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HEALTH PHYSICS AND SAFETY DIVISION
Informal Report

SAMPLING AND ANALYSIS OF
RADIOACTIVE SUBSTANCES IN THE ATMOSPHERE

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INTRODUCTION

The Radioactive Substances Subcommittee of the Intersociety Committee on Methods for Air Sampling and Analysis (ISC) has formulated and published⁽¹⁻⁵⁾ nine tentative methods for the sampling and analysis of radioactive substances, and has several more under consideration. Together these include most of the nuclides or classes of nuclides commonly encountered in the environment. A description of these methods, with some of the considerations underlying them, should therefore be illustrative of the overall subject of the sampling and analysis of airborne radioactive substances.

In contrast to the rather specific types of pollutants considered by most of the other ISC Subcommittees, the concerns of the Radioactive Substances Subcommittee are very broad. These include several types of radioactivity: alpha, beta and gamma, which may be emitted by a variety of natural or man-made radionuclides, each with its own characteristic combination of decay scheme, type or types and energies of radioactive emissions, and half-life. These radionuclides may be airborne in the environment in gaseous, vapor or solid (particulate) forms. From this it should be obvious that there is no one single method of sampling or analysis appropriate for all airborne radioactive substances, but rather that a separate and more or less unique method is required for each.

The interdisciplinary nature of the ISC and make-up of its subcommittees has therefore been essential to the functioning of the Radioactive

Substances Subcommittee. In addition to drawing on its own competence, the Subcommittee has from its inception (in 1966) established a close liaison with other groups with corresponding or overlapping interests. In particular this has included the Referee Committee on Air of the Subcommittee for Radiological Methods for Biological and Environmental Samples (RMBES), which was being created at about the same time by the Coordinating Committee on Laboratory Methods of the American Public Health Association (APHA), itself an ISC participant. The potential for a duplication of effort, through this classic example of the right hand not knowing what its left hand is up to, was minimized by the deliberate naming of an overlapping membership to the two groups. The ISC Radioactive Substances Committee has since become de facto the RMBES Referee Committee for Air, thus eliminating the problem.

Only recently, with the expansion of the scope of the ISC, has the Health Physics Society (HPS) become a member of it. Thus, although several HPS members happened to be serving on the Subcommittee on Radioactive Substances, the Society was not officially represented. In recognition of its interest and expertise in this field, the HPS was invited to appoint a liaison, which it did early in 1967.

At the outset of its activities, the Subcommittee assessed the radio-nuclides for which it appeared that methods of sampling and analysis were most needed. This initial list included ^3H , ^{85}Kr (and other noble gases), ^{89}Sr and ^{90}Sr , ^{210}Po , ^{210}Pb , ^{222}Rn , uranium, plutonium, gross alpha and gross beta. Priorities for the development of methods within this list were established on the basis of the environmental importance of the nuclide, and on the basis of the completeness of existing methods known to one or more Subcommittee members.

An individual on the Subcommittee was designated to take primary responsibility for the preparation of a first draft for a given nuclide. This was circulated and then critiqued at a subsequent Subcommittee meeting. The process was repeated until the Subcommittee was satisfied with a final draft, which was then submitted to the full ISC Executive Council. To date the Subcommittee has completed tentative methods for all the nuclides on its initial list but Kr, ^{210}Po and uranium. It has not as yet found a suitable method for any radioactive fission gases at generally prevailing concentrations. The Subcommittee has reconsidered the need for a ^{210}Po method. It has also found uranium to be primarily of "in-plant" rather than of environmental concern.

METHODS

Tentative methods for ^{210}Pb and ^{222}Rn were published in Health Laboratory Science⁽¹⁾ in 1969. In principle they are:

Lead-210

Lead-210 has a half-life of 21 years. Its principal radioactive emission is a beta particle, with a maximum energy of 0.061 million electron volts (MeV). It is a trace component of the normal atmosphere and is produced through decay of ^{222}Rn , which diffuses into the air from radium sources in the soil. It is removed by washout, by precipitation, and by dry-deposition processes. The normal ^{210}Pb concentrations over land rarely exceed 25 pCi/1,000 m³. Consequently large volumes of air must be sampled to obtain a statistically significant count rate. Analysis is performed by dissolution of a filter through which a known volume of air has passed. Inactive bismuth is added as a carrier for the 5.0 day half-life ^{210}Bi daughter of ^{210}Pb , which decays by beta emission with a maximum energy of 1.16 MeV and is thus much easier to detect than the weak ^{210}Pb emissions. Separation and radiochemical purification of the ^{210}Bi is accomplished by repeated precipitation as bismuth sulphide.

