PLUTONIUM: A REVIEW OF MEASUREMENT TECHNIQUES
FOR ENVIRONMENTAL MONITORING

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SUMMARY

An overview is provided of the techniques for measuring plutonium
in various media. The emphasis is on measurements for surveillance and
protection in environmental and occupational situations. Overviews are
first provided for the characteristics of, sources of, and typical levels of
plutonium concentrations. The various measurement techniques are then
discussed.

INTRODUCTION

Plutonium is by far the most important of the transuranic elements
(elements heavier than uranium). Its use in atomic (fission) weapons has
made it a strategically important material, and it is the cornerstone in
the fast-breeder-reactor system which is now under development. Pluton-
ium is also highly toxic, a fact recognized very early in its history. This
toxicity makes measurements of plutonium in environmental media
very important.

We shall deal primarily with the measurement of plutonium con-
centrations in environmental media. We shall concentrate on methods
for determining low levels of plutonium in air, water, soil, and certain
other environmental media; but bioassay methods will not be discussed
in detail.

We will first provide overviews of the physical characteristics used
in the detection of the important isotopes; of the radiation protection
guides for plutonium concentrations; and of the sources of and typical
ranges of plutonium concentrations in the natural environment. We
shall then discuss the various measurement techniques for plutonium.
This discussion will concentrate on the various broad categories of
instruments and techniques for plutonium measurements, their sen-
sitivities, areas of applicability, and limitations. Four recent pub-
lications[1-4] provide detailed information on a number of subjects
concerning plutonium.

PHYSICAL CHARACTERISTICS

The isotopic states which concern us are plutonium-238 through
-242. Some physical properties of these isotopes are shown in Table 1.
The isotope americium-241, the immediate daughter of ^{241}Pu, is also
listed in Table 1 because its properties are used in some plutonium
measurements.

The half-lives of the three most important isotopes are all
relatively long: ^{238}Pu (86 years); ^{239}Pu (24,400 years); and ^{240}Pu
(6580 years). The alpha energies are grouped such that present alpha
spectrometry systems cannot separate ^{239}Pu from ^{240}Pu, but can
cleanly resolve all of the other plutonium isotopes.

The fact that ^{239}Pu fissions under the impact of slow neutrons is
the physical property which has made plutonium so important. However,
the fission property has for our purposes very little direct consequence,
either as a hazard or as a means for measuring plutonium in the
environment.

RADIATION PROTECTION GUIDES

Plutonium is relatively hazardous, compared to many of its neigh-
boring elements in the periodic table. The various hazards have been
taken into account in the establishment of the radiation protection
guides. The toxicity depends on the medium, of course: airborne
soluble plutonium transfers across the lung mucosa and ultimately is
largely deposited in bone, where its tumor-forming hazard is greater
than that of radium-226. As soluble plutonium in water, it is absorbed
by the GI tract and again deposits preferentially in bone. When pluton-
ium is insoluble, the critical organs are the sites of direct exposure, the
lungs and GI tract. Recently, concern has also been expressed that the
limiting effect for insoluble airborne plutonium might be the dose to
the pulmonary lymph nodes,[6] autopsies having shown significant
plutonium burdens there.[7]

TABLE 1.

Some Properties of the Important Plutonium Isotopes, and of Americium-241
(from Ref. 5)

Isotope	Half-Life (years)	Main Decay Products and Energies (MeV)
Plutonium-236	2.85	α (5.72, 5.77)
Plutonium-237	0.12	electron capture
Plutonium-238	86.	α (5.46, 5.50)
Plutonium-239	24,400.	α (5.16, 5.15, 5.11) x-rays (0.017, 3.8%)
Plutonium-240	6,580.	α (5.12, 5.17)
Plutonium-241	13.2	β⁻ (0.021 maximum)
Plutonium-242	379,000.	α (4.86, 4.90)
Americium-241	433.	α (5.44, 5.49) γ-ray (0.060, 36%) x-ray (0.014, 0.017, others)

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TABLE 2.

*168-Hour/Week Occupational Maximum Permissible Concentrations in Air
and Water, and Maximum Permissible Body Burdens*

(from ICRP Pub. 2, Ref. 8)

Isotope	Soluble or Insoluble	Critical Organ	$(MPC)_w$ μCi/liter	$(MPC)_a$ pCi/liter	MPBB (μCi)
Plutonium (238, 239, 240, 242)	Soluble	Bone	0.05	0.0006	0.04
Radium (226)	Soluble	Bone	0.0001	0.01	0.10
Plutonium (238, 239, 240, 242)	Insoluble	Lung	---	0.01	---
Radium (226)	Insoluble	Lung	---	0.02	---
Natural Uranium	Insoluble	Lung	---	0.02	---
Plutonium (238, 239, 240, 242)	Insoluble	GI tract	0.30	---	---
Natural Uranium	Insoluble	GI tract	0.20	---	---

For 168-hour occupational exposures, the maximum permissible concentrations in air and water, $(MPC)_a$ and $(MPC)_w$, are given in Table 2. The maximum permissible body burdens (MPBB) are also given. Note that for individuals in the general public, the applicable MPC values are a factor of 10 smaller than those tabulated in Table 2; and for exposure to a suitably large sample of the general population, another factor of 3 smaller still.[8]

Note the comparisons in Table 2 with radium-226 and natural uranium. In insoluble form Pu, U, and Ra have comparable MPC values. However, the MPC for soluble plutonium in air is a factor of 15 more restrictive than that for ^{226}Ra. In water, on the other hand, the MPC is 500 times less restrictive than for radium. These differences are direct manifestations of the biomedical-pathway toxicities.

