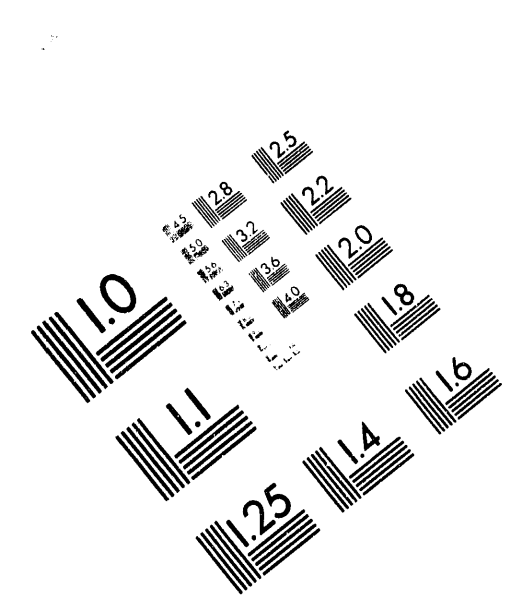
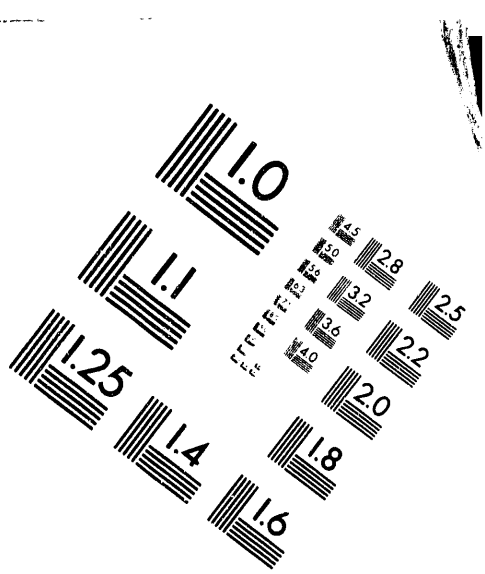
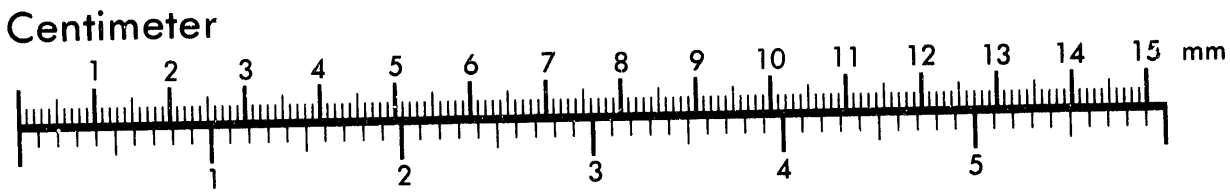
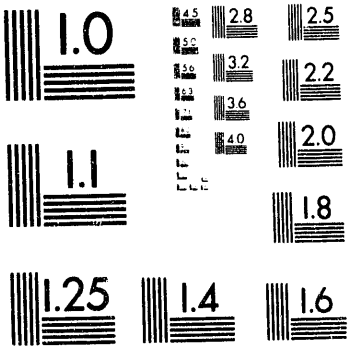
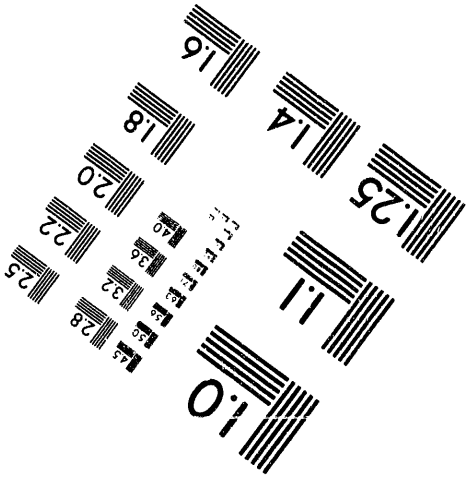


