Comparison with alternative procedures of measuring Pb-210 was made to determine efficiencies.

C. With a possible environmental measurement scheme under development, the next task was to construct a theoretical model for the ingrowth of Pb-210 into an atmosphere contaminated with radon under certain specified conditions. Without such a model, there was no means for comparing measured values with expected values.

D. Having some idea of what Pb-210 concentration levels to expect under certain conditions of radon and its short-lived daughter concentrations provides the opening for relating Pb-210 levels to the currently used measure of exposure, the "working level". The details of this relation were studied again under certain specified ideal conditions.

E. A problem which has proven difficult to resolve is that of determining the relation between Pb-210 activity on a sample filter which is due to the deposit of short-lived radon daughters and background Pb-210 activity which is due to the direct deposit of airborne Pb-210.

F. Another difficult problem is the development of a practical sampling program which will yield reliable data concerning actual exposure of miners to radon and its short-lived daughters under current mining conditions.

Each of these points will be discussed in considerable detail in the following report. Together they constitute a brief history of the project and provide some glimpse of the motivation for the various studies undertaken in this project.

ACKNOWLEDGEMENTS

I wish first of all to thank Mr. Edward L. Kaufman and the staff of the Radiation Protection Section of the New Mexico Environmental Improvement Agency for their encouragement and support throughout this entire project. Mr. Kaufman provided those administrative and technical supports which are vital to the successful completion of a project of this type. Mr. Mike Hill contributed much to the collection of data, both in working mines and the Agency's experimental mine.

Mr. James Cleveland and others with the Kerr McGee uranium mining operations in Grants, New Mexico, provided valuable assistance and complete cooperation in matters of obtaining samples from working mines.

The sharing of supplies and technical information by Dr. Richard Blanchard was crucial to the progress of this project at several points. His advice and encouragement are deeply appreciated.

TABLE OF CONTENTS

ABSTRACT . . . . . .

INTRODUCTION 1

PART I. Theoretical Considerations 4

A. The nature of the ingrowth of lead-210 in an atmosphere into which radon-222 is eminating

1. The case of the assumption of constant radon activity level: the first model

2. The ingrowth process in a hypothetical ventillated tunnel: the second model

3. Ingrowth in a fixed volume of air: the third model

B. The relation between the WL of the air and the contribution of radon daughters to lead-210 activity on a sample: the fourth model

C. Summary of theoretical results

PART II. Counting Technique and Sample Collection and Preparation 26

A. Instrumentation

B. An extraction technique for sample preparation for liquid scintillation counting of lead-210

C. Sample collection considerations

PART III. Environmental Investigations 35

A. Interlaboratory comparison check of dithizone extraction techniques applied to environmental samples

B. Field studies of the extent of background contributions to lead-210 samples

C. Experimental studies of lead-210 ingrowth patterns

1. The relation between WL and lead-210

2. Test of the third model

3. Tests of the second model

PART IV. Conclusions and Discussion 51

A. Liquid scintillation as a technique for counting lead-210 in mine air

B. Relating measured lead-210 to the average WL exposure

C. Applications to bioassay techniques

Appendix 1. Fairman's Ion Exchange Procedure 60

Appendix 2. Dithizone Separation Technique (Summary) 61

Translation of "The Use of Dithizone for Separation and Purification of RaDEF" by Bouissierres and Ferradini

BIBLIOGRAPHY 65

ABSTRACT

A technique for monitoring the average alpha-exposure due to the airborne decay products of radon-222 (i.e., working level) in a uranium mine atmosphere on a long term, continuous basis is described. The strategy of the approach investigated is to collect a long term, high volume sample, let the short-lived daughters decay to lead-210, and rapidly separate and count the lead-210 using liquid scintillation counting techniques. Experimental testing of the technique reveals that while countable quantities of lead-210 can be accumulated, only a fraction of the activity can be attributed to the direct collection of short-lived daughters. The remainder is shown to be due to a variety of indeterminate background sources. This result raises serious problems for any continuous monitoring technique based on measuring accumulated levels of lead-210, whether it be on an air filter or in a miner's blood.

INTRODUCTION

The principle objective of the lead-210 project is the determination of the feasibility of employing lead-210 as a quantitative indicator of exposure to radiation in uranium mine atmospheres.

The primary source of radiation exposure in uranium mines is the presence of radon-222 and its daughters in the atmosphere.

Radon-222 is a noble gas, and as such, readily diffuses into the air directly out of the ore body; or, because of its slight solubility in water, it may be transported into a mine environment via water percolation. The short-lived daughters of radon (RaA, RaB, RaC and RaC') are each both chemically and electrically active atoms, and upon formation rapidly diffuse and become attached to the first surface they encounter. Since most, if not all, aerosol particles in a mine are of respirable size (5 microns or less in diameter), essentially all the radon and its short-lived daughters in a mine atmosphere exist either as free atoms or molecules, or attached to respirable aerosols. The aerosol composition is chiefly water vapor, diesel fume, and ore dust. Under current mining practice, control of radon and its daughters is achieved by mechanically ventillating the mine with large volumes of fresh air. As a result, in many locations in a mine, particularly the haulageways mined through waste rock, the level of activity is very low and is due chiefly to radon and RaA alone. Elsewhere, there is invariably a state of disequilibrium between radon and its daughters, the principle components of a typical composition being radon, RaA and RaB, with smaller amounts of RaC.

The foregoing briefly describes the principle inhalation exposure situation in a mine atmosphere. The determination of dose from a given exposure context is a very complex matter, depending as it must, on the fraction of the various radionuclides deposited in the respiratory tract and the sites of deposition. The study which is the subject of this report, is concerned with the measurement of radiation exposure in uranium mine atmospheres, but there are certain results which have potential application to the problems of determining dose which will be discussed below.

The most widely used method for measuring exposure for purposes of ventillation control and exposure record-keeping is that developed by Kusnetz. The unit of exposure on which this method is based is the "working level", equivalently defined either as a concentration of 100 pCi/l of Rn-222 in secular equilibrium with its short-lived daughters, or as 1.3×10^5 Mev of potential alpha-energy per liter of air. The sampling procedure typically involves taking a five-minute air sample at a known sampling rate through a suitable filter medium and alpha-counting the filtered aerosol with a portable alpha-scintillation counter after an interval of decay time (optimally, at 40

minutes after the sample is taken). Clearly this procedure and the instrumentation used in the field produce certain definite constraints on the type and quality of data which can be obtained concerning a given exposure context. One result of such constraints is that the method has a lower limit of applicability at a concentration of about 0.3 WL. Below that level, the errors can be in excess of 15%. Another result, which is of particular concern as far as exposure monitoring is concerned, is that only a limited number of samples of small volume (usually 10 liters) can be practically taken and measured from a number of representative sites in a mine. From this limited amount of concentration data and other appropriate information such as stay-time of miners at given locations and certain weighting factors, a cumulative exposure value can be obtained. In spite of the fact that cumulative exposure values obtained in this fashion can be quite accurate, there is widespread agreement that much of the exposure data available is in practice, somewhat inaccurate. Sources of the errors include the difficulties with the Kusnetz method and field instrumentation already mentioned; and probably more significant are the errors introduced by infrequent WL measurements in a given exposure context, poor choice in location of samplers, and incomplete or inaccurate stay-time records. However, it has proven difficult to confidently assign magnitudes to these sources of error.

Various suggestions for improving the current exposure determination have been made, but in the absence of reliable information on the sources and magnitudes of contributing errors in these methods, there is considerable uncertainty about where to place emphasis on corrective measures.

The strategy of the present study, in order to improve exposure assessment, is to sample the air in an exposure context continuously and at a high sampling rate so as to yield a long term, high volume, integrated sample, as opposed to the usual short term, low volume, "grab sample" taken only a few times a month.

The feasibility of obtaining such a sample is based on the following considerations. Instead of sampling the mine air for the short-lived daughters of radon, the sample is collected and counted for lead-210, the first long-lived daughter. Because lead-210 has a 22 year half-life, and since the maximum concentration of activity which can be collected on an air filter is directly proportional to the mean life of the radionuclide being collected, it is the only radon daughter which has the linear accumulation properties necessary for a week or month long sampling period. A key factor in relating accumulated lead-210 activity to the WL exposure average over the same time-span would be a definite correlation between accumulated lead-210 atoms and WL which is relatively insensitive to variations in the composition of the air which has a given WL. Such a correlation will be demonstrated below. Another factor in this relation is that there must be a determinate relation between radon daughter concentrations or WL and back-

ground lead-210 concentration.

The lead-210 collected on an air sampling filter could come from (a) short-lived daughters collected from the air which decayed to lead-210 on the filter; (b) lead-210 formed from the decay daughters while in the air, and (c) resuspended aerosols or highly contaminated air which has entered the air stream from unventillated worked-out areas. Since only the fraction from source (a) is directly relatable to the average WL of the air which was sampled, some means must be provided for determining the contributions of (b) and (c). This potentially troublesome factor will be considered in some detail below.

Because lead-210 is a low energy beta emitter, special techniques must be employed to count it rapidly and efficiently. The development of liquid scintillation spectrometry to the level of standard laboratory procedure has opened the possibility for rapid, direct counting of lead-210 if appropriate sample preparation is realized. A sample preparation technique especially tailored for liquid scintillation counting of lead-210 collected in mine atmospheres has been developed during this study and will be described below.

It is in the context of the special problems associated with the determination of the exposure situation in working uranium mines, and the proposed means for dealing with them that the following detailed material is presented.

Theoretical Considerations

Part I.

A. The nature of the ingrowth of lead-210 in an atmosphere into which radon-222 is eminating:

The growth of activity of each of the decay products of radon in an atmosphere containing initially only pure radon is described by the Bateman equations. For radon and its successive decay products, the subscripts R, A, B, C, C', and D will be used and assigned to the symbols N (number of atoms), λ (decay constant), I (activity $N\lambda$), τ (mean life, $1/\lambda$) and T (half-life, $0.693/\lambda$).[1]

The form of the solution of the Bateman equations depends on the assumption made concerning the state of the parent radon. One can assume a source of radon isolated from a radium source and hence deal with a constantly decaying radon level, or one can consider the parent radon activity to be constant, which would describe fairly accurately local conditions in a well-ventilated mine where fresh radon is constantly supplied from radium in the rocks and is mixed with fresh air. This second case can be made more realistic by integrating the effects of mixing fresh air and radon over a length of tunnel. A third possibility would be to consider the case where fresh radon is eminating at a given rate into a fixed volume of air with the result that the parent radon activity is constantly increasing. This condition would describe the state of affairs in a mine where a given volume of air was stagnating such as in sealed-off, mined-out areas or even unsealed side rooms. It would also describe the situation where a given volume of air stream was moving through ore rock constantly picking up radon without any additional fresh air.

1. The case of the assumption of constant radon activity I_R = constant, has been treated by Evans.[7] These results will be cited without proof and extended to RaD. The following, then, are solutions for the growth of activity accumulating in a constant radon source:

For RaA:

$$I_A = I_R \left[1 - e^{-\lambda_A t}\right] \qquad \text{(Evans' eq. 17)} \ldots\ldots\ldots\ldots 1.$$

For RaB:

$$I_B = I_R \left[1 - \frac{\lambda_B}{\lambda_B - \lambda_A} e^{-\lambda_A t} - \frac{\lambda_A}{\lambda_A - \lambda_B} e^{-\lambda_B t}\right] \text{(Evans' eq. 18)} \ldots 2.$$

For RaC:

$$I_C = I_R \left[1 - \frac{\lambda_B}{\lambda_B-\lambda_A} \cdot \frac{\lambda_C}{\lambda_C-\lambda_A} e^{-\lambda_A t} - \frac{\lambda_A}{\lambda_A-\lambda_B} \cdot \frac{\lambda_C}{\lambda_C-\lambda_B} e^{-\lambda_B t} - \frac{\lambda_A}{\lambda_A-\lambda_C} \cdot \frac{\lambda_B}{\lambda_B-\lambda_C} e^{-\lambda_C t} \right]$$ (Evans' eq. 19)..... 3.

For RaC':

$I_{C'} = I_C$ (on account of the very short half-life of RaC')
(Evans' eq. 20)..... 4.

To extend this series to RaD, it requires the solution of the equation,

$$\frac{dN}{dt} D = N_C\lambda_C - N_D\lambda_D \quad \text{..... 5.}$$

For the successive coefficients of the expoentials in line 3, writing K_1, K_2, K_3; and substituting into line 5, we have:

$$\frac{dN}{dt} D = I_R \left[1 - K_1 e^{-\lambda_A t} - K_2 e^{-\lambda_B t} - K_3 e^{-\lambda_C t} \right] - N_D\lambda_D \quad \text{..... 6.}$$

OR

$$\frac{dN}{dt} D + N_D\lambda_D = I_R \left[1 - K_1 e^{-\lambda_A t} - K_2 e^{-\lambda_B t} - K_3 e^{-\lambda_C t} \right] \quad \text{..... 7.}$$

Multiplying 7. through by the integrating factor $e^{\int \lambda_D dt} = e^{\lambda_D t}$, and integrating:

$$N_D e^{\lambda_D t} = \int I_R \left[1 - K_1 e^{-\lambda_A t} - K_2 e^{-\lambda_B t} - K_3 e^{-\lambda_C t} \right] e^{\lambda_D t} dt + C \quad \text{.... 8.}$$

$$N_D e^{\lambda_D t} = I_R \left[\frac{e^{\lambda_D t}}{\lambda_D} - \frac{K_1 e^{(\lambda_D-\lambda_A)t}}{\lambda_D-\lambda_A} - \frac{K_2 e^{(\lambda_D-\lambda_B)t}}{\lambda_D-\lambda_B} - \frac{K_3 e^{(\lambda_D-\lambda_C)t}}{\lambda_D-\lambda_C} \right] + C$$

..... 9.

Assuming that when t=0, N_D=0, the integrating constant is:

$$C = I_R \left(\frac{K_1}{\lambda_D-\lambda_A} + \frac{K_2}{\lambda_D-\lambda_B} + \frac{K_3}{\lambda_D-\lambda_C} - \frac{1}{\lambda_D} \right) \quad \ldots\ldots\ldots 10.$$

Dividing out $e^{\lambda_D t}$ and substituting in C:

$$N_D = I_R \left[\frac{1}{\lambda_D} - \frac{K_1 e^{-\lambda_A t}}{\lambda_D-\lambda_A} - \frac{K_2 e^{-\lambda_B t}}{\lambda_D-\lambda_B} - \frac{K_3 e^{-\lambda_C t}}{\lambda_D-\lambda_C} \left(+ \frac{K_1}{\lambda_D-\lambda_A} + \frac{K_2}{\lambda_D-\lambda_B} + \right. \right.$$

$$\left. \left. \frac{K_3}{\lambda_D-\lambda_C} - \frac{1}{\lambda_D} \right) e^{-\lambda_D t} \right] \ldots\ldots\ldots 11.$$

Multiplying through by λ_D and collecting:

$$\lambda_D N_D = I_R \left[1 - \frac{K_1}{\lambda_D-\lambda_A} \left(e^{-\lambda_A t} - e^{-\lambda_D t} \right) - \frac{K_2}{\lambda_D-\lambda_B} \left(e^{-\lambda_B t} - e^{-\lambda_D t} \right) - \right.$$

$$\left. \frac{K_3}{\lambda_D-\lambda_C} \left(e^{-\lambda_C t} - e^{-\lambda_D t} \right) \right] \quad \ldots\ldots\ldots 12.$$

Substituting for K_1, K_2, K_3:

$$\lambda_D N_D = I_D = I_R \left[1 - \frac{\lambda_B \cdot \lambda_C}{(\lambda_D-\lambda_A)} \frac{\left(e^{-\lambda_A t} - e^{-\lambda_D t} \right)}{(\lambda_B-\lambda_A)(\lambda_C-\lambda_A)} - \frac{\lambda_A \cdot \lambda_C}{(\lambda_D-\lambda_B)} \frac{\left(e^{-\lambda_B t} - e^{-\lambda_D t} \right)}{(\lambda_A-\lambda_B)(\lambda_C-\lambda_B)} - \right.$$

$$\left. \frac{\lambda_A \cdot \lambda_B}{(\lambda_D-\lambda_C)} \frac{\left(e^{-\lambda_C t} - e^{-\lambda_D t} \right)}{(\lambda_A-\lambda_C)(\lambda_B-\lambda_C)} - e^{-\lambda_D t} \right]$$

This can be put into symmetrical form following Bateman, (H. Bateman, Proc. Cambridge Phil. Soc., 15:423 (1910):

$$I_D = I_R \left[1 - \frac{\lambda_B}{\lambda_B-\lambda_A} \cdot \frac{\lambda_C}{\lambda_C-\lambda_A} \cdot \frac{\lambda_D}{\lambda_D-\lambda_A} \cdot e^{-\lambda_A t} - \frac{\lambda_A}{\lambda_A-\lambda_B} \cdot \frac{\lambda_C}{\lambda_C-\lambda_B} \cdot \frac{\lambda_D}{\lambda_D-\lambda_C} \cdot e^{-\lambda_B t} - \frac{\lambda_A}{\lambda_A-\lambda_D} \cdot \frac{\lambda_B}{\lambda_B-\lambda_D} \cdot \frac{\lambda_C}{\lambda_C-\lambda_D} \cdot e^{-\lambda_D t} \right] \quad \ldots\ldots\ldots\ldots\ldots 13.$$

From this it can be seen that, since $\lambda_A > \lambda_C > \lambda_B >> \lambda_D$, for times on the order of even 10 mean lives of the longest lived of the group RaA, RaC ($\sim$ 386 min.), this expression simplifies to:

$$I_D = I_R \left(1 - e^{-\lambda_D t} \right) \quad \ldots\ldots\ldots\ldots\ldots 14.$$

This result indicates that under the assumption of conditions under which the radon activity would stay constant in a given volume of air, a very long time would elapse before the RaD activity level would even approach the level of activity of the radon. See Table 1 for a numerical example. Of course, the atom concentration of RaD would increase quite a bit faster due to the very low specific activity of RaD. In a sense, the atom concentration is actually of more interest than the activity concentration. The point is that we are concerned not with exposure to RaD, but with the use of it as an indicator of exposure to the short-lived daughters. This result will be referred to below as the first model for RaD ingrowth.

2. Now it should be noted that there is something odd about the condition of constant radon activity concentration in a given mine context. The oddity is the fact that the condition of uniform concentration of radon is assumed to be the result of the combined processes of constant emination of radon into the mine air and constant dilution of radon with ventilation air. Under such assumption, the static radon concentration condition is strictly only a local condition; in as much as, if one were to go from place to place in a mine, the radon level would be different (higher or lower depending on whether one is moving downstream or upstream in the air current), but constant in time for each location. Accordingly, it doesn't make sense to calculate the ingrowth of daughters in a constant radon source and imagine it to apply to a given location in a mine over a period of time. Rather, for that location, under specified conditions of radon emination rate and ventilation rate, the radon concentration, and concen-

TABLE 1

Predicted Lead-210 Ingrowth in a Tunnel Atmosphere From the Decay of Radon Daughters in the Air According to the First Model.

