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ARH-SA-29

CONF-690606--3

IMPROVEMENTS IN RADIOCHEMICAL ANALYSIS
AND DATA REDUCTION OF ENVIRONMENTAL AIR SAMPLES

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ABSTRACT

An environmental air sample radioactivity monitoring program used at the Redox Analytical Laboratory is described. A proposed revision and computerization of this program to meet the current and projected needs is outlined. The limits specified by the existing authority are referenced and explained. Methods of attaining improved lower detection limits and computer calculated results together with computer plots of long term data are outlined.

INTRODUCTION

To ensure safe working conditions, it is necessary to provide rapid detection of biologically significant levels of radioactivity by automatic continuous monitoring alarm systems. It is also necessary to provide accurate analysis as part of a well documented permanent record.

This is required to assure compliance with AEC policy (1) "... contractor operations shall be conducted in a manner that will limit personnel radiation exposures to the lowest practical levels".

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In order to supply accurate and meaningful analytical data for historical and legal purposes, it is necessary to provide a valid system of analysis which is capable of meeting the requirements (Table I) specified by the existing authority.

One method (2) of complying with these standards is to demonstrate that "concentrations in effluents released to uncontrolled areas do not exceed the radiation protection standards specified (3) . . . ". Thus the release of effluents is limited by the possible effect on exposures in uncontrolled areas.

The following concepts must also be kept in mind: 1) "Radioactive wastes released to the atmosphere should be minimized to the fullest extent technically and economically feasible" (4). 2)

"Representative measurements should be made and documented for all wastes discharged, along with identification of the radionuclides so disposed" (5).

TABLE I
CONCENTRATIONS IN AIR ABOVE NATURAL BACKGROUND

Isotope		AEC Chapter 0524 Annex 1 Table II	Guidelines - AEC Routine Operating Levels	Guidelines - ARHCO Desired Maximum Levels	Analytical Capabilities	
		Air (uc/ml)	Air (uc/ml)	Air (uc/ml)	Current LDL Air (uc/ml)	Potential LDL Air (uc/ml)
Am ²⁴¹	S*	2×10^{-13}	2×10^{-14}	2×10^{-15}	1.8×10^{-14}	1.8×10^{-15}
	I*	4×10^{-12}	4×10^{-13}	4×10^{-14}	1.8×10^{-14}	1.8×10^{-15}
SB ¹²⁵	S	2×10^{-8}	2×10^{-9}	2×10^{-10}	6.6×10^{-13}	6.6×10^{-14}
	I	9×10^{-10}	9×10^{-11}	9×10^{-12}		
Ce ¹⁴⁴	S	3×10^{-10}	3×10^{-11}	3×10^{-12}	2.1×10^{-12}	2.1×10^{-13}
	I	2×10^{-10}	2×10^{-11}	2×10^{-12}		
Cs ¹³⁷	S	2×10^{-9}	2×10^{-10}	2×10^{-11}	4.5×10^{-13}	4.5×10^{-14}
	I	5×10^{-10}	5×10^{-11}	5×10^{-12}		
Co ⁶⁰	S	1×10^{-8}	1×10^{-9}	1×10^{-10}	8.5×10^{-13}	8.5×10^{-14}
	I	3×10^{-10}	3×10^{-11}	3×10^{-12}		
I ¹³¹	S	1×10^{-10}	1×10^{-11}	1×10^{-12}	2.2×10^{-13}	2.2×10^{-14}
	I	1×10^{-8}	1×10^{-9}	1×10^{-10}		
Nb ⁹⁵	S	3×10^{-8}	3×10^{-9}	3×10^{-10}	8.6×10^{-13}	8.6×10^{-14}
	I	3×10^{-9}	3×10^{-10}	3×10^{-11}		
Pu ²³⁹	S	6×10^{-14}	6×10^{-15}	6×10^{-16}	1.8×10^{-14}	1.8×10^{-15}
	I	1×10^{-12}	1×10^{-13}	1×10^{-14}		
Pm ¹⁴⁷	S	2×10^{-9}	2×10^{-10}	2×10^{-11}	3.4×10^{-13}	3.4×10^{-14}
	I	3×10^{-9}	3×10^{-10}	3×10^{-11}		
Pa ²³³	S	2×10^{-8}	2×10^{-9}	2×10^{-10}	4.2×10^{-13}	4.2×10^{-14}
	I	6×10^{-9}	6×10^{-10}	6×10^{-11}		
Ru ¹⁰³	S	2×10^{-8}	2×10^{-9}	2×10^{-10}	2.9×10^{-13}	2.9×10^{-14}
	I	3×10^{-9}	3×10^{-10}	3×10^{-11}		
Ru ¹⁰⁶	S	3×10^{-9}	3×10^{-10}	3×10^{-11}	3.0×10^{-12}	3.0×10^{-13}
	I	2×10^{-10}	2×10^{-11}	2×10^{-12}		
Sr ⁹⁰	S	3×10^{-11}	3×10^{-12}	3×10^{-13}	2.1×10^{-13}	2.1×10^{-14}
	I	2×10^{-10}	2×10^{-11}	2×10^{-12}		
Zr ⁹⁵	S	4×10^{-9}	4×10^{-10}	4×10^{-11}	4.3×10^{-13}	4.3×10^{-14}
	I	1×10^{-9}	1×10^{-10}	1×10^{-11}		

