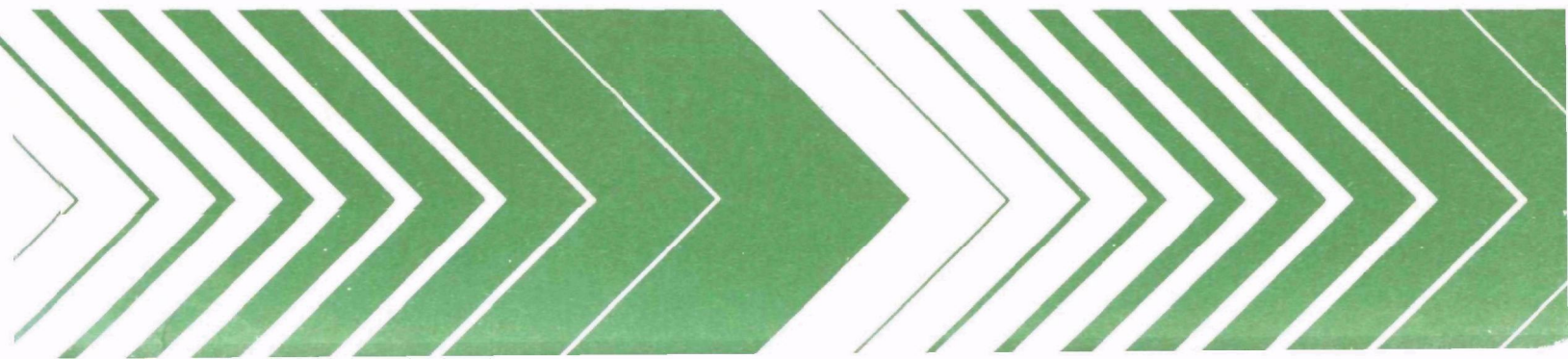$EPA

Analysis of Radioactive Contaminants in By-Products From Coal-Fired Power Plant Operations

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ANALYSIS OF RADIOACTIVE CONTAMINANTS IN BY-PRODUCTS

FROM COAL-FIRED POWER PLANT OPERATIONS

by

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise, and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water and land. The Environmental Monitoring and Support Laboratory contributes to the multidisciplinary focus through progress engaged in:

·Studies on the effects of environmental contaminants on the bio-sphere, and

·A search for ways to prevent contaminaton and to recycle valuable resources.

This report focuses on the radioactive contaminants released to the environment in the course of fossil fuel power plant operations and ascertains whether it has a deleterious effect on the population.

Dwight G. Ballinger
Director
Environmental Monitoring and
  Support Laboratory

ABSTRACT

Electrical power requirements for the next 200 years will necessitate a doubling of our present generating capacity. Even with the imposition of strong conservation measures, additional facilities and sources of fuel must become available. Because of restrictions on construction of nuclear installations, coal-fired power plants have to assume most of this burden. Since environmental discharges associated with the coal power industry contain not only the oxides of sulfur and nitrogen, but also significant concentrations of natural radioactivity, a potential radiation hazard from radium, thorium and uranium could result as more coal is burned.

In this study, the major radionuclides detected in fossil fuel power plant operations have been identified and quantified. Samples of coal, fly ash, bottom ash and scrubber sludge were collected from different regions in the U.S. and analyzed for radium, thorium and uranium. The standard radiochemical procedures were modified in order to obtain reproducible results for the variety of samples analyzed, which then can be used to calculate a radioactivity balance on the basis of normal operations.

The report tabulates the spectrum of activity levels in a variety of samples, and compares the results from non-destructive spectrometry and from radiochemical separations. The environmental impact of an expanding fossil-fuel power plant operation is discussed, and it is concluded that for the present, no radiation hazard exists.

This report covers a period from January 1976 to December 1977 and work was completed as of February 1978.

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ACKNOWLEDGMENT

The cooperation of the Cincinnati Gas and Electric Company and of the Radiation Control Branch, Bureau of Health Services, Frankfort, Kentucky, is gratefully acknowledged. Their engineers and technicians were most helpful in obtaining and delivering the representative samples required.

The thorium and uranium analyses were performed by the analytical section under Mrs. Ann Strong, EERL, Montgomery, Alabama, and the dose determinations were computed and interpreted by Dr. R. L. Blanchard, EERL, Montgomery, Alabama. This assistance is deeply appreciated.

SECTION 1

INTRODUCTION

Today, the vulnerability and future needs of the U.S. in the area of
electrical power are uppermost in the minds of the consuming public. The
energy crisis has become a complex of economic, environmental, conservation
and cost-benefit issues that must be resolved to preserve the way-of-life as
we now know it. The oil embargo showed how dependent we were on foreign
nations for the raw materials to keep oil-burning engines in operation; the
extremely cold winters of 1977 and 1978 cautioned us about our depleted
natural gas reserves and the importance of energy conservation; and the
environmental battle against nuclear power stations, coupled with the
presidential edict against fuel reprocessing operations, emphasized our
energy predicament. In addition, the latest energy plan stressed both fuel
conservation and a penalty for those industrial consumers who would not or
could not convert to coal, the dwindling coal reserves resulting from labor
disputes notwithstanding.

The search for alternative sources of energy plus the need for energy
conservation is a must. But the fact that population growth and electrical
power requirements have been increasing more rapidly than electricity
generating capacity has aggravated this problem.[1] This observation is
graphically depicted in Figure 1, and predicts the situation that will be in
existence at the turn of the century. In spite of the most stringent
conservation efforts or the effectiveness of alternative sources of
electricity, power requirements should more than double over the next 20
years.

The alternative sources of electrical power do not give us cause to
be optimistic. Solar, hydroelectric and geothermal power are potential
sources, but in the opinion of the experts, their full-scale operation is at
least 10 years away. A similar prediction is made for coal degasification
operations, which will utilize all types and grades of coal without
pretreatment. Since the present state of the art is pilot plant evaluation,
since gas and oil reserves are severely limited, and since there remain many
environmental problems connected with the construction and operation of
nuclear power stations, the main thrust in the energy picture today is that
additional coal burning power plants must be built. Our electrical needs
may be satisfied if these are brought rapidly into operation, but to
accomplish this, the fossil fuel economy must undergo major changes, and
energy consumption must be controlled.

The United States has an almost inexhaustible supply of fossil fuel,
which today accounts for more than half of the thermal electrical energy
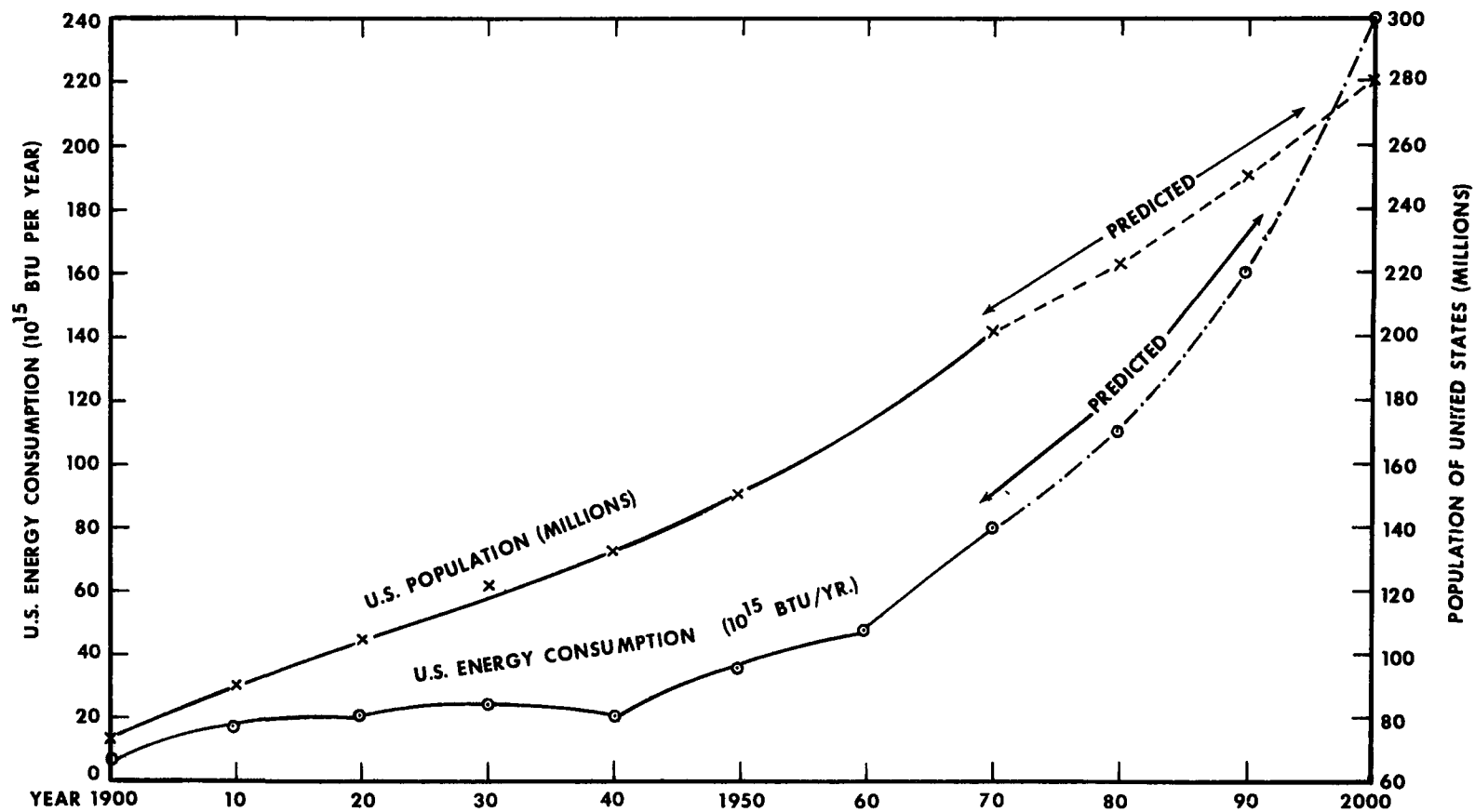production. A conservative estimate[2] puts the availability of our coal