Assumptions:

1. The parent radon source is of constant activity: I_R = 100 pCi/l.

2. No plate-out of daughters.

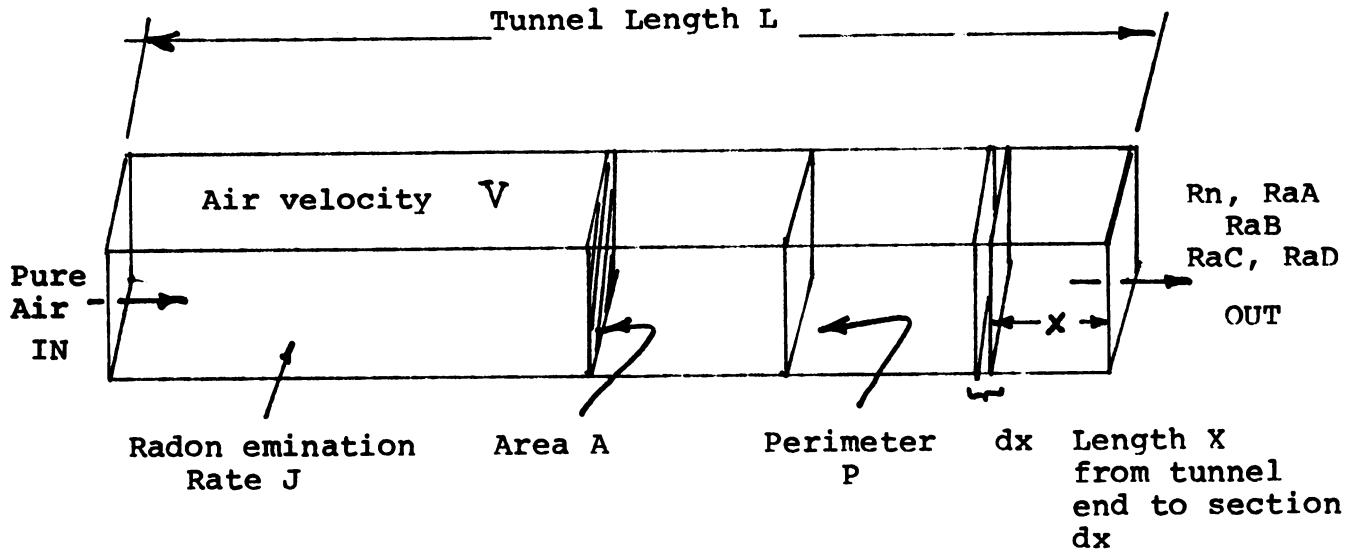
Elapsed time t min.	RaD concentration I_D pCi/l
10	5.94×10^{-5}
100	5.94×10^{-4}
10,000	5.94×10^{-3}
100,000	5.94×10^{-1}
500,000	2.93
10^6	5.76
10^8	99.73

Clearly the ingrowth rate is very slow according to this model, and the maximum concentration will never exceed 100 pCi/l.

tration of each of the daughters as well, will be nearly a constant. The degree of equilibrium between the parent radon and each of the daughters will depend principally, then, on the distance of the given location from the source of fresh air and the rate at which the air moves through the mine.

A model which describes the growth of radon daughters in a ventilated mine has been developed by Thomas and Epps.[8] Given the above derivation of RaD ingrowth in a constant radon source, the extension of the Thomas and Epps tunnel model to include RaD is straight forward.

Here the same notation and tunnel parameters, as shown in the sketch of the hypothetical mine tunnel below, will be used.



As the authors point out, the radon concentration at the tunnel end is composed of radon of different ages, so the equations giving concentrations of radon daughters as a function of radon age must be integrated over the different radon ages to get the daughter concentrations. From an area Pdx cm^2 in the tunnel, there will eminate JPdx pCi/min of radon, and this radon will be diluted into a volume VA cm^3/min of air.

Hence from each section dx of the tunnel, there will be produced a concentration of JPdx/VA pCi/cm^3 at the tunnel end. Hence,

$$dI_R = \frac{JPdx}{VA} \qquad \text{..... 15.}$$

The age of this radon concentration is X/V=t min. Using the approximation of equation 14 above,

$$I_D = I_R \left(1 - e^{-\lambda_D t} \right),$$

an expression for I_D at the tunnel end can be derived. Since here each infinitesimal radon concentration at the tunnel end has a different age t, this equation must be rewritten in differential form:

$$dI_D = dI_R \left(1 - e^{-\lambda_D t} \right) \qquad \ldots\ldots\ldots 16.$$

Combining lines 15 and 16 and integrating from t=0 to t=T, the time of flight for the entire tunnel,

$$I_D = \int_{t=0}^{t=T} \left(1 - e^{-\lambda_D t} \right) \frac{JP}{VA}\, dx \qquad \ldots\ldots\ldots 17.$$

Since x=Vt, dX=Vdt, and when X=L, t=T, line 17 can be rewritten as,

$$I_D = \frac{JP}{A} \int_{t=0}^{t=T} \left(1 - e^{-\lambda_D t} \right) dt \qquad \ldots\ldots\ldots 18.$$

Integrating:

$$I_D = \frac{JP}{A} \left[T - \frac{1}{\lambda_D} \left(1 - e^{-\lambda_D T} \right) \right] \qquad \ldots\ldots\ldots 19.$$

This equation is the second model for RaD ingrowth.

Using this equation, expected concentrations at various locations in a mine can be calculated under ideal assumptions concerning loss of daughters due to plate out, uniform air flow, uniform tunnel cross-section, smooth tunnel walls and so forth. The results of detailed calculations from this model are presented in Table 2. These results will be discussed along with the results of the third model which will be analyzed next.

TABLE 2

Predicted Lead-210 Ingrowth in a Tunnel Atmosphere From the Decay of Radon Daughters According to the Second Model.

Assumptions:

1. 8' x 10' tunnel, ventilation rate = 50,000 CFM.
2. T = 30 pCi/cm^2 min of Rn-222.
3. T = time of flight in tunnel.
4. No plate-out.

T min.	I_D (pCi/l) @ J=30
1.0	1.32×10^{-5}
5.0	3.28×10^{-4}
10.0	1.31×10^{-3}
15.0	2.94×10^{-3}
20.0	5.30×10^{-3}
50.0	3.28×10^{-2}
70.0	6.44×10^{-2}
100.0	1.31×10^{-1}

On this model, airborne background RaD due to the prompt decay of radon daughters increases very rapidly: A 10^4 fold increase in I_D with a 10^2 fold increase in time of flight in the tunnel.

3. The third case, which for example, has bearing on the problem of determining the contribution of stale mine air to background RaD, is that of the ingrowth of RaD in a volume of air having a constantly increasing radon level. In other words, suppose the following situation--given a fixed volume of air, which at time t=0 has no radon or daughters, let radon eminate into it at a fixed rate (say, K atoms/min.). What is the nature of the ingrowth of the radon daughters RaA through RaD under these circumstances?

The prescribed conditions have the following consequence--that the time rate of change in the number of radon atoms equals the rate of decay due to their being radioactive. Mathematically,

$$\frac{dN_R}{dt} = K - N_R\lambda_R \qquad \text{..... 20.}$$

proceeding as before

$$\frac{dN_R}{dt} + N_R\lambda_R = K$$

$$\frac{d}{dt}\left(N_R e^{\lambda_R t}\right) = Ke^{\lambda_R t}$$

$$N_R e^{\lambda_R t} = \frac{K}{\lambda_R} e^{\lambda_R t} + C'$$

where C' is the constant of integration. When t=0, $N_R = 0$, so $C' = K/R$, hence,

$$N_R e^{\lambda_R t} = \frac{K}{\lambda_R} e^{\lambda_R t} - \frac{K}{\lambda_R}$$

$$N_R = \frac{K}{\lambda_R} - \frac{K}{\lambda_R} e^{-\lambda_R t}$$

$$I_R = N_R\lambda_R = K\left(1 - e^{-\lambda_R t}\right) \qquad \text{..... 21.}$$

From this result, we see that the condition for maximum activity is just as one would expect--it is when the rate at which atoms are entering the volume, K, equals the rate at which they are leaving, I_R. Noting now that line 21 has exactly the same form as line 1, the equation for the ingrowth of RaA from a constant source of radon, we can proceed to write down by inspection the growth equation for RaA, RaB, and RaC under these new circumstances:

For RaA:

$$I_A = K\left[1 - \frac{\lambda_A}{\lambda_A-\lambda_R} e^{-\lambda_R t} - \frac{\lambda_R}{\lambda_R-\lambda_A} e^{-\lambda_A t}\right] \qquad \text{(from 2.)} \qquad \ldots\ldots\ldots 22.$$

For RaB:

$$I_B = K\left[1 - \frac{\lambda_A}{\lambda_A-\lambda_R}\cdot\frac{\lambda_B}{\lambda_B-\lambda_R} e^{-\lambda_R t} - \frac{\lambda_R}{\lambda_R-\lambda_A}\cdot\frac{\lambda_B}{\lambda_B-\lambda_A} e^{-\lambda_A t} - \frac{\lambda_R}{\lambda_R-\lambda_B}\cdot\frac{\lambda_A}{\lambda_A-\lambda_B} e^{-\lambda_B t}\right] \qquad \text{(from 3.)} \qquad \ldots\ldots\ldots 23.$$

For RaC:

$$I_C = K\left[1 - \frac{\lambda_A}{\lambda_A-\lambda_R}\cdot\frac{\lambda_B}{\lambda_B-\lambda_R}\cdot\frac{\lambda_C}{\lambda_C-\lambda_R} e^{-\lambda_R t} - \frac{\lambda_R}{\lambda_R-\lambda_B}\cdot\frac{\lambda_B}{\lambda_B-\lambda_A}\cdot\frac{\lambda_C}{\lambda_C-\lambda_A} e^{-\lambda_A t} - \frac{\lambda_R}{\lambda_R-\lambda_B}\cdot\frac{\lambda_A}{\lambda_A-\lambda_B}\cdot\frac{\lambda_C}{\lambda_C-\lambda_B} e^{-\lambda_B t} - \frac{\lambda_R}{\lambda_R-\lambda_C}\cdot\frac{\lambda_A}{\lambda_A-\lambda_C}\cdot\frac{\lambda_B}{\lambda_B-\lambda_C} e^{-\lambda_C t}\right] \qquad \ldots\ldots 24.$$

Then, following the pattern implicit in equations 21, 22, 23 and 24, we can write the extension of this analysis to RaD:

$$I_D = K\left[1 - \frac{\lambda_A}{\lambda_A-\lambda_R}\cdot\frac{\lambda_B}{\lambda_B-\lambda_R}\cdot\frac{\lambda_C}{\lambda_C-\lambda_R}\cdot\frac{\lambda_D}{\lambda_D-\lambda_R} e^{-\lambda_R t} - \frac{\lambda_R}{\lambda_R-\lambda_A}\cdot\frac{\lambda_B}{\lambda_B-\lambda_A}\cdot\frac{\lambda_C}{\lambda_C-\lambda_A}\cdot\right.$$

$$\frac{\lambda_D}{\lambda_D-\lambda_A} e^{-\lambda_A t} - \frac{\lambda_R}{\lambda_R-\lambda_B} \cdot \frac{\lambda_A}{\lambda_A-\lambda_B} \cdot \frac{\lambda_C}{\lambda_C-\lambda_B} \cdot \frac{\lambda_D}{\lambda_D-\lambda_B} e^{-\lambda_B t} - \frac{\lambda_R}{\lambda_R-\lambda_C} \cdot$$

$$\frac{\lambda_A}{\lambda_A-\lambda_C} \cdot \frac{\lambda_B}{\lambda_B-\lambda_C} \cdot \frac{\lambda_D}{\lambda_D-\lambda_C} e^{-\lambda_C t} - \frac{\lambda_R}{\lambda_R-\lambda_D} \cdot \frac{\lambda_A}{\lambda_A-\lambda_D} \cdot \frac{\lambda_B}{\lambda_B-\lambda_D} \cdot$$

$$\left. \frac{\lambda_C}{\lambda_C-\lambda_D} e^{-\lambda_D t} \right) \qquad \text{..... 25.}$$

But once again, since $\lambda_A > \lambda_C > \lambda_B > \lambda_R >> \lambda_D$, for times on the order of several half-lives of the short-lived daughters, line 25 reduces to:

$$I_D = N_D\lambda_D = K \left(1 + \frac{\lambda_D}{\lambda_R-\lambda_D} e^{-\lambda_R t} - \frac{\lambda_R}{\lambda_R-\lambda_D} e^{-\lambda_D t} \right) \qquad \text{..... 26.}$$

Numerical values for this equation are tabulated in Table 3 under ideal assumptions which parallel those used in the previous models. The particular values would perhaps reflect the situation one would find in a sealed-off abandoned section of a mine. Line 26 is the third RaD ingrowth model.

4. There are several conclusions which can be drawn from an examination and comparison of the three models of RaD ingrowth just described.

   First of all, the simplest ingrowth model would lead one to anticipate that the RaD level in a working mine (where the radon and daughter concentrations are kept low by ventilation) would be extremely low, even under ideal conditions. On the basis of this model one might be tempted to suppose that one could sample the mine air at various locations, trap out the short-lived daughters and let them decay to RaD on the filter, and count them indirectly in this fashion with negligible contribution of RaD from the decay of daughters to RaD in the air stream as it moves through the mine. Moreover, one would suppose that the variation in background RaD, whatever it was, would be relatively slight at least as far as the contribution from the prompt decay of daughters to RaD in the air is concerned.

   But if we look at the second model, which integrates the effects of increasing the air burden of radon and aging it as a given volume of air

TABLE 3

Predicted Lead-210 Ingrowth in a Sealed Tunnel Atmosphere From the Decay of Radon Daughters According to the Third Model.

Assumptions:

1. 8' x 10' tunnel, 1 mile long.
2. No ventilation, no plate-out of daughters.
3. $J = 30$ pCi/cm^2 min. of Rn-222.
4. At $t = 0$, $I_D = 0$.

Time Since Mine Was Sealed t Min.	RaD Concentration pCi/l
1	1.313×10^{-3}
10	1.313×10^{-1}
100	1.306×10^{-1}
1000	1.30×10^{-3}

On this model, RaD concentrations will build up very quickly and continue to grow to very high levels in stagnant air into which radon gas is constantly eminating.

moves through a mine tunnel, we see that surprisingly high concentrations of RaD can accumulate very quickly and increase appreciably as one moves down the tunnel. Of course, the numbers in Table 2 are probably high on account of the assumption of no plate-out. If a plate-out effect is assumed which reduces the effective emination rate of radon by several orders of magnitude, then more modest levels of RaD result, levels which are more realistic given the known rapid plate-out processes which occur, and which are closer to measured values. These tables reveal another important effect of integrating the contributions along a mine tunnel, namely, that the expected background RaD concentrations resulting from the decay of the short-lived daughters while in the air will increase 10 to 100 times going from the 1/8 mile location to the 1 mile location in the tunnel. The rate of increase is seen to vary depending on the emination rate assumed. Thus one cannot, for example, measure the RaD concentrations near the beginning and end of a tunnel and from the difference arrive at a number which represents an "average" for the whole tunnel. Put another way, each sampling location would, on this model, have a particular RaD background due to the decay of airborne daughters, a value which may be several times higher or lower than other locations depending on relative positions in the air course. Certainly the background RaD situation is not entirely accounted for by the ingrowth of RaD from airborne short-lived daughters. Probably much more comes from the leakage of stale air from poorly ventilated areas or sealed-off, worked out portions of a mine. Table 3, generated from the third model, shows that very large concentrations of RaD can accumulate quickly in such areas. Even small leaks through bulkheads could contribute comparatively large quantities of RaD to the air stream.

A detailed model of a working mine aimed at providing a theoretical basis for analyzing the RaD sampling problem would have to be built on the assumption that the processes described in the last two models were both going on.

B. <u>The relation between accumulated RaD on a filter bed and working level of radon contaminated air</u>:

1. Thus far, only the problem of building mathematical models of the ingrowth of RaD in a radon atmosphere has been addressed, along with the immediate application to the question of assigning a magnitude to background levels. But what is the relation between the levels of concentration of the three short-lived daughters, which are responsible for the principle exposure in a mine, and the RaD that would be measured on an air filter sample of the air containing those radionuclides?

   There are three sources of accumulated RaD on a filter: airborne RaD from the prompt decay of radon and daughters, resuspended RaD in dust or RaD in stale air leaks, and finally, the decay of accumulated quantities of RaA, RaB, and RaC from the air being sampled. Ignoring

for the moment the background contributions of the first two sources, we will consider the relation between the last source alone and accumulated RaD. It is this relation which is a key to the use of RaD as an indicator of exposure in a mine.

Conceivably, the relation could be quite complex since there are, in effect, three sources of potential RaD atoms in the air at one time, and equilibrium mixtures of these three with the parent radon are never observed in well-ventilated working areas of mines. The ideal relation would be to develop a one parameter correlate between RaD activity on a sample and the combined activities of the short-lived daughters. The "Working Level" (WL) is the standard single parameter of exposure in use today, so it is a likely candidate for the needed correlate in this context. The WL is defined as any combination of the short-lived decay products (RaA, RaB, RaC, and RaC') in one liter of air that will result in the ultimate emission by them of 1.3×10^5 MeV of alpha-ray energy. The value of 1.3×10^5 MeV potential alpha energy is derived from summing the alpha-decay energy emitted by the decay of 100 pCi each of RaA, RaB, and RaC through RaC'.

In the following discussion, it will be shown that there is a direct correlation between Lead-210 accumulated on a filter bed (including the lung, for example) and the working level (WL) of air the filter was exposed to, based on the assumptions listed below. The correlation is practically (but not absolutely) independent of the radon and short-lived daughter concentrations and age of the air at the given WL. The relation is a power relation of the form:

$$N_T = A\ (WL)^b$$

Where N_T is the ultimate number of Pb-210 atoms which would accumulate on a filter (assuming 100% efficiency of collection) per liter of air sampled which had a given WL.

The analysis will be made using the following procedures and assumptions:

a) It will be assumed that a given radon concentration is a constant over the times involved.

b) Any mixture being sampled will be assumed to be in state of stable disequilibrium or equilibrium. Thus, for example, if it is three minute old air which is being sampled, in the sense that the radon has aged three minutes before being sampled, it will be assumed that all the air sampled was this old even if the sampling extended over a week's time.

c) Every parent atom will be assumed to become a daughter without loss due to plate-out.

d) It will be assumed that the only sources of Pb-210 on the filter are the radon daughters.

e) The calculations are intended to be heuristic only, and hence, are partly analytic, partly numerical and graphic.

Under these assumptions, we have the following sampling situation:

There are a certain number of RaA atoms (N_A), a number of RaB atoms (N_B), and a certain number of RaC atoms (N_C), per liter of air due to the decay of radon gas over a given period of time. (This number can be quantified conveniently as the number of atoms per liter per 100 pCi of radon per liter. This seems awkward, but is the procedure followed by R. Evans in his "Engineer's Guide to the Elementary Behavior of Radon Daughters", Health Physics, 17 (1969), and leads to a number of simplifications). Each of these radon daughter atoms which is collected becomes a Pb-210 atom on the filter, and due to the long half-life of Pb-210 (22 years), remains on the filter as Pb-210. Thus, per liter of air sampled, the eventual number of Pb-210 atoms on a filter, N_T, will be:

$$N_T = N_A + N_B + N_C \quad \ldots\ldots\ldots 27.$$

where

$$N_A = I_A\ (2.22)\ \left[\tau_A\right]$$

OR

$$N_A = 9.77\ I_A \quad \ldots\ldots\ldots 28.$$

and similarly

$$N_B = 85.8\ I_B \quad \ldots\ldots\ldots 29.$$

$$N_C = 63.1\ I_C \quad \ldots\ldots\ldots 30.$$

By definition of the working level

$$WL = 0.00103\ I_A + 0.00507\ I_B + 0.00373\ I_C \quad \ldots\ldots\ldots 31.$$

(See Evans p. 240)

Substitution of 28, 29, 30 into 31 yields:

$$WL = 0.000105\ N_A + 0.000059\ N_B + 0.000059\ N_C \quad \ldots\ldots\ldots 32.$$

As a check, the accumulated decay products per 100 pCi Rn-222 per liter, are $N_A = 483$, $N_B = 176$, $N_C = 5$ and the WL should be 0.061.