SOURCES AND LEVELS OF ENVIRONMENTAL PLUTONIUM

Plutonium is produced by certain nuclear reactions, mainly in nuclear reactors. Its isotopic composition is variable, depending upon the method and conditions of production. The most important production mechanism creates ^{239}Pu by neutron capture on ^{238}U to form ^{239}U, which β-decays (23.5 minutes) to ^{239}Np, which in turn β-decays (2.3 days) to ^{239}Pu. Plutonium-240, the next most abundant isotope after ^{239}Pu, is formed by a second neutron capture on one of the 239 isotopes. In plutonium being produced for weapons, the ^{240}Pu concentration must be kept below the few-percent level; otherwise, too many spontaneous neutrons from ^{240}Pu will either set off a premature chain reaction or decrease the energy yield of the explosion.[10] In plutonium for commercial power-reactor use, on the other hand, ^{240}Pu is expected to be present at about 30% abundance.[10] At Rocky Flats (where weapons-grade plutonium is produced), a typical mixture contains the following isotopic fractions:[11]

^{238}Pu	0.04 ± 0.01%	
^{239}Pu	93.34 ± 0.5 %	
^{240}Pu	6.00 ± 0.5 %	
^{241}Pu	~0.58	%
^{242}Pu	~0.04	%

The concentration of americium-241 is dependent upon the time for ingrowth from its parent, ^{241}Pu (13.2 years).

Nearly all of the plutonium in the world today exists at only a few types of locations: in nuclear weapons; in the nuclear-reactor fuel cycle; and in stockpiles. The most probable sources of plutonium in the environment are equally easy to classify: nuclear weapons already exploded; wastes or leaks from the reactor fuel cycle, most likely around plutonium production facilities or fuel reprocessing plants; and occasional unique events, such as the burnup of a plutonium-fuelled power cell in a satellite accident.[12, 13]

Studies of plutonium in surface air have been carried out for several years by the U.S.A.E.C. Health and Safety Laboratory. A recent compilation[14] indicates that in 1969, typical ^{239}Pu world-wide concentrations were in the range from 1 to 50 x 10⁻⁸ pCi/liter of air. The higher number is a factor of 40 lower than the MPC$_a$ value for exposure to large general populations; the smaller number is 2000 times lower. In 1966, the average ^{238}Pu/^{239}Pu ratio in air[14] was 0.04, and the monthly surface deposition of ^{239}Pu from precipitation[15] ranged from about 0.5 to about 1.0 pCi/m². Studies of plutonium in surface soil in the Livermore Valley of California[16] have found ^{239}Pu surface levels of 200 to 2000 pCi/m². Children's diets in 1966 showed ^{239}Pu concentrations[16] of about 0.002 to 0.006 pCi/kg. This is more than 5 orders of magnitude smaller than the general-population MPC$_w$.

These world-wide distributions are mostly due to fallout from nuclear weapons tests, plus the aforementioned satellite accident, which deposited 11,000 curies of ^{238}Pu in the stratosphere over the Indian Ocean in 1964.[12, 13] As the numbers reveal, the world-wide levels are not now significant fractions of the MPC limits for general-population exposure; and since fallout hopefully will not increase dramatically, the levels should also not increase dramatically. The main radiological hazard is thus more likely local than worldwide in scope. Local concentrations can range up to values much higher than the worldwide averages just mentioned. One example is at the Nevada Test Site, where many locations have ^{239}Pu in soils at levels of 100's to 1000's of pCi/gram over several acres.[17] Another example is near the Rocky Flats plutonium production facility, where plutonium air concentrations have occasionally reached as much as 30% of the soluble MPC$_a$ for individuals in the general public.[18]

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One important point which must be borne in mind is that plutonium deposited on soil is not a significant direct public health hazard. One prime pathway to man is resuspension from the ground into the air, which can result in widespread distribution of an originally well-localized source, and which in turn may lead to more widespread public health exposures. This possibility has motivated a program within the U.S.A.E.C. to study the problems of resuspension.[19]

MEASUREMENT CONSIDERATIONS

Among the environmental media requiring measurement of plutonium activity are silt and soil; natural and waste waters; food; and air. The techniques which have been developed fall into several categories. We shall discuss them separately below. These categories are:

    a.   Radiochemical Analysis Followed by
           Counting or Spectroscopy
    b.   Air Filter Collection Followed by
           Counting
    c.   Gamma and X-Ray Spectroscopy
    d.   Other Methods

Because plutonium concentrations in most samples are small, and because the decay alphas have such short ranges in matter (~ 5 to 10 mg/cm^2), direct alpha counting of environmental samples is seldom practical.

Radiochemical Analysis Followed by
Counting or Spectroscopy

A wide variety of techniques for radiochemical analysis have been developed for plutonium determinations in various media. Chemical separation produces enrichment with respect to the matrix in which the plutonium is found, and makes possible alpha counting or alpha spectroscopy with increased sensitivities.

The main difficulty in alpha detection is the extremely short range of the alphas (5 to 10 mg/cm^2), which requires preparation of a nearly 'weightless' sample. An important chemical-analysis difficulty is that the weight of the plutonium in samples may be minute: 1 pCi of ^{239}Pu weighs only 16 pg.

