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VEGETATION AND SOIL SAMPLING FOR DETECTION OF ENRICHMENT FACILITIES

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ABSTRACT

The issues involved in acquiring environmental samples from around nuclear facilities are discussed, with the primary application being safeguards. Sampling plans, sample acquisition, analytical techniques, and data interpretation are described.

I. INTRODUCTION

The concept of being able to detect clandestine nuclear operations rests on the fact that they invariably lose material characteristic of the process to the environment. This material can be collected and characterized using highly sensitive analytical techniques. The extent to which these signatures penetrate the environment depends on the type of process and the care taken at the facility to control losses. An enrichment facility that uses UF_6 , a gas, will tend to lose more than a reactor because gases are harder to contain than solids. Any nuclear facility, like industrial processes everywhere, loses some characteristic material to the environment.¹ The challenge to the analyst is to find and analyze it.

Recent world events have led to a call for strengthening international safeguards. There are two situations for which the International Atomic Energy Agency's safeguards program must be prepared to address. One is the detection of nuclear activities occurring at undeclared sites. The other is to detect undeclared activities at declared sites. In the first of these, the operation has been previously unsuspected and its location must be pinpointed; in the second, some, probably small, undeclared activity is being carried on at a much larger site. In the latter case, the larger activity tends to mask the smaller, making detection difficult. An example might be a centrifuge enrichment plant with only a small fraction of its capacity being devoted to producing weapons grade uranium. The analytical challenge is to identify the smaller operation.

This little essay concentrates on detection of enrichment activities through analysis of environmental uranium, but the principles are equally applicable to any nuclear facility and any element that is to be detected in solid samples. Material is lost from nuclear facilities by many different routes. There is probably no single sampling medium that is best in all cases, and intelligent evaluation of various pathways to the environment is an important element in devising a sampling plan. General guidelines can be prescribed, however, that will be helpful in determining location, type, and number of samples. For example, any waste stream that either originates inside the plant or passes through it is a prime candidate for sampling. If there is a laundry on site, the stream to which its waste is discharged will be a good source for samples; both the stream itself and the sediment that settles from it are attractive media for sampling.

Solid samples can be generated from virtually any sampling medium, including water and air. Water can be evaporated and the residue analyzed; air can be drawn through a filter

and the particulate matter analyzed. The emphasis of this monograph, however, is the acquisition of environmental samples directly in the solid state.

II. AIR-BORNE LOSSES

One of the primary routes for loss from nuclear facilities, especially enrichment plants, is through the air. UF_6 is a gas, and all enrichment facilities employing this compound have a means to draw off product-level material; there may be other access points as well. UF_6 hydrolyzes on contact with water vapor in the air, forming UO_2F_2 , a solid. This material usually coalesces on air-borne dust particles and is carried by the wind some distance from the facility before it is deposited upon whatever surface it chances to fall. It is these particles and these surfaces that are the subject of the remainder of this essay.

III. DEVELOPING A SAMPLING PLAN

The specific sampling plan to be used in a given situation is dependent on the conditions obtaining. If the facility in question is a declared one and the goal to determine whether or not undeclared activities are taking, or have taken, place, swipe samples within the facility are the best choice. The larger, declared, operation will mask the smaller, undeclared, one at any distance from the plant.

Swipes should be taken as close to critical points as possible. For an enrichment facility, wipes should be taken at the product withdrawal point, at any purge point, and at the tails withdrawal point. Feed material should be sampled if desired, although its composition is in general known from other sources.

If the object of the exercise is to detect an undeclared facility, it is highly desirable to have some idea of where it might be; trying to find a site whose location is completely unknown is a difficult job. On the assumption that a specific location is to be tested, and access to the facility is not available, samples should be taken at several distances from it. The exact distances are not critical; something approximating 1, 2, 3, 5, and 8 km (in the same direction) is reasonable. If the suspect site has in fact been engaged in undeclared enrichment operations, the ^{235}U abundance will be greatest close to the facility and decline with distance, at some point reaching natural.

The reason the direction from the suspect facility is prescribed is because concentrations of effluent in the environment vary with wind direction. It is desirable, but

not mandatory, to sample in the direction that dominates the wind pattern about the facility. Effluent concentration will be greatest in this direction. This topic is discussed further in the Interpretation Section. Vegetation, if possible pine needles, is recommended as the sample medium; see the section on vegetation samples below.

It is strongly recommended that a meeting with all parties be conducted prior to sample taking. Representatives of the site should be present; their local knowledge is often invaluable in setting up a sampling plan.