Substitution above yields:

WL = 0.0507 + 0.0138 + 0.00029 = 0.065 (a difference of only 0.05%)

Let $K_1 = 0.000105$ and $K_2 = 0.000059$, then line 32 becomes:

$$WL = \left(K_1 \cdot N_A\right) + \left(K_2 \cdot N_B\right) + \left(K_2 \cdot N_C\right) \quad \ldots\ldots\ldots 33.$$

Substitution from 33 into 27 gives N_T as a function of WL:

$$N_T = \left[WL - K_2\left(N_B + N_C\right)\right] / K_1 + \left(WL - K_1N_A - K_2N_C\right) / K_2 + \left(WL - K_1N_A - K_2N_B\right) / K_2 = WL/K_1 + 2WL/K_2 - K_2\left(N_B + N_C\right)/K_1 - 2K_1N_A/K_2 - N_C - N_B$$

$$N_T = WL\left(K_2 + 2K_1\right)/K_1 \cdot K_2 - \frac{2K_1}{K_2} N_A + \left(\frac{K_2}{K_1} + 1\right)N_B + \left(\frac{K_2}{K_1} + 1\right) N_C \quad \ldots\ldots\ldots 34.$$

Line 34 gives us an expression for the total number of potential Pb-210 atoms (N_T) per liter of air sampled as a function of WL, N_A, N_B and N_C and age of air implicity since there is a unique correlation between all these terms only for a given decay period. Now we ask, (in anticipation of the result to be shown), is the variation in N_T with respects to WL a simple one--constant, for example? We will consider a number of particular cases and then generalize. For a particular fixed time t_1, our question translates into the problem of evaluating $\partial N_T/\partial WL$ at $t = t_1$.

From line 8, we have, taking derivatives of both sides, for $t=t_1$:

$$\frac{\partial N_T}{\partial WL} = \left(\frac{K_2 + 2K_1}{K_1 K_2}\right) - \frac{2K_1}{K_2} \frac{\partial N_A}{\partial WL} + \left(\frac{K_2 + K_1}{K_1}\right) \frac{\partial N_B}{\partial WL} + \left(\frac{K_2 + K_1}{K_1}\right) \frac{\partial N_C}{\partial WL} \quad \ldots\ldots 35.$$

The first term is a constant, so to evaluate this derivative $\frac{N_A}{WL}$, $\frac{N_B}{WL}$ and $\frac{N_C}{WL}$ must be determined first. This can be done for particular times numerically rather easily. Referring to the next table which tabulates N_A, N_B, N_C and WL:

	Concentrations per 100 pCi Rn/l				Slopes at Specific Times		
t	N_A	N_B	N_C	WL	$\frac{dN_A}{dWL}$	$\frac{dN_B}{dWL}$	$\frac{dN_C}{dWL}$
3	483	176	5	0.061	7,918	2,885.2	81.9
10	876	1219	114	0.17	5,152.9	7,170.6	670.5
15	950	1970	296	0.25	3,800	7,880	1,184
20	960	2720	541	0.3	9,200	9,066	1,803.3
30	965	4120	1158	0.42	2,297	9,809	2,757

On the left as functions of time, it can readily be seen that, for example, since these values are in terms of units per 100 pCi Rn per liter, 20 min. air containing 500 pCi Rn per liter will have 4800 atoms RaA per liter, and so on, and 1.5 WL. 1000 pCi Rn per liter will correspond to 9600 atoms RaA per liter and 3.0 WL. The graph of N_A vs. WL for t=20 min., then, will be a straight line with a slope, dN_A/dWL of 3200. In an entirely analogous fashion, the slopes of the other atom concentrations vs. WL can be numerically determined. Substitution into line 30 for each time yields the results tabulated in the following table:

Numerical Solutions of Line 30

t_1	$\partial N_T/\partial WL$ $t=t_1$	% variation from average
3	1.06×10^4	-23%
10	1.28×10^4	-7%
15	1.57×10^4	+12%
20	1.51×10^4	+8%
30	1.56×10^4	+12%
average	1.39×10^4	±12.4%

This indicates a remarkable stability in the rate of change in N_T with respect to changes in WL over times ranging from very "young" radon to near equilibrium radon under the assumption of constant radon activity.

This result can be seen even more dramatically by plotting the data of the third table on log-log paper as in Figure 1.

N_T and WL as functions of Rn Concentration and Time

t \ Rn	100 pCi/l		200 pCi/l		500 pCi/l		1000 pCi/l	
	N_T	WL	N_T	WL	N_T	WL	N_T	WL
3 min.	664	.061	1328	.12	3320	.3	6640	.61
10 min.	2209	.17	4418	.34	11045	.85	22090	1.7
15 min.	3216	.25	6432	.5	16080	1.25	32260	2.5
20 min.	4221	.3	8442	.6	21105	1.5	42210	3.0
30 min.	6244	.42	12488	.82	31220	2.1	62440	4.2

It can be seen from the graph that the data plots as a family of straight lines all having approximately the same slope. Moreover, the intercepts at WL=1 are seen to vary only slightly and are, in fact, the values of N_T/ WL tabulated in Table 2. The intercept of the median line (only approximately situated) is 1.3×10^4 which is very close to the average value of Table 2 which is 1.39×10^4. The equation of the median line by graphical analysis is:

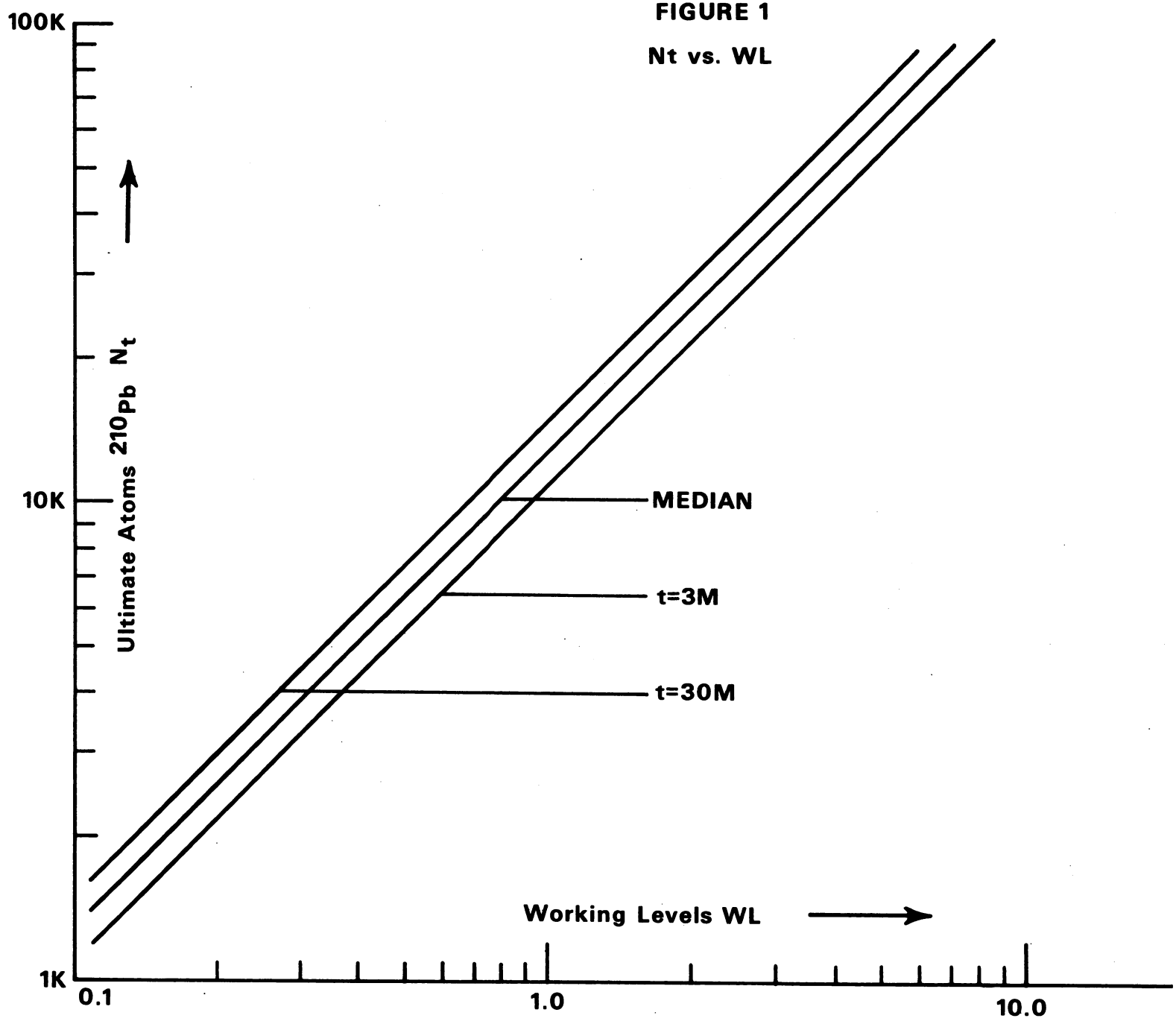
$$N_T = 1.3 \times 10^4 \ (WL)^{.884} \qquad \ldots\ldots\ldots \ 36.$$

This relation shows that the WL is a practical (though not exact) single parameter correlated to the total number of radon daughter atoms which would be collected on a sample taken from an air mixture of practically any sort, the only condition being that it have a certain WL value. Since these short-lived daughters will all eventually decay to lead-210, the correlation obviously translates to a correlation between WL and total number of lead-210 atoms on a sample just from the deposit of radon daughters from the sampled air.

These results apply also in the context where the filter bed in question is the lung tissue of a miner exposed to radon daughters in a uranium mine. The relation between body burdens of lead-210 and cumulative exposure (usually expressed in working level months of exposure) has been studied extensively in various aspects. From the foregoing considerations alone, one would conclude that a correlation should exist (if at all) only between WL and that fraction of the body burden of lead-210 due to the direct deposit of the short-lived radon daughters. As was seen in Part A above, the background contributions from various sources to sample activity or body burden of lead-210 can be expected to be quite high. Moreover, it could be quite difficult to accurately apportion the quantitative contribution of each of the potential sources of lead-210 discussed. Further consideration of the problem of relating sample

FIGURE 1

Nt vs. WL



quantities of lead-210 and a given exposure context will be made in the final section of this report where experimental data will be taken into account.

The correlation just derived is based on the assumption of simple growth from a constant parent radon activity source, and so does not explicitly take into account possible effects of mixing different aged air. But an entirely analogous derivation can be made on the Thomas and Epps tunnel model which would cover integrated growth effects and mixing over the entire length of a hypothetical tunnel. The details will not be presented here since the derivation is step by step the same, with the exception that the concentrations are all referenced to the tunnel end and time of flight of air in the tunnel. The derived exponential relation between N_T and WL of the air is somewhat different from that derived above:

$$N_T = 1.42 \times 10^4 \ (WL)^{1.045} \qquad \ldots\ldots\ldots 37.$$

The preceding discussion completes the development of a fourth mathematical model which , in this case, described the relation between measured lead-210 and an exposure value. These four models and turbulent diffusion models such as derived by Jacobi to account for processes such as the suspension of dust and other aerosols in the air for which no model was developed here, would have to be appropriately combined to produce a composite picture of lead-210 in the environment of a uranium mine.[9] It is considered beyond the scope of the present study to attempt to produce such a detailed composite model.

C. Summary of Theoretical Results

In the foregoing discussion, several mathematical models were developed for describing growth and decay processes leading to lead-210 under certain specified ideal conditions. Several observational consequences which might be expected under the assumption of various combinations of the principle processes of interest will now be briefly considered. The processes are, once again: the prompt decay of daughters in the air to lead-210, the rapid accumulation and subsequent mixing of the short-lived daughters and lead-210 in stagnant air, and the collection of daughters on a filter bed followed by decay to lead-210.

Certainly the process of most interest, as far as relating lead-210 measurements to exposure values in uranium mines is concerned, is the accumulation of airborne radon daughters followed by their subsequent decay to lead-210. It is quite clear from a comparison of figures tabulated in the fourth table that this process can be a weak competitor to the other two potential sources of lead-210. Under the sort of ideal conditions assumed above, the collected daughters source exceeds the airborne background source from the prompt decay of daughters at least during the first 21 minutes of aging of the air coming into a mine tunnel.

Whether or not it could be expected to exceed the contribution from stagnant air sources, such as small side rooms or air pockets along the ribs and back of the tunnel, would depend on the number and volume of them and the degree of mixing taking place.

Under current mining conditions, where every effort is made to supply all work areas with as fresh air as possible, most miners are exposed to air with a very short residence time and only slightly contaminated with stagnant air. Evidence for this can be seen in the impressive reduction in the presence of miners being exposed to WL values in excess of 1.0 WL in recent years. Then the chief sources of both exposure and of lead-210 collected at typical locations would be RaA, which quickly grows in from radon mixed in the air, and the whole spectrum of radon daughters (RaA, B, C and D) which would be added from stagnant air mixing into the fresh air stream. The prompt decay of radon daughters to lead-210 in the air would not have a prominent role in this situation, presuming that the residence time of most of the ventilation air in work areas is less than six minutes. But airborne ore dust and other resuspended aerosols could contribute appreciable amounts of activity under certain conditions (e.g. drilling or mucking).

However, if one is considering the past exposure of miners who have worked in some of the early uranium mining conditions where poor ventilation was the rule, then undoubtedly all three processes under discussion here (plus ingested and inhaled ore dust) contributed heavily to the body burden of lead-210 which would be measured today. But here we have a reversal of the priority of contributors to measured lead-210. Since the residence time of the air under minimal ventilation conditions is long, the background lead-210 sources would be expected, on the basis of the models, to dominate the contribution from the decay of airborne daughters collected. The exact character of the relative contributions would, of course, depend on the specific conditions in a given working environment.

These, then, are some of the theoretical expectations derivable from models developed above. They raise some interesting questions with regard to published studies of the possibility of using lead-210 in a bioassay technique for determining exposure in uranium mines. It has been shown, for example, that while there exists a relationship between the concentration of radon daughters in a uranium mine atmosphere and the concentration of lead-210 in the skeleton of a miner, the concentration may be well in excess of that expected from the inhalation of the short-lived radon daughter atoms alone.[13] The models under discussion provide an indication of the complexities which must be dealt with in developing a realistic account of the relation between exposure and body burdens of lead-210. Further consideration of bioassay will be made in a subsequent section.

TABLE 4

Predicted Relative Contributions to RaD Samples of Mine Air.

Assumptions:

1. Assume a Thomas-Epps type tunnel, 8' x 10'.
2. Let the ventiliation rate be 50,000 CFM.
3. Suppose the only two sources of RaD collected on air samples to be the decay on the filter of collected short-lived radon daughters (indicated by WL), and a background airborne concentration of RaD which is solely due to the decay of daughters in the air to RaD.

Sampling Conditions			Sources of RaD	
L (ft.)	Time of flight	WL	I_D (pCi/l) from daughters	I_D (pCi/l) from background
600	1.056	0.0598	2.02×10^{-5}	1.32×10^{-5}
1,320	2.112	0.203	7.25×10^{-5}	5.80×10^{-4}
2,640	4.224	0.775	2.94×10^{-4}	2.32×10^{-4}
3,960	6.338	1.665	6.54×10^{-4}	5.22×10^{-4}
5,280	8.448	2.848	1.145×10^{-3}	9.26×10^{-4}
6,600	10.560	4.296	1.761×10^{-3}	1.47×10^{-3}
13,200	21.12	15.268	6.62×10^{-3}	5.84×10^{-3}

Evidently the background contribution is quite high from the start, and at about 20 minutes time of flight has reached 88% of the contribution of RaD to the sample from the decay of the short-lived daughters.

Part II. Counting Technique and Sample Collection and Preparation

The direct measurement of lead-210 has always been difficult on account of the low end-point energy of its beta-emissions: 61 KeV (19%) and 15 KeV (81%). If it is known that the parent lead-210 is in secular equilibrium with its daughters bismuth-210 and polonium 210, one or both of these can be immediately separated and counted to determine the quantity of the parent present. Otherwise it is necessary to separate the lead-210 away from its decay products and wait a period of days or even months until the daughters grow-in significantly.

The relatively recent development of liquid scintillation spectroscopy and its successful application to counting the weak beta from tritium (18.6 KeV) opened a new approach to the direct counting of lead-210. It was found that in spite of the fact that 81% of the beta emissions from lead-210 are less energetic than that of tritium, an overall counting efficiency of between 97% to 98% can be achieved. This unexpectedly greater counting efficiency can be explained by reference to the decay scheme of lead-210. The 15 KeV beta decay leads to a meta-stable energy state of bismuth-210 which very quickly converts to the ground state with the emission of an internal conversion electron having an energy of approximately 30 KeV. The conversion is so rapid that the electron and beta particle appear in coincidence and so are counted simultaneously by a liquid scintillation spectrometer as a single event having an energy equal to the sum of the two events (45 KeV). Such an energy is sufficiently high to be counted at essentially 100% efficiency. The unconverted 46 KeV gamma-rays are weak enough that most of them are totally absorbed in the scintillation solution producing monoenergetic electrons which are counted at 100% efficiency.[1]

The process of setting up a measurement technique for counting lead-210 quantitatively and applying the result to determining exposure involves (A) first calibrating the instrument using standard dilutions of lead-210 and its daughters; and then, (B) once the optimum instrument settings have been determined for the standards procedures can be worked out to deal with the complications, introduced by the complex chemistry of the environmental sample matrix. Finally, (C) given a sample preparation and counting procedure whose quantitative efficiency is known, and given the expected concentrations of lead-210 from various sources from the theoretical mine models, possible sampling schemes aimed at relating measured lead-210 concentrations to exposure values can be studied. Each of these steps will be discussed below.

A. The instrument used in the present study is Packard Tri-Carb Liquid Scintillation Spectrometer, Model 3375. This instrument has the capability of three independent counting channels, each with its own single channel analyzer.

Initial calibration tests were carried out the following procedures outlined by Fairman and Sedlet as far as practicable.[1]

The choice of a suitable liquid scintillation solution ('scintillation cocktail') was narrowed considerably by the fact that the RaDEF standards are supplied as solutions in 1N HNO_3. Also it was anticipated that a small quantity of 1N HNO_3

would have to be added to the environmental sample cocktail to keep the lead-210 activity in suspension and thus maintain constant counting geometry. In either event, a cocktail had to be chosen which was compatible with the addition of small amounts of aqueous solutions.

After experimentation with several of the possible solutions, it was determined that either of the two formulations listed below were quite satisfactory; the second having the advantage of ease of preparation and the fact that a thin gel forms on the addition of water which helps to provide suitable nucleation for maintaining activity in suspension.