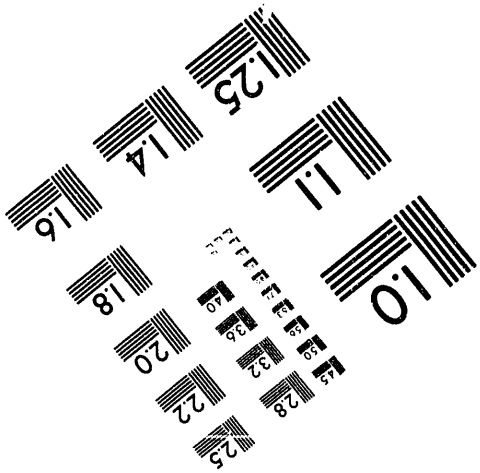
Association for Information and Image Management
1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202











MANUFACTURED TO AIIM STANDARDS
BY APPLIED IMAGE, INC.

1 of 1

March 30, 1993 K/NSP-129

DETECTION OF URANIUM ENRICHMENT ACTIVITIES USING ENVIRONMENTAL MONITORING TECHNIQUES

W. L. Belew, J. A. Carter, D. H. Smith, and R. L. Walker
Martin Marietta Energy Systems, Inc.*
Oak Ridge, Tennessee, U.S.A.

Presented at the
International Atomic Energy Agency Consultant Group Meeting
on Environmental Monitoring and Special
Analysis Methods for Safeguards
Vienna, Austria
March 30–April 2, 1993

*Managing contractor for the U.S. Department of Energy
under contract No. DE-AC05-84OR21400

DETECTION OF URANIUM ENRICHMENT ACTIVITIES USING ENVIRONMENTAL MONITORING TECHNIQUES*

W. L. Belew, J. A. Carter, D. H. Smith, and R. L. Walker
Martin Marietta Energy Systems, Inc.†
Oak Ridge, Tennessee, U.S.A.

ABSTRACT

Uranium enrichment processes have the capability of producing weapons-grade material in the form of highly enriched uranium. Thus, detection of undeclared uranium enrichment activities is an international safeguards concern. The uranium separation technologies currently in use employ UF_6 gas as a separation medium, and trace quantities of enriched uranium are inevitably released to the environment from these facilities. The isotopic content of uranium in the vegetation, soil, and water near the plant site will be altered by these releases and can provide a signature for detecting the presence of enriched uranium activities. This paper discusses environmental sampling and analytical procedures that have been used for the detection of uranium enrichment facilities and possible safeguards applications of these techniques.

INTRODUCTION

Uranium enrichment processes used for production of low-enriched uranium (LEU) for commercial uses can also be capable of producing direct-use nuclear weapons grade material in the form of highly enriched uranium (HEU). Thus, the verification of the absence of HEU at declared enrichment plant sites is an important international safeguards goal. The International Atomic Energy Agency (IAEA) currently implements safeguards inspection procedures at uranium enrichment facilities that use gas centrifuge and advanced vortex tube separation technologies. These safeguards inspections are based on the traditional approach of material balance verification, containment, and surveillance monitoring, supplemented by techniques for detection of HEU production. Recent activities have resulted in increased interest in implementing international safeguards techniques for detection of undeclared uranium enrichment facilities in countries with full-scope safeguards. Activities involving enriched uranium can leave unique signatures in the environment that may be detectable in samples of soil, vegetation, or water by use of sensitive analytical techniques. This paper discusses signatures from uranium enrichment facilities inclusive of U.S. experience and possible safeguards applications of these analytical techniques.

---

†Managing contractor for the U.S. Department of Energy.

URANIUM ENRICHMENT TECHNOLOGY AND SAFEGUARDS APPROACHES

The concentration of the ^{235}U isotope in natural uranium can be increased by several different isotope separation technologies. The technologies which have been used in large-scale facilities and in pilot plant operations or research and development efforts are listed in Table 1. Other technologies, such as plasma and thermal diffusion, are of theoretical interest.