It is then plancheted and determination of its count rate relative to a ^{210}Bi standard is made, preferably using a low background beta counter. The method is sensitive to concentrations as low as $1 \text{ pCi}/1,000 \text{ m}^3$.

Radon-222

Radon is the daughter product of Radium-226 in the uranium decay chain, and is ubiquitous in the terrestrial environment. Gaseous radon atoms, released to the atmosphere from soil, decay to polonium, lead and bismuth daughter atoms. These radionuclides in turn become attached to solid matter in the environment, forming a radioactive aerosol. The decay series for Radon is as follows:

Table 1 presents a summary of representative concentrations of airborne radon.

Due to the range of naturally occurring concentrations of radon in different environments, several choices were offered for its sampling and analysis. These included:

- 1) Filter paper collection and alpha activity measurement of the radon daughters (assumed to be in equilibrium). The method is simple, rapid and inexpensive. It is sensitive to concentrations as low as $30 \text{ pCi}/\text{m}^3$.
- 2) Filter paper collection and beta activity measurement of the radon daughters. This method is similar to the first, except that radon beta-emitting daughters are counted. It

is therefore useful where dust-loadings may interfere with alpha counting, and is sensitive to concentrations down to 15 pCi/m^3 .

- 3) Absorption of the radon itself onto activated charcoal, with a subsequent de-emanation (at an elevated temperature) and transfer to a cell for alpha counting. This method requires more complicated equipment, including a special radon counting cell, but does not depend on assuming that equilibrium exists between the ambient radon and its daughters. It is sensitive to amounts of radon as small as 3 pCi .
- 4) Absorption from the atmosphere onto activated charcoal and the direct gamma measurement of the ^{214}Bi radon daughters. Since this method requires no transfer of radon, it is in principle the simplest. However, it requires a shielded NaI (or GeLi) detector and a multichannel pulse height analyzer which are more complicated and expensive than the counting apparatus required for the preceding methods. It is sensitive to concentrations as low as 120 pCi/m^3 .

Tentative methods for gross alpha, gross beta and ^{131}I were published in Health Laboratory Science⁽²⁾ early in 1970. Their principles are:

Gross Alpha

Since a given alpha emitter cannot be present in air in a greater concentration than the overall alpha concentration of a mixture of otherwise unidentified radionuclides, a gross alpha analysis may eliminate the need for a more time consuming and expensive analysis for specific alpha emitters. In this method, air particulates are collected on a high-surface retention

filter paper, then counted with an alpha detector. Loading should be kept to less than 1 mg/cm^2 to minimize self-absorption. If long-lived alpha emitters are of primary concern, it may be necessary to differentiate between these and the naturally occurring short-lived radon and thoron daughters by energy discrimination or by waiting for the latter to decay sufficiently. Concentrations as low as 60 pCi/l,000 m^3 may be ascertained by this method.

Gross Beta

In reasoning and principle, this method is analogous to the gross alpha procedure, except that the requirement for surface collection is not as stringent. The naturally occurring radon and thoron daughters are also a consideration. With proper control of counter background, concentrations as low as 3 pCi/m^3 may be ascertained in a counting interval as short as ten minutes.

Iodine-131

Iodine-131 decays principally by the emission of a 0.61 MeV maximum energy beta and an 0.36 MeV gamma transaction. Iodine is volatile at only slightly elevated temperatures, has multiple pathways through the environment, and is selectively taken up by the thyroid. Although several radio-iodines (^{131}I - ^{135}I) have large fission yields (3% - 6%), ^{131}I has the longest half-life (8.05 days) and therefore the greatest persistence in the environment. It is found in the routine effluents of nuclear facilities, as well as in the fallout debris from nuclear weapons tests.

Since radioactive iodine may be introduced into the atmosphere as an elemental or chemically combined vapor, as a vapor adsorbed on particulate matter, or as a particulate iodine compound, it presents a unique sampling problem. The method involves sampling radioiodine in its solid and gaseous states with an "absolute" particulate filter in series with an activated charcoal cartridge. The amount of the ^{131}I (and any other radioiodines which

may be present) on each element is then quantitatively determined by gamma spectroscopy.