Liquid Scintillation Solutions Suitable for Counting Lead-210

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1. 7 grams PPO, 2,5-diphenyloxazole and 100 grams reagent grade naphthalene dissolved in 1,4 dioxane to make 1 liter.

2. A solution containing 1 part Triton X-100 and 2 parts toluene scintillator solution composed of 8.25 grams PPO and 0.25 grams M_2POPOP, 1, 4-bis-2-(4-methyl-5 phenyloxazole) - benzene, per liter of toluene.

The choice of amplifier gain settings and energy-window counting channels had to be made by generating spectra of the RaDEF secular equilibrium standard solution, and later, spectra of the separated isotopes. Spectra were obtained by counting in from 15 to 100 narrow energy windows selected by settings of the upper level and lower level discriminators of the single channel analyzers. This procedure is very time consuming, but is necessary in the absence of multichannel pulse height analysis capability.

Figure 2 is the spectrum of the RaDEF standard at 3% amplification. All three isotopes can be seen together at this gain. The lead-210 beta and conversion electron pulses are compressed into the first 200 channels or so, and the resultant peak clearly sits on top of the low energy end of the broad bismuth-210 beta spectrum. At the high energy end of the bismuth-210 spectrum indicates the possibility for counting lead-210 even in the presence of its daughters. However, due to the overlapping of spectra, a careful determination of the relative contributions of lead-210 and bismuth-210 to the low energy peak has to be made.

Increasing the gain to 17% spreads the spectrum out to the extent that the lead-210 and lower end of the bismuth-210 spectra occupy the whole 1000 window divisions, as seen in Figure 3. The spectrum of background noise generated in a blank solution reveals that almost all background counts occur in the first 50 channels at this amplification. Such a disposition of spectra suggests that lead-210 can be counted in the window from 50 to 700 divisions, and the remaining divisions, 700-1000, can be used as a quantitative indicator of the contribution of bismuth-210 to the lead-210 peak. The 17% gain was chosen as optimum for this instrument and scintillation cocktail chosen.

FIGURE 2

Spectrum of 100 Lambda of Standard RaDEF Solution in Triton Cocktail
3% AMPL., WINDOW DIVISIONS + 4%

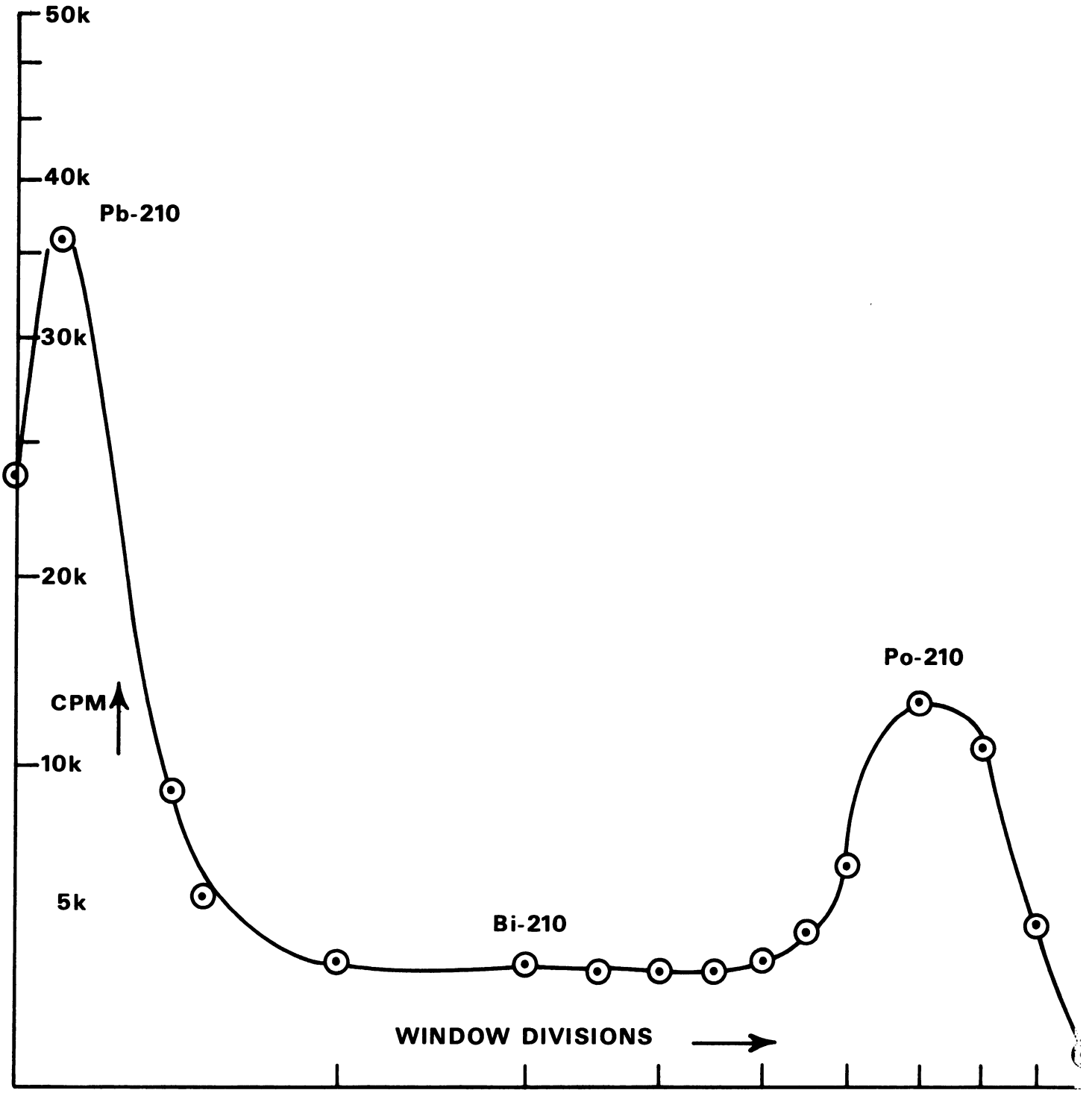
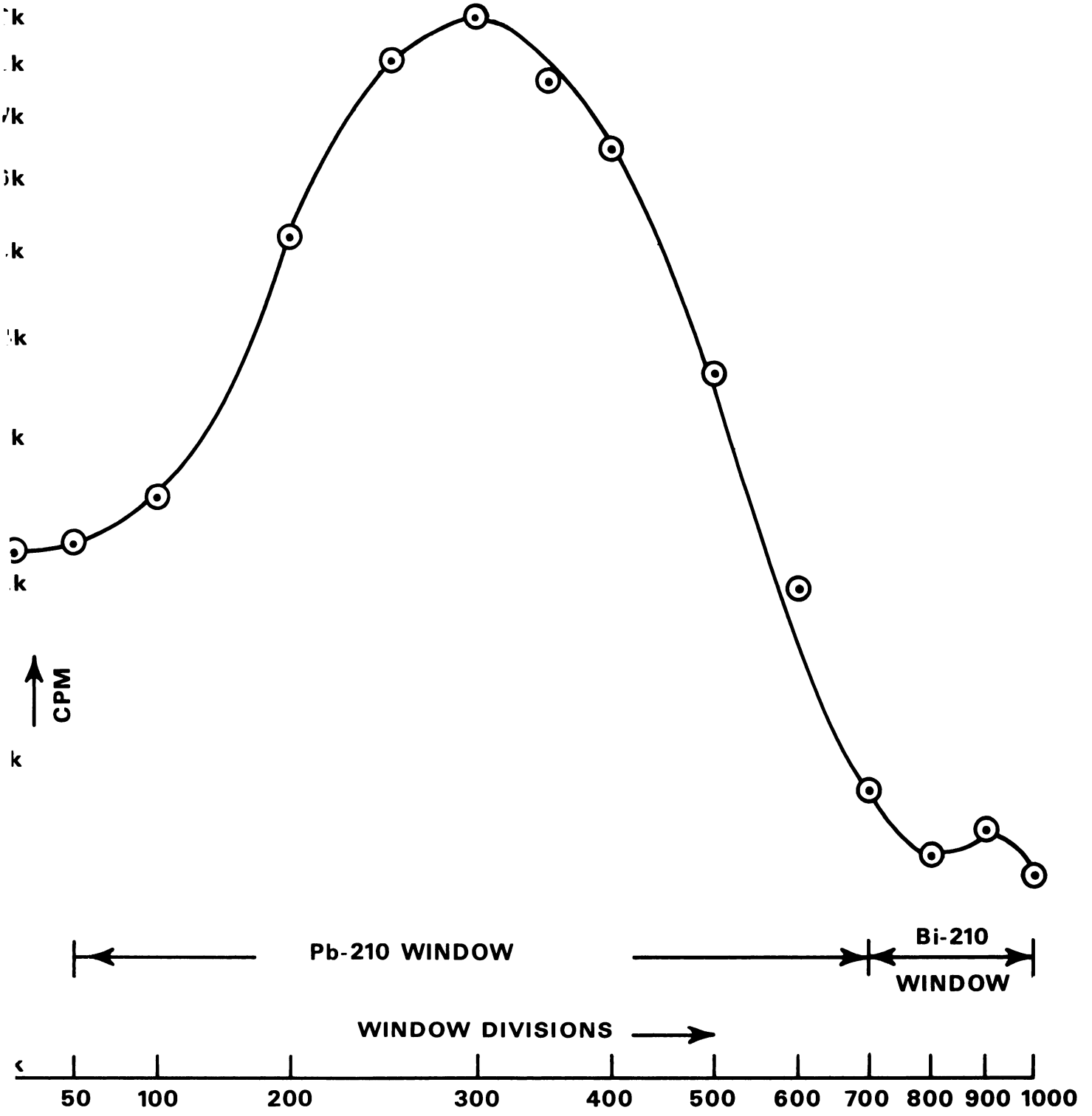


FIGURE 3

Spectrum of 100 Lambda of Standard RaDEF
Solution in Triton Cocktail
17% AMPL., WINDOW DIVISIONS + 4%



Putting these counting parameters into practice requires generating pure samples of lead-210 and bismuth-210 from the standard solutions and determining: a) the extent that the tail of the lead-210 peak extends into the bismuth-210 spectral region, and b) the exact ratio of bismuth counts in the bismuth-210 spectral region to bismuth counts in the lead-210 spectral region. From this ratio the quantitative contribution of bismuth counts to lead counts can be made.

The first attempts at separation were made using an ion-exchange procedure developed by Fairman (See Appendix 1).[1] The separation of lead-210 was clean, but it was not determined just how quantitative the procedure is. The spectrum of the pure lead aliquot at 17% amplification revealed that there is only a very slight tail of the lead peak into the bismuth spectral region.

Unfortunately, the next step in the ion-exchange separation, which was to yield a pure bismuth aliquot, was not clean. That is to say, despite repeated attempts, the bismuth separation always seemed to carry out some portion of lead. Also, the necessity of using stronger reagents caused considerable difficulty in sample preparation.

This necessitated research for an alternative separation procedure. A successful alternative was developed from a procedure described by G. Bouissiers in an article (partially translated from the French in Appendix 2, titled, "The Use of Dithizone for Separation and Purification of RaDEF").[2] THe procedure proves quite straightforward in application. The bismuth separation is clean of any trace of lead as revealed by a nearly flat spectrum across the entire spectral region from 50 to 1000 window divisions. See Figure 4.

By repeatedly separating and counting bismuth aliquots in the 50-700 (lead), and 700-1000 (bismuth) windows, a ratio or relative efficiency factor was computed. In principle, the following relation should correctly describe the calculation of lead-210 DPM given the gross CPM counted in the lead and Bismuth windows, C_{Pb} and C_{Bi}, and the gross background CPM in those respective windows B_{Pb} and B_{Bi}:

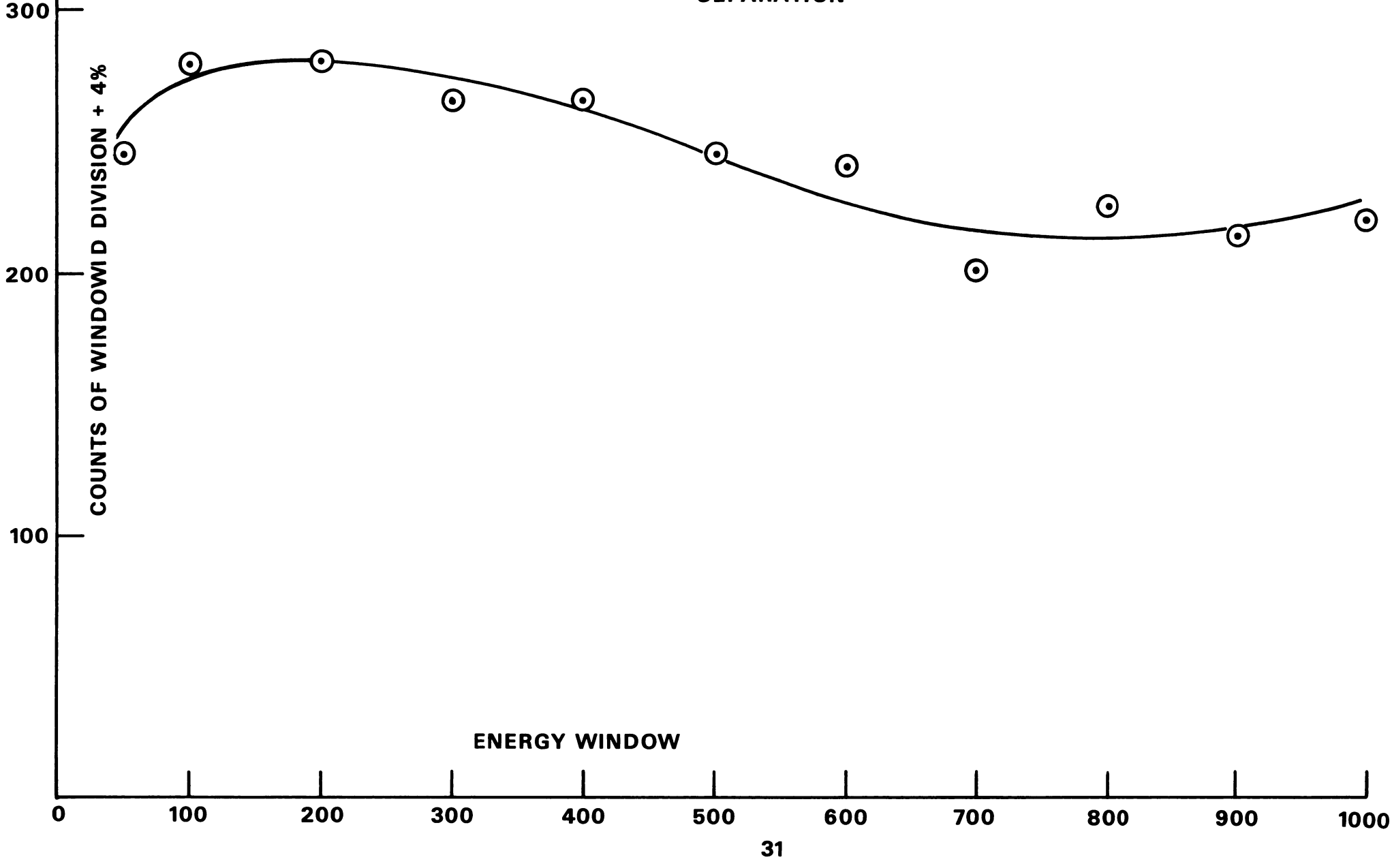
$$\text{Total DPM } {}^{210}Pb = \frac{(C_{Pb} - B_{Pb}) - [(C_{Bi} - B_{Bi}) \ / \ E_{Bi}]}{E_{Pb}}$$

where E_{Bi} is the relative efficiency factor which converts the net bismuth counts in the bismuth window into the bismuth background CPM to the lead counts. And E_{Pb} is the overall efficiency for counting lead-210 in the presence of its first daughter.

Note that as the term 'relative efficiency' implies, no determination of total bismuth activity in a given sample need be known, provided the ratio of bismuth counts in the lead spectral region is very nearly stable for the range of activities encountered. Such appears to be the case for samples dealt within this study. Furthermore, since the stability of this ratio rests on the stability of the spectral distribution of counts over the period of counting times necessary, it should be noted that careful control must be maintained over sample chemistry to insure that no spectral shifting occurs as a result of color or chemical quenching. In particular, all standard and sample aliquots should have been evaporated to

FIGURE 4

SPECTRUM OF BISMUTH
Bi-210 ALIQUOT FROM DITHIZONE
SEPARATION



dryness and taken up in a standard amount of 1N HNO_3 before adding to the scintillation cocktail.

The best estimate of $1/E_{Bi}$ using the instrument settings and cocktail described above is 2.79. Using this value in the equation above the date obtained from a 5770 $\pm$ 248 DPM aliquot of a standard solution, a measured value of 5716.36 DPM was obtained. Thus, the observed value is 99% of the expected, including the effects of the separation process. Tests with much smaller amounts of activity show a lower overall efficiency undoubtedly due to variable losses in the separation process. A good average value of E_{Pb} seems to be 90%.

The foregoing describes the complete calibration process for the instrument used in this investigation. The next step is to apply these procedures to environmental samples.

B. An Extraction Technique for Sample Preparation for Liquid Scintillation Counting of Lead-210:

In application to environmental samples, the utility of this approach depends on the quality of sample preparation. Among possible difficulties are color quench, chemical quench, and homogeniety of sample and counting solution ('cocktail'). In each of these complications, the observed effects include loss of scintillation events with a change in counting efficiency, shifting of spectral peaks which can also result in a change in counting efficiency, and a change in background count rate. Clearly, if liquid scintillation counting of lead-210 is to be successful, sample preparation must be performed with considerable care.

Below a technique is described for counting lead-210 which is collected on air sampling filters in active uranium mine atmospheres containing large quantities of black diesel exhaust fume, ore dust, and blasting powder smoke. Clearly, all of the difficulties mentioned above are present, and a rapid and sample procedure that would isolate the lead-210 into a homogeneous, colorless sample of controlled chemistry is needed.

Solvent extraction techniques using dithizone which have been employed to extract lead-210 from various sample media proved applicable to this problem. The successful use of dithizone separation in the calibration phase suggested its use in environmental sample preparation. Although there are many variations of the dithizone extraction technique, none described in the current literature are applicable for liquid scintillation counting under the conditions indicated above.[4] In the following procedure, the sample is collected on a microsorban filter medium, which is completely soluble in chloroform. The filter is dissolved in a chloroform-dithizone solution, and the lead-210 and a portion of the bismuth-210 are extracted into a weak acid solution. The carbon-black and other aerosols are retained in the chloroform dithizone layer, while the aqueous layer, containing the lead and bismuth is pipetted off. The aqueous solution is evaporated to dryness and taken up in a small quantity of standard acid to be counted in a suitable scintillation cocktail (i.e., dioxane or Triton X-100 which are miscible with small volumes of water).[5]

After collecting the air sample on one inch microsorban filter material, the filter is added to approximately 5 ml of the chloroform dithizone solution in a separatory funnel. Slight agitation takes the filter into solution and the aerosol into suspension. Five milliliters (5 ml) of the 0.01N HCl are added and the contents of the funnel shaken for at least two minutes. The supernatant aqueous layer is pipetted off leaving about one milliliter which is difficult to collect without including some dithizone.* Then the extraction procedure is repeated with another 5 ml of 0.01N HCl. The extracts are combined and evaporated to dryness over a water bath.** A third wash may be necessary to complete the separation and to check on the degree to which the separation is quantitative. Higher temperature evaporation could result in loss of lead-210. Following evaporation, 0.25 ml to 0.5 ml of 1N HNO_3 is added to the evaporating beaker, washing down the sides as carefully as possible. Scintillator cocktail is added to the acid in the beaker and the mixture transferred quantitatively to a counting vial, the beaker being successively washed with small amounts of scintillator cocktail. A total volume of 20 ml of cocktail is usually required.