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Figure 1.   Growth of population and energy consumption from 1900 to present and predictions to 2000.

reserves at 200 years or more, with deposits in more than 30 states that are potentially developable for commercial purposes. Fuel production operations, however, have not been able to keep up with the unusual increase in coal consumption, especially during periods of labor disputes.

The ineffectiveness of present mining techniques usually results in the discarding of potential coal reserves in the overall process. Because of the projected heavy demand for fuel, this waste product needs to be recovered. And, as these demands increase, mining operations will become less selective, and a poorer grade of ore will be extracted. This projected increase in coal consumption, coupled with the decreasing quality of available coal, will also result in substantially increased quantities of coal ash.

The geological and geographic factors associated with the fossil fuel beds determine the nature of the ultimate residue; the actual mining devices determine the extent of environmental insult. Even with low sulfur coal, mined primarily in Western U.S., several million tons of SO_2, NO_2 and particulates find their way into the environment as emissions from coal burning plants. Projecting this into the future, it is evident that double this volume may be released in 1999.[3] The bulk of this solid waste will be recovered from scrubber operations and therefore its disposal needs to be considered.

The schematic diagram that shows the flow of air, fuel and ash in a typical fossil fuel plant is depicted in Figure 2. By analyzing each segment of the coal burning process, and with the information available regarding plant operation, a material balance could be made and a dose committment from releases could be calculated.

There have been investigations into the health hazards resulting from increased use of coal and other fossil fuels - the effect of NO_2, SO_2 and particulates that are found in plant exhaust. These, however, are the non-radioactive components from fossil fuel combustion.

There have been studies that have measured the concentration of radium, thorium, and uranium that have been released to the environment as fly ash from the combustion of coal in fossil-fuel plant operations.[4-5] There have been investigations that have compared stack discharges from coal-fired plants with that from nuclear power plants and have determined that a greater hazard results from the ^{226}Ra emitted from fossil fuel than from the noble gases and ^{131}I released from a comparable size nuclear plant.[6-8]

Therefore, if the radiation hazard from coal burning plants is to be determined, the activity in coal and its operational by-products must be obtained. With this information available, dose commitment results for each component can be estimated.
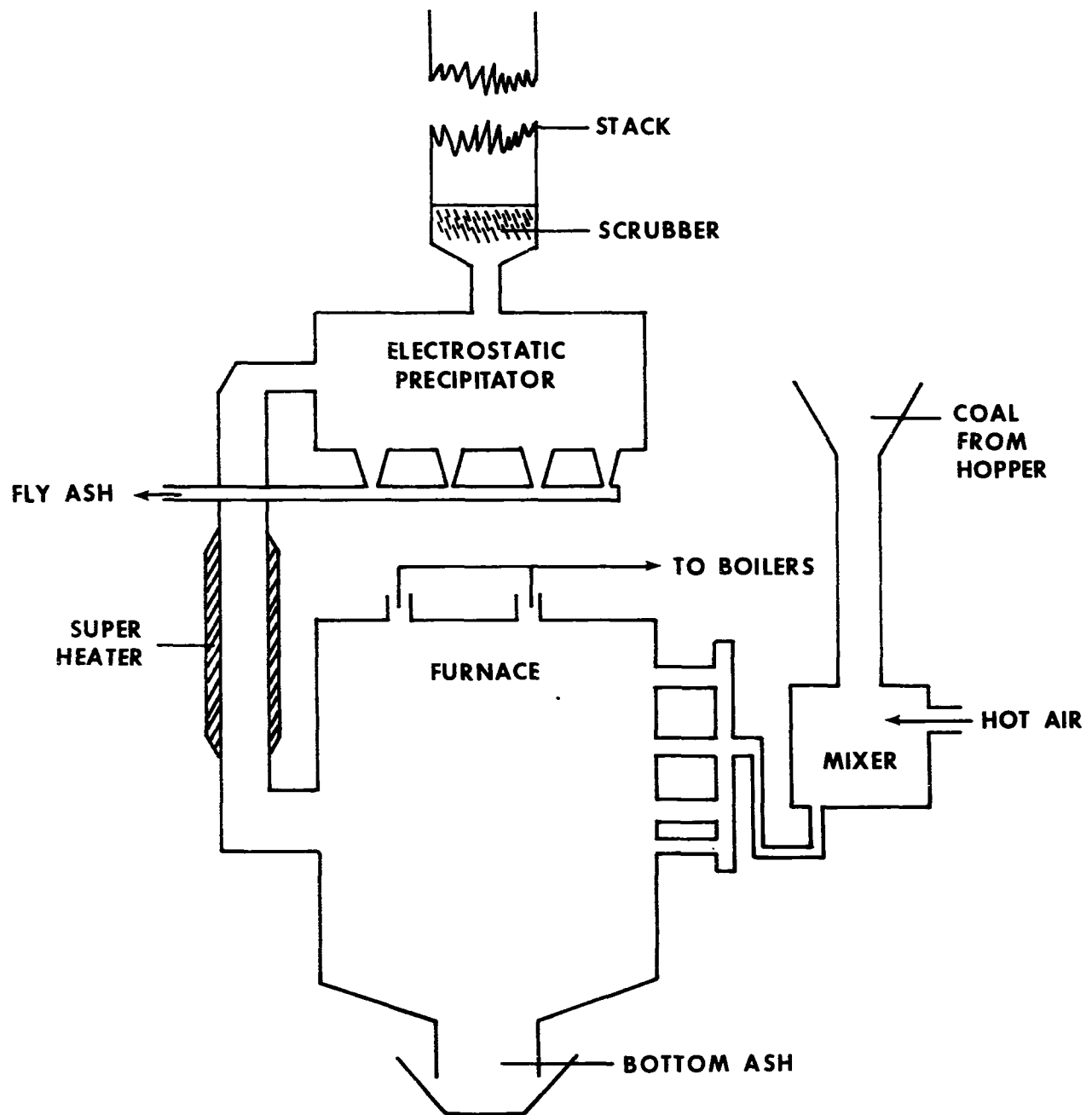
Figure 2. Schematic of coal burning plant depicting sampling ports.

SECTION 2

EXPERIMENTAL

Through the assistance of the radiation representatives of several regional offices, samples of coal and combustion by-products were collected during fossil-fuel plant operations. Additional coal samples were obtained from different mines in the United States.

During this study, 75 samples of coal and products of combustion were collected during actual operations, and shipped to the laboratory for analysis. The quality control data relating to these aliquots, obtained from the Federal Power Commission, indicated the annual operating experience of these plants. The radionuclides present in these fossil fuels were then determined using radiochemical procedures applicable to liquid samples. The methods had to be modified to assure quantitative recovery of all activity.

Each sample was air dried, pulverized if necessary, and homogenized until uniform. In a few instances the samples were sieved to a 60 mesh size in order to separate any non-uniform aggregates. Each sample was placed in a 400 ml polyethylene container and filled to the mark. After recording the tare weight, the gamma radioactivity in the sample was determined. Radionuclides that emit gamma rays were identified by their characteristic gamma-ray energies. A 2048-channel spectrometer and a Ge(Li) detector were employed to obtain the spectra. Because of the low activity and the low abundance of these nuclides, overnight and long week-end counting times were required. Once the gamma emitters were identified, the activities of several of them were determined and concentration factors were calculated.

The radium, thorium and uranium concentrations were ascertained by radiochemistry using methodology applicable to aqueous samples that had to be modified to accommodate the variety of samples and sample sizes. Testing continued until reliable and reproducible results were obtained on replicate determinations. The selected methods were effective for all kinds of fossil-fuel and by-product samples and assured that all the activity was completely solubilized at the start of the analysis.