Radioiodine adsorbed on solid particles and possibly some vaporous iodine will be deposited on the "absolute" filter, while the remaining vaporous iodine will be adsorbed on or absorbed in the activated charcoal. For that portion which is collected by the charcoal, at a sampling rate of $0.01 \text{ m}^3/\text{min}$, the practicable minimum detectable concentration in a seven day sample is 0.1 pCi/m^3 . Decay measurements of the ^{131}I photopeak can be used to evaluate it in the presence of other long-lived gamma emitters, which are likely to be collected on the particulate filter. Spectral stripping may be employed if quicker results are desired.

In addition to the customary sampling apparatus, this method requires a NaI (or GeLi) detector and multichannel pulse height analyzer.

Tentative methods for ^{89}Sr , ^{90}Sr and Pu were published in Health Laboratory Science⁽³⁾ in mid-1970. Several isotopes of Sr are produced in large fission yields (~ 5%) during the fission process, of which 50.5 day ^{89}Sr and 27.8 year ^{90}Sr have half-lives long enough to be of environmental significance. The principles of the methods for their sampling and analysis are:

Strontium-89

Strontium-89 decays by beta emission with a maximum energy of 1.46 MeV. Since it is usually determined at the same time as ^{90}Sr , using the separated strontium fraction, the radiochemical procedures are those used for ^{90}Sr . The ^{89}Sr content of the sample is calculated by correcting the total counting rate of SrCO_3 fraction for the ^{90}Sr present, and for the ^{90}Y which grows in between separation and counting. The procedure is simple chemically, but requires rather complex calculations, particularly in obtaining the estimate of counting error.

Strontium-90

Strontium-90 decays by beta emission with a maximum energy of 0.55 MeV. Its 64.0 hour half-life daughter ^{90}Y also decays by beta emission with a maximum energy of 2.27 MeV. ^{90}Sr is one of the longer lived radionuclides produced by nuclear fission. It follows calcium in the body, and thus accrues principally in bone where it is retained indefinitely. Therefore, it constitutes one of the more hazardous fission product radionuclides which may be present in ground-level air.

The analysis is performed by dissolution of a filter through which a known volume of air has been passed. Strontium is separated from calcium, other fission products, and natural radioactive products. Nitric acid separations are used to remove the calcium and most other interfering ions. Radium, lead and barium are removed with barium chromate. Traces of other fission products are scavenged with iron hydroxide. After ^{90}Sr and ^{90}Y equilibrium is established, the ^{90}Y is precipitated as the hydroxide and converted to the oxalate for counting. Strontium chemical yield is determined gravimetrically as strontium carbonate. 0.5 pCi of ^{90}Sr can be determined by this method, employing a low background (< 1 cpm) counter.

Plutonium

This procedure may be applied to the analysis of ^{238}Pu and $^{239}\text{Pu}^*$ in air filters. These are artificial radionuclides, produced by the irradiation of ^{238}U in nuclear reactors. Both are alpha emitters, 86.4 year ^{238}Pu with energies of 5.50 MeV (72%) and 5.46 MeV (28%), and 24,390 year ^{239}Pu with energies of 5.16 MeV (88%) and 5.11 MeV (11%). ^{238}Pu is employed as a heat source in small self-powered devices, while fissionable ^{239}Pu is employed as

* ^{239}Pu is usually accompanied by a small amount of 6,580 year ^{240}Pu . Its decay energies, 5.17 MeV (76%) and 5.12 MeV (24%), are so close to those of ^{239}Pu that the two cannot be distinguished by alpha spectroscopy.

a nuclear reactor fuel and in nuclear weapons, which uses have resulted in environmentally detectable levels of both radionuclides.

In the procedure, the plutonium in the sample is equilibrated with ^{236}Pu tracer and isolated by co-precipitation with cerium and yttrium fluorides. The plutonium is further purified by a double anion-exchange column technique, first by adsorbing from a hydrochloric acid medium, the second time from a nitric acid medium. Finally the plutonium is electrodeposited onto a platinum disc. The plutonium isotopes are resolved by a solid state alpha spectrometer. The ^{236}Pu is used to determine the chemical yield.* Counting is performed using a solid state silicon surface-barrier alpha detector linked to a multichannel analyzer in order to make an energy resolution between ^{236}Pu , ^{238}Pu and ^{239}Pu . With a 1,000 minute counting time, the minimum detectable concentration of plutonium is about $1 \times 10^{-4} \text{ pCi/m}^3$.