As previously mentioned, the separation of lead-210 from its daughter bismuth-210 is not complete. Invariably a small quantity of the bismuth-210 on the filter goes into the aqueous phase. But the success of the technique does not depend on the complete separation of these two nuclides. All that is required is that for a given instrument setting the efficiency for counting bismuth-210 in the lead-210 counting window be well known.***

As is evident from the spectra, the bismuth contributes a moderate relatively even count rate to the lead-210 peak. As before, if the lead is counted in the 50-700 channel, and the bismuth in the 700-1000 channel, the contribution of bismuth to lead counts will be somewhat more than twice the counts observed in the bismuth window.

C. Sample Collection Considerations

The establishment of an environmental sampling procedure can proceed on the basis of the sort of instrument calibration parameters just presented. What is needed are

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*Pipetting the aqueous layer was found to be cleaner than draining the chloroform layer since a thin film of microsorban forms at the interface of the two layers, interfering with the separation.

**A small 20 ml beaker held in place over a 600 ml beaker of boiling water was found to be quite satisfactory. Evaporation could be carried out directly in the scintillation counting vial, but no increase in efficiency was observed.

***The technique used here is a simple variation of the channels ratio technique first described by L.A. Baillie (Inter. J. Appl. Rad. and Isotopes, 8, 1 (1960), and further discussed by R. J. Herberg in Packard Technical Bulletin No. 15 (1965).

estimates of the qualitative and quantitative determination limits of the whole counting system and the expected concentrations of radon daughters and lead-210 in mine air. For on the basis of these two estimates, one can anticipate first, how much activity will have to be collected on a given sample in order that either a qualitative detection or a statistically significant quantitative measure can be made and second, knowing how much activity is needed and the anticipated concentration in the air, a working estimate of the necessary volume to be collected and hence the sampling period can be determined.

The detection limit L_D and the quantitative determination L_Q for the counting system can be estimated using working formulas derived by Currie[6] under the assumption that sufficient control is maintained over sample preparation that a well known sample blank can be used to obtain a mean number of background counts in the channel in interest, μ_b.

Currie shows that:

$$L_D = 2.71 + 3.29\sqrt{\mu_b}$$

and

$$L_Q = 50\left\{1 + \left[1 + \frac{\mu_b}{25}\right]^{\frac{1}{2}}\right\}$$

For the plastic counting vials and Triton cocktail used in this study the average background in the lead-210 spectral region is 31.4 cpm. Substitution in the Currie formulas yields:

L_D = 21.15 DPM + 9.53 pCi and L_Q = 125.1 DPM or 56.35 pCi

Since most mining companies are attempting to bring WL concentrations down to the new standard of 0.3 WL in work areas, it is useful to use this value together with the relation derived above relating WL and expected lead-210 on a sample from the decay of collected daughters to calculate the order of magnitude of sample volumes necessary to detect and quantitatively measure lead-210 for the purposes of this investigation. From the WL formula we should expect 1×10^{-4} pCi/l of lead-210. Hence the sample volume must be approximately 195,000 liters for reliable qualitative estimates and about 520,000 liters for quantitative measure. The assumption here is that there is no background contribution to the sample. Addition of background could appreciably reduce sample volume. At a low sampling rate of 12.5 liters per minute these volumes would require sampling periods of approximately 11 days and 29 days respectively.

Now since lead-210 has a very long half-life, loss of collected activity due to decay is no problem in such long term samples. However, if there is very much aerosol in the atmosphere being sampled, there can be serious difficulty extracting the collected activity out of the sample matrix. There are other problems typical of long term, high volume samples such as increased uncertainty in sample volume, or possible change in filter efficiency.

PART III - ENVIRONMENTAL INVESTIGATIONS

A. Interlaboratory Comparison Check of Dithizone Extraction Techniques Applied to Environmental Samples:

Before the dithizone extraction technique described in Section II could be applied to field investigations, a test of the overall effectiveness of it for removal of lead-210 collected on air filter samples taken in working mines had to be made. The plan of the test was to collect at least two long-term samples in duplicate in an environment containing a relatively large amount of both radon and its decay products, and typical mine aerosols such as diesel exhaust, dust, blasting smoke and so forth. One of each pair was collected on one inch diameter metrical membrane filter medium and was sent to another laboratory for wet ashing and counting, using the established techniques of spontaneous deposition and alpha counting of the second lead-210 daughter, polonium-210. The other sample of each pair was collected on one inch diameter microsorban filter medium and was processed and counted by the techniques described above.

The samples were collected over two consecutive 24 hour periods of time at the same location in the same mine. High sampling rates of 30 liters per minute were used in order to obtain large sample volumes. At the end of each sampling period, 5 minute samples were taken and counted by the modified Tsivoglou method to provide data on radon daughter concentrations and working levels. The results of these measurements are tabulated in Table 5. Taking the results of the gas proportional alpha measurement as a primary measure, the overall efficiency of the dithizone extraction, liquid scintillation beta-counting measure of lead-210 is on the order of 90% for levels of sample activity on the order of those collected (i.e., 1000 pCi).

These results are quite satisfactory in light of the anticipated losses in extraction and liquid scintillation counting. They are particularly encouraging in view of the fact that the measure resulting from techniques developed in the present study can be obtained in a matter of several hours, as compared with the several months time required by the other technique, and still be highly efficient.

TABLE 5

Results of Interlaboratory Comparison

Sample Collection Data:

Samples 2 and 3 collected on microsorban filter material.
Samples 4 and 5 collected on metrical membrane filter material.
Sample volume of 2 and 4: 4.72×10^4 liters.
Sample volume of 3 and 5: 4.14×10^4 liters.
All samples collected at a sampling rate of 30 lpm.
Samples 2 and 4 approximate working level: 22.3.
Samples 3 and 5 approximate working level: 24.7.

Sample Counting Data:

A. Dithizone Extraction, LSC Counting Procedures

Sample No. 2: Counting times are all 100 min.

	Pb-210 Channel CPM	%Std.Dev.	Bi-210 Channel CPM	%Std.Dev.
1st Extraction	3697.4	0.2	273.3	0.7
2nd Extraction	121.9	1.0	10.6	2.5
Sample Blank	33.8	2.5	5.7	4.5

Pb-210 CPM 1st extraction = 3663.6.
Bi-210 CPM 1st extraction = 267.6.
Bi-210 contribution to Pb-210 counts = 267.6 x 2.79 = 746.6.
Net Pb-210 CPM 1st extraction = 2917.0.
Pb-210 CPM 2nd extraction = 88.1.
Bi-210 CPM 2nd extraction = 4.9.
Bi-210 contribution to Pb-210 counts = 4.9 x 2.79 = 13.67.
Net Pb-210 CPM 2nd extraction = 74.4.
Total Pb-210 CPM = 2991.4 CPM.

Sample No. 3: Counting times are all 100 min.

	Pb-210 Channel CPM	%Std.Dev.	Bi-210 Channel CPM	%Std. Dev.
1st Extraction	2858.7	0.2	213.7	0.7
2nd Extraction	95.1	1.5	7.5	4.5
Sample Blank	33.8	2.5	5.7	4.5

Pb-210 CPM 1st extraction = 2824.9.
Bi-210 CPM 1st extraction = 208.0.
Bi-210 contribution to Pb-210 counts = 208.0 x 2.79 = 580.3.
Net Pb-210 CPM 1st extraction = 2244.6.
Pb-210 CPM 2nd extaction = 61.3.
Bi-210 CPM 2nd extraction = 1.8.
Bi-210 contribution to Pb-210 counts = 1.8 x 2.7 = 5.0.
Net Pb-210 CPM 2nd extraction = 56.3.
Total Pb-210 CPM = 2300.9 CPM.

B. Spontaneous Deposition, Gas Proportional Alpha-Counting

Sample No. 4:

Pb-210 DPM = 3237.83 $\pm$ 73 DPM ($\pm$ 2 sigma).

Sample No. 5:

Pb-210 DPM = 2637.76 $\pm$ 64 DPM ($\pm$ 2 sigma).

Comparing Samples 2 and 4: $\frac{2991.4}{3237.83} = 0.923.$

Thus Sample 2 is 92.3% of Sample 4.

Comparing Samples 3 and 5: $\frac{2300.9}{2637.76} = 0.872.$

Thus Sample 3 is 87.2% of Sample 5.

The average of these results indicates an overall extraction efficiency E (CPM/DPM) of 89.8%.

B. Field Studies of the Extent of Background Contributions to Lead-210 Samples:

The many complexities involved in the experimental determination of the type and relative magnitudes of contributions of lead-210 atoms to any given environmental samples were studied by several approaches. One procedure was straightforwardly to obtain a series of long-term samples in as many types of mine environments as time and circustance would allow. Unfortunately, collateral data on such parameters as radon and daughter concentrations and working levels were not always complete. However, it should be emphasized that under the best of circumstances, the collateral data were obtained by standard 'grab sample' procedures (Kuznetz and Tsivoglou), and hence the data only approximately specifies the conditions under which the long term (several days), high volume (several tens to hundreds of thousands of liters) samples were taken for the lead-210 measurement.

Table 6 contains a compilation of the most useful of the data collected. The 'measured lead-210 total' represents the total lead-210 activity measured from the sample, divided by the sample volume. As such, it is an average value of air concentration over several consecutive 24 hour periods. The 'expected lead-210 from collected daughters' was determined from one of two sources. When the WL value was either the only available, or most reliable, data on the daughter concentrations, the mathematical relation between WL and lead-210 atom concentration described above in equations 36 and 37 was used to calculate the quantity of 'potential lead-210 atoms' per liter that would be collected (as one of the three short-lived radon daughter atoms) by sampling air of that WL. The other procedure, when usable radon daughter concentration data was available, was to transform the concentration values into atoms per liter, and divide the total daughter atoms concentration by the number of lead atoms per pCi of lead-210, and thus obtain a value of the number of pCi per liter of lead-210 that would be expected in the sample of the air from this source.

TABLE 6

BACKROUND CONTRIBUTION TO LEAD-210 SAMPLES

Sample	WL	Measured ^{210}Pb Total (pCi/1)	Expected ^{210}Pb from Collected Daughters (from WL or Tsivoglou Data) (pCi/1)		Difference due to Background Sources (pCi/1)	% of Total Attributable to Background
			WL	Tsivoglou		
HS1	0.014	8.75×10^{-5}	a) 8.07×10^{-6} b) 4.38×10^{-6}		a) 7.94×10^{-5} b) 8.31×10^{-5}	a) 90.7 b) 94.9
HS2	0.02	9.0×10^{-5}	a) 1.106×10^{-5} b) 6.37×10^{-6}		a) 7.89×10^{-5} b) 8.36×10^{-5}	a) 87.7 b) 92.9
KM33A	0.30	1.81×10^{-4}	a) 1.21×10^{-4} b) 1.087×10^{-4}		a) 0.60×10^{-4} b) 0.723×10^{-4}	a) 33.1 b) 39.9
DK1A	1.0	1.31×10^{-3}	a) 3.51×10^{-4} b) 3.83×10^{-4}		a) 9.59×10^{-4} b) 9.27×10^{-4}	a) 73.2 b) 70.76
DK1B	2.9	7.7×10^{-3}	a) 0.90×10^{-3} b) 1.19×10^{-3}		b) 6.5×10^{-3}	b) 84.4
DK2A	2.10	3.46×10^{-3}	a) 6.76×10^{-3} b) 8.55×10^{-4}		b) 2.61×10^{-3}	b)75.3
DK2B	2.90	9.26×10^{-3}	a) 0.90×10^{-3} b) 1.19×10^{-3}		b) 8.07×10^{-3}	b) 87.15
DK3A	1.63	1.54×10^{-3}	a) 0.54×10^{-3} b) 0.64×10^{-3}		b) 9.0×10^{-4}	b) 58.4
DK3B	0.44	5.40×10^{-4}	a) 1.7×10^{-4} b) 1.6×10^{-4}		a) 3.7×10^{-4} b) 3.8×10^{-4}	a) 68.5 b) 70.4
KM24A	31.38	4.40×10^{-2}	a) 0.74×10^{-2} b) 1.42×10^{-2}	1.5×10^{-2}	b) 2.98×10^{-2} 2.90×10^{-2}*	b) 67.7 65.9*
KM24B	22.28	3.90×10^{-2}	a) 5.46×10^{-3} b) 9.908×10^{-3}	1.07×10^{-2}	b) 2.91×10^{-2} 2.02×10^{-2}*	b) 74.5 65.3*
KM24C	24.75	2.87×10^{-2}	a) 0.59×10^{-3} b) 1.106×10^{-2}	1.23×10^{-2}	b) 1.76×10^{-2} 1.64×10^{-2}*	b) 61.4 57.1*
DK4A	0.199	2.58×10^{-3}	a) 8.43×10^{-5} b) 7.074×10^{-5}	1.4×10^{-4}	a) 2.49×10^{-3} 2.44×10^{-3}*	a) 96.5 94.6*
KM33C	0.30	5.69×10^{-4}	a) 3.767×10^{-5} b) 2.740×10^{-5}		a) 0.773×10^{-5} b) 1.80×10^{-5}	a) 17.0 b) 39.6
KM33D	0.08	4.54×10^{-5}	a) 3.767×10^{-5} b) 2.740×10^{-5}		a) 0.773×10^{-5} b) 1.80×10^{-5}	a) 17.0 b) 39.6
KM33E	0.02	2.61×10^{-5}	a) 1.106×10^{-5} b) 6.37×10^{-6}		a) 1.504×10^{-5} b) 1.97×10^{-5}	a) 57.6 b) 75.6

*Calculated using Tsivoglou data.

a) Calculated using $Pb = 1.3 \times 10^4 (WL)^{0.884}$

b) Calculated using $Pb = 1.42 \times 10^4 (WL)^{1.045}$

The difference between the 'measured total' and the 'expected from daughters' value should be an approximate value of the contribution to lead-210 on the sample filter due to the various background sources. The degree to which the difference is a good approximation of the magnitude of the combined background sources depends largely on how representative the data on daughter concentrations is of the conditions during the interval the sample was taken.

The results of the 1969 HASL investigation of the radiological characteristics of uranium mine atmospheres indicate that the greatest variability in WL and daughter concentration values is to be expected for conditions of low concentrations (WL values between 0 and 1).[10] The net coefficient of half-hourly variation changed from near 0.6 at 0.25 WL down to almost 0.2 at 1.0 WL. In individual mines, the range was even greater. The HASL report indicates that 85% of the atmospheric fluctuations had a net coefficient of variation which was ≤ 0.3.

Based on the apparent rule that the lower the concentrations, the greater the fluctuations, the greatest uncertainty in these determinations of background lead-210 would be expected with that data obtained in atmospheres of less than one WL.

Just to illustrate what effect variability in low level WL determinations might leave on these background effect calculations, suppose that, for sample HS2, 0.02 WL represented a sample mean, and that the coefficient of variation is 0.9. Then the anticipated standard deviation would be S = 0.018, indicating that the majority of WL determinations would be in the range of 0.002 WL and 0.038 WL. This implies a range of expected lead-210 from collected daughters of between 5.71×10^{-7} pCi/l and 1.25×10^{-5} pCi/l. Thus, even the high end of the range would represent only 4.3% of the total concentration measured. What is even more significant than this, as far as an indication that the background contribution is in excess of 70%, is the fact that two-thirds of the data is from air concentrations greater than or equal to one WL, for which the coefficient of variation is 0.2 or less. And for this group, the average percentage of the total lead measured attributable to background is 70.5%. The average for the whole data is 72.7%, with a standard deviation of 16.53 percentage points, and hence a coefficient of variation of 0.23. The 95% confidence limits of the mean percent of total lead-210 measured on a sample which is due to background are $\pm$ 10.02%. So not only is the background contribution high, there can be expected to be a fairly large variation in level from place to place.

C. Experimental Studies of Lead-210 Ingrowth Patterns:

Several mathematical models which describe various aspects of the ingrowth processes of lead-210 under different conditions were developed as described above. A series of experimental tests of these models were attempted in order to confirm the applicability of them to complex environmental contexts.

1. Two numerical relations between the WL of a given air and the anticipated contribution of lead-210 to a sample of that air from the decay of collected short-lived daughters of radon-222 were derived. It will be recalled that one was based on the assumption that ingrowth of daughters occurs in a constant radon concentration level. The other was derived using the assumptions of the Thomas and Epps' tunnel model which entail the constant influx of radon

Table 7.

Comparison of Different Estimates of
Pb-210 Contributions from Radon Daughters
(Field Data from D.A. Holaday, Final Report BOSH 099-T1-2)

Sample	WL	RaA(pCi/l)	RaB(pCi/l)	RaC(pCi/l)	I_D Using Tsivoglou Data	I_D Using $1.34 \times 10^{-4}(WL)^{0.884}$	I_D Using $1.42 \times 10^{-4}(WL)^{1.045}$
1. KM-1	3.60	746.0	395.6	242.9	1.528×10^{-3}	1.090×10^{-3}	1.463×10^{-3}
2. KM-2	0.70	151.4	76.4	51.0	3.04×10^{-4}	2.56×10^{-4}	2.64×10^{-4}
3. KM-3	0.96	174.2	101.7	71.1	4.03×10^{-4}	3.38×10^{-4}	3.67×10^{-4}
4. KM-4	0.16	42.6	17.1	7.8	6.40×10^{-5}	6.95×10^{-5}	5.65×10^{-5}
5. KM-5	0.49	117.7	51.3	28.3	1.98×10^{-4}	1.87×10^{-4}	1.82×10^{-4}
6. KM-6	1.69	274.7	174.0	145.0	7.23×10^{-4}	5.59×10^{-4}	6.64×10^{-4}
7. KM-15	0.23	104.5	21.6	3.6	9.58×10^{-5}	8.38×10^{-5}	8.26×10^{-5}
8. KM-29	1.93	388.7	201.4	136.5	8.02 x10-4	6.28 x10-4	7.62×10^{-4}
9. KM-32	1.58	309.8	165.4	115.4	6.62×10^{-4}	5.26×10^{-4}	6.18 x10-4
10. UH-5	0.72	132.3	73.6	55.1	$2,99 \times 10^{-4}$	2.63×10^{-4}	2.72×10^{-4}
11. UC-15	0.30	82.7	30.4	17.8	1.23×10^{-4}	1.21×10^{-4}	1.09×10^{-4}
12. UC-23	0.32	63.7	33.3	23.9	1.35×10^{-4}	1.28×10^{-4}	1.16×10^{-4}
13. UC-26	2.04	256.6	198.3	208.8	8.84×10^{-4}	6.59×10^{-4}	8.08×10^{-4}
14. UH-3	0.57	105.4	57.8	44.4	2.38×10^{-4}	2.14×10^{-4}	2.13 x10-4
15. UC-1	0.48	66.4	48.3	44.1	2.05×10^{-4}	1.84×10^{-4}	1.28×10^{-4}
16. UC-5	0.33	95.6	33.1	16.7	1.30×10^{-4}	1.32×10^{-4}	1.20 x10-4
17. UC-27	2.18	351.5	215.9	197.4	9.30 x10-4	6.99×10^{-4}	8.99 x10-4
18. UC-28	1.21	184.3	121.3	108.2	5.14×10^{-4}	4.16×10^{-4}	4.68×10^{-4}
19. UC-30	0.55	128.0	51.9	40.4	2.23×10^{-4}	2.07 x10-4	2.05 x10-4
20. UC-31	0.41	95.0	44.2	23.6	1.68×10^{-4}	1.59×10^{-4}	1.51×10^{-4}

into the airstream as it moves through the tunnel and ages. But, of course, neither set of assumptions completely matches the actual conditions typical of a working mine. The model based on a constant radon level would be expected to predict a more rapid initial growth rate than that based on the assumption of a continual influx of radon starting at zero concentration. However, as air moves through a mine picking up an increasing amount of radon and aging, the continual influx model would be expected to show the expected continuing growth pattern while the constant radon level model would tend to show a leveling off. Refer to Table 7, which tabulates published field data on radon daughter concentrations obtained using the modified Tsivoglou method, the expected lead-210 on a sample from these daughter concentrations, the expected lead-210 based on the constant radon level model (pCi/l Pb-210=$1.34X10^4$ (WL) 0.884, and then the expected lead-210 based on the tunnel model (pCi/l Pb-210=$1.42X10^4(WL)^{1.045}$). It will be seen from this data that empirically, the constant radon level model fits the data better than the tunnel model does for low WL's up to approximately 0.6 WL, where the two predicted values are approximately the same. But for all WL's larger than these values, the tunnel model provides a better approximation to the data. The behavior of these two models suggested by the empirical data is borne out in the theoretical graphical comparison of the two models in Figure 5. Note that the intersection of the two graphs occurs in the vicinity of 0.68 WL.