Perhaps the greatest problem with plutonium radiochemistry is the insolubility of one common chemical form, plutonium oxide. We quote from Healy:[20]

> "Plutonium oxide fired at high temperatures is a
> notoriously insoluble ceramic. If present at larger particle
> sizes it is exceedingly difficult to put into form for a
> chemical separation. However, very small particles such
> as are found in natural fallout or other materials, includ-
> ing oxide which has been formed at a lower temperature,
> are much more soluble and can be leached from the sample
> with relatively mild treatment."

The media requiring chemical analysis are usually of three general classes: water samples, air-filter samples, and soil samples. Other possible media are food, urine, and biological and fecal samples. The general problem of low solubility may be present in nearly all of these media.

Chemical methods can be divided into two general classes: those that bring the entire sample into solution, and those that use a leaching technique to extract the plutonium from the matrix. The leach methods are generally easier, but are also more liable to error . . . hence, periodic total-dissolution and cross-comparisons are often used to check the yields from the leach methods.

In all of the radiochemical analyses, the use of either plutonium-236 or plutonium-242 as a tracer for chemical yield is common. Both ^{236}Pu (5.72, 5.77 MeV) and ^{242}Pu (4.86, 4.90 MeV) decay by emitting alphas of sufficiently different energy that they can be resolved from ^{239}Pu by using spectroscopy. The tracer should be added at the earliest possible state, of course. Unfortunately, the tracer technique cannot adequately correct for insolubility losses, one of the commonest problems, since

soluble tracer does not exchange with insoluble ^{239}PuO$_2$ unless there is complete dissolution to soluble ionic forms.[22] Another consideration, emphasized by Sill,[22] is that at least as much tracer should be used as unknown Pu being determined. Otherwise, the statistical uncertainty in the determination is limited by the ^{236}Pu statistics. Lindeken[23] has pointed out that one advantage of ^{242}Pu is that it has a lower energy, so that there are no contributions to the ^{239}Pu energy region from possible energy degradation of the tracer's alpha.

Sill[24] describes a method for soils, in which "the sample is decomposed completely by a combination of potassium fluoride and silicon tetrafluoride. The cake is dissolved in dilute HCl and all alpha emitters are precipitated with barium sulfate." Sill claims recoveries of 94 $\pm$ 3% for all elements from thorium through plutonium, and describes a method for separating and electrodepositing three fractions for separate alpha spectroscopy: (Am, Cm, and Cf), (Th), and (Pa, U, Np, and Pu). Sill also claims that the method is reliable "in soils in which complete dissolution of both the siliceous matrix and the most insoluble forms of plutonium oxide that can be produced can be guaranteed routinely".[24]

Another total-dissolution method has been described by Talvitie,[25] in which adsorption from a hydrochloric acid medium is followed by a nitric acid wash for removal of iron. Anion exchange is then used for plutonium separation, followed by electrodeposition.

The leaching methods, which are commonly used for soil analysis, are claimed to be easier and faster than the total dissolution methods. One method prominently mentioned in the literature is that of the U.S.A.E.C. Health and Safety Laboratory.[26, 27] This method is designed for 100-gram soil samples. Soil is leached with a mixture of HNO$_3$ and HCl. Leached Pu is converted to Pu(IV) with sodium nitrite and absorbed from 8N HNO$_3$ for electroplating.

This method presents problems in the presence of highly insoluble PuO$_2$, and the U.S.A.E.C. Nevada Applied Ecology Group[28] has adopted instead a Los Alamos-modified technique, the so-called "modified HASL-LASL" method, [29] which uses HF as well as HCl in the leach process to improve the yield. After leaching, an anion exchange resin column is used for Pu separation followed by electroplating. The electroplating step may present an important roadblock, because it limits the number of samples which can be run in parallel unless many electroplating cells are available. Also, even this improved method may suffer from yield difficulties when very large samples are analyzed.

Levine and Lamanna[30] describe methods in which "solubilized plutonium as the chloride is reduced to the tri-valent state, co-precipitated with lanthanum carrier as the fluoride, dissolved in acid aluminum nitrate and extracted with thenoyltrifluoroacetone (TTA) for separation and removal of impurities and carrier. The plutonium is then back-extracted with strong acid, oxidized and electrodeposited on stainless steel for counting." Bowen et al.[31] report a similar procedure.

Air Filter Collection Followed by
Counting

The most common method for monitoring plutonium in air is by the collection of activity on an air filter, followed by direct counting of the collected activity. Unless an identification of the isotopes is possible from separate knowledge, this type of measurement is really a "gross-alpha" determination. The MPC$_a$ for soluble plutonium is 6×10^{-9} pCi/liter for individuals in the general public. The counting rate from such an activity level is extremely low: 6×10^{-6} pCi gives about 1.3 disintegrations per week. Measurement of such activities requires the sampling of many liters of air. There are two different classes of measurements: those which measure continuously while the activity accumulates, and those which measure the activity after a fixed collection period. The latter are the more sensitive, and the more frequently used.

In all of the methods to be described below for air filters, no distinction is made between soluble and insoluble plutonium. Thus the measurement must be considered as, and compared to, the soluble MPC$_a$ (which is the more restrictive).

One common collection system has been used by Lawrence Livermore Laboratory personnel at the Nevada Test Site.[32] An air sampler with a pumping speed of 10 ft³/min (1 ft³/min = 28.4 liters/min) pulls air through a convoluted fiberglass filter. Particles as small as 0.025 μm are collected at >99% efficiency, and 90% efficiency can be obtained even at sizes as large as 50 μm.