The use of bar codes to identify samples is also strongly recommended. Labels with the bar codes on them should be affixed to the polyethylene bags that hold the samples themselves, to the secondary container, and in the log book or sample sheet where notes of the sampling campaign are kept.

IV. SAMPLING

There are two principal ways of collecting solid environmental samples: by removing a specimen of the selected medium (e.g., vegetation) and by collecting only air-borne dust that has accumulated. The two methods complement each other.

IV.A. Wipe Samples

Analysis of dust can pinpoint specific features of the plant itself; such samples should thus be collected within the facility or in its near vicinity from areas where mixing of various effluent streams is low. Samples can be collected by taking wipes (or smears) of a suitable surface; the area sampled should be 10-30 cm on a side. Another method that works well for collecting samples for particle analysis is to pick up dust using acetone-soluble tape. A length of tape 30-35 cm long should be used. Not enough material is collected by this technique for bulk analysis.

The areas to be sampled by either of these techniques should be chosen with care. Basically, the more dusty the surface is, the better. For example, tops of door jambs, blackboard frames, etc., are rarely cleaned and can be sampled using sticky tape; if sufficient surface area is available, a wipe is also viable. Computer monitor screens tend to pick up static charge and are often dusty. Car glass, especially back windows, is another good source. If a sample can be taken on a roof, there are almost always nooks and crannies that are protected from the rain and almost never cleaned. Signs and fences near roads are often very dusty. Areas underneath equipment tend to be seldom cleaned. It is clearly not possible to

produce an exhaustive list; this is an area where the person collecting the samples must exercise good judgment.

Wipe samples are very sensitive to effluents in the immediate vicinity. For example, a wipe sample taken near the top end purge of a gaseous diffusion plant cascade will invariably show enriched uranium; a sample taken near the tails purge will show depleted uranium. The uranium in samples taken some distance from both will be a mixture of the two (and any other sources as well), but in general enriched uranium will dominate the assay. This is in part because an enrichment of, say, 3% ^{235}U differs from natural abundance substantially more than the depleted tails, which is usually about 0.3%.

IV.B. Other Samples

The second common way of collecting environmental samples is to remove material in which plant effluent has been assimilated. Water is one example of such a medium. Others are soil, including sediment, and vegetation.

IV.B.1 Soil

Soil itself, as represented by the earth of the fields, so to speak, is in general not a good choice for samples. Most soil has a natural uranium background of a few ppm, which is high enough to obscure the usually small effect of plant effluents. Soil used for agricultural purposes should be avoided. Fertilizers are rich in phosphates and other salts that almost always have high uranium content. On the other hand, sediments deposited downstream from the facility from streams passing through it can be good samples. Sediment produced by parking-lot run-off is often a good choice.

If soil is to be sampled, an attempt should be made to collect only the top few millimeters. This region will contain the air-borne particulate matter deposited there in the recent past; such samples will, of course, include uranium from sources other than the target facility. Various means have been devised to collect these samples. A small, hand-held, battery-powered vacuum cleaner works well, but is cumbersome to use. A small, soft paint brush can be used to sweep an area. A small laboratory scoop can be used. All of these have been tried; all are satisfactory. Dry soil is easier to sample than wet. One of the laws governing sample collection, however, is that, if it isn't actually raining, it has only just stopped. The laboratory scoop is the only useful method for sampling wet soil.

IV.B.2 Vegetation

Vegetation is usually the sample medium of choice when the location is far enough removed from effluent points to render wipe samples of dubious value. This will, of course, be the case if the goal is to detect an undeclared nuclear operation. Most vegetation has uranium at ppb levels; for example, the NIST 1575 pine needle standard has a certified uranium concentration of 20 ± 4 ppb (dry weight).

There are two routes by which uranium is incorporated into vegetation. One is through the plant's uptake of water from the surrounding soil; this uranium reflects the isotopic composition it has in that soil. The other route is through the air, and this is the uranium representative of the facility's operation; the sample medium should be selected with this in mind. Species of high surface area with sticky surfaces should be chosen if possible.

Historically, the most important vegetation sample medium has been evergreen, specifically pine, needles. There are several reasons for this. Pine trees are common to much of the northern hemisphere. The needle structure packs a lot of surface area into a relatively small volume. The surfaces are sticky--just feel them! The resin inherent in pine trees tends to bind particles to the needles, making them resistant to being washed away by rain. Many species of pine retain their needles for two years, making the older needles integrators over that period. The older needles are thus the more desirable sample.