A possible explanation for the failure of the tunnel model to accurately predict the expected lead-210 from daughters at very low WL's is that most often fresh surface air is brought into a mine directly at the working stopes which naturally are the most gassy areas. There the air quickly picks up a heavy burden of radon. Initially, then, the air behaves as though it has started aging with a certain relatively constant radon concentration. But as it moves out through the exhaust air cicuits it continues to pick up additional radon and begins to look more like air which has been moving through a tunnel whose walls are emanating radon at some average rate.

Referring again to Table 7, it is seen that in almost every case the daughter concentration data yields an expected lead-210 atom contribution which exceeds those values predicted from the WL by either model. The differences are not large in most instances. For example, of five samples in this group ranging from 1.59 WL to 2.18 WL, the average discrepancy between the tunnel model relation and the Tsivolgou data is that the former is low by a factor of only 7% of the latter's value.

The most likely explanation for the consistently low estimates based on the WL value is that the situation in actual mine conditions inevitably represents a significant departure from processes of the simple growth of daughters into a parent radon concentration. Thus, while both models are partially compatible with the presumption of mixing of differently aged air, they would tend not to accurately reflect all the varied mixing processes that could be expected to actually occur, particularly the leakage and mixing of very stale air out of sealed off mined-out areas, which would lead to an underestimation by the models.

Under the widely varying circumstances encountered in the field, the estimate of lead-210 contribution from the decay of daughters by the numerical relations using the WL prove to be actually quite good.

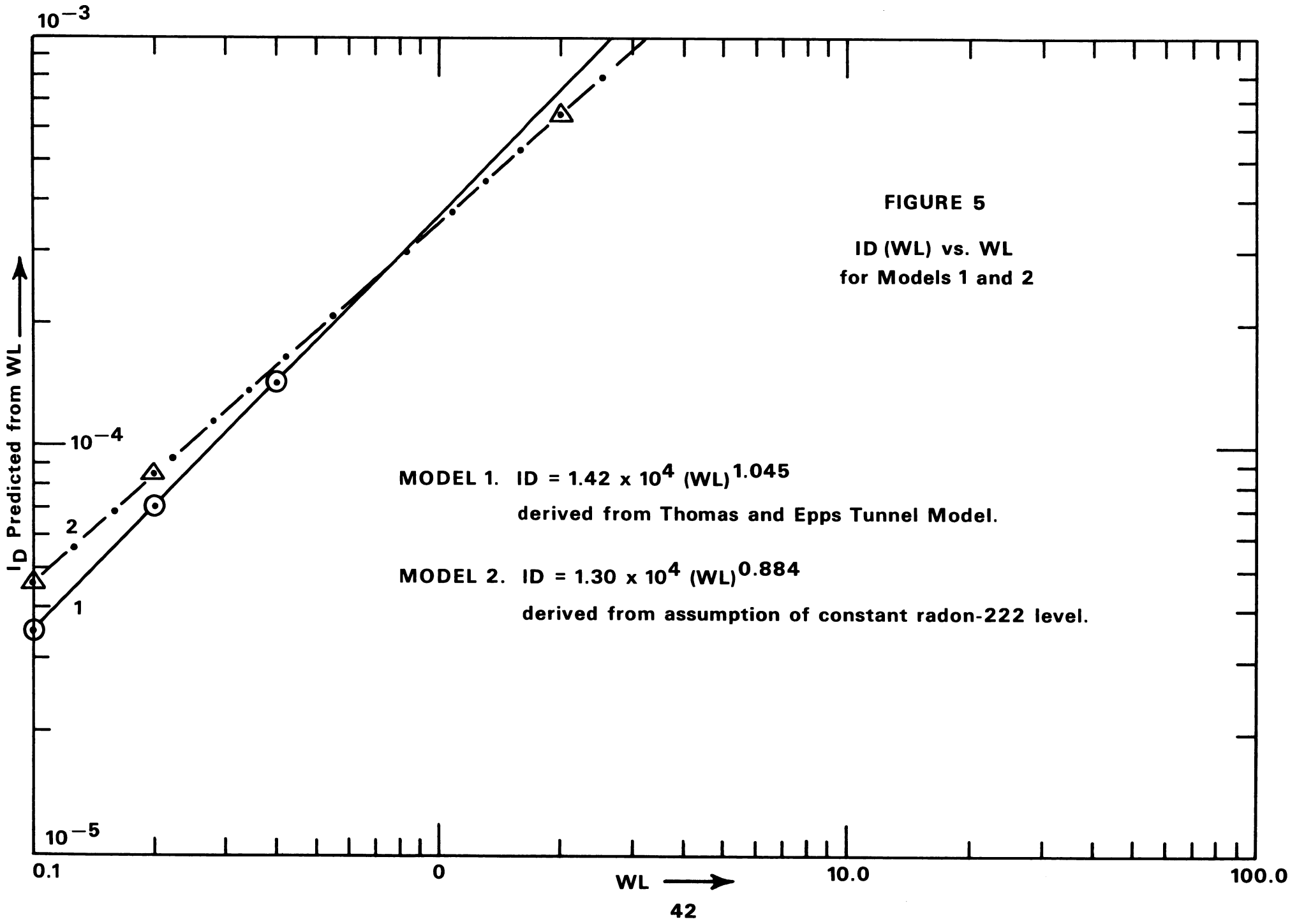


FIGURE 5

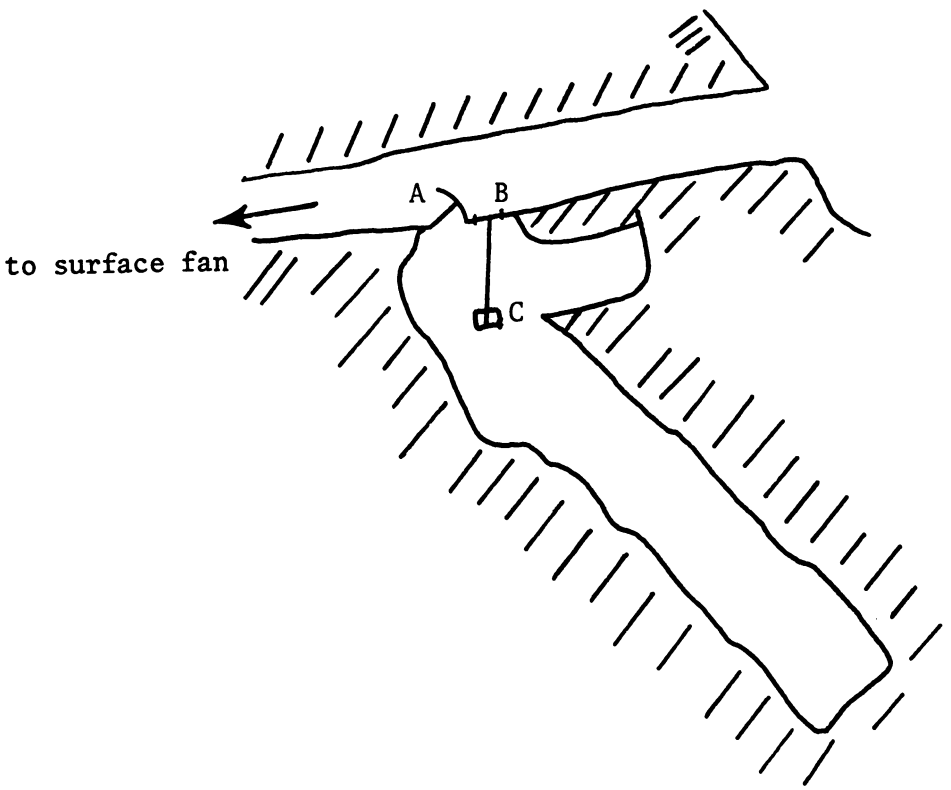
ID (WL) vs. WL
for Models 1 and 2

MODEL 1. $ID = 1.42 \times 10^4 (WL)^{1.045}$
derived from Thomas and Epps Tunnel Model.

MODEL 2. $ID = 1.30 \times 10^4 (WL)^{0.884}$
derived from assumption of constant radon-222 level.

Figure 6.

Dakota Test Chamber 3



Scale = 1"20'

A. Door into chamber through bulkhead

B. Sampling Port in bulkhead

C. Pulley stand where samples are taken

Chamber data:

Chamber Volume: 5,460 ft^3 = 154,674.2 l

Wall rock area: 2,801 ft^2 = 2.603 x 10^6 cm^2

Grade of ore: 0.05 to 0.10% U_3O_8

2. The third mathematical model developed above (line 26) leads to the prediction that whenever mine air stagnates, a rapid ingrowth of lead-210 can occur, particularly if the radon-222 emanation rate is high. The significance of this prediction for the present study is that the anticipated background contributions to airborne lead-210 concentrations can be significantly higher than on might anticipate from the assumption of ingrowth in a more or less stable radon concentration. An experimental test of this model was set up in the State of New Mexico's experimental uranium mine, Project Dakota.

One of the sealed off chambers was prepared by sealing a port into the bulkhead of the chamber which would allow samples to be taken without radically altering the air concentrations of radon and daughters. A pulley system was arranged to allow samples to be taken from the interior of the chamber away from the walls and floor. See Figure 6 for details of the experimental setup.

Before sealing off the test chamber at the start of the experiment, fresh air, provided by a downcast surface fan delivered at an approximate rate of 4000 CFM through vent tubing, was used to flush out all the stale air in the chamber. Flushing out continued for approximately 4 hours to insure many complete exchanges of air in the chamber.

Since surface air must flow a considerable distance through ore-bearing rock before delivery into the mine, and thus is slightly contaminated, and since quite long term samples are necessary to measure low level lead-210 air concentrations, the initial, baseline level of lead-210 was established by sampling the air in the haulageway outside the test chamber. The baseline sample was collected over a period of 45 hours and 40 minutes. In the meantime, the first lead-210 sample was started in the sealed chamber. After 17 hours 5 minutes, the sampler was stopped. Tsivoglou data was taken at this point and then a second sample started. The record sample was terminated after 28 hours 25 minutes. Again, Tsivoglou data was taken. Following completion of the second sample, the Dakota facility was shut down for routine maintenance, and when power was later restored (over the weekend), it was discovered by sampling the test chamber that stopping and starting the main ventilation fan had markedly disturbed conditions in the chamber so the experiment was terminated. Sufficient data was obtained, however, to establish that indeed the growth pattern predicted by the mathematical model. Test results are tabulated in Table 8.

A double precision computer program was used to generate a theoretical growth curve for the chamber environment with the emanation constant derived from the radon ingrowth data obtained from the test chamber. The calculations and tabulated predicted values are to be found in Table 9. A graphical comparison of the predicted growth and the observed averages is made in the accompanying graph. See Figure 7.

From the graph it is readily seen that the predicted and observed growth rates agree quite well, although the values differ by a constant. This indicates that the measured radon-222 emanation rate, from which the emanation constant was derived, was higher than would be implied by the lead-210 measurements.

Table 8.

Experimental Data from Lead-210 Ingrowth
Experiment Dakota Test Chamber 3

1. Baseline Data:

RaA (pCi/l) = 61.46 pCi/l

RaB (pCi/l) = 27.83 pCi/l

RaC (pCi/l) = 22.32 pCi/l

WL = 0.29

Rn-222 (pCi/l) = 48 pCi/l

LSC lead-210 activity measurement = 61.9 pCi
Sample Volume = 23,9751
Concentration = 0.00258 pCi/l
Expected lead-210 from deposited radon daughters calculated from Tsivoglou data
= 0.00014 pCi/l
Hence, the net baseline lead-210 concentration is = 0.00244 pCi/l

2. 1st Sample data: Elapsed time = 17h 5m

RaA (pCi/l) = 6,552.74 pCi/l

RaB (pCi/l) = 7,132.01 pCi/l

RaC (pCi/l) = 6,283.94 pCi/l

WL = 66.3

Rn-222 (pCi/l) = 6,513 pCi/l

LSC lead-210 activity measurement = 672.13 pCi
Sample volume = 10762.51
Concentration = 0.0625 pCi/l
Expected lead-210 from deposited radon daughters calculated from Tsivoglou data
= 0.0329 pCi/l
Net lead-210 on sample = 0.0296 pCi/l
Baseline lead-210 level = 0.0024 pCi/l
Net lead-210 ingrowth above baseline = 0.0272 pCi/l

3. 2nd Sample Data: Elapsed time = 1.812 d

RaA (pCi/l) = 8,828.2 pCi/l
RaB (pCi/l) = 8,860.6 pCi/l

RaC (pCi/1) = 8,006.3 pCi/1
WL = 85.79
Rn-222 (pCi/1) = 8,562.5 pCi/1
LSC lead-210 activity measurement = 6,170.67 pCi
Sample Volume = 16,624 1.
Concentration = 0.3712 pCi/1
Expected lead-210 from deposited radon daughters calculated from Tsivoglou data = 0.0414 pCi/1
Net lead-210 on sample = 0.3298 pCi/1
Baseline Lead-210 level = 0.0024 pCi/1
Net lead-210 ingrowth above baseline = 0.3274 pCi

Table 9.

Predicted Lead-210 Ingrowth in Dakota Chamber 3

For the Dakota Chamber #3, the radon-222 flux was measured to be 8,514 pCi/l concentration increase in 1.81 days, in a chamber volume of approximately 154, 674 liters.

Thus there was a flux rate of radon-222 of:

$$C\ (pCi/d) = 8{,}514\ (pCi/l) \times 154{,}674\ (l) \times \frac{1}{1.81}\ (d)$$

$$= 7.276 \times 10^{8}\ pCi/d\ \text{influx radon-222}$$

Now since I (dpm) = $N\lambda$, the atom flux rate must be:

$$C(\text{atoms/min}) = 7.276 \times 10^{8}\ \frac{(pCi\ ^{222}Rn)}{d} \times 222\ (dpm) \times 5.5\ (d)$$

$$= 8.883 \times 10^{9}\ \text{atoms/min influx radon-222}$$

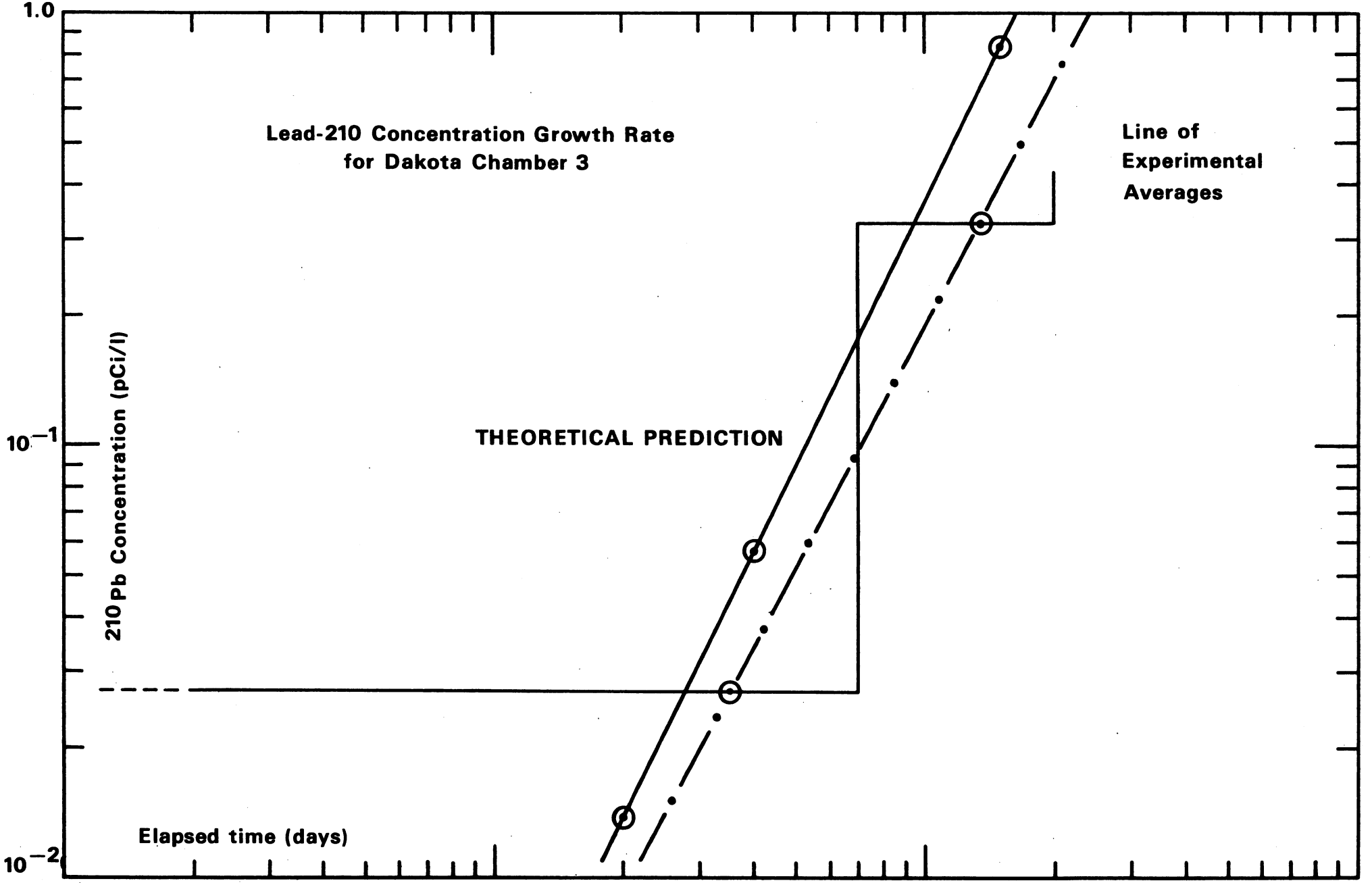
With $C = 8.883 \times 10^{9}$ (atom/min), the predicted ingrowth of lead-210 using the model

$$I_D = C\left[1 + \frac{\lambda_D}{\lambda_R - \lambda_D} e^{-\lambda_R t} \frac{\lambda_R}{\lambda_R - \lambda_D} e^{-\lambda_D t}\right]$$

is indicated in the following table of values:

t(Min)	I_D (pCi)	I_D (pCi/l) Assuming V=154,647 l
1.0	3.32×10^{-2}	2.146×10^{-7}
1.7	9.60×10^{-2}	6.207×10^{-7}
5.2	8.99×10^{-1}	5.812×10^{-6}
16.4	8.93	5.773×10^{-5}
51.8	89.0	5.754×10^{-4}
175.0	8.88×10^{-2}	5.741×10^{-3}
570.0	8.88×10^{-3}	5.741×10^{-2}
1870.0	8.88×10^{-4}	5.741×10^{-1}
6100.0	8.88×10^{-5}	5.741

FIGURE 7


Lead-210 Concentration Growth Rate
for Dakota Chamber 3
Line of
Experimental
Averages
THEORETICAL PREDICTION
210Pb Concentration (pCi/l)
Elapsed time (days)
1.0
10−1
10−2
0.01
0.1
1.0
10

Since the latter represent averages over nearly 24 hours in each case, it may well be that the average emanation rate of radon in the test chamber was indeed lower.