At Rocky Flats, sampling at about 1 ft³/min is used.[33] Using a rate of 10 ft³/min, and with an air concentration equal to one general-public-MPC_a, it would take about 1 hour of sampling to collect 1 pCi (= 2.2 dpm) on the filter.

The most important background is usually from the daughters of radon-222. The MPC_a for radon daughters is about 5 orders of magnitude higher than for plutonium, and radon occurs naturally in typical surface air at concentrations of 0.1 to 1 pCi/liter. In some locations (for example, in some areas in the Rocky Mountains) even higher ambient concentrations are found. Radon-220 (thoron gas) and its daughters can also provide a similar type of background, but usually at much smaller concentrations. Since the filters are efficient collectors of radon and thoron daughters, any measurement system for plutonium must be able to discriminate against the much larger radon background.

There are four techniques which are commonly used to achieve the necessary discrimination:

i.   alpha spectroscopy
ii.   alpha-to-beta ratio method
iii. radiochemical analysis
iv.   4-day hold-up to allow for decay of
      the short-lived activities.

i. _Alpha Spectroscopy._ Measurement of the alpha energy spectrum from the activity deposited on an air filter is very effective for discrimination against radon and thoron daughters. The alpha energies from decay of radon-222, polonium-218, and polonium-214 are 5.49, 6.00, and 7.69 MeV, respectively. The highest-energy alpha from an important plutonium isotope is ^{238}Pu's 5.50 MeV, which would be difficult to resolve in the presence of large amounts of ^{222}Rn. ^{239}Pu emits in the 5.15 MeV region, which is easily resolvable. The daughters of radon-220 (thoron) all emit alphas with energies above 6 MeV, and are therefore quite easily rejected. At Rocky Flats, Griep[33] has performed alpha spectroscopy using a large surface-barrier detector, with an area of 350 mm². An earlier device using a different solid-state detector was developed at Lawrence Livermore Laboratory.[34] These types of instruments are capable of discriminating between ^{239}Pu and the higher-energy backgrounds with plutonium activity of less than 1 pCi/m³ of air, sampled for 8 hours. Both of the instruments just mentioned were designed primarily for occupational rather than environmental monitoring. The Livermore instrument can easily detect one 40-hr-occupational MPC_a with an 8-hr sampling time at 1 ft³/min: this concentration yields about 15 counts/min in the detector, which has a 25% overall efficiency.
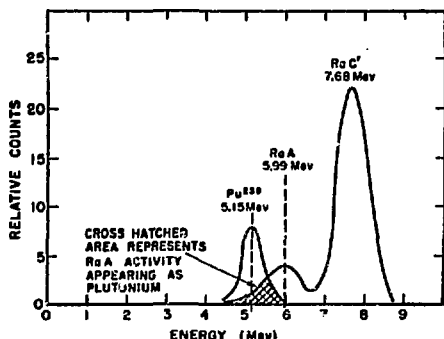
Figure 1 shows the spectrum from the Livermore detector when radon daughters are present together with plutonium. The sampling parameters are 1 ft³/min for 8 hr. The radon daughters reach equilibrium very quickly: Ra A (^{218}Po) has a 3.05 min half-life. Therefore their activity levels on the filter are smaller by orders of magnitude than their total collected activities.

Use of an internal gas proportional counter for alpha spectrometry yields resolutions nearly as good as with a solid-state detector, with the added ability to count larger filter areas.

ii. _Alpha-to-Beta Ratio Method._ In this method, plutonium is distinguished from the radon and thoron daughters using the fact that the important natural alpha emitters have a special signature using $\alpha\,\beta$ coincidence counting. Ra C (^{214}Bi) emits a β^- almost immediately before Ra C´ (^{214}Po) emits its alpha . . . the same is true of Th C (^{212}Bi) and Th C´ (^{212}Po). This is because the half-lives of Ra C´ and Th C´ are so short: 164 μsec and 0.30 μsec, respectively. Thus $\alpha\,\beta$ coincidences can be used to measure the level of the radon/thoron-daughter activities. One difficulty with this technique is that it relies on comparing two (sometimes large) numbers to obtain the (sometimes small) plutonium activity.

When a filter is measured by two different (alpha- and beta-sensitive) detectors, lack of 100% detection efficiencies means that there cannot generally be a one-to-one subtraction of the $\alpha\,\beta$ coincidences. Rather, the $\alpha\,\beta$ coincidence rate must be electronically weighted before subtraction. Given a fixed resolving time and fixed detection efficiencies it is theoretically possible to cancel out both the radon and the thoron chains exactly, aside from statistical fluctuations,[36] provided the deposited daughters are in equilibrium. To do this subtraction properly, very careful calibrations are required. Because thoron daughters have a longer average half-life, they will dominate for collection periods in the 10 hr range, while for a 1-hr collection period radon daughters usually dominate.[30] However, for a given detector, one must take care to equalize the detection efficiencies for the Th C and Ra C betas, which have very different energy spectra. This can be done by using an appropriate absorbing foil to compensate properly for the different energies.