Mosses and lichens are good vegetation sampling media. They, too, have large surface areas. Samples of these species are usually more difficult to locate and collect than pine needles. Areas deep in moss are best in order to reduce picking up soil with the samples. Deciduous leaves are acceptable, but, unless fallen leaves are sampled, their length of exposure to air-borne particulate matter is dependent on the time of year; and the sampling team cannot always dictate the season in which samples will be taken. Grasses are acceptable samples. Both fallen leaves and grasses tend to pick up uranium from the soil, and are thus less desirable than evergreen foliage. Nearly any kind of vegetation will give satisfactory results, but evergreen vegetation should be given priority over other types. Tree bark can be used if desired, but it is less satisfactory than foliage. Pine bark is preferred for the same reason cited earlier--pine resin tends to lock particles in place.

The amount of uranium in samples is by itself of little value in this application, but when combined with the isotopic composition, can be extremely useful. The weather--how recently it has rained, how strong the wind is--will affect the amount of originally air-borne

matter on the vegetation at the time of sampling, making conclusions from total uranium alone suspect. On the other hand, using total uranium in conjunction with the isotopic composition yields the amount of ^{235}U in excess of natural (see interpretation section), which is of great diagnostic value. An additional benefit from using the ^{233}U spike for quantification is that it provides the analyst with a strong, stable signal to use in focusing the instrument without fear of losing the sample. Too high a temperature for a filament holding a very small amount of uranium can sometimes deplete it enough to make a good analysis impossible. A ^{233}U spike of high purity should be used so the isotopic composition of uranium in the sample can be reliably calculated.

No matter what kind of samples are to be collected, care must be taken to preclude contamination. In the opinion of the author, cross-contamination between locations around a given facility is not a major issue for the IAEA; the goal is to determine whether or not undeclared operations are being carried out at the facility, and a little contamination from sample A getting into sample B will have no effect on the conclusions. On the other hand, every possible precaution should be taken to preclude cross-contamination between facilities. For obvious reasons, this is particularly important if the facilities are in different countries. For bulk samples, the measures necessary are neither difficult nor intrusive. Lint-free gloves should be worn, used for one sampling location, and discarded. Tools should be cleaned between each use.

A location is defined as the place where a sample is taken, as opposed to the facility of interest. There will usually be several sample locations for each facility. If more than one sample is to be taken at a given location (e.g., two trees are to be sampled), it is not necessary to change gloves. When one moves to a new location (e.g., from the 3 km to the 5 km point), gloves should be changed. Note that more extreme precautions are required when particle samples are to be collected than for bulk.

IV.C. Priority List for Samples

Pine needles are the first choice for vegetation samples for the reasons enumerated above. Here is a list of various types of vegetation in approximate order of priority, with soil bringing up the rear.

1. Pine needles
2. Cedar foliage
3. Other evergreen foliage

4. Mosses and lichens
5. Deciduous leaves
6. Grasses and shrubs (e.g., sagebrush, tumbleweed)
7. Bark and soil

Bark should only be considered if there is no viable alternative, and, of course, when there is bark, there is usually foliage. The choice among the others will be dictated by conditions at the site and at specific locations--Mother Nature doesn't always provide a pine tree where we want one!

IV.D. Storage of Samples

It is important to store samples properly to maintain long-term integrity. Water samples should be acidified (1% HNO₃ by volume). Vegetation samples should be kept in a freezer to prevent bacterial decomposition. Decomposition does not, of course, affect uranium composition, but analysts are noticeably happier if they don't have to handle rotting vegetation.

V. ANALYSIS

There are three ways to analyze solid samples to obtain uranium information. The method used is dependent on various parameters, including the number of samples to be analyzed, the type of information sought, and the degree of certainty with which conclusions can be made.

V.A. Delayed Neutron Counting

For situations where large numbers of samples are to be processed, preliminary screening by delayed neutron counting should be considered.² No isotopic information is obtained by this method, which is sensitive only to ²³⁵U; neutrons generated by Br and I isotopes, fission products of ²³⁵U, are counted. What is provided is total amount of ²³⁵U in the sample. This can be converted to total uranium by assuming an isotopic composition. Normal abundance (0.720% ²³⁵U) is the most common assumption made. Enriched uranium in the samples will then give anomalously high concentration values, signalling that further investigation is called for. Precision and accuracy are about 10%. What makes the technique attractive for screening purposes is that throughput is high and cost is low, especially in comparison to the other techniques. Many (n > 50) samples a day can be analyzed at a cost

of \$100 - \$200 per sample, figures well above and well below, respectively, the other techniques.