Various methods were evaluated for solubilizing the sample matrices. These included hydrogen fluoride digestion, Parr bomb ignition and fusion with different flux combinations. The modified procedures appear in the Appendix*, and are summarized as follows.

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*We appreciate the cooperation and assistance of Mrs. Ann Strong, Chief, Analysis Section, Eastern Environmental Research Laboratory, Montgomery, Alabama, for the thorium and uranium analyses.

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1. ^{226}Ra: The fossil-fuel sample is dried at 110°C for a few days, cooled, pulverized and sieved for homogeneity using a sixty mesh sieve. In order to avoid activity loss during ignition, a weighed aliquot (5-10 g) is carefully pre-ashed with a Meker burner.

The pre-ashed sample is placed in a muffle furnace and ashed overnight or longer if the ashing is incomplete. During this operation the temperature is slowly increased to 600°C. The sample is cooled and weighed to determine ash content. For the initial solubilization, a 1-gm aliquot is fused with an alkaline flux and dissolved with strong acid. The BaSO$_4$, carrying the radium activity, is precipitated, dissolved and transferred to a radon bubbler. The radon in the sample is deemanated, and the bubbler is set aside for about a week for the ingrowth of ^{222}Rn from its ^{226}Ra parent.

The radon that has grown in is deemanated into a calibrated scintillation cell, and the radon and its alpha-emitting daughters are allowed to come to equilibrium. The ^{222}Rn in the cell is determined with an alpha scintillation counter.

This modification of the radon emanation technique[9] assures complete dissolution of the sample and quantitative measurement of radium activity.

2. Uranium and Thorium: The fossil-fuel sample is dried at 110°C overnight, cooled, pulverized and sieved for homogeneity using a sixty-mesh sieve. Up to 5 g of sample is ashed in the muffle furnace at 550°C overnight.

The ashed sample is transferred to a teflon beaker and standardized ^{232}U and ^{234}Th tracers are added for yield calculations. After an HF digestion, the residue is transferred to a platinum crucible for a pyrophosphate fusion. Sulfuric acid digestion, evaporation to fumes and dissolution in hydrochloric acid complete the solubilization.

Uranium is extracted into triisoctylamine and coprecipitated with lanthanum fluoride. The thorium in the acid phase of the extraction is purified by anion exchange and coprecipitated with lanthanum fluoride.

The planchets are counted by alpha spectroscopy to determine the uranium and thorium isotopes, respectively. This improvement of existing methodology[10-11] enables all the activity to be determined on the same aliquot.

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SECTION 3

RESULTS

Gamma Spectroscopy - The gamma-ray activities in the coals, ashes and sludges were found to be a function of the source and type of fuel combusted—a fact which was recently reported.[12] Although most of the nuclides were evident in all samples, there were some differences. As evidenced by differences in photopeak height, none of the activities were lost during combustion, but were concentrated in the ash. The Ge(Li) spectra of these samples revealed the presence of the ^{238}U and ^{232}Th series and indicated qualitatively what could be expected in stack releases.

An indication of what activities may be present can be obtained by comparing the gamma photopeaks of the coal and fly ash samples with that of normal background. The peaks that have been identified verify the presence of ^{214}Pb, ^{226}Ra, ^{214}Bi, and ^{40}K. These scans are shown in Figure 3, and refer to coal and by-products collected from operating plants in Ohio and Kentucky. A similar compilation was made recently on Western Pennsylvania coal plant operations. The small differences that existed were attributed to differences in equilibrium that had been attained in the respective coal fields and to different coal mining operations.

Radiochemical Analyses - Methodology for determining radium, thorium and uranium in aqueous samples have been tested and found quite reliable for many years. The scientific literature has described these procedures, and reported on modifications that were required when samples of silt, biota and vegetation were analyzed. Several procedures were evaluated by replicate analyses of the coal and ash samples. The non-agreement of results suggested that the sample was not completely in solution, and initial treatment had to be more rigorous to overcome this obstacle.

Investigations involving replicate analysis of coal and ash samples demonstrated that an acceptable treatment consisted of ashing and hydrofluoric acid digestion in platinum, ashing overnight at high pressure in a Parr bomb capable of handling one gram samples and finally an assortment of flux fusions. For some samples one of these treatments was sufficient, but it was generally agreed that a universal dissolution technique for all coal and by-product samples would assure uniformity of analytical results and provide reliable values for dose calculations. An alkaline borax flux was determined as satisfactory for all samples. Using 8 g of flux per gram of sample assured complete dissolution of the sample which was subsequently purified as the sulfate and dissolved for radon emanation analysis.
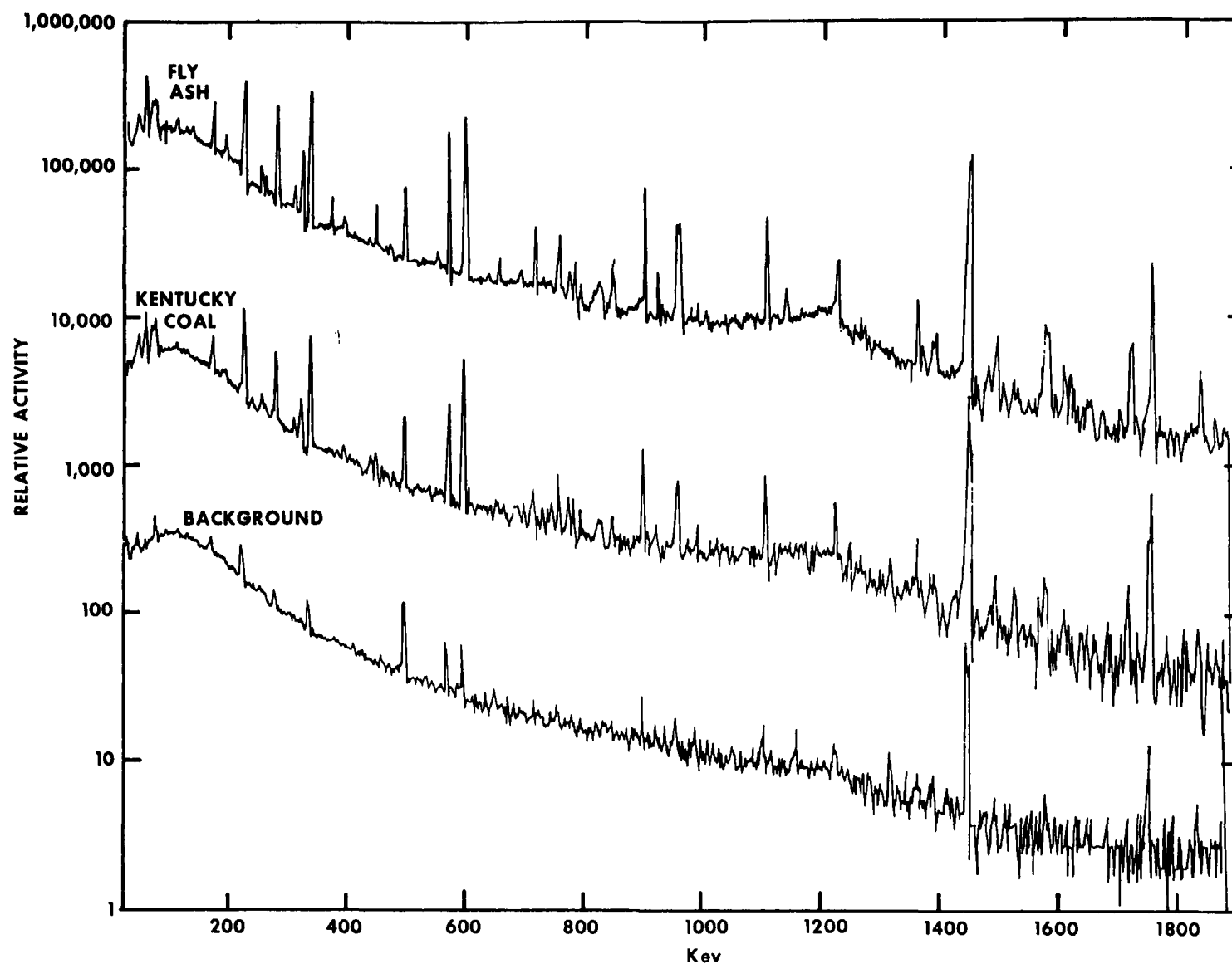
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Figure 3. Ge(Li) spectra comparing instrument background, Kentucky coal, and electrostatic precipitated fly ash.

The initial preparation of samples for the uranium and thorium procedures included prior ashing, a hydrofluoric acid digestion, plus a pyrosulfate fusion. This meant that for the uranium and thorium extractions to be considered complete, both a digestion and fusion technique were necessary.

Although the same procedure was employed on all samples, obvious differences were noted in the appearance of the ash initially and in subsequent steps. Dependent on the nature of the coal sample, the ash took on a reddish, whiteish or grayish texture. Despite differences in appearance, the ash was readily solubilized during the fusion treatment, and the final separation was a purified precipitate.