This experiment does confirm that quite rapid ingrowth of lead-210 will occur in stagnant air even at relatively low radon emanation rates. (The Dakota mine emanation rate is approximately ten times lower than rates published for commercially operating mines in the Ambrosio Lake area). Thus, for example, it can be seen from these graphs that the MPC for occupationally exposed persons to lead-210, which is $2X10^{-1}$ pCi/1, is reached in from 0.8 to 1.0 day starting from clean air!

Of course, under most circumstances encountered in actual mining conditions today, air which miners are exposed to is not nearly 24 hours old. But occasionally men are exposed to air which has a portion of air which is at least that old or older. The consequences in terms of a resultant body burden of lead-210 are probably minor, but it certainly would complicate efforts to relate body burdens of lead-210 to a cumulative WLM exposure record. No doubt many men who were working in uranium mines years ago before extensive ventilation was used were exposed to quite high lead-210 levels which would be reflected in their present body burdens of this isotope. Another aspect of the surprisingly rapid ingrowth pattern lead-210 exhibits, one which was not discussed previously, is that since the half-life of lead-210 is so very much longer than radon-222, the activity ratio of daughter to parent increases continuously as time increases. Furthermore, for times much larger than the half-life of radon (3.82 days), the initial stock of short-lived parent atoms becomes a stock of long-lived atoms which decay at the low daughter rate. Thus the effects of, say, a week or more of high radon emanation, would persist for quite a long time in stagnant air even though the measured radon level might have dropped considerably. So if one were to obtain a radon sample from a stagnant air source, it would be difficult to predict the lead-210 level in that same air just from the radon and WL information without knowing the prior history of radon levels there.

Thus this third model provides useful insight into the complexities of the determination of the nature and magnitude of one class of background lead-210 sources, stagnant mine air.

3. The most difficult model of lead-210 ingrowth to study experimentally proved to be the second model, in which the effects of the continual emanation of radon into an air stream moving through a tunnel are integrated over the entire length of tunnel.

Two series of experiments were undertaken in the course of the study of this model. The plan in each case was essentially the same. Since the ingrowth of lead-210 from radon contaminated air is small in short time intervals and low radon levels, the background lead-210 would have to be eliminated at the outset of the growth period. Then all the lead-210 measured on a sample would be attributable either to the decay of short-lived daughter atoms collected, or to lead-210 atoms which had grown into the air as it aged. The pure radon and air mixture was prepared by passing all the air to be later sampled through HEPA (High Efficiency Particulate Air) filters which are capable of removing

essentially all aerosol (and all radon daughters) from the air. Aerosol for short-lived radon daughter attachment was to be later added.

In the first series of experiments, the 600 feet of incline leading from the surface down to the station area in the Dakota mine was planned as the ingrowth tunnel. A tightly sealed bulkhead with provision for installation of a large HEPA filter and access doors was constructed at the bottom of the incline. Then, with the doors closed and filter in place, the smaller of the two surface fans was turned on in the downcast operating mode. This forced air contaminated with radon from the mine area through the filter and up the incline. When it later became apparent that in spite of considerable effort to make tight seals, enough of the radon decay products were getting through the bulkhead to upset the required controlled growth conditions, the HEPA filter was installed in a sealed box with a separate fan which pulled mine air through the filter and discharged it through the sealed bulkhead into the incline. Thus the incline was in effect over-pressured relative to the rest of the mine, and accordingly all leaks would be from the incline into the rest and thus were neutralized.

Other problems materialized soon after the problem of leaks was resolved: first of all, there was so much turbulence in the air coming into the incline from the filter fan through an eight inch vent tube that considerable recirculation of air occurred immediately causing an initial uncontrolled aging of the air; second, the volume of air into the incline was so small that the air flow pattern up the incline was exceedingly complex, including unexpectedly large counter currents of surface air down the incline. The subsequent mixing with aged air slowly moving up produced unpredictable air concentrations of radon daughters. Third, there was considerable difficulty generating an adequate aerosol which would persist all the way up the incline. The cumulative effect of all these difficulties was to render the lead-210 measurements of samples taken at the bottom and top of the incline unusable as a check of the second model since all control of relevant growth parameters was lost.

It was then decided to redesign the experiment on a reduced scale. In this second series of experiments radon contaminated air was to be pulled through a HEPA filter, aerosol added, and the resultant air mix moved up the incline through eight inch collapsible vent tubing. Measurements of radon daughters at various points in the airstream of this long tube indicates that, provided adequate aerosol is added, a nearly idealized growth pattern can be realized.

Unfortunately, this series of experiments was not completed before the termination of the project and so a usable set of samples was not obtained from the tube.

Part IV - Conclusions and Discussion

There were several problem areas set forth in the original Lead-210 Project Proposal which were to be studied in the course of the investigation. Each of these will be discussed in this concluding section in light of the theoretical and experimental results which have been set forth in the preceding sections of this report.

A. The development of liquid scintillation beta-counting (LSC) procedure for lead-210 which is collected in uranium mine air samples was an early target of this project. Although it had been previously demonstrated that LSC could be used to count lead-210 with high efficiency, no technique for preparing environmental air samples for counting lead-210 had been developed. A suitable technique was successfully developed for the purposes of this project. That is to say, a technique was developed which would enable the efficient extraction of lead-210 in quantities on the order of magnitude of the quantitative detection limit of the liquid scintillation counting system which is approximately 56 pCi of lead-210. The sample matrix from which the lead-210 to be extracted is presumed to be microsorban filter medium and typical mine aerosols such as are dust and diesel smoke.

   The specific conditions of the applicability of the techniques described in this report are being stressed here because other potentially useful applications of the technique, such as in various bioassay schemes, have not been investigated in the present study. There could well be certain difficulties in attempting to extend the techniques to other sample matrices such as strongly interferring reactions of the chloroform-dithizone extraction solvent with biological materials. It seems likely that such difficulties could be resolved; the point here is only that the conclusion warranted by this study is that dithizone extraction and liquid scintillation counting can provide a rapid, sensitive technique for measuring very low levels of lead-210 in mine atmospheres. Concentrations a thousand times smaller than the occupational MPC for lead-210 were successfully measured, although long term sampling obviously was required. Smaller concentrations were detected, but were not, strictly speaking, measured at the quantitative detection level for the system.

B. The principal target of the project, once a suitable measurement system was readied, was the development of an accurate means for relating measured lead-210 on a long term mine air sample to the cumulative WLM exposure which men who were working in the area the sample was taken from would have received. The rationale for this exposure determination technique is presented in the introduction of this report.

   At the outset, it was clear that there would be several potential sources for lead-210 on a sample of mine air. It was unknown just what the magnitude of each of these would be, and in particular, whether that portion of the sample attributable to the decay of the short-lived daughters of radon collected during sampling could be uniquely specified and thus be related to the cumulative inhalation exposure of miners during that sampling period. If the other background sources proved not

to be negligible by comparison with the target source, a possible means for accounting for background had to be sought. Both theoretical and experimental investigations were needed since neither aspect of the growth properties of lead-210 had previously been extensively studied.

The results of measurements in mine air concentrations ranging from hundredths to several tens of working levels reported in this study clearly indicate that the magnitude of the background contribution to the samples are, in fact, the dominant source of lead-210. Thus, the theoretical prediction to this effect is borne out. The average percentage attributable to background, 73.6%, is smaller than the average which can be calculated from the data of Blanchard's 1969 Study, 80.2%. See Table 10. This difference is perhaps attributable to the fact that much of his data was obtained from mine atmospheres where the control of radon daughter concentrations was much worse than is typical for the samples obtained from mines in this present study. For example, only two of the samples in Blanchard's study are from air less than 2WL, while in the present study, only three samples are from air above 3WL. Alternatively, the difference may be due to inaccuracies in the determination of daughter concentrations.

The consequences of finding very high background levels of lead-210, even in quite low WL air, for the proposal to count the short-lived daughters of radon after they have decayed to lead-210, is clear: since the activity of interest on a sample will almost certainly be masked by background of unknown and possibly variable origin, the chances of making an accurate estimate of the average exposure during the sampling period based on a measured quantity of lead-210 attributable to the short-lived daughters, must be low.

But a number of bioassay studies have indicated that there is a reasonably good correlation between body burdens of lead-210 and cumulative WLM exposure in uranium mines. If these results and the finding that the radon daughter contribution to lead-210 collected on a filter bed is very low are to be consistent, there must be a strong correlation between the total lead-210 that would be measured on a filter sample and the WL of the air that sample was taken from. Indeed, the data of this study supports that hypothesis. The regression line of WL on total lead-210 for 14 of the data points from the field studies is: $WL = 709.15\ (Pb\text{-}210)^{1.06155}$. The correlation coefficient is $\Gamma = 0.94$. Also, there is a good correlation between atoms of lead-210 per liter of mine air attributable to daughters, Pb_d, and atoms of lead-210 per liter of mine air attributable to background Pb_f: $Pb_d = 0.0866\ (Pb_f)^{1.10639}$, with a correlation coefficient $\Gamma = 0.915$. See Figures 8 and 9 for graphical results.

It is worthwhile to look more closely at the correlation between the WL data from a variety of mines and the corresponding total lead-210 on the samples from these sources.

Table 10

BLANCHARD'S 1969 DATA ON LEAD-210 BACKGROUND

(NATURE, 223, July 19, 1969)

Sample	Pb-210 Atoms from Rn-222 Daughters	Background Lead-210 Atoms	% Attributable to Background
1A	0.25×10^5	1.97×10^5	88.7
2A	13.9×10^5	125×10^5	89.9
3A	1.01×10^5	1.72×10^5	63.0
1B	4.35×10^5	8.7×10^5	66.7
2B	6.78×10^5	21.5×10^5	76.0
3B	2.39×10^5	7.6×10^5	76.1
4B	0.23×10^5	2.4×10^5	91.3
5B	1.56×10^5	2.6×10^5	62.5
6B	0.94×10^5	6.9×10^5	88.0
7B	4.41×10^5	13.8×10^5	75.8
8B	0.52×10^5	1.3×10^5	71.4
9B	1.31×10^5	6.5×10^5	83.2
1C	10.5×10^5	228×10^5	95.6
2C	6.38×10^5	172×10^5	96.4
3C	1.39×10^5	4.9×10^5	77.9
		Avg.	80.17%

The correlation is quite strong, but even judging from the obvious scatter of the data points, the 95% confidence limits of the regression equation have to be large, indicating that another set of data points representing another sample from the same population could very well be quite different. In other words, we can apparently confidently assert that a correlation exists, but we cannot say (from this data set, at any rate) what the exact form of the relation is. It would be very surprising, however, if the general trend of the data (the slope of the regression line) were very different.

Very likely one reason for the wide dispersion of this data set is the fact that these samples were drawn from a variety of mines, and even a variety of locations in a given mine. Accordingly, there are likely to be a number of different radon-222 emination rates and background lead-210 sources represented here.

Still, for all this variety, there are some surprisingly useful insights into the processes going on to be had by superimposing on the data some predictions based on the theoretical investigations developed in the preceeding discussion and a single boundary condition, namely, an estimate of the radon-222 emination rate J for the ore body in which the mines sampled in these investigations are located. The value is $J = 3.9$ pCi/cm^2 min reported in another study conducted in a mine in this same ore body.

Assuming an 8' x 10' tunnel in ore eminating radon-222 at this rate (these are generous estimates of mine dimension which would tend to overestimate the radon accumulation rate), from the Thomas and Epps tunnel model the radon daughter contribution to lead-210 on the sample can be calculated. And from the extension of this model to the prediction of background lead-210 in the air of the hypothetical tunnel, one source of background can be approximated.

The sum of these values represents the total lead-210 on a sample which could be anticipated by theory. A comparison of the graphs of these calculated values with the least-squares fitted graph of the data in Figure 8 reveals that theory predicts quite well the general trend of the growth of sample lead-210 with increasing WL! The essential difference between the predicted and observed lead-210 for a given WL is an additional background contribution which shifts the line to the right (increasing lead-210 for a given WL).

Now, subtracting the predicted total from the observed total at several points yields an approximation of the growth patter of the remaining background lead-210 unaccounted for. The resultant graph, shown in Figure 9 along with the others, has a steeper slope than the rest. The result is that a greater contribution to background occurs at lower WL's than at higher. Perhaps a way to express this result with an example would be to say that a leaky bulkhead contributes more background to relatively fresh air than it does to relatively stale air.

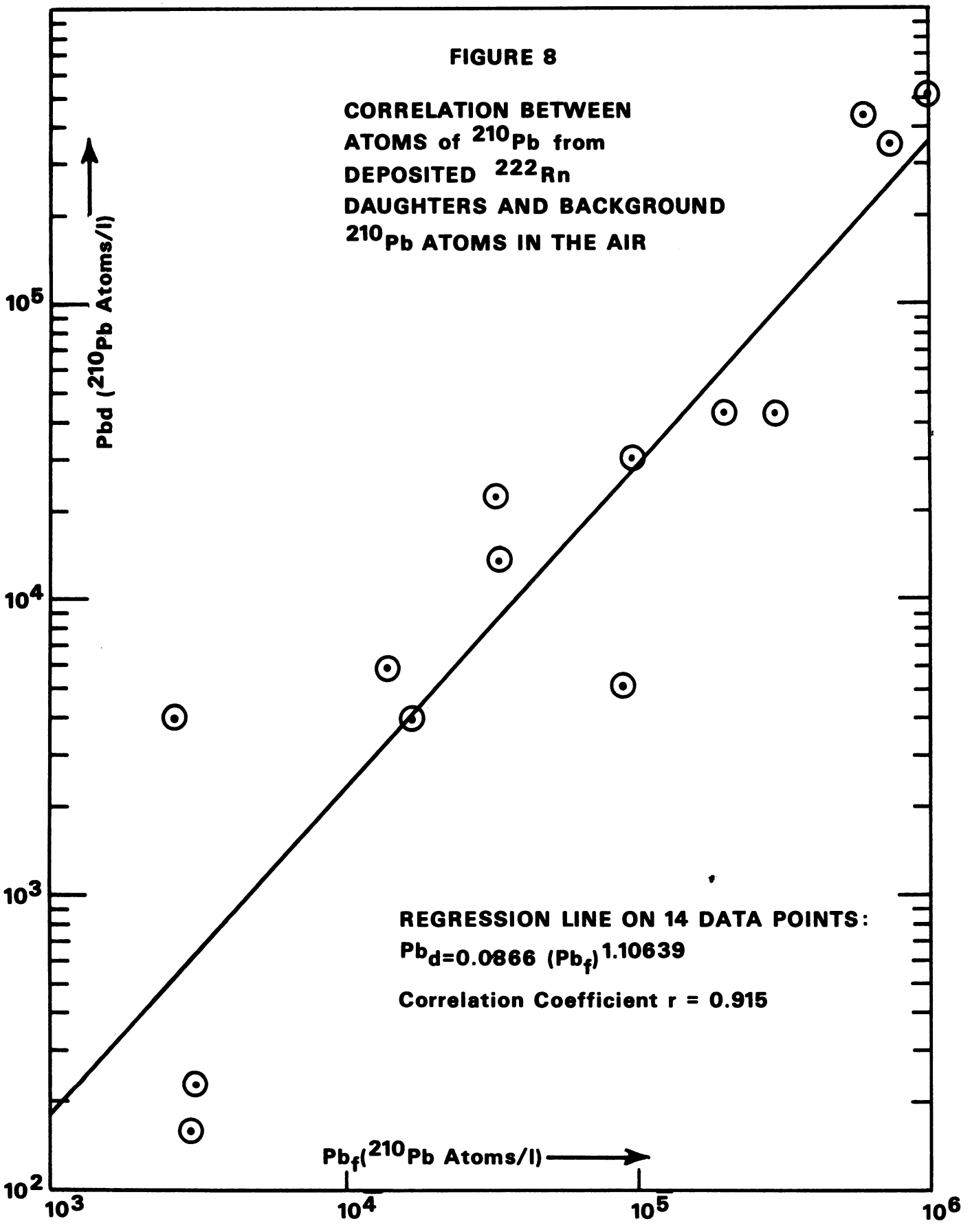
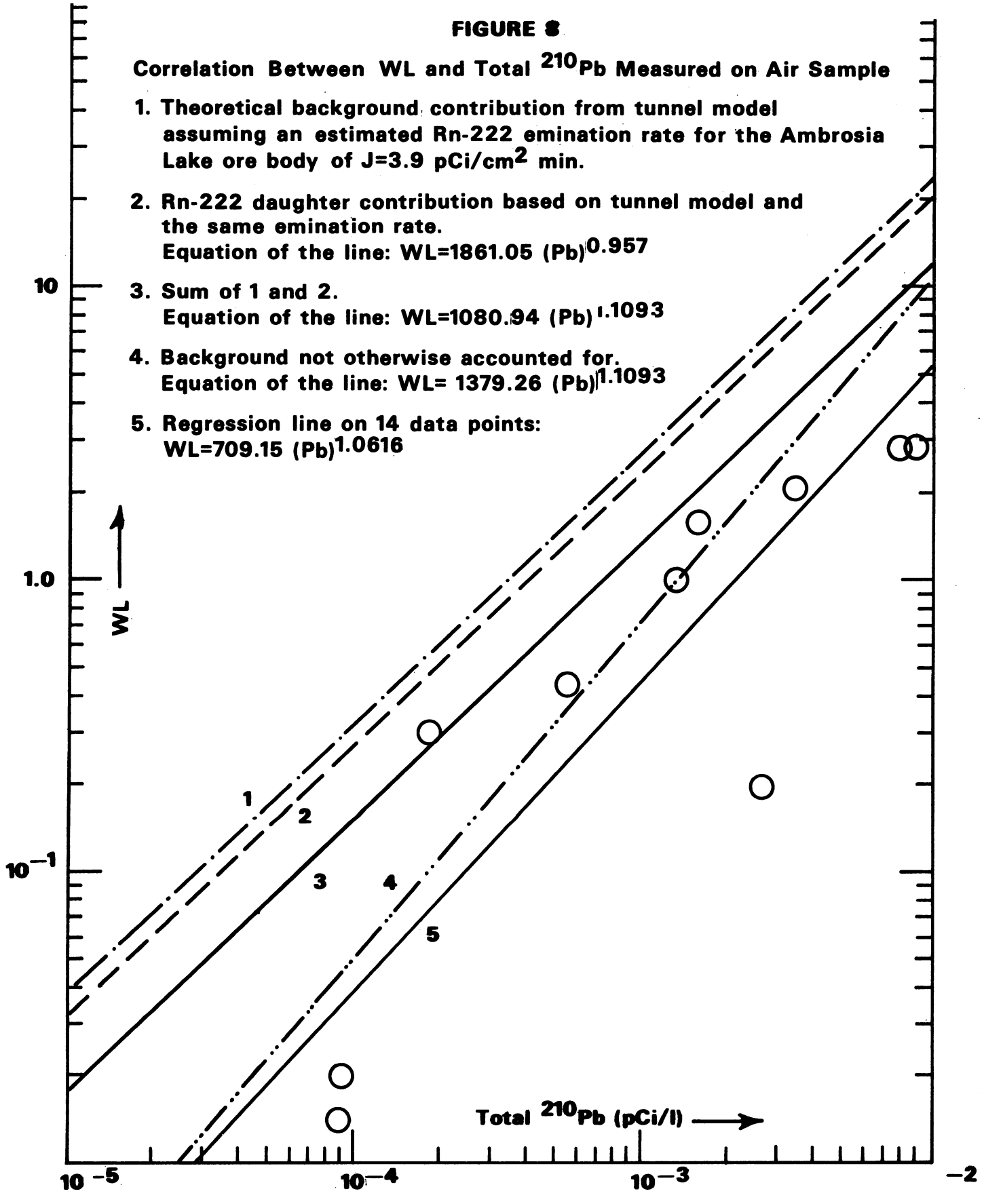