V.B. Bulk Analysis

The second method of addressing solid samples is bulk analysis of uranium. This requires chemically extracting uranium from the sample and measuring its isotopic composition mass spectrometrically. Because quantities of uranium from the samples are low (typically tens of nanograms), meticulous attention to cleanliness must be observed. A class 100 clean room is recommended. Highly sensitive, pulse-counting mass spectrometers must be employed; conventional Faraday cup detection systems do not have the necessary sensitivity. For some studies, complete dissolution of the sample is required, but for most purposes leaching of surface uranium is just as informative, with the advantage that the natural uranium background is usually lower. Substantial time is saved in sample preparation if leaching is used.

Thermal ionization mass spectrometry requires a sample of reasonable chemical purity. Ultra-pure samples are not generally required, but too much of any contaminant causes problems. Because ions are made on a hot filament, there is a fixed amount of energy available for the ionization process. Readily ionized elements (Na, K, Ca, Ba, etc.) tend to bleed energy away from the process of interest: $U \rightarrow U^+ + e^-$. These elements are often among the most common in abundance in the earth's crust. Some elements cause interferences difficult to predict in advance and impossible to correct for. Potassium, for example, generates K_6^+ , which falls at mass positions 234 and 236, right on top of the minor uranium isotopes. Too much acid on the filament leads to formation of ReO_3^+ , which is observed at mass positions 233 and 235--again undesirable for uranium analysis. Many other elements cause problems as well.

With this in mind, it is essential to separate uranium from the sample, either via solvent extraction or ion-exchange chromatography. The chemical procedures to achieve good separation with good recovery have been in place for many years.³

An alternative to thermal ionization is to use inductively coupled plasma mass spectrometry (ICP-MS). Dissolution of uranium is still required; at the time of writing, it was unclear whether or not a clean-up step would be required. In either case, a solution of suitable uranium concentration is aspirated into the ICP. Results are less precise than those for thermal ionization, but instrumental sample throughput is greater. But, like the other

mass spectrometric techniques discussed here, the limiting factor in sample throughput is preparation time and not the time required for the measurements.

V.C. Particle Analysis

The third method of analysis of uranium in environmental samples is through analysis of individual particles. Such analyses require highly specialized instrumentation and are the most costly of the three analytical approaches. On the other hand, particle analysis is the most sensitive and the results obtained are usually definitive.⁴

Because the quantities of uranium are so small, a class 100 clean room is mandatory. Each sample collected in the field can produce dozens of particles containing fissionable material, sometimes so many that it is not practicable to analyze them all. In such cases, sufficient particles must be analyzed to establish statistical confidence in one's conclusions. This is one reason particle analysis is so expensive: In addition to the costs inherent in operating expensive specialized equipment (reactor, clean room, mass spectrometer), it is necessary to analyze multiple particles per sample.

The procedure involves irradiating the particles in a high neutron flux, identifying those that have fissionable components, and analyzing the individual particles mass spectrometrically. Particles can be obtained from any of the media discussed above. In the laboratory, the particles are isolated and dispersed on a medium that will register fission tracks. The choice of medium is usually dictated by the reactor used for irradiation. For example, lexan was the medium of choice for the old Oak Ridge Research Reactor, but the flux in the High Flux Isotopes Reactor (HFIR), the only reactor currently operational at ORNL, is so high that it fogs the lexan, making it impossible to identify individual fission tracks. Supersil works well for HFIR.

Once isolated, the particles are dispersed on the registration medium in a 10% solution of collodion in methanol. The collodion remains after the methanol evaporates and serves to bind the particles to the medium. The particles, together with the supporting medium, are subjected to irradiation. Fission occurs in those particles containing elements of interest. The fission products ejected are both heavy and energetic, and they damage the medium through which they pass, generating what are called fission tracks.

Once enough time has elapsed (a few days) for the short-lived species created during irradiation to have decayed, the particles (still affixed to the medium) are returned to the laboratory. Registration marks are made in the collodion and the medium. The collodion

is peeled off, taking the particles with it. The medium is etched with acid to render the fission tracks visible. Inspection through a microscope allows identification of particles of interest. Each set of fission tracks radiates from a central point that corresponds to a particle. When the registration marks on the collodion and medium are adjusted to be slightly offset from one another, identification of the particle containing fissionable material is easy. Particles to be analyzed are then cut out of the collodion and loaded directly onto mass spectrometer filaments. Since uranium is often present in subnanogram quantities, mass spectrometers of high sensitivity are required.