After obtaining the gamma spectra for these samples, the areas under the 187 keV ^{226}Ra and the 1462 keV ^{40}K photopeaks were summed and quantified. The ^{226}Ra was then determined by radiochemical analysis using the modified radon emanation technique. Comparing the values listed in Table I, it can be concluded that the 2 error associated with gamma spectral analyses, results in values that are significantly higher even with a 1000-minute counting time. This difference may be attributed to the ^{235}U contribution to the 0.186 MeV peak. As an indication of the presence of ^{226}Ra and other nuclides in the uranium and thorium series, non-destructive spectral analysis is satisfactory if long counting time is available, but for the measurement of this activity and the calculation of a radiation dose, radiochemical analysis is required.

The analytical results indicate small differences in the ^{226}Ra in coal, the average value being less than 1.0 pCi/g. The activity in the ash, however, varies as a function of the plant operation and possible prior treatment of the fossil fuel following mining operation. A 4-10 fold concentration has been observed and similar results have been described in the literature. Generally speaking, the levels in fly ash and bottom ash indicate possible differences in mining and coal washing operations, and differences in the source of the fossil fuels.

The results from the radiochemical analyses of samples from the Louisville, Kentucky power plant one year apart are listed in Table II. No stack samples could be collected, so no activity balance is possible. The aliquots for the uranium, thorium and ^{226}Ra analyses were taken at the same time so that a close correlation of all activities could be made. From this data it can be concluded that radioactive composition varies as coal sources vary. This will result when the natural acitivity is in a different state of equilibrium at the time of mine operations.

It is generally accepted that a 1000-megawatt power plant, the average capacity for a fuel plant, burns 2×10^6 tons of coal annually. Even though the sources of coal in the United States do vary with respect to chemical composition, ash content, burn-up and activity, average values have been selected in order to calculate a radiation dose. The Louisville Gas and Electric Company has indicated that the ash content of coal last year averaged 15%. This value is a little higher than the norm, and indicates

Table 1

Comparison of Non-Destructive and Radiochemical Analyses of ^{226}Ra

Sample Identification	^{40}K pCi/g	^{226}Ra, pCi/g Spectral Result	Radiochemical Analysis
Coal:			
W. Ky 3/76	3.6 + 1.0	1.7 + 1.2	0.49 + 0.01
W. Pa 4/76	8.3 + 0.5	1.0 + 0.2	0.49 + 0.01
E. Pa 4/76	8.1 + 0.05	1.1 + 0.2	0.55 + 0.01
E. Ky 11/76	4.2 + 0.4	1.3 + 0.5	0.49 + 0.02
Ohio 6/76	4.4 + 0.3	0.4 + 0.3	0.29 + 0.01
W. Montana 5/76	1.1 + 0.2	0.7 + 0.5	0.65 + 0.20
E. Ky 4/77	6.2 + 0.4	1.6 + 0.4	0.56 + 0.01
W. Ky 4/77	4.6 + 0.2	1.1 + 0.3	0.59 + 0.04
Fly Ash:			
W. Pa 4/76	23.0 + 0.9	4.6 + 0.3	1.36 + 0.02
Ohio 6/76	18.0 + 1.0	8.8 + 0.6	4.04 + 0.07
E. Ky 11/76	18.0 + 2.0	5.8 + 1.0	3.86 + 0.07
W. Ky 4/77	19.0 + 1.0	7.2 + 0.5	3.92 + 0.07
Bottom Ash:			
E. Ky 6/76	15.0 + 1.0	10.6 + 1.0	4.89 + 0.11
E. Ky 6/77	18.5 + 0.7	7.5 + 0.7	3.08 + 0.07

Table 2

Radiochemical Analysis of Coal and Coal By-Products, pCi/g

Date	Identification	^{226}Ra	^{234}U	^{235}U	^{238}U	^{228}Th	^{230}Th	^{232}Th
6/76	E. Ky. Coal	0.28±0.01	0.54±0.07	0.03±0.01	0.51±0.07	0.40±0.04	0.46±0.03	0.30±0.03
	W. Ky. Coal	1.98±0.01	0.80±0.10	0.04±0.01	0.78±0.03	0.21±0.03	0.71±0.05	0.19±0.02
	W. Ky. Fly Ash	7.0 ±0.1	6.3 ±1.1	0.33±0.09	8.6 ±1.1	1.9 ±0.1	6.5 ±0.3	1.8 ±0.1
	W. Ky. Bottom Ash	5.0 ±0.1	5.6 ±0.8	0.22±0.07	5.5 ±0.8	1.9 ±0.4	6.0 ±0.7	1.6 ±0.3
6/77	E. Ky. Coal	0.46±0.01	0.56±0.16	0.07±0.02	0.58±0.12	0.60±0.08	0.61±0.13	0.39±0.09
	W. Ky. Coal	0.72±0.01	0.92±0.10	0.05±0.02	0.92±0.10	0.34±0.04	0.85±0.05	0.27±0.03
	W. Ky. Fly Ash	3.8 ±0.1	4.2 ±0.5	0.20±0.07	4.4 ±0.5	1.8 ±0.2	4.5 ±0.3	1.57±0.18
	W. Ky. Bottom Ash	3.1 ±0.1	2.7 ±0.4	0.09±0.04	2.7 ±0.3	1.7 ±0.2	2.7 ±0.3	1.3 ±0.2

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the possibility of poorer grade of coal being mined. Continued deterioration can be expected in the future.

With this information and with our results, the following calculations evolve:

The annual total ash production would be 3×10^5 tons (2×10^6 tons x 0.15); divided into bottom residue (15%) and fly ash (85%). The quantity of bottom ash, 4.5×10^4 tons (3×10^5 tons x 0.15) is normally buried and completely covered for disposal. Airborne pollution will be negligible from this operation, and no hazard from the alpha activity will result.

The 3×10^5 tons of fly ash that are generated annually are collected by electrostatic precipitation followed by stack scrubbers. This fly ash is normally used in the building trades or road improvement operations. If the coal ash is incorporated in concrete and concrete products as a replacement for cement, radon emanation may become a problem, and regular monitoring would then be required. Past experience has shown that a radiation problem may result from possible radioactive emanations from walls and floors of buildings constructed from this material. Other uses of the fly ash have been in reclaiming surface mine spoil and as a soil nutrient.

The efficiency of electrostatic precipitators has been rated at 90-95%. Hence most of the fly ash will be trapped in this operation. Effectively operating scrubbers which can clean up about 80-90% of the stack influent will collect that fraction of the residue. Hence, about 5000 tons of fly ash could find its way into the environment as stack gas effluent.

Subsequent methods development and radiochemical analysis for [226]Ra and the other important nuclides entering the fossil fuel plant stack as gaseous effluent may provide a more accurate determination of the activity balance that is experienced when coal is burned in 1000 megawatt fossil fuel power plants for one year. The data obtained in the radiochemical analysis of coal, fly ash and the other by-products were used to calculate the following assessment which is shown in Table III.

This assessment is based only on the grab samplings of the coal, fly ash and scrubber sludge and the [226]Ra content as determined by our procedures. Levels of [226]Ra in coal as indicated in the literature ranged from 0.2 - 4.0 pCi/gm of coal, from 3.0 - 10.0 pCi/gm of fly ash and from 0.2 - 1.0 pCi/gm dried scrubber sludge. Depending on the source of mining operations, the 20 mCi [226]Ra that is calculated as an average discharge from a 1000 megawatt plant may be a conservative estimate. The activity levels selected for this assessment can also be much higher. In any event, direct measurement of the activity in the stack effluent will provide a more reliable estimate of radiation dose.

Table 3

By-Product Production and ^{226}Ra Activity Data
for a 1000 Megawatt Fossil Plant

Component	Annual Production, tons	Average Activity, pCi/g	Total Activity Available Annually, Ci/yr	Potential Annual Discharge, Ci/yr
Coal	2×10^6	0.9	1.65	----
Bottom Ash	0.05×10^6	5.0	0.23	----
Fly Ash	0.3×10^6	5.0	1.35	----
Scrubber Sludge	0.1×10^6	0.5	0.05	----
Stack Effluent	5000	5.0	----	0.02

The foregoing analytical and calculated results plus general operation data and assumptions are to be utilized to calculate the annual dose rate. The criteria have been compiled in a report soon to be published.[13]

These then are the assumptions:

1. Electrostatic precipitators and stack scrubbers operate at maximum efficiency.

2. Operating information:

Stack height - 500 ft. (150 m.)
Average stability -neutral condition
Max. downwind concentration - at 5.5 km (3.4 mi.)
Wind direction - SSW to NNE - 15% of the time
Average wind speed - 8.4 mph
Regular source of fuel

3. Relatively flat terrain between stack and receptor.

4. No plume rise due to buoyancy of heated effluent.

The critical organ for ^{226}Ra, which is designated as a "W compound*", is the bone, where the dose limit has been set at 25 mrem/yr. The average annual concentration of ^{226}Ra that is released from a 1000 megawatt coal burning plant is 20 mCi or 2.4×10^{-11} Ci/m^3. The dose to the bone for this activity is 3.7×10^{-2} mrem/yr. or 2×10^{-3} of the bone dose limit. The radiation dose to the lungs for the ^{226}Ra discharge is about a factor of 10 lower.