A tentative method of analysis for tritium content of the atmosphere (as tritium vapor) was published in Health Laboratory Science⁽⁴⁾ early in 1971. With a half-life of 12.26 years, tritium has the lowest known beta emission energy, 0.0186 MeV maximum. It is therefore difficult to detect and to quantify. Tritium is naturally produced by cosmic radiation, in a concentration as vapor of about $3 \times 10^{-8} \text{ } \mu\text{Ci/ml}$. The corresponding concentration in air is a function of relative humidity and temperature; at 15°C and 50% R.H. it would be 0.27 pCi/m^3 . Additions from weapons tests during the past two decades have resulted in current environmental concentrations about ten times those occurring naturally. It may also be found in the effluents from nuclear reactors, fuel reprocessing plants and other nuclear facilities.

* 2.85 year ^{236}Pu decays by alpha emission, with energies of 5.77 MeV (69%) and 4.72 MeV (31%). It is available on special order from Isotope Sales, Oak Ridge National Laboratory (615-483-8611X3-6661).

In the procedure, air is pumped through a column containing a desiccant such as silica gel. The collected moisture is then removed (by a heating and condensation train) from the column. Alternatively, a cold finger or dehumidifier may be used, in which case the temperature and relative humidity must be known to establish the absolute moisture capacity of the ambient air. The collected moisture is mixed with a scintillation solution and counted in a liquid scintillation beta counter. The tritium vapor concentrations obtained from air approaching environmental concentration guide levels ($2 \times 10^{-7} \mu\text{Ci}/\text{cm}^3$) will be sufficient to produce acceptable precision in short counting intervals. However, the tritium vapor concentrations from current ambient atmospheric levels are below the minimum detection capability of conventional beta scintillation counters and require electrolytic enrichment prior to counting.

CURRENT AGENDA

The ISC Radioactive Substances Subcommittee is currently assessing the available methods for the collection and analysis of ^{85}Kr . Although a variety of radioactive noble gases (Xe and Kr) are produced in the fission process, 10.76 year ^{85}Kr is the only one with a half-life of more than a few days, and therefore the only one of general environmental concern. Most of the sampling methods under consideration involve the adsorption of Kr onto activated charcoal at liquid nitrogen temperatures, its subsequent separation by cryogenic techniques and introduction into scintillation solution for liquid scintillation counting. The much higher than generally prevailing concentrations which may exist briefly downwind in the immediate vicinity of nuclear reactors or nuclear fuel reprocessing facilities produce radiation levels which may be evaluated by sensitive CaF thermoluminescent dosimeters.

Additionally, the Committee is considering a general gamma analysis method, which would be applicable to any gamma emitting nuclides which may

be present in ambient air samples. It is also currently considering the need for a method for the specific analysis of ^{14}C and ^{129}I .

However, the principal unfinished business of the Committee is the collaborative testing of the tentative methods already devised, so that they may be established as standard methods. In addition to securing a sufficient number of collaborators, it appears that a competent laboratory would have to be funded to carry out the preparation and distribution of suitable samples and tabulation of the data. The Analytical Quality Control Program of the International Atomic Energy Agency has recently scheduled the distribution of simulated air filters containing many of the nuclides of interest to the Subcommittee on Radioactive Substances, which may in part facilitate some aspects of the collaborative analysis for these nuclides. Funding to enable a full scale collaborative effort has been proposed to interested agencies, but has not been forthcoming to date.

TABLE 1
REPRESENTATIVE CONCENTRATIONS AND ESTIMATED DOSES
FROM AIRBORNE RADON

Concentrations

1. Ground Level Air over Continents⁽⁶⁾ - 30 to 300 pCi/m³
⁽⁷⁾ - 100 to 3900 pCi/m³ surface
2. Over Oceans (between one and two orders of magnitude lower than land concentrations).
3. Uranium Mines in Colorado Plateau - 3×10^6 pCi/m³ (average) to 58×10^6 pCi/m³.

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