* The criteria for determining whether a compound is soluble (S) or insoluble (I) is based on whether it may remain in lungs or become dissolved and be absorbed by the body, actually entering the blood stream. Since it is usually impossible to determine what combination of compounds may be involved in a particular case, the more restrictive case is used as the limit.

In order to meet these requirements it is therefore necessary to perform analysis at extremely low levels on some samples (see Table I).

While we are now capable of analyzing samples at the routine operating levels suggested by the AEC Guidelines, it is felt that the following areas could be improved:

1. Lower detection limit capability should be at least an order of magnitude below release guidelines.
2. Our ability to calculate large numbers of routine samples could be expanded by use of a computer with a saving of time, and a possible improvement in accuracy.
3. The analytical results could be presented in a format which could be more readily digested and interpreted, thus being more meaningful.

Description of Sample Collection

Samples of the radioactivity present in the air at various locations are collected on four-inch circular filters by the radiation monitoring groups. The sampling points include air in laboratories, exhaust air from laboratories, gaseous effluent from waste tanks, and emission from production plant stacks.

These samples are submitted to Technical Services Analytical Laboratories for analysis.

The collection rate is assumed to be constant throughout the sampling period. This involves both a constant uc/cc radioactivity level in

the area sampled and constant air flow through the sampler during the collection period.

The curve (see Graph I) shows the observed activity level approaching a maximum due to the decay of the collected material. The activity level will remain constant when sufficient material has been collected that the decay rate is equal to the collection rate.

When the sample is removed from the sampler it then continues to decay, approaching the activity level of the isotopes of very long half life if any are present.

(Definition for Graph I)

C = Counts on filter at time T_2

AT_2 = uc on filter at time $T_2 = \frac{C}{(\text{eff.}) (0.7) (2.22 \times 10^6)}$

AT_1 = uc on filter at time $T_1 = AT_2 e^{+\lambda \Delta T_2}$

$\Delta T_2 = T_2 - T_1$

Graph I
Collection and Decay Curve for Air Samples

Radioactivity (optional scale)

It is assumed that k = constant collection rate = Q (F.R.)

Where Q = uc/cc (constant concentration)

F.R. = flow rate of sampler in cc/minute

Let a = activity in uc on filter at time t , ($t > \gamma$) which remains from the activity collected on the filter between time γ and $\gamma + d\gamma$,

Therefore $a = (k d\gamma) e^{-\lambda(t-\gamma)}$.

$$\begin{aligned} \text{Then: } A_t &= k \int_0^t e^{-\lambda(t-\gamma)} d\gamma \\ &= \frac{k}{\lambda} e^{-\lambda t} [e^{\lambda \gamma}]_0^t = \frac{k}{\lambda} e^{-\lambda t} (e^{\lambda t} - e^0) \\ &= \frac{k}{\lambda} (1 - e^{-\lambda t}) \end{aligned}$$

$$\text{Or: } Q = \frac{AT_1 \lambda}{1 - e^{-\lambda T_1}} \cdot \frac{1}{\text{F.R.}}$$

In the case of a very long lived isotope such as Pu^{239} where the half life ($T_{1/2}$) is much greater than $4T$, or essentially "infinity", causing λ to approach zero, the above equation becomes:

$$Q = \frac{A_{t1}}{(4 t1) \text{ (F.R.)}}$$

Analytical Methods and Calculations

We are now using the general method suggested by G. Koval. (7)

This method is based on the fact that after six hours the half life of the natural alpha emitters is 10.6 hours (Pb^{212} , thorium B in the thorium natural decay series). It is therefore possible to calculate the amount of long lived alpha radioactivity by taking the initial count at least six hours after the sample is removed from the sampler, and the second count at least four hours later. The initial six hours is required to allow the very short lived isotopes of the uranium series to decay.