Similar calculations for the ^{232}Th and ^{238}U being emitted from the plants indicated only a small fraction of the allowable radiation dose occurring. The chemical toxicity from these was more significant.

In summary, then, a very minimal radiation hazard results from the discharges from present-day coal plants under the optimum conditions stated. However, if scrubbers are not employed, or if these collectors operate at less than maximum efficiency, the radiation hazard may become significant. If present coal supplies are replaced with fuel of a higher radioactive and ash content, an increase in the radiation hazard could result. For the present, the greater hazard results from mining and pre-combustion operations, and it is these activities that must be carefully monitored. Therefore, if plant operations are carefully monitored, an expanding fossil-fuel economy need not have a serious environmental radiation impact.

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*A "W compound" is defined as one having a clearance time of a few days to a few weeks.

The procedures which have been developed for measuring ^{226}Ra, ^{232}Th and ^{238}U in coal and coal by-products have been instrumental in calculating an activity balance in a coal plant operation. From these radiochemical results, the minimal radiation hazard could be calculated.

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APPENDIX
Methods of Analysis

I. Pretreatment of Samples (Note 1)

A. Coal - Take an aliquot (20-30 g), grind in a mortar and put through a 60-mesh sieve. Transfer to a tared porcelain dish, weigh and pre-ash with a Meker burner. The pre-ashing must proceed carefully and slowly. Starting with a low flame, to keep losses at a minimum, gradually increase the flame until all gases are released and the carbon deposits are burned off the rim of the dish. Continue ashing overnight in a muffle furnace at 600°C. After cooling and weighing, take a 1 gm aliquot of the ash for the initial alkaline fusion step.

B. Bottom Ash - Take an aliquot (5-10 gm), grind in a mortar, put through a 60-mesh sieve and transfer to a porcelain dish. Ash overnight in a muffle furnace at 600°C, cool, weigh and take a 1 gm aliquot for the initial alkaline fusion step.

C. Fly Ash - Ash an aliquot (1-2 g) overnight in a muffle furnace at 600°C. After cooling, take a 1 gm aliquot for the initial alkaline fusion step.

D. Scrubber Sludge - Dry an aliquot (5-10 g) in a drying oven overnight at 105°C. Transfer to a mortar and grind till uniform. Ash overnight in a muffle furnace at 600°C. After cooling, take a 1 gm aliquot for the initial alkaline fusion step.

II. Radiochemical Analytical Procedures

A. Radium-226 Analysis - Radon Emanation Technique (Fig. 4).

1. Principle of Method

The radium in the coal and by-product sample is recovered by an alkaline fusion of a pretreated ash. The melt is dissolved in sulfuric acid and the activity is concentrated and separated by coprecipitation with barium as the sulfate. The precipitate is dissolved in EDTA, placed in a bubbler, deemanated, sealed and stored for ingrowth of ^{222}Rn.

2. Reagents

Radioactive tracer standard: ^{226}Ra
Alkaline flux reagent - prepared reagent
Ammonium hydroxide, NH_4OH: 15 $\underline{N}$ (conc.)
Ascarite: drying reagent, 8-20 mesh

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Barium carrier: 16 mg/ml
EDTA reagent: 0.25 $\underline{M}$ (Note 2)
Helium gas
Hydrochloric acid, HCl: 12 $\underline{N}$ (conc.)
Hydrogen peroxide, H_2O_2: 3%
Magnesium perchlorate, $Mg(ClO_4)_2$
Potassium carbonate, K_2CO_3
Sodium carbonate, Na_2CO_3
Sodium borate decahydrate, $Na_2B_4O_7 \cdot 10H_2O$
Sodium hydroxide, NaOH: 10 $\underline{N}$
Sulfuric acid, H_2SO_4: 36 $\underline{N}$ (conc.), 18 $\underline{N}$, 0.1 $\underline{N}$

3. Procedure

a. Prepare an alkaline flux reagent (Note 3), and store in an air-tight bottle.

b. For each gram of ashed sample, mix thoroughly with 8 g of the alkaline flux reagent in a 100 ml platinum dish. Fuse the sample by heating with a blast burner, swirling until the melt is a clear red, then continue heating for 20 minutes. Cool.

c. Place crucible with melt in a covered beaker containing 120 ml water, 20 ml 36 $\underline{N}$ H_2SO_4 and 5 ml 3% H_2O_2 for each 8 g of alkaline flux reagent. When solids are dissolved, remove and rinse dish, adding rinse to beaker. Heat solution and slowly add 2.0 ml barium carrier. Continue stirring and heating for 30 minutes. Allow the precipitate to settle overnight, decant and discard supernatant.

d. Slurry the precipitate and transfer to a centrifuge tube with a minimum amount of 0.1 $\underline{N}$ H_2SO_4. Centrifuge and discard supernatant. Wash twice with 0.1 $\underline{N}$ H_2SO_4 and discard washes.

e. Add 20 ml EDTA reagent, heat in a hot water bath and stir well. Add a few drops 10 $\underline{N}$ NaOH if the precipitate does not readily dissolve (Note 4).

f. Transfer the solution to a radon bubbler (Fig. 5). Open both the upper and lower stopcocks and deemanate the solution by slowly passing helium gas through the bubbler for about 20 minutes.

g. Close the two stopcocks, and record time. Store the solution for 4 to 8 days for ingrowth of ^{222}Rn (Fig. 6).

h. At the end of the storage period, fill the upper half of an absorption tube with magnesium perchlorate and the lower half with ascarite (Note 5). Attach the tube to the radon bubbler and then attach the evacuated scintillation cell (Fig. 7) to the tube.

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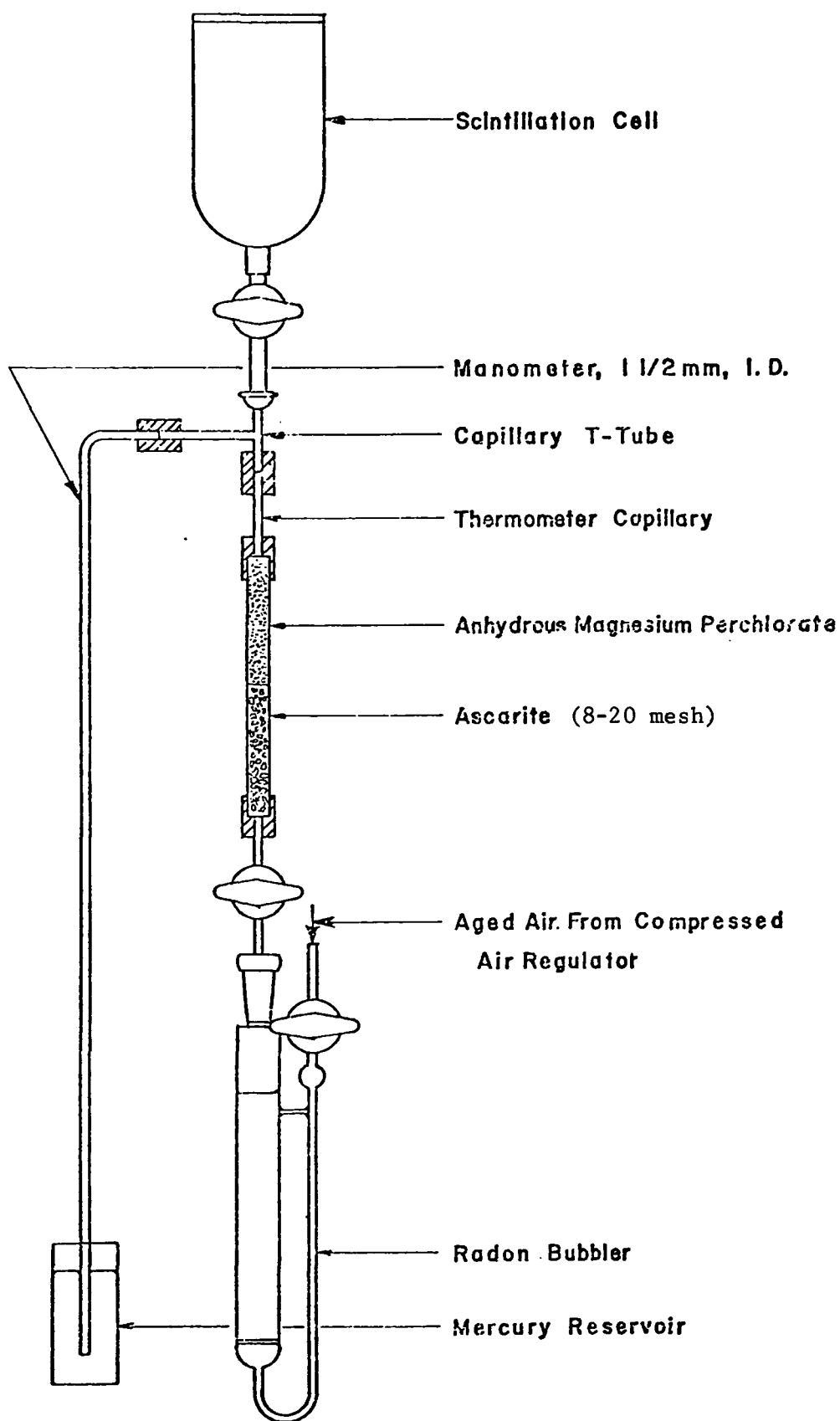
Figure 4. Radon Emanation Apparatus with Scintillation Cell

7mm O.D.