Typical instruments of this design have been described by Spaa,[36] Rankin,[37] and Gupton,[38] among others. Spaa's design aims for continuous alarm capability. A filter paper is moved semi-continuously (stepwise) across a 70 liter/min pump. Continuous counting is performed during activity accumulation, using a ZnS(Ag)/photomultiplier alpha detector and an end-window G-M beta counter. Every 12 hours the filter is automatically moved stepwise, and is available for more precise measurements if required. In the presence of radon daughters at 10 pCi/liter of air, plutonium at 0.002 pCi/liter was the approximate limit of detection after about 1 hr of sampling.

Rankin,[37] using solid scintillation detectors for both α and β counting, detected plutonium at a lower limit of about 800 pCi in the presence of 0.1 pCi/liter of radon-222. With a 24-hr sampling time at 10 ft³/min, this also corresponds to a plutonium concentration of 0.002 pCi/liter of air. Gupton's instrument[38] is very similar, but also provides another G-M detector which is not exposed to the filter, for external gamma compensation.

Tanaka et al.[35] describe an improvement of the technique in which an alpha spectrometer is used to further select the ^{239}Pu signal. A CsI(Tl) scintillation spectrometer is used, and alpha particles are selected from beta particles by pulse-shape discrimination. In 24 hours, it can detect plutonium levels as low as 10^{-6} pCi/liter in the presence of radon at about 0.1 pCi/liter.

iii. _Radiochemical Analysis of Air Filters._ A method for radiochemical analysis of air filters has been adopted as a tentative method by the Intersociety Committee.[39] This method is similar to one found in the HASL Manual.[27] "The plutonium is . . . isolated by co-precipitation with cerium and yttrium fluorides . . . further purified by a double anion-exchange column technique . . . finally electro-deposited onto a platinum disk".[39] The first ion-exchange process is from HCl, the second from an HNO_3 medium. A solid-state spectrometer determines the Pu isotopes; ^{236}Pu is used as a tracer. This method claims a practical detection limit of about 8×10^{-8} pCi/liter with ±10% error(1 σ), when air is collected at about 700 liters/min for about one week. For

FIGURE 1. _Radium A (Polonium-218) interference in plutonium detection (from Ref. 34)._

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smaller volumes of air, sensitivity is reduced proportionally. The difficulty with this method is, as might be expected, that dissolution of high-temperature-fired PuO_2 is not necessarily complete, leading to possible underestimation of the concentration. However, since the MPC_a for soluble plutonium is smaller by a factor of 16 than that for insoluble plutonium, the problem of insolubility losses is usually not serious for air-filter measurements.

Gamma and X-Ray Spectroscopy

Gamma and x-ray spectroscopy is an important plutonium measurement technique in some situations, and may be thought of as complementary to the radiochemical assay methods, since the applications of this type of spectroscopy are usually for measurements of an entirely different class.

The field survey of large surface areas for possible plutonium contamination is one such application: for example, much effort has gone into large-area surveys around the Nevada Test Site. Another application is for plutonium assay in media which are not accessible to radiochemical analysis: examples are large soil samples, bioassay of plutonium in lungs, or plutonium detection in a solid-waste container.

This method usually relies on detecting decay photons from one of two important phenomena. The first phenomenon is the 59.6-keV gamma ray emission which accompanies 36% of the decays of [241]Am, the daughter of [241]Pu. [241]Pu is seldom the main plutonium isotope present, and even if it were it is not usually the main hazard, being a beta-emitter. Therefore, this method is useful for gross-plutonium measurement only if one knows both the 'age' of the plutonium (to determine ingrowth of [241]Am) and the original isotope ratios.

The second phenomenon is the 17-keV x-ray emission group which accompanies about 3.8% of the [239]Pu decays. Actually, the emissions are L x-rays from the daughter [235]U. The energies[40] of the three most prominent lines are 13.6, 17.2, and 20.2 keV with relative intensities 100:120:35. Americium-241 decays are also accompanied by x-rays in the same 17-keV region (actually the L x-rays of its daughter, [237]Np). The energies of the americium lines[41] are 14.0, 17.8, 20.8, and 26.3 keV, with relative intensities (photons/alpha) of 12%, 13%, 3%, and 2.5%. (Note again for comparison the 36% 59.6-keV americium gamma.)

The task of field-surveying for plutonium contamination on the ground has received considerable attention, although it actually has a rather narrow range of application such as at the Nevada Test Site, near plutonium production facilities, and so on. Here the goal is to locate and quantify the surface activity ($\mu Ci/m^2$), rapidly and conveniently. The presumption is made that detailed soil sampling must be relied on for more refined measurements.

One instrument type often used for this task is a thin NaI(Tl) crystal of large area, coupled to a photomultiplier tube. The archetype specifically for plutonium contamination is the FIDLER detector developed at Lawrence Livermore Laboratory.[42] It has a 5" diameter 1/16" thick NaI(Tl) crystal, and is designed to be carried by hand over the terrain at about one foot above ground level. The battery-operated electronic circuitry separates and counts two 'windows' in the energy spectrum, one around 17 keV and the other around 60 keV. These are shown, along with a spectrum from a pure [241]Am source, in Fig. 2. An instrument of this type must be calibrated against several variables. First, its response is sensitive to activity distributed over a wide area. Further, the thickness and composition of any overburden material, as well as the plutonium isotopic distribution, will affect the interpretation of the results.

Assuming a 12-second time-constant for the count-rate meter and that the instrument is being carried slowly over the terrain, the minimum detectable [241]Am point source is about 9400 pCi, and the minimum detectable area-distributed source is 19,200 pCi/m², both at 3.3 σ above a natural background of about 200 counts/min.