FIGURE 8
CORRELATION BETWEEN ATOMS of 210Pb from DEPOSITED 222Rn DAUGHTERS AND BACKGROUND 210Pb ATOMS IN THE AIR
Pbd (210Pb Atoms/l)
10^5
10^4
10^3
10^2
REGRESSION LINE ON 14 DATA POINTS:
Pbd=0.0866 (Pbf)1.10639
Correlation Coefficient r = 0.915
Pbf(210Pb Atoms/l)
10^3
10^4
10^5
10^6

FIGURE 8

Correlation Between WL and Total ^{210}Pb Measured on Air Sample

1. Theoretical background contribution from tunnel model assuming an estimated Rn-222 emination rate for the Ambrosia Lake ore body of J=3.9 pCi/cm^2 min.
2. Rn-222 daughter contribution based on tunnel model and the same emination rate.
   Equation of the line: WL=1861.05 $(Pb)^{0.957}$
3. Sum of 1 and 2.
   Equation of the line: WL=1080.94 $(Pb)^{1.1093}$
4. Background not otherwise accounted for.
   Equation of the line: WL= 1379.26 $(Pb)^{1.1093}$
5. Regression line on 14 data points:
   WL=709.15 $(Pb)^{1.0616}$



Combining these several graphs, the measured lead-210 can be used to predict the WL (as an average) in a given context according to a two-component relation of the form: $WL = (A + B)(Pb)^a + C(Pb)^b$ where the first term represents the contribution to the sample of the radon daughters and lead-210 which has grown into the air up to the time of sampling, and the last term represents the lead-210 contribution from stale air, ore dust and the like. For the data obtained in this study, A = 1861.055, B = 1080.937, C = 1379.257, a = 0.952, and b = 1.10934.

These results indicate that the measure of the total lead-210 collected on a mine air sample is a usable indicator of the average WL of the air sampled, in spite of the variety and potential variability of background sources. It is not possible to make good assessment of the accuracy of exposure measurements using lead-210 on the basis of data collected for this study. What would be needed would be a mine-scale comparison study between the present recordkeeping procedures and an appropriate application of lead-210 measurement. The extent of the sampling that would be involved is considerable. For example, there are at least eight types of work areas in a mine (surface, haulage development, stope development, stope production, raises, lunch room, track haulage, and miscellaneous others), and numerous examples of each type in each mine.

The problem being indicated here concerns the difficulty in devising an appropriate application of lead-210 measurement. The samplers in any mine scale experiment must be located and operated in such a fashion that the resultant integrated samples accurately reflect the actual exposure context of the men working in the mine. Only then could the results of lead-210 measurements be compared with the presently used grab-sample techniques.

There are several factors which must be taken into account here. First, it has been shown by AEC studies that the WL values throughout a mine fluctuate significantly, depending on the mining activities going on, and are at their lowest when all activity ceases. Thus, at the very least, sampling should be made only during times men are in the mine and at the location being monitored. This requires either automatic timing devices, or the active participation of miners and mine supervisors. Secondly, the WL of any given air stream will vary from place to place transversely, often being higher near the ribs and back of a tunnel than near the center. Also, it tends to be higher at any location along the length of the tunnel where air velocity drops significantly, such as near short side rooms, or even a widening of the tunnel. There can evidently be a conflict then between the demand for not obstructing movement in the tunnel and the demand that the air being sampled is accurately representative of the air being breathed.

Additional complications can arise, for example, in areas where men are actively mining high grade ore in large stopes where there is a potential for high radon emanation and poor ventilation. Then the men must be provided with fresh air discharged from a vent tubing outlet nearby. In such a situation one could want to sample just the air in the vicinity of the men, not upstream or downstream of their location in the stope. Again, this requirement tends to conflict with the necessity for having the

sampler, its power line, and so forth, out of the miners' way. Third, the necessity for obtaining high volume samples introduces another set of complications in itself. High volume samplers typically require a source of power other than batteries which introduces a logistics problem. Also, they are typically quite noisy and hence are uncomfortable to have in a work environment. While this third set of complications perhaps seems minor in comparison with some of the others, in the field work for this project such concerns produced definite constraints on the sampling activity.

These considerations are being advanced here as an indication of the kinds of operational considerations one would have to deal with in order to attempt to set up an exposure measurement system for an operating mine. No one of them seems to present an insurmountable difficulty. However, collectively, they might prove to make the implementation of such a system both in accurate and impractical, particularly in some of the older mines. In this regard, it might be worthwhile considering whether or not the appropriate kinds of sampling gear, power lines and other needed equipment could not be engineered into the plans for a new mine, and in so doing create a quite acceptable alternative to the present record-keeping scheme.

C. The possibility of applying the techniques for counting lead-210 described above to various lead-210 bioassay systems which have been reported in the literature has not been extensively studied in the present investigation. A few remarks concerning the potential of the system are in order, however.

The advantages LSC counting of lead-210 would bring to bioassay are clearly the savings in counting time required since no ingrowth of the daughters of lead-210 is necessary, and the potential for high counting efficiency due to the 4π counting geometry.

But there is an immediate drawback to such a proposed use, and that is the relatively high background count rate found in this study. There was not an emphasis put on optimizing the counting system parameters. But it soon became evident that the most desirable choice of amplification, made on the basis of a study of a number of the relevant parameters, such as the presence of an interfering beta-emitter and low lead-210 beta energy, entailed a moderately high background. The reason for this is that the region of highest background is naturally the low pulse-height region, and low amplification places a portion of the broad range beta signal in this region. The detrimental consequence of high background is that the minimum amount of lead-210 which can be measured quantitatively is large. For example, if one takes the value of 20 cpm background rate reported by Fairman and Sedlet as a nearly optimum value since this refers to counting a separated lead-210 standard, the minimum quantitative detection level is still nearly 53 pCi (as opposed to the 65 pCi reported in this study).

If the range of lead-210 in biological materials reported by Blanchard *et al* is considered typical (i.e., from 0.006 to 0.158 pCi/g of blood, and 0.12 to 10 pCi/g of bone), then quite large samples would be required. In fact, they might be too large to be considered practical in most circumstances.

Still, there does seem to be a place for the theory and counting techniques developed in this study in the continuing study of the uranium miners' problem through the application of bioassay techniques. And that is, since one of the largest unknowns in the lead-210 bioassay technique concerns the nature and extent of background contributions to a miner's body burden of lead-210, and since the theory and techniques of the present study are tailored to provide that kind of information, a joint investigation of both the airborne activities and resultant biological concentrations in certain specified contexts could prove to be a most rewarding approach to the problem of dosimetry in this area.

APPENDIX 1

Fairman's Ion Exchange Procedure

Column: 7 mm I.D., 2 cm, long

Resin: Dowex 21K (Cl-form) anion exchange

Flow Rate: 1 ml/min.

Steps:

1. Evaporate (.2 ml of 1.725 x 10^6 dpm/ml = 345,000 dpm) RaDEF solution and take it up in 2 ml 0.1 N HCl. Put it on the column.

2. Add 18 ml of 0.1N HCl slowly and collect 2 ml aliquots. The 3rd ml fraction should be clean lead-210 usable for spectrum. 500 lambda is evaporated in scintillation vial. Add 0.2 ml 1 N HNO_3. Add 10 ml of counting cocktail.

3. Add 20 ml concentrated HCl in different portions to the column: 2 ml (for acid change and to clear remaining lead); 3 ml; 5 ml; 5 ml; 5 ml; the 5th 2 ml aliquot should contain pure bismuth-210 and so can be used for analysis as above.

4. Put 1 ml of water through column to wash acid off. Then add 19 ml concentrated HNO_3 in 2, 2, 5, 5, 5 ml portions. Again the 5th 2 ml fraction is selected for polonium-210 analysis.

5. Make direct plates of solutions in 3 & 4. Check alpha to to beta ratio. Calculate polonium activity from alphas and bismuth activity from betas.

APPENDIX 2

Dithizone Separation Technique (Summary)

Reagents:

1. Chloroform - dithizone solution 0.1 g/l
2. HCl pH 2 (approximately 0.01 N HCl)
3. 0.3 - 0.5 N HCl
4. 1.0 N HNO_3

Procedure:

1. Evaporate an aliquot of RaDEF solution to dryness using a double-boiler arrangement. Take up residue in 5 ml of 0.01 N HCl.
2. Add the solution to 5 ml chloroform-dithizone solution in separatory funnel and shake vigorously for 2 minutes.
3. The aqueous phase, now containing most of the lead, is separated off, evaporated to dryness and taken up in 0.5 ml 1N HNO_3 and counted.
4. The chloroform solution is returned to the funnel and 5 ml of fresh 0.01 N HCl is added as a wash. Steps 2 and 3 repeated.
5. The chloroform aliquot is returned to the funnel and 5 ml of 0.3 - 0.5 N HCl is added. Shake for 2 minutes; the aqueous phase now contains most of the bismuth. Evaporate to dryness and take up in 0.5 ml 1N HNO_3 and count.

The Use of Dithizone for Separation and Purification of RaDEF,
by George Bouissierres and C. Ferradini
Analytica Chemica Acta, Vol. 4 (1950)

The complexes formed by dithizone* with metallic ions are soluble in chloroform and are stable in a pH interval whose limits vary with each element. As a consequence, one is able to extract certain cations in aqueous solution by means of a combined solution of chloroform and dithizone, or inversely, to convert an organic medium to an aqueous one, under the condition of fixed conversion pH. The principle application of this method is the extraction and micro-determination of lead, although it has turned out to have interesting application in the

* Diphenylthiocarbazone

separation and verification of elements which actively deposit in the series RaDEF.

With this objective, we have from the very first verified and completed the experimental results relative to lead and bismuth, and studied the behavior of the isotopes RaD and RaE, and at the same time determined the conditions for the extraction of polonium. For this assay, we have adopted the following mode of operation: In a flask, vigorously shake for a few minutes 5-10 ml of a solution having 0.1 g/l of dithizone in chloroform with an equal volume of an aqueous solution of the radioactive elements whose activity and acidity are known. After resting 1/20 of a minute, the two phases are separated by decantation and evaporated to dryness on a glass double-boiler arrangement. One then measures the α, β and γ activities of each portion, according to whether it is a matter of measuring the amount of Po, RaE or RaD.

The measurement of RaD γ's has been carried out by M. Riou using a geiger counter after eliminating the RaE β's by means of an appropriate magnetic field. The β's were measured using an ionization chamber connected to electrodes at quadrants.

The activities initially employed in the assay were on the order of 1μCi Po, 100μCi RaE and 100μCi RaD.

For each radio-element we have verified that the coefficient of separation is the same as the activity which was initially in the aqueous or organic phase.

Experimental Results

1. Radium D (^{210}Pb)

   In using radio-lead, we have confirmed the results of Bamback & Bronner who found the extraction of lead is accomplished with excellent yield when the pH of the aqueous solution is near 9; but then, on the contrary, the totality of the lead remains or passes back in the aqueous layer when the pH of it is less than 3.

2. Radium E (^{210}Bi)

   We have studied the extraction of radium E, in as many chlorhydric solutions (as needed). The curves of Figure 1 indicate the variation in yield of the extraction as a function of pH. The curves are not modified when one adds to these solutions 10 mg of bismuth per liter - that which modifies the concentration in the ratio of 4×10^5 to 1.

   Note that the retention depends on the nature of the anion persent in the aqueous phase. When the solution is chlorhydric the extraction is 97% at pH1 and only 2% at pH0; whereas, if the solution is nitric, it is still 80% at that pH. That difference in the behavior of Bi in chlorhydric and nitric solutions is explained by the formation of a chloride complex of

the form $(Bi\ Cl_x)^{(x-3)}$ which prevents the metallic ion from passing to the state of dithizone. In order to give evidence of that action of the complex of the chlorhydric ion, we have made the following experiment:

To a solution of RaE without salts with pH equal to 3, we added Na Cl. On the one hand, so long as the concentration of this salt is less than 0.25 mol/l the yield of extraction remains unchanged at 95%, but if the concentration of Na Cl is up to 1 mol/l, there is no further extraction. On the other hand, under the same conditions, the presence of $Na\ NO_3$ is not troublesome.

We found a maximum of extraction for nitric solutions toward pH 4-5, which is in accord with the indications of Wichmann. But we found the onset of extraction with a much stronger acidity than that indicated by that author.

3. Polonium

Preliminary assays have demonstrated that polonium is not extracted from chlorhydric or nitric solutions by pure chloroform at whatever acidity. But with a dithizone-chloroform solution extraction attains 95% if the pH of the solution is between 0 and 5 (Fig. 2).

Contrary to what we observed with bismuth, the results are essentially the same with chlorhydric and nitric solutions. This justifies the conclusion that Po forms a stable dithizonate with dithizone which is stable at pH 0 to pH 5. If one compares the pH's corresponding to maximum of extraction the order is Po, Bi, Pb which conforms to the Wichmann rule: the more noble the metal, the more base is the pH for optimum extraction.

Applications

1. Extraction of RaD from old radium ampoules (not translated here).

2. Chemical and radiological purification of solutions of RaE. In the course of manipulations, radium E is often associated on the one hand, with radium D and polonium, or on the other hand, with nickel and aluminum. The solution, preferably chlorhydric, is neutralized to pH 2.

   In this condition Po and RaE are separated, with dithizone, from RaD, Ni and Al which remain quantitatively in the aqueous phase. Then the chloroform solution is agitated with 0.3-0.5N HCl which extracts more than 95% of the RaE but only 3 to 5% of the Po present. If one desires a greater purity from Po, the polonium residue can be eliminated by treating the chlor-hydric solution of RaE, without changing its acidity, one or two times with a fresh solution of dithizone in chloroform.

   This technique presents several advantages over the classic methods. For one, it allows the simple and rapid preparation of RaE without associated matter, which is important for the preparation of strong sources. For

another, it allows the elimination, in a manner more rapid and more complete, of the polonium present in the solutions of RaE which naturally are spontaneously deposited from the parent metal.

The use of dithizone has, as well, the advantage over the former procedures of avoiding the presence in solution of metallic ions which are capable of being troublesome, for example, in the process of electrolysis of RaE. (rest of the paragraph untranslated here)

3. Preparation of Pure Polonium

If a chlorhydric solution 0.3 to 0.5N of RaDEF is treated with the dithizone solution, Po is extracted as well as 3 to 4% of RaE. The chloroform solution is then washed with 0.5N HCl to eliminate traces of RaE, and then with 4N HCl which passes the Po into the aqueous phase. (the rest untranslated here)

BIBLIOGRAPHY

1. W.D. Fairman and J. Sedlet, Determination of Lead-210 by Liquid Scintillation Counting, Analytical Chemistry, 40, 2004 (1968).

2. G. Gouissieres and C. Ferradini, Emplor De La Dithizone Pour Separer et Purifier Le Radium D, Le Radium E, et Le Polonium, Analytica Chemica Acta, 4, 610 (1950).

3. R. L. Blanchard, Rapid Determination of Lead-210 and polonium-210 in Environmental Samples by Deposition on Nickel, Analytical Chemistry, 38, 189 (1966).

4. H. A. Talvitie and W. J. Garcia, Radiochemical Determination of Lead-210 after solvent Extraction as Iodidide and Dithizonate, Analytical Chemistry, 37, 851 (1965).

5. M.S. Patterson and R.C. Greene, Measurement of Low Energy Beta-Emitters in Aequous Solution by Liquid Scintillation Counting of Emulsions, Analytical Chemistry, 37, 854 (1965).

6. L. A. Currie, Limits for Qualitative Detection and Quantitative Determination, Analytical Chemistry, 40, 586, (1968).

7. R. D. Evans, Engineers' Guide to the Elementary Behavior of Radon Daughters, Health Physics, 17, 229 (1969).

8. J. W. Thomas and R. Epps, Radium A, B, and C concentrations and Working Levels from Radon Emination in a Mine Tunnel, HASL TM 70-4, Sept. 1970.

9. N. Jacobi, Activity and Potential Alpha Energy of Radon-222 and Radon-220 Daughters in Different Air Atmospheres, Health Physics, 22, 441 (1972).

10. A. J. Breslin, A. C. George, and M. S. Weinstein, Investigation of the Radiological Characteristics of Uranium Mine Atmospheres, HASL-220, December, 1969.

11. R. L. Blanchard, Radon-222 Daughter concentrations in Uranium Mine Atmospheres, Nature, 223, 287 (1969).

12. R. D. Evans, The Atomic Nucleus, Twelfth Printing, McGraw-Hill (1969).

13. R. L. Blanchard, V. E. Archer, G. Saccomanno, Blood and Skeletal Levels of Pb-210, Po-210 as a Measure of Exposure to Inhaled Radon Daughter Products, Health Physics, 16, 585 (1969).

14. Richard B. Holtzman, Sources of Lead-210 in Uranium Miners, Health Physics, 18, 105 (1970).

15. Charlot and Beziers, Analyse Quantitative, p. 275, Hopkins and Williams, Reactif Organiques en Analyse Minerale, p. 59.

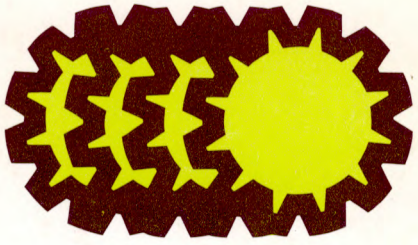
16. Bombach and Burdey, Ind. Eng. Chem. Anal. Ed., 15 (1942), 904.

17. Wichmann, Ind. Chem. Anal. Ed., 7 (1935), 285.

18. Irene Curie, J. Chem. Phys., 22 (1925), 285.

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