Corning No. 2
or Equivalent

$ 10/30

Bubble Trap
7 mm I.D.

Liquid
Level

Rigidity Brace

135 mm

7 mm Capillary Tubing
1 1/2 mm I.D.

17mm
O.D.

Fritted Glass Disc
10-15 micron pores
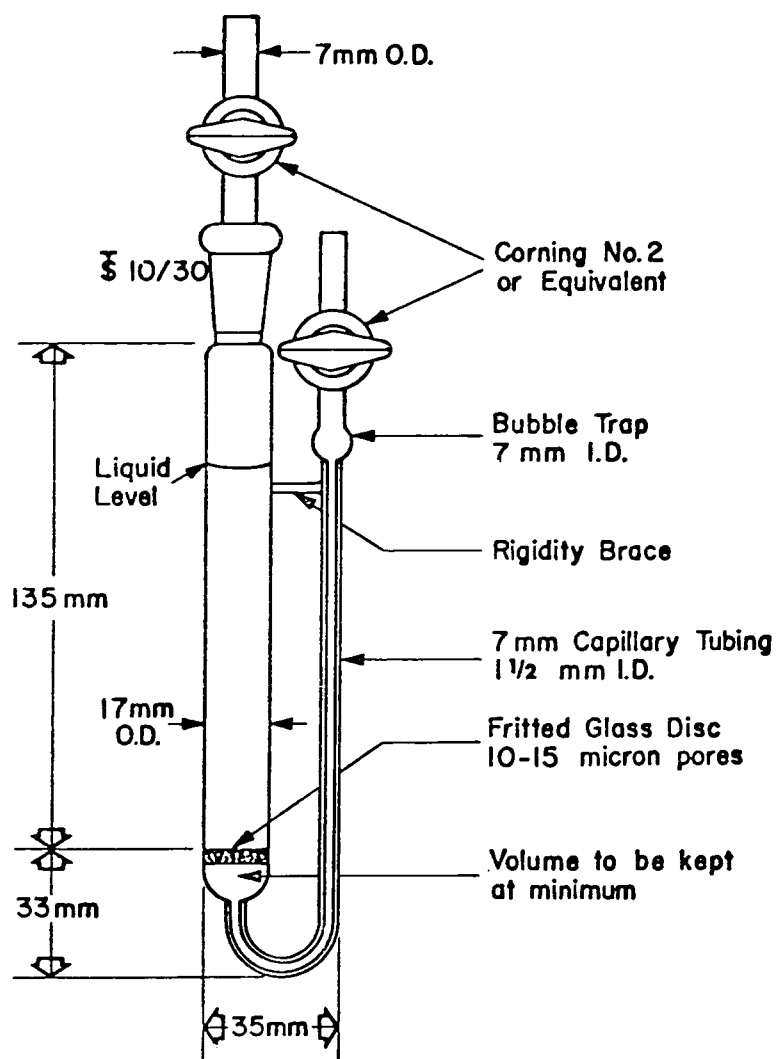
WATER

Volume to be kept
at minimum

33mm

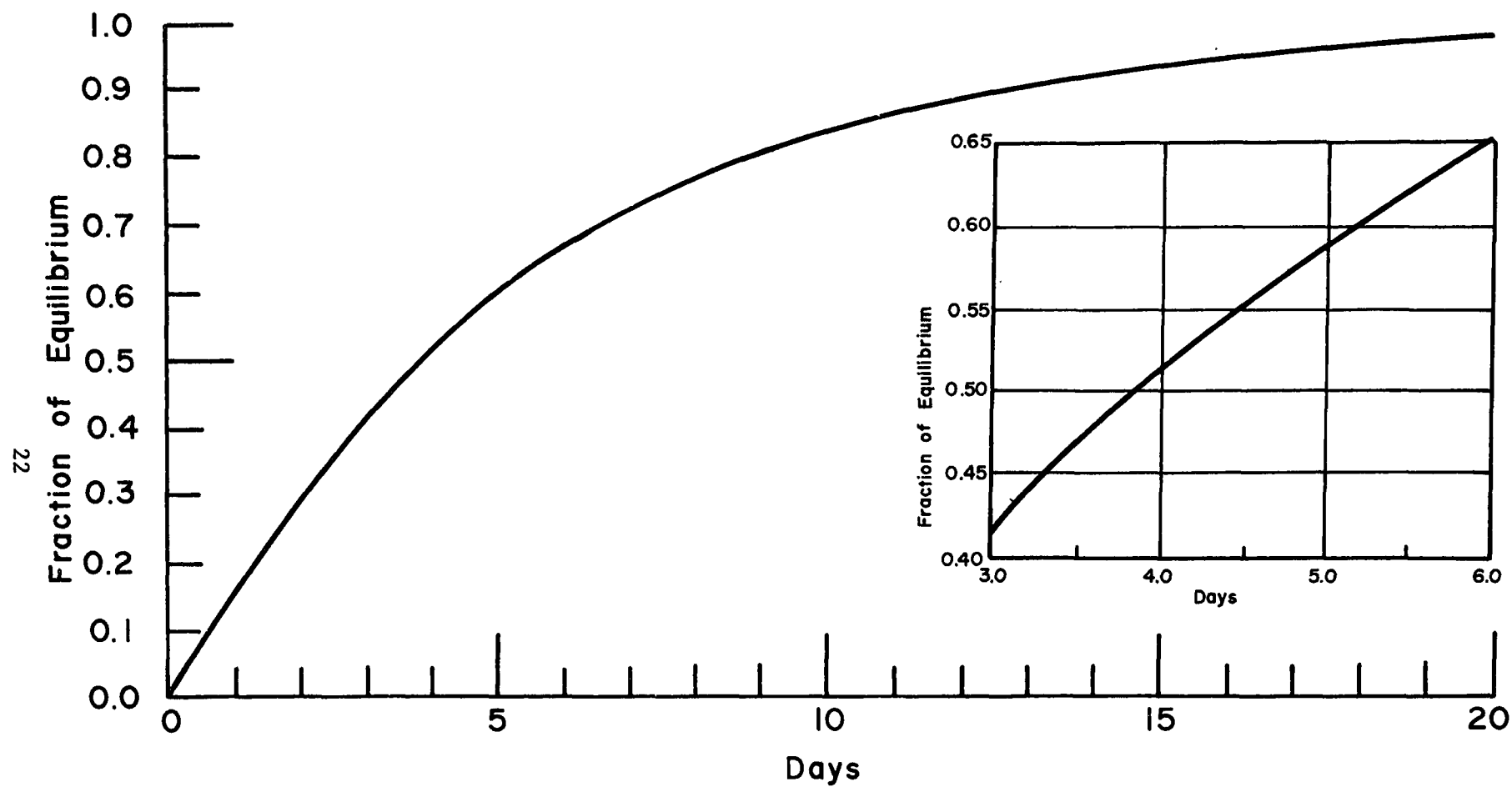35mm

Figure 5. A Typical Radon Bubbler (emanation tube)

Figure 6. The Growth of Radon-222 from Radium-226.

i. Open the stopcock on the cell and check the assembly for leaks. Gradually open the outlet stopcock on the bubbler, and when the stopcock is fully open and no further significant bubbling takes place, close the stopcock.

j. Adjust the aged air or helium gas pressure so that the gas flows at slightly above atmospheric pressure.

k. Connect the hose to the bubbler inlet and gradually open the inlet stopcock using the bubbling as a guide. When the stopcock can be fully opened without a significant amount of bubbling, the bubbler is essentially at atmospheric pressure again.

l. Open the outlet stopcock very slightly and allow bubbling to proceed at a rate, determined by experience, such that 15 to 20 minutes are required to complete deemanation.

m. Toward the end of the deemanation, when the vacuum is no longer effective, gradually increase the helium gas pressure. When the system is at atmospheric pressure, shut off the helium gas, disconnect the tubing from the bubbler inlet and close the inlet and outlet stopcocks of the cell and bubbler, and record time. This is the beginning of ^{222}Rn decay and ingrowth of ^{222}Rn daughters.

n. Store the scintillation cell for at least 4 hours to ensure equilibrium between radon and radon daughters. Count the alpha scintillations from the cell in a radon counter with a light-tight enclosure that protects the photomultiplier tube. Record the counting time to correct for the decay of ^{222}Rn.