The long lived alpha activity is calculated using the following formula: (8)

$$A_{LL} = \frac{A_2 - (A_1 e^{-\lambda \Delta T_2})}{1 - e^{-\lambda \Delta T_2}}, \quad t_2 - t_1 = \Delta T_2$$

t_1 = time of first count

t_2 = time of second count

a_1 = alpha radioactivity recorded at first count.

a_2 = alpha radioactivity recorded at second count.

$$\lambda = \frac{\ln 2}{10.6} = 0.0654$$

The initial alpha count is decay corrected to the time of the second count, using the half life of the natural activity. This expected count (if all count is due to natural activity) is then subtracted from the second observed count.

The result is corrected to the initial count time and used as the quantity of long lived (QLL) alpha activity. There are three cases which can occur as shown by the QLL portion of table II.

The "quantity of short lived" (QSL) alpha activity may also be calculated as shown in the QSL portion of table II. This usually consists primarily of natural activity.

Since the observed activity may consist of various combinations of long and short lived isotopes, it should be noted at this point that knowing what the observed effective half life was may be an advantage. Half life may in fact be a better criteria than activity levels on which to base judgment of hazard on some cases.

Derivation of formula to calculate half life from two counts:

$$\lambda = \frac{\ln 2}{T_{1/2}}$$

$$A_2 = A_1 e^{-\frac{\ln 2 (\Delta t)}{T_{1/2}}}, \quad (11)$$

$$\frac{A_2}{A_1} = e^{-\frac{\ln 2 (\Delta t)}{T_{1/2}}}$$

$$\frac{\ln (A_1)}{(A_2)} = \frac{\ln 2 (\Delta t)}{T_{1/2}}$$

$$T_{1/2} = \frac{\ln 2 (\Delta t)}{\ln \frac{(A_1)}{(A_2)}}$$

TABLE II
DECISION TABLE

TO BE USED IN CALCULATION OF QSL AND QLL ALPHA ACTIVITY

Condition	Procedure		Explanation
	QSL Eq. #	QLL Eq. #	
$A_2 \geq A_1$	1	4	All long lived activity
$A_1 e^{-\lambda \Delta t_3} > A_2$	2	5	All short lived activity
$A_1 > A_2 > A_1 e^{-\lambda \Delta t_3}$	3	6	Mixture of short and long lived activity

QSL means Quantity of Short Lived Alpha Activity.

QLL means Quantity of Long Lived Alpha Activity.

QSL Eq. #1: $\text{uci/cc} < \frac{(1) (e^{\lambda \Delta t_2}) (8.33483 \times 10^{-14})}{(1 - e^{-\lambda \Delta t_1}) (F.R.)}, < 1 \text{ c/m short lived.}$

Eq. #2: $\text{uci/cc} = \frac{(A_1) (e^{\lambda \Delta t_2}) (8.33483 \times 10^{-14})}{(1 - e^{-\lambda \Delta t_1}) (F.R.)}, \text{ all short lived.}$

Eq. #3: $\text{uci/cc} = \frac{\left[\frac{A_1 - (A_2 - A_1 e^{-\lambda \Delta t_3})}{1 - e^{-\lambda \Delta t_3}} \right] (e^{\lambda \Delta t_2}) (8.3348 \times 10^{-14})}{(1 - e^{-\lambda \Delta t_1}) (F.R.)}$

QLL Eq. #4: $\text{uci/cc} = \frac{(A_2) (1.2796 \times 10^{-12})}{(F.R.) (\Delta t_1)}, \text{ all long lived.}$

Eq. #5: $\text{uci/cc} = \frac{(1) (1.2796 \times 10^{-12})}{(F.R.) (\Delta t_1)}, < 1 \text{ c/m long lived.}$

Eq. #6: $\text{uci/cc} = \frac{(A_2 - A_1 e^{-\lambda \Delta t_3}) (1.2796 \times 10^{-12})}{(F.R.) (\Delta t_1)}$

Where:

FR = flow rate of sampler in cubic feet per minute (cfm)

EFF = counts per minute per disintegration per minute (c/m) / (d/m)

0.7 = efficiency of air sample filter

A₁ = first count (c/m)

A₂ = second count (c/m)

$$\lambda = \frac{\ln 2}{10.64 \text{ hr.}} = 0.065145$$

$\Delta T_3 = T_3 - T_2$, time elapsed between first and second count (hours).