Table 1. Uranium enrichment processes in commercial use or the subject of research and development activities

- Electromagnetic isotope separation (EMIS)
- Gaseous diffusion
- Gas centrifuge
- Jet nozzle/vortex tube
- Molecular laser isotope separation (MLIS)
- Atomic vapor laser isotope separation (AVLIS)
- Chemical exchange (CHEMEX)
- Ion exchange

To date three of these technologies—electromagnetic isotope separation, gaseous diffusion, and gas centrifuge—have been used to produce HEU in large quantities for use in nuclear weapons. The EMIS process was used to produce the first HEU in the United States. Until the discoveries in Iraq, the EMIS process was considered only of historical interest from a proliferation viewpoint. All large-scale uranium enrichment facilities currently in operation are based on gaseous diffusion or gas centrifuge separation technology. However, HEU production in quantities sufficient to fabricate a nuclear weapon could conceivably be carried out in small-scale facilities using any one of the technologies listed in Table 1. Pilot plant enrichment facilities have operated, with varying degrees of success, using the jet nozzle, MLIS, AVLIS, CHEMEX, and ion exchange technologies. Therefore, for purposes of this paper, detection of undeclared enrichment facilities using any of these technologies is considered a safeguards objective. Production of HEU by declared low-enrichment gas centrifuge facilities has been a primary safeguards concern: international safeguards approaches have been defined and are being applied to these facilities. The safeguards approaches being implemented are intended to detect diversion of LEU, which could be used as feed for undeclared facilities or unauthorized production of HEU in declared facilities. A primary technique under consideration for detection of undeclared enriched uranium facilities is environmental monitoring using other-than-natural uranium as the detection signature.

EFFLUENTS FROM URANIUM ENRICHMENT ACTIVITIES AND PATHWAYS TO THE ENVIRONMENT

In general, environmental monitoring of uranium effluents from uranium enrichment and uranium processing facilities has not been as high a priority as that for reprocessing facilities and reactors. The health and safety hazards associated with uranium are not as serious as those associated with fission products and highly radioactive materials from reactors or nuclear fuel reprocessing facilities. Uranium is present in the environment as a trace element. The low levels of uranium that are typically contained in normal effluents from uranium enrichment facilities do not significantly alter the concentration of uranium in the environment and, therefore, do not present a major environmental concern. Consequently, few technical publications exist on the subject of detection possibilities using the sensitive analytical techniques for enriched uranium signatures.

The current large-scale uranium enrichment facilities use gaseous diffusion or the gas centrifuge as the separation technology. These facilities use uranium hexafluoride (UF_6) gas in the separation process. The purge and light gases released from these facilities have passed through a series of cold traps and chemical traps before being released to the atmosphere. These traps minimize the uranium-bearing material that is released to the environment. However, some small fraction of the UF_6 inevitably escapes in the gas phase and reacts immediately with water upon release to the atmosphere to form uranyl fluoride (UO_2F_2). The UO_2F_2 coalesces around dust particles in the air. The particles grow larger with time and eventually fall to earth in the vicinity of the enrichment facility. The released uranium can blend with natural uranium in the environment, altering the isotopic content found in the sample and leaving a unique signature of the presence of activities involving enriched uranium. This isotopically altered uranium can be detected in samples of soil, vegetation, or water using sensitive analytical techniques.

Facilities using the vortex tube or jet nozzle separation technology also use gaseous UF_6 as a separation medium, and releases to the environment would be similar to those from gaseous diffusion and gas centrifuge facilities. Other separation technologies that do not use gaseous UF_6 as a process medium may have different release materials and pathways to the environment. Facilities using the electromagnetic enrichment technology would typically use uranium tetrachloride (UCl_4) as a source of uranium. This compound is volatile (melting point 690°C) and reacts with water on exposure to the air. Thus, some release of uranium-bearing compounds into the air, either as gas-phase molecules or fine particles, would be expected. Uranium isotopic separation processes based on ion exchange, chemical exchange, or laser excitation techniques would be expected to release different forms of uranium through the ventilation and wastewater effluents from the facility. Information on the environmental signature of these processes can best be addressed by states having operating pilot facilities using these technologies.