4. Calculation

Calculate the concentration, D, of the ^{226}Ra activity in picocuries per gram as follows:

$$D = \frac{C}{2.22\ EV} \times \frac{1}{1-e^{-\lambda t_1}} \times \frac{1}{e^{-\lambda t_2}} \times \frac{\lambda t_3}{1-e^{-\lambda t_3}}$$

where:

C = net count rate, counts/minute (Note 6),
E = calibration constant for the deemanation system and the scintillation cell in counts per minute/disintegrations per minute of ^{222}Rn (Note 7),
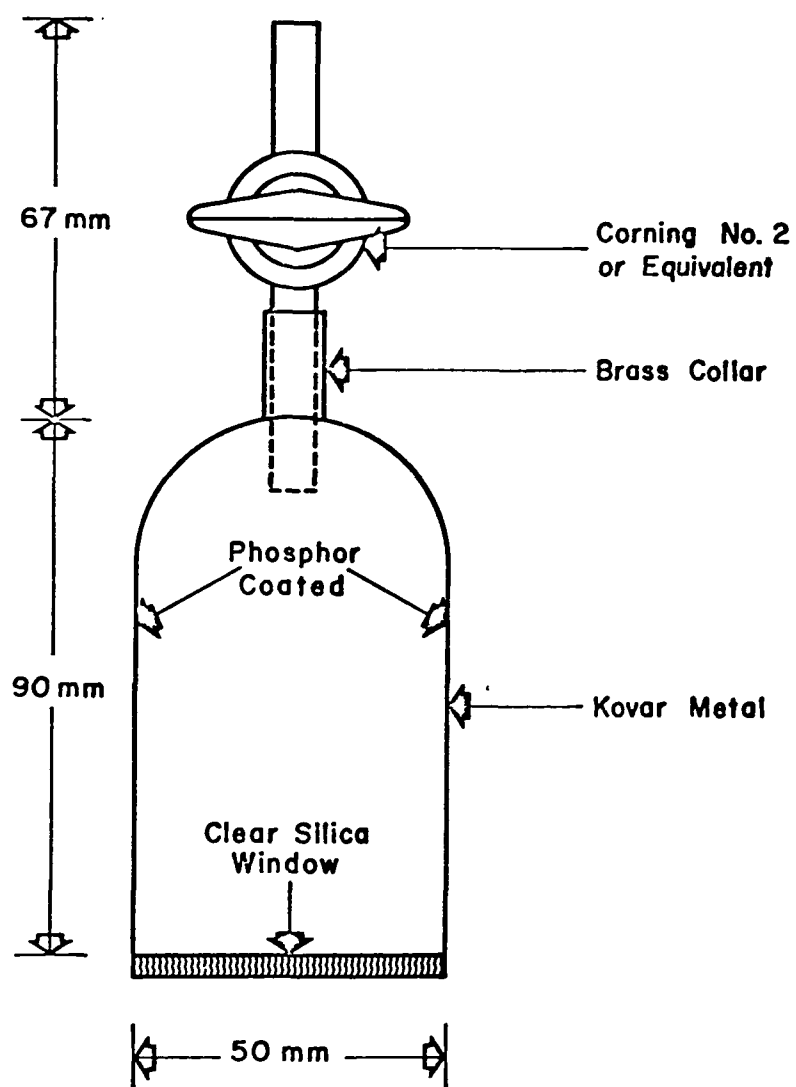
67 mm

Corning No. 2
or Equivalent

Brass Collar

Phosphor
Coated

90 mm

Kovar Metal

Clear Silica
Window

50 mm

Figure 7. A Typical Scintillation Cell for Radon Counting

V = sample aliquot in grams,

t_1 = the elapsed time in days between the first and second deemanations (steps g and m) and λ is the decay constant of ^{222}Rn (0.181 d^{-1}),

t_2 = the time interval between the second deemanation and counting and λ is the decay constant of ^{222}Rn (0.00755 hr^{-1}), and

t_3 = the counting time in minutes and λ is the decay constant of ^{222}Rn (1.26 x 10^{-4} min^{-1}).

Notes:

(1) Sample weight prior to ashing should be obtained, as well as the weight of the ashed aliquot used in analysis. This information is of value for relating pCi/g ash to pCi/g original sample.

(2) Preparation of 0.25 $\underline{M}$ EDTA reagent - Dissolve 20 grams NaOH in about 750 ml water, heat and slowly add 93 grams $Na_2C_{10}H_{14}O_8N_2 \cdot 2H_2O$ (disodium ethylenedinitri-loacetate dihydrate) while stirring. After the salt is in solution, filter through coarse filter paper and dilute to 1 liter.

(3) An alkaline flux reagent is prepared by mixing thoroughly 30 mg $BaSO_4$, 65.8 g K_2CO_3, 50.5 g Na_2CO_3 and 33.7 g $Na_2B_4O_7 \cdot 10H_2O$ in a 500 ml platinum dish. Heat cautiously to expel water. Using a blast burner, fuse the mixture by swirling constantly during the heating. Cool the mixture, transfer to a large mortar and grind until the fines pass through a 10-mesh screen. Store in an air-tight bottle.

(4) The volume of these bubblers is usually greater than 20 ml allowing for at least a 1 cm air space between the bubbler and the stopper. In those instances where the solution volume exceeds the capacity of the bubbler, it will be necessary to continue the boiling in the water bath until the volume is reduced.

(5) For minimizing corrections that would be required in subsequent calculations, the voids above the bubbler must be kept very small. Capillary tubing should be used whenever possible, and the drying tube volume with the Ascarite and magnesium perchlorate must be kept to a minimum. A typical system consists of a drying tube 10 cm x 1.0 cm (I.D.), with each of the drying agents occupying 4 cm and being separated by small glass wool plugs. The column can be reused several times before the chemicals need to be replaced.

(6) After each analysis, flush the cell three times by evacuation and filling with helium, and store filled with helium at atmospheric pressure. This procedure removes radon

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from the cell and prevents the build-up of radon daughter products. Before each analysis, the scintillation cell should be evacuated, filled with helium and counted to ascertain the cell background.

(7) The calibration constant, E, is determined as follows:

(a) Place 50 pCi of the ^{226}Ra standard solution in a bubbler (50 pCi of ^{226}Ra will produce about 6 pCi ^{222}Rn in 18 hours). Attach the bubbler to the assembly as shown in Fig. 4.

(b) With the scintillation cell disconnected, bubble helium gas through the solution for 20 minutes.

(c) Close both stopcocks on the bubbler to establish zero time for ingrowth of ^{222}Rn. Set aside for approximately 18 hours.

(d) Evacuate the scintillation cell and attach to the column and bubbler.

(e) Proceed with steps i-m, ^{226}Ra-Radon Emanation Technique.

(f) The calibration constant, E, is determined from the ^{226}Ra activity in the bubbler and the ingrowth time of ^{222}Rn by the equation:

$$E = \frac{C}{A(1-e^{-\lambda t_1})(e^{-\lambda t_2})}$$

where:

C = net count rate, counts/minute,
A = activity of ^{226}Ra in the bubbler (d/m),
t_1 = ingrowth time of 222Rn in hours,
t_2 = decay time of ^{222}Rn in hours occurring between deemanation and counting, and
λ = decay constant of ^{222}Rn, 0.00755 hour $^{-1}$.

The calibration constant, E, includes the deemanation efficiency of the system, the counting efficiency of the cell, and the alpha activity contributed by ^{218}Po and ^{214}Po, which will be in equilibrium with ^{222}Rn when the sample is counted 4 hours after the deemanation. A 100-minute counting time will be sufficient for the standard and will eliminate the need to correct for decay of ^{222}Rn, which occurs during counting.

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The bubbler used for the ^{226}Ra standardization should not be used for sample analysis. It should be set aside to be retained for future calibrations. Each scintillation cell should be calibrated periodically with the ^{226}Ra standard to ensure instrument quality control.

B. Uranium and Thorium Analysis

1. Principle of Method

^{232}U and ^{234}Th tracers are added to a pretreated ash of a coal or by-product sample. Silicates are removed by repeated HF evaporations. A pyrosulfate fusion solubilizes the residue, and the final solution is made 8 $\underline{N}$ in HCl. Uranium is separated by extraction with triisooctylamine, back extracted with water, coprecipitated with lanthanum fluoride for counting by alpha spectroscopy. Thorium activity, which is not extracted, is concentrated on an anion column, eluted with HCl, and coprecipitated with lanthanum fluoride for counting by alpha spectroscopy.