An instrument similar to the FIDLER but using a 5"-diameter, 1/8"-thick CaF_2(Eu) scintillator has been developed by Nuclear Chicago.[43] The claimed advantages of CaF_2(Eu) are that it does not require the careful hermetical sealing characteristic of NaI(Tl); and that there is better optical coupling to a tapered conical light pipe, which partially compensates for the lower light output (40-50% of that for NaI(Tl)).
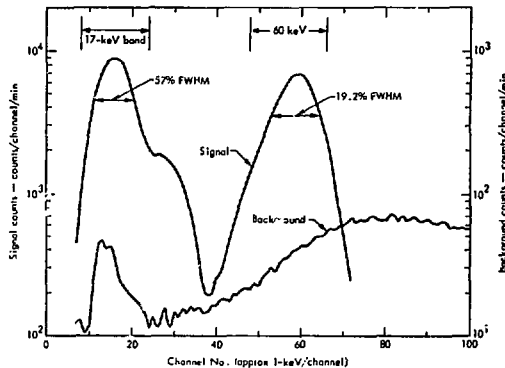

FIGURE 2. Spectra for [241]Am and background as measured with a 5-in.-diam by 1/16-in.-thick NaI(Tl) scintillation detector. Source was 10.7-µCi [241]Am, and source-to-detector distance was 30.5 cm. Optimum discriminator settings for 17-keV band and 60 keV are shown (from Ref. 42).

A similar instrument, but using an 8"-diameter, 0.2"-thick NaI(Tl) crystal, has been used for assay of the lung burden of exposed individuals.[44] For a 100-minute counting time, the minimum detectable activity (3 σ) was found to be 6200 pCi of [239]Pu. Counting efficiency must be determined with a phantom, because absorption and scattering of the low-energy photons is very large. The counting efficiency (counts per [239]Pu disintegration) was measured to be only about 4×10^{-4}, the majority of the x-rays being absorbed or scattered. The principal irreducable background is from degraded gammas due to the decays of [40]K and ^{137}Cs in a normal body.

Use of twin large-area gas proportional counters is also common for Pu lung assays. With this technique Tomitani and Tanaka[40] report 12.6% resolution (full width half maximum) on the 13.6 keV line; this is shown in Figure 3. With an outer ring of wires for anti-coincidence shielding to provide a veto whenever cosmic ray particles traverse the chamber, the minimum detectable activity (3 σ) is 6000 pCi of [239]Pu, using a 100-minute counting time.

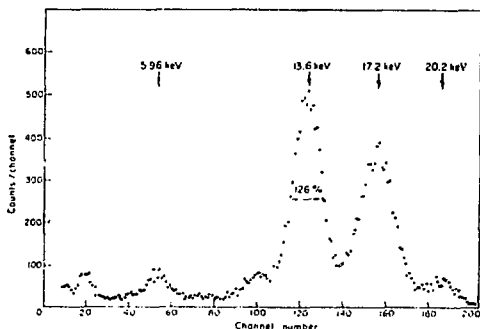FIGURE 3. X-ray spectrum of [239]Pu. 13.6, 17.2 and 20.2 keV X-rays are L_α, L_β and L_γ characteristic X-rays of [235]U, respectively. X-rays of energy about 5.96 keV are the fluorescent X-ray of the stainless steel housing (from Ref. 40).

The backgrounds are higher using NaI(Tl) for lung-counting applications, but the detection efficiencies are also higher. It seems that the proportional counters as described by Tomitani and Tanaka are more difficult to construct and operate. Overall, the two types of instruments have comparable sensitivities.

A solid-state Ge(Li) assay technique has been developed by Tyree and Bistline.[46] This system can resolve the 51.6-keV gamma ray from [239]Pu in the presence of the 59.6-keV [241]Am gamma. The 51.6-keV [239]Pu gamma occurs with an 8.4% branching ratio. Using this system and a 1-hr counting time, minimum detection (3 σ) of a few thousand pCi of [239]Pu was possible. These authors also report detection of the 14.0-keV [241]Am line with 3.7% resolution (full width, half maximum) using a Si(Li) detector, compared to 14% using a proportional counter.[46] This is shown in Fig. 4.
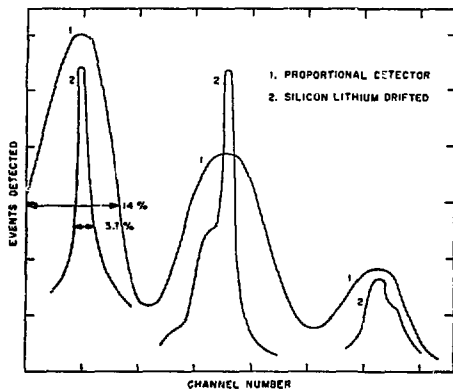
FIGURE 4. *Proportional and Si(Li) detector spectra from americium-241. The three peaks shown have energies of 14.0, 17.8, and 20.8 keV, and are actually L x-rays from neptunium-237 (from Ref. 46).*

Tyree and Bistline[46] report use of the relative attenuation of the various x-ray lines to give a measurement of the depth of a contaminating source, such as plutonium in a wound. Several-mm depths are measured to fractions of one mm. The relative attenuations of the 13 and 20 keV uranium L x-ray lines with thickness are shown in Figure 5.
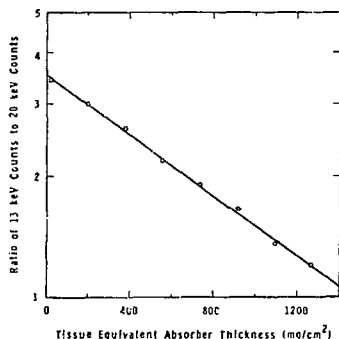
FIGURE 5. *Plot of the ratio of the 13 and 20 keV uranium L x-ray intensities as a function of increasing absorber thickness (from Ref. 47).*