Regardless of the chemical form reaching the environment, the presence of isotopically altered uranium in a state with no declared uranium enrichment or enriched uranium processing facilities would provide unambiguous rationale for "special inspections" or other steps by the IAEA to resolve the inconsistency.

ENVIRONMENTAL SAMPLING TECHNIQUES FOR DETECTION OF ENRICHED URANIUM PROCESSING ACTIVITIES

The effect of the natural uranium background in the environment must be considered in the selection of sample media, sampling sites, and analysis techniques and in the interpretation of the results. Environmental samples taken from streams and vegetation always contain natural uranium. Typical concentrations of natural uranium in the environment are listed in Table 2.

Table 2. Typical concentrations of natural uranium in the environment

• Soil	≥ 1 ppm
• Vegetation	10 to 100 ppb
• Inland lake	0.3 ppb

The natural uranium concentration in the environment will vary from sample to sample, and identifying increases in uranium concentration due to uranium processing is difficult unless it significantly exceeds the normal variations in the background. The isotopic content of natural uranium is constant at values of 0.72% for ^{235}U and 0.0055% for ^{234}U, and any change from these values can easily be detected by sensitive isotopic analysis techniques. Thus, while increases in uranium concentration in an environmental sample could indicate that uranium processing activities have been or are occurring, it does not prove that a sensitive activity is present. However, variation of the isotopic ratios from their natural abundances is unequivocal evidence that enriched uranium processing activities have been or are being carried out in the vicinity.

Simple bulk sampling of vegetation, water, or soil, followed by isotopic analysis of the uranium present, has been used to detect the presence of enriched uranium processing activities. The sampling techniques used and some advantages are described below.

Vegetation Samples. Samples of vegetation, if available, have the following advantages: (1) the background uranium concentration found in vegetation is typically lower than that in soil or water samples, (2) bulk samples are easily collected with minimum equipment, and (3) uranium-containing particles collect on the surfaces of vegetation over a period of time, which increases the probability of detection. Evergreen foliage, for example, serves as a good sample source. Evergreen needles typically have life cycles of 2 to 3 years and tend to integrate particles from the atmosphere which fall to earth over an extended period of time. In the absence of evergreen growth in a given

area of interest, virtually any vegetation sample will suffice. Vegetation samples can be collected in polyethylene bags, which are sealed with tape and placed in plastic or cardboard containers. This procedure provides a double barrier against external contamination. The amount of vegetation collected is not critical; approximately 10 g is required per analysis.

Water Samples. A grab sample of about 100 mL of water is sufficient for analysis. The sample should be stored in a water-tight container. The sample is usually acidified with nitric acid to keep metallic elements, including uranium, in solution.

Soil Samples. Small samples of soil within the top 1 cm can be taken in plastic vials and sealed with tape to prevent contamination.

ANALYTICAL TECHNIQUES

Accurate measurements of the isotopic abundances of ^{234}U, ^{235}U, and ^{238}U are necessary. These measurements are typically performed using thermal ionization mass spectrometry with pulse-counting capabilities that permit analysis of nanogram-size samples. Any change in ^{234}U or ^{235}U abundance is unequivocal evidence that man-altered uranium is present. The presence of ^{236}U would, of course, indicate that the uranium in the sample had been exposed to a neutron flux. Separation of uranium from other elements in the sample is necessary before analysis begins, and a "clean room" environment is usually necessary for sample preparation. Samples of vegetation are dried, ashed, dissolved, and the uranium separated by solvent extraction techniques. Soil samples are prepared by dissolution of the sample and purification of the uranium with techniques similar to those used for vegetation samples. The purified uranium is usually transferred to the mass spectrometer filament using a resin bead to concentrate the solution in the center of the filament and to take advantage of its superior ion emission characteristics.

RESULTS FROM ENVIRONMENTAL SAMPLES TAKEN NEAR A LARGE GASEOUS DIFFUSION URANIUM ENRICHMENT FACILITY

A study was conducted over a period of several years to determine the extent of enriched uranium in the environment in the vicinity of a large-capacity gaseous diffusion uranium enrichment facility. A summary of the results from this study is presented below. Approximately 190 samples were analyzed over a period of