2. Reagents

Radioactive tracer standards: ^{232}U and ^{234}Th
Ascorbic acid, $C_6H_8O_6$: Crystals
Ethanol, C_2H_5OH: 95%
Hydrochloric acid, HCl: 12 $\underline{N}$ (conc.), 8 $\underline{N}$, 6 $\underline{N}$, 2 $\underline{N}$, 1 $\underline{N}$
Hydrofluoric acid, HF: 28 $\underline{N}$ (conc.), 5% (3 $\underline{N}$)
Lanthanum carrier: 0.10 mg/ml
Nitric acid, HNO_3: 8 $\underline{N}$, 6 $\underline{N}$, 0.1 $\underline{N}$
Perchloric acid, $HClO_4$: 70% (conc.)
Potassium fluoride, KF: solid
Potassium pyrosulfate, $K_2S_2O_7$: solid
Sulfuric acid, H_2SO_4: 6 $\underline{N}$
Titanium trichloride, $TiCl_3$: 0.4% (freshly prepared)
Triisooctylamine/xylene solution, TIOA/xylene: 10%

3. Procedure

a. Add 1-5 g (Note 1) of ashed sample to a 50 ml teflon beaker. Add 1.0 ml each of ^{232}U and ^{234}Th tracer solutions. Mix.

b. Add 28 $\underline{N}$ HF (5 ml HF per gm ash) and evaporate to dryness at a low heat. Repeat 3 more times with 10 ml volumes of HF to volatilize the silica. Additional treatment may be necessary if residue remains.

c. Add 25 ml 12 $\underline{N}$ HCl and evaporate to dryness.

d. Transfer the powdery residue to a platinum crucible. Add 2 g KF for each gram of ash used and fuse with a Meker burner for

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30 minutes. Continue swirling, then add 3 g $K_2S_2O_7$ for each gram of ash and continue fusion for another 30 minutes.

e. Cool the crucible in an ice bath, add 15 ml 12 $\underline{N}$ HCl and evaporate to dryness. Slurry residue with water, transfer to a beaker, bring volume to 150 ml, and evaporate to dryness.

f. Take up residue with 100 ml 6 $\underline{N}$ H_2SO_4 and evaporate past white fumes.

g. Add 10 ml 12 $\underline{N}$ HCl and evaporate to dryness. Repeat.

h. Add 115 ml 8 $\underline{N}$ HCl to dissolve residue and transfer to a 1 liter separatory funnel.

i. To the solution in the separatory funnel, add 100 ml of a 10% TIOA/xylene solution. Shake for 2 minutes and after the phases separate, drain the aqueous acid solution into a beaker and reserve for thorium analysis, step s.   ·

j. To the organic phase add 50 ml 8 $\underline{N}$ HCl and shake for 20 seconds. Discard the aqueous wash solution.

k. Add 100 ml 0.1 $\underline{N}$ HNO_3 to the separatory funnel and shake for 2 minutes. Drain the aqueous layer into a 250 ml beaker.

l. Repeat step k, adding the aqueous fraction to that in the 250 ml beaker. Evaporate to dryness.

m. Add 10 ml 8 $\underline{N}$ HNO_3, evaporate to dryness. Repeat.

n. Wet ash again with 5 ml 8 $\underline{N}$ HCl and 5 ml $HClO_4$ and evaporate to dryness.

o. Add 10 ml 12 $\underline{N}$ HCl, evaporate to dryness. Repeat.

p. Dissolve residue in 10 ml 1 $\underline{N}$ HCl, plus a pinch of ascorbic acid to reduce the iron. Add 1.0 ml lanthanum carrier, 1 ml of freshly prepared 0.4% $TiCl_3$ and 2 ml 5% HF. Stir well, and let stand 30 minutes.

q. Filter through a 25-mm nucleopore filter (0.2 u pore size). Wash three times with 10 ml portions of alcohol. Mount on a s.s. planchet using double-stick tape to secure the sample.

r. Count for 1000 minutes, using an alpha spectrometer to determine ^{234}U, ^{235}U, and ^{238}U; and for the chemical recovery of ^{232}U. (Note 2).

s. Evaporate to dryness the aqueous acid solution from step i which contains the thorium activity.

t. Wet ash the residue with 10 ml 8 $\underline{N}$ HNO$_3$ and evaporate to dryness. Repeat.

u. Add 5 ml 8 $\underline{N}$ HCl and 5 ml HClO$_4$ and evaporate to dryness.

v. Add 10 ml 8 $\underline{N}$ HNO$_3$ and evaporate to dryness.

w. Take up the residue in 100 ml 6 $\underline{N}$ HNO$_3$ and heat until dissolved.

x. Cool and pass over prepared anion resin column (Note 3) at gravity flow. Discard effluent.

y. Wash the resin column with 100 ml 6 $\underline{N}$ HCl and collect the eluate in a 400-ml beaker; evaporate to dryness.

z. Add 10 ml 8 $\underline{N}$ HNO$_3$ and evaporate to dryness. Repeat.

aa. Add 10 ml 2 $\underline{N}$ HCl and evaporate to dryness. Repeat.

bb. Dissolve residue in 10 ml 1 $\underline{N}$ HCl, add 1.0 ml lanthanum carrier, 2 ml 5% HF and stir well. Let stand for 30 minutes.

cc. Filter through a 25-mm nucleopore filter (0.2 u pore size). Wash three times with 10 ml portions of alcohol. Mount on a s.s. planchet using double-stick tape to secure the sample.

dd. Beta count for 10 minutes to obtain ^{234}Th recovery (Note 4). Count for 1000 minutes, using an alpha spectrometer to determine ^{232}Th, ^{230}Th, ^{228}Th, and ^{227}Th.

Notes:

(1) If only 1 g samples are used, the fusion step (d) can be eliminated, since the HF and HCl treatments will completely solubilize the sample. The procedure can continue with step (h).

(2) A ^{232}U standard used for determining chemical recovery of uranium is prepared by pipetting 1.0 ml ^{232}U tracer ($\sim$3 dpm) into a beaker and coprecipitating as described in steps p and q. Count 1000 minutes using an alpha spectrometer.

(3) Preparation of anion resin - Slurry anion resin (Dowex 1-X8 or equivalent) (50-100 mesh) with water and transfer to a column 1.0 cm (I.D.) x 20 cm until a layer 10 cm deep is formed. Wash with 25 ml 6$\underline{N}$ HCl followed by 100 ml water before use.

(4) A ^{234}Th standard used for determining chemical recovery of thorium is prepared by pipetting 1.0 ml ^{234}Th tracer ($\sim$ 1000 dpm) into a beaker and coprecipitating as described in

steps cc and dd. Beta count for 10 minutes on the same day samples are counted in the alpha spectrometer.

4. Calculations

(1) Uranium

Sum the counts in the ^{232}U standard under the ^{232}U peak (5.32, 5.27 MeV), and compare with the counts in the sample under the ^{232}U peak. For calculating the specific isotopes of uranium, sum the counts under the following peaks:

^{234}U (4.77, 4.72 MeV)

^{235}U (4.37, 4.40, 4.58 MeV)

^{238}U (4.20, 4.15 MeV)

$$\text{pCi } ^{234}U/g = \frac{\text{cpm } ^{232}Th}{\dfrac{\text{cpm } ^{232}U \text{ in sample}}{\text{cpm } ^{234}U \text{ in standard}} \text{ X Eff. } \dfrac{\text{cpm}}{\text{dpm}} \text{ X } \dfrac{\text{sample}}{\text{size}} \text{ X } 2.22}$$

(2) Thorium

Compare the ^{234}Th beta counts in the sample to those in the standard to determine chemical recovery. For calculating the specific isotopes of thorium, sum the counts under the following peaks:

^{232}Th (4.01, 3.95 MeV)

^{230}Th (4.68, 4.62 Mev)

^{228}Th (5.43, 5.34 MeV)

$$\text{pCi } ^{232}Th/g = \frac{\text{cpm } ^{232}Th}{\dfrac{\text{cpm } ^{234}Th \text{ in sample}}{\text{cpm } ^{234}Th \text{ in standard}} \text{ X Eff. } \dfrac{\text{cpm}}{\text{dpm}} \text{ X } \dfrac{\text{sample}}{\text{size}} \text{ X } 2.22}$$

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(Please read Instructions on the reverse before completing)

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

The major radionuclides detected in fossil fuel power plant operations have been identified and quantified. Samples of coal, fly ash, bottom ash and scrubber sludge were collected from different regions in the U.S. and analyzed for radium, thorium, and uranium. The standard radiochemical procedures were modified in order to obtain reproducible results for the variety of samples analyzed, which then can be used to calculate a radioactivity balance on the basis of normal operations.

The report tabulates the spectrum of activity levels in a variety of samples, and compares the results from non-destructive spectrometry and from radiochemical separations. The environmental impact of an expanding fossil-fuel power plant operation is discussed, and it is concluded that for the present, no radiation hazard exists.

17. KEY WORDS AND DOCUMENT ANALYSIS

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