Another detector type useful for this class of measurement consists of a thin NaI(Tl) crystal optically coupled to a much thicker CsI(Tl) crystal behind. This system is usually called a 'phoswich' detector. The low-energy x-rays are totally absorbed by the NaI(Tl), while higher-energy photons (or charged particles) come in the CsI(Tl). Both scintillators are viewed by the same photomultiplier tube (see Fig. 6), and the signals can be differentiated by pulse-shape analysis since NaI(Tl) has a 250-nsec optical decay time compared to 1100 nsec for CsI(Tl). This type of instrument can suppress high-energy backgrounds by factor of 3 to 10.

Koranda et al., [48] have developed a semi-portable Ge(Li) spectrometry system for field surveys of soil. The system rides in a van, and is designed to combine the better resolution of a solid-state detector system with the needs for mobile surveying in the field. The system seems more valuable for the higher energy gammas from fission products and natural emitters, rather than for the low-energy plutonium photons.
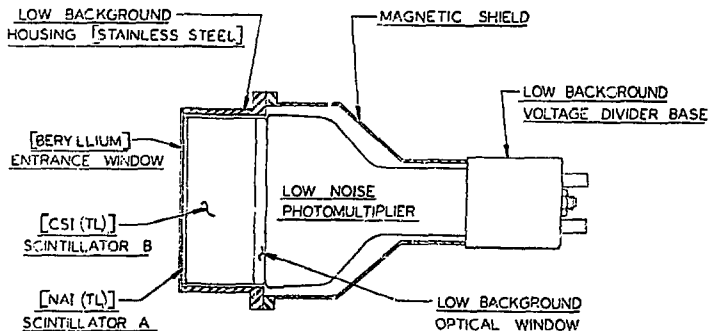
FIGURE 6. *Harshaw phoswich detector: matched window type for x-ray and low energy gamma detection.*

Other Methods

Several other types of determinations, which do not ultimately rely on alpha or gamma counting for the plutonium measurement, have been developed. We shall not discuss these here at all, but shall merely refer the reader to some references for details. Generally these methods are not sufficiently sensitive for environmental measurements. (i) Controlled-potential coulometry[49] is useful when Pu concentrations are high ($\gtrsim 0.1\ \mu$Ci/liter) and accuracy is required. (ii) Constant-current potentiometric titration[50] is also commonly used at these concentrations. (iii) Amperometric techniques[51] can be used for accurate work with very large ($\gtrsim 10\ \mu$Ci/liter) concentrations. (iv) Spectrophotometry[52] is applicable above about 0.1 μCi/liter. (v) Square wave polarography[53] is sensitive down to $\sim 0.1\ \mu$Ci/liter.

CONCLUSIONS

In this section we have given overviews of the typical levels at which plutonium is found in environmental media; of the radiation protection guides; and of some of the types of measurement techniques which have been developed for plutonium measurements in the environment.

The material is very dangerous and the radiation protection guides are necessarily very restrictive. Fortunately, important plutonium contamination in the environment is not widespread. A small level of world-wide plutonium from fallout is supplements by higher concentrations in only a few well-localized areas, where plutonium contamination may be an important radiobiological factor.

The ideal instrument or technique for plutonium determinations should be capable of measuring concentrations down to fractions of MPC levels in the appropriate medium. There are two main classes of measurements, field and laboratory measurements. Of the type of measurements considered here, only two are of the field-type: surveys of plutonium deposition on the ground, and air concentration measurements. Even the latter are often performed by laboratory analysis of an air filter after field sampling.

We shall summarize the situation in each of the various measurement areas separately:

Measurements of Plutonium on and in Soil

There are two basically different techniques: first, field surveying; and second, radiochemical analysis followed by alpha counting or spectroscopy. The field-survey measurements demand less accuracy, and are now performed by carrying counting instruments above the terrain. The archetype of this class is the FIDLER, which has a thin, large-area NaI(Tl) scintillation detector. Instruments of this type seem adequate for most rough field-survey measurements. Radiochemical analysis techniques are intrinsically much more sensitive and accurate, but suffer from their own types of difficulties. The most precise and surefire techniques involve total dissolution . . . but these are laborious, time-consuming, and expensive. There are a number of leaching methods which are intrinsically faster and cheaper. Many of these present difficulties in the presence of insoluble matter, such as high-temperature-fired PuO_2. There certainly seems to be need for further improvement in the analytical chemical methods. In particular, the development of a faster and less expensive leach method possessing a high yield would be desirable.

Measurements of Plutonium in Air

Measurements of plutonium in air are nearly always made by collecting particulate activity on an air filter for counting. The main background is usually due to daughters of radon, which must be discriminated against. One method is to perform radiochemical analysis, followed by spectroscopy. This technique, while intrinsically sensitive and accurate, is expensive, time-consuming, and liable to radiochemical-yield errors. The two most common methods which use direct counting of the filter are the alpha beta coincidence technique and alpha spectrometry. Both are sensitive and precise; perhaps α spectrometers are to be preferred for the most precise and background-free requirements, but the $\alpha\,\beta$ coincidence technique is advantageous since it has been adapted for

continuous measurements during sample collection. However, because of the very low MPC_a value, none of the methods presently available combines rapid or continuous detection with sensitivity well below MPC_a.