$\Delta T_2 = T_2 - T_1$, time elapsed between removal from sampler and first count (hours).

$\Delta T_1 = T_1 - T_0$, time elapsed on sampler, collection period (hours).

Equation #5 is therefore the case involving a lower detection limit for long lived alpha activity. The "normal case" would be for a collection period of 24 hours and a flow rate of 3 cfm. The "best case" (i.e. lowest detection limit) would be for a 168 hour collection period and a sampler flow rate of 6 cfm. The lower detection limits (LDL) are therefore:

$$1) \text{ "normal case" LDL uci/cc} = \frac{(1) (1.2796 \times 10^{-12})}{(3 \times 24)} = 1.78 \times 10^{-14}$$

$$2) \text{ "best case" LDL uci/cc} = \frac{(1) (1.2796 \times 10^{-12})}{(6) (168)} = 1.27 \times 10^{-15}$$

Beta radioactivity is also measured calculated and reported. It is assumed to be long lived (it may include some short lived natural activity) and is calculated using the second beta count in the following formula:

$$\text{ucc/cc} = \frac{(\text{c/m Beta}) (9.889 \times 10^{-13})}{(\text{F.R.}) (4 T_1)}$$

$$\text{"Total curies beta emitted"} = \frac{(\text{uc}) (\text{stack flow cfm}) (10^{-6})}{(0.7) (\text{F.R.})}$$

At the present a gamma energy analysis is requested only when the "total curies of beta radioactivity emitted" is above a certain specified limit for each sampling location. (9)

Problems and Proposed Solutions

Because of the work which has been done, we are now in a position to solve the following problems. We need to know what level the alpha, beta, and gamma radioactivity is when released to the environment. We need to know also what level it is in relation to previous history. This information needs to be readily available without a great deal of research and interpretation. The "total beta" results are rather ambiguous since they could have different meanings depending on the circumstances. For instance, observe the results shown below in Table III comparing what a "total beta" indicates in relation to what is actually present as shown by a more comprehensive analysis. The total beta must be calculated without benefit of knowing what isotopes are actually present unless additional analyses are performed, such as a gamma energy analysis (GEA), to identify the particular isotopes present which are contributing to the observed beta count. The calculations for "total beta" are therefore based on assumptions which are not necessarily valid.

"Total beta" activity is calculated as a hypothetical, non-volatile, isotope of long half life emitting a mono-energetic beta particle of energy 0.3 Mev. A "total beta" analysis is in fact only slightly more

meaningful than the "total gamma" analysis formerly used (prior to development of gamma energy pulse height analysis). This fact is explained to customers requesting analysis, but the explanation usually has little effect.

In the case of environmental air sample monitoring this fact deserves more consideration.

What is needed, and in fact is specified as being required, (12) IS TO "assure that the release of wastes capable of adversely effecting the environment is limited to the lowest practical level".

This means that releases shall not merely comply with whatever release guides are set up but will in fact be continually held as low as possible.

This therefore implies that the analysis will be capable of measuring what is actually released, (if any).

Lowering the lower detection limit (LDL) can only be accomplished by performing and reporting the most comprehensive analyses of which we are capable. If this is then done routinely, and the data analyzed properly, what was once an analytical lower detection limit may become a routine operating level. It also provides a means of more critically evaluating problem areas as they arise, and in fact predicting them in advance, thus avoiding many serious errors. For example, when the Redox Plant was in operation an alpha count on an air sample was observed to be

"higher than normal". It was not over the limits specified nor even close to them, but merely higher than usual. A gamma energy analysis showed the absence of the expected fission products, but gave an indication of Bi^{210} . An alpha energy analysis (AEA) then showed the sample to be mostly Po^{210} . A potentially serious problem was avoided as a result.

TABLE III

Comparison of UQ/cc "total beta" to actual uCi/cc present

The formula $UQ/cc = \frac{(c/m \text{ beta}) (3.7875 \times 10^{-13})}{(\text{efficiency}) (F.R.) (\Delta T_1)}$ is used in both cases,

with efficiency factor 0.383 for "total beta". The proper efficiency factor is used in the case where the actual isotope is known. Flow rate (F.R.) = 3, sampling period (ΔT_1) = 24 hours, c/m beta = 1000.