VI. INTERPRETATION

It is perhaps of interest to investigate the effect of highly enriched uranium on the natural in vegetation. Table 1 contains the results of calculating the impact of one part of 93% ^{235}U on various amounts of natural.

Impact of Enriched Uranium on Isotope Composition				
Atom %	234	235	238	235/238
Natural	0.0055	0.7200	99.275	0.00725
HEU	1.00	93.00	6.00	15.5
HEU/Nat				
1/20	0.053	5.11	94.85	0.0539
1/100	0.015	1.63	98.35	0.0166
1/1000	0.0065	0.8112	99.18	0.00819
1/10000	0.0056	0.729	99.265	0.00734

Thus, for example, a pine needle sample with 200 ng of natural uranium having 2 ng of HEU would give a 235/238 ratio of 0.017. Ratios this high are observed only quite close to enrichment facilities (a few kilometers). Ratios representative of one part HEU per 1000 parts of natural can be found many kilometers from a large enrichment facility.

Because of complexities in sample dispersion and vagaries of the weather, concentration measurements in bulk samples are difficult to correlate with losses from the facility. They are necessary, however, to calculate excess ^{235}U in the sample. A plot of excess ^{235}U vs. distance is a powerful help in locating an undeclared facility.

Excess ^{235}U is defined as the quantity of ^{235}U present in the sample in excess of that contributed by natural. It is calculated from the following equation:

$$\text{XS}_{235} = (A_{\text{sam}} - A_{\text{nat}})/100 * C_u$$

where XS_{235} is excess ^{235}U

A_{sam} is atom percent ^{235}U in the sample

A_{nat} is atom percent ^{235}U in natural (= 0.720)

C_u is the concentration of U in the sample

It is usually expressed in parts per trillion (ppt). As an example, from Table 1, if the measured abundance of ^{235}U is 0.812 and the uranium concentration is 75 ppb, the calculation is: $\text{XS}_{235} = (0.812 - 0.720)/100 * 75 = 69 \text{ ppt } ^{235}\text{U}$

The use of excess ^{235}U is illustrated in Figures 1 and 2. Together these represent the eight octants of the wind rose around an enrichment facility; two figures were used only because eight data sets on a single plot resulted in cluttered, difficult-to-read figures. These figures also illustrate the fact that, for many facilities, one need not be fanatical about following the direction of the prevailing wind. While the NNE octant is most favorable, the operation is readily observed in all other directions except perhaps the WSW. Conditions around the facility prevented taking samples closer than about 3 km for the WSW octant, eliminating its most sensitive points. This is not unusual: parking lots, corn fields, large rivers--all these and more can make it impossible to sample a given location.

The isotopic composition of uranium in bulk samples is by itself usually not a definitive indicator of enrichment activity. Plant effluent is usually mixed with enough natural uranium that the abundance of ^{235}U is below alarm levels (e.g., 3% for facilities producing fuel for commercial reactors). Only samples taken very close to an enrichment facility producing weapons-grade material will show ^{235}U abundances higher than 3%.

It is important to note that close agreement between duplicate samples taken at the same location should not be expected. Needles taken from different branches of the same pine tree usually have different $^{235}\text{U}/^{238}\text{U}$ ratios. Some other means of evaluating the data is thus required.

Figure 1

Figure 2

One indicator is ^{236}U . Its presence, even at low ppm levels, is unequivocal evidence that the uranium has been subjected to a neutron flux; ^{236}U does not occur naturally. ^{236}U is often a constituent of feed material of an enrichment plant; this will be the case when spent uranium fuel is recycled through the enrichment process. Note that the presence of ^{236}U says nothing about enrichment activities.

A powerful technique for aiding interpretations calculate the ratio of excess ^{235}U to excess ^{234}U . "Excess" in this case means the abundance of the two isotopes over what is attributable to natural uranium. For example, if the measured ^{235}U abundance is 1.76% and ^{234}U 0.016%, the calculation would look like this:

$$(1.76 - 0.72)/(0.016 - 0.0055) = 99.$$

This ratio in natural uranium is about 131. The value of the excess ^{235}U /excess ^{234}U should, within experimental error, represent some point in the process declared for that facility. For a gaseous diffusion plant, it should reflect some point on the enrichment cascade, and that point will usually be the one where the most losses occur--often product level uranium.

A similar approach is applied to analyzing data acquired from particles. In this case, however, the contribution from natural uranium is often quite small, and that from the effluent dominates the measured isotopic composition. It takes no great interpretive insight to conclude that, when a number of particles containing uranium with 93% ^{235}U are found, the facility in question has been enriching natural material beyond the declared 3%!

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