Measurements in Soil or Bioassay Using Gamma Spectroscopy

Bioassays of lung or other body burdens, and also measurements in bulky samples such as large amounts of soil, can be performed with gamma spectrometers, typically using either NaI(Tl) or Ge(Li) detectors. These methods all suffer from one intrinsic problem: it is necessary to trade off resolution for sensitivity. High resolution Ge(Li) detectors capable of high detection efficiency are available only at great expense; on the other hand, the much larger NaI(Tl) crystals suffer from poor resolution which is a handicap especially in the presence of higher-energy gamma fluxes. This problem is inherent to the method.

Measurements in Other Media

Measurements in media such as urine, plants, food, and tissue are typically made radiochemically. There is also a wide variety of chemical methods (coulometry, spectrophotometry, polarography, etc.), which are mainly useful at relatively high concentrations. The radiochemical analyses of various media usually consist of initial sample-treatment steps designed to bring all of the plutonium into solution, followed by analysis identical to that used in the analysis of soil or water.

It seems probable that more sensitive and faster methods for measurements of plutonium in man can be developed, using extensions of presently-available technology. The motivation for this is probably not great at the present time since its application would be limited largely to measurements in a few occupational-exposure situations.

Overview

At present, measurements at levels significantly below MPC values for individuals in the general public are possible in each of the main measurement situations where public health is involved or where pathways in the environment require study. In particular, radiochemical analyses in the laboratory followed by alpha spectroscopy are quite sensitive and suffer from few interferences. Unfortunately, the best of these methods are expensive and time-consuming.

Given the probable growth in use of plutonium as the nuclear power industry expands and as the breeder-reactor program grows, it seems important that methods be developed which enable sensitive but inexpensive determinations of plutonium in air and water effluents, as well as in soil and biomedical media.
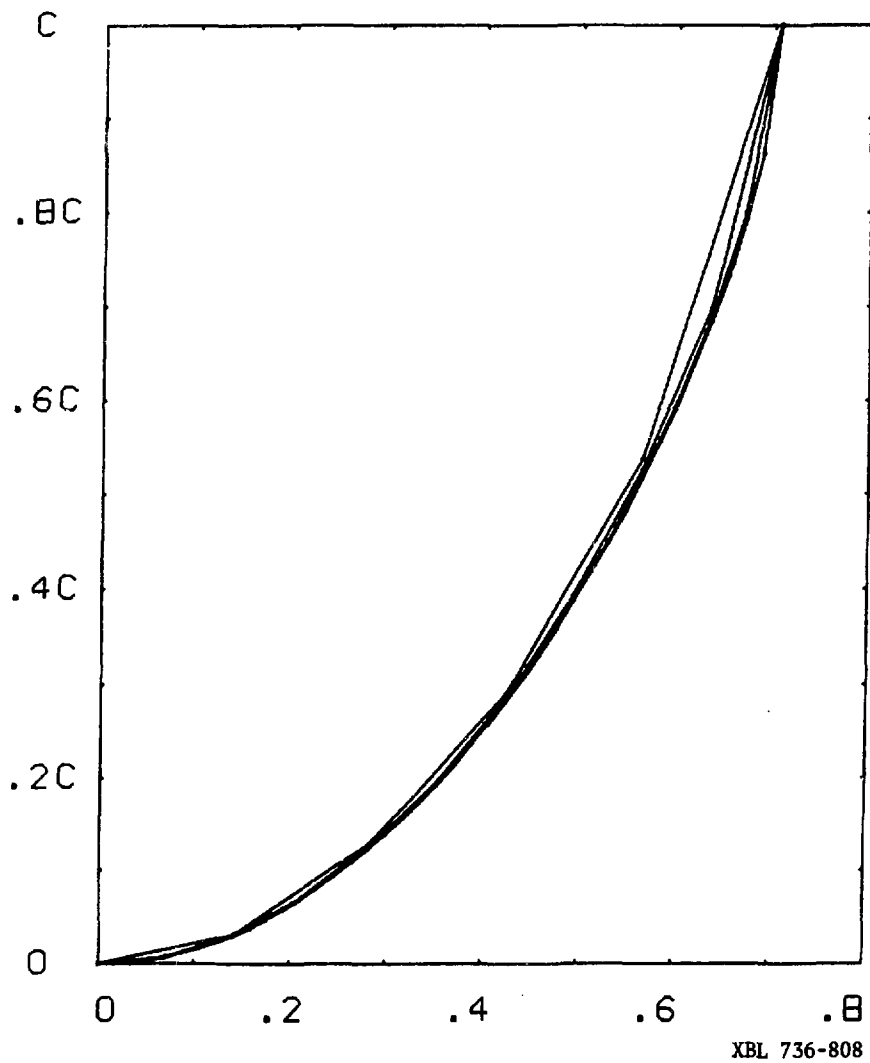
XBL 736-808

Figure 7.   Same as Fig. 4 except that $c = 0.1$

50. C. E. Pietri and A. W. Wenzel, Talanta 14, 215 (1967).

51. C. E. Herrick, C. E. Pietri, A. W. Wenzel, and M. W. Lerner, Anal. Chem. 44, 377 (1972).

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