<u>Isotope</u>	<u>"Total Beta" uQ/cc Isotope Unknown</u>	<u>Beta in uCi/cc Isotope Known</u>
⁶⁰ Co	1.37×10^{-11}	1.37×10^{-11}
⁹⁰ Sr	"	1.05×10^{-11}
⁹⁵ ZrNb	"	1.96×10^{-11}
¹⁰³ Ru	"	2.63×10^{-11}
¹⁰⁶ RuRh	"	1.75×10^{-11}
¹²⁵ Sb	"	1.58×10^{-11}
¹³¹ I	"	1.10×10^{-11}
¹³⁴ Cs	"	1.4×10^{-11}
¹³⁷ Cs	"	1.04×10^{-11}
¹⁴⁴ CePr	"	1.19×10^{-11}
¹⁴⁷ Pm	"	1.74×10^{-11}
¹⁵¹ Sm	"	1.78×10^{-11}

Methods instituted or suggested to attain increasingly lower LDL:

We are now using 1c/m net alpha, and 20c/m net beta as LDL. In order to improve on this, we must attain lower background and utilize a larger count time as well as change some of the other variables in the calculation such as the sampler flow rate where possible. The collection period could be lengthened but may be defeating the purpose because of the short half lives which may be involved.

Longer collection periods would also effect the premise that the radio-activity collected is deposited at a uniform rate (activity/time).

A reduction in background can be facilitated by: 1) further removal of the instrument from an area where high level samples are also handled, 2) a reduction in the "dust" commonly found in laboratories which can contribute to the background. This can best be accomplished in the present facility through the use of a remote "clean room".

Automation of Calculations and Reports

The format in which information is collected and reported can be as important as the analysis itself, especially if the most constructive results are to be provided.

In order to present more meaningful results on air sample analysis, it is necessary to compile large volumes of information which individually can be almost meaningless and in the past have not usually been understood nor used to best advantage. It is necessary to computerize the data and analysis if this is to be accomplished. Some programs have been written (and others are now being written) which can most effectively accomplish the required tasks.

These tasks include the following:

I. Write a computer program capable of:

A. Accepting the raw input data.

1. In the form of paper punch tape.
2. Storing the first counts until calculation can be performed.
3. Storing gamma contributions.

B. Calculating

1. Microcures per cubic centimeter (on all samples)
 - a. Alpha uc/cc
 - b. Beta uc/cc
2. Total curies emitted (on appropriate locations)
 - a. Alpha curies
 - b. Beta curies
 - c. Gamma curies
3. Effective half life observed
 - a. Alpha $T_{1/2}$
 - b. Beta $T_{1/2}$

C. Reporting

1. Microcuries per cubic centimeter
 - a. Long lived alpha
 - b. Total beta
 - c. Gamma corrected beta
2. Total curies emitted (daily and year to date)
 - a. Long lived alpha
 - b. Beta
 - c. Each gamma isotope

3. Observed half life

a. Alpha

b. Beta

D. Plotting

1. The observed activity level each day for the previous month (monthly).
2. The average for the month together with the previous monthly averages for a year (annually).

II. Implementing the program by automatically submitting to the computer.

A. The sampling information needed to perform the requested calculations.

1. Alpha and Beta

- a. Date and time on sampler
- b. Date and time off sampler
- c. Sampler flow rate
- d. Gross count beta
- e. Alpha
- f. Background beta
- g. Background alpha

B. The microcuries of each isotope found present on the gamma scan of each sample (when applicable) together with the time of each GEA.

Flow Chart

Automatic Data Processing System

EXAMPLE OF REPORT

Report of Air Sample Analysis for September 9, 1968

#	T _{1/2} day	uc/cc	Long Lived		Total Curies (LL)			
			Beta	CorrBeta	Alpha	Beta	Isotope	Curies
001	9.4	2.95E-10	3.75E-10	1.84E-10	1.38E-05	1.75E-05	ZrNb-95	1.48E-06
							Ru-103	5.36E-09
							RuRh-106	1.18E-05
							Co-60	8.46E-08
003	0.7	2.34E-13	7.31E-12					
234	1.0	8.54E-13	5.24E-12					

GRAPH II

HYPOTHETICAL AIR SAMPLE ACTIVITY FOR A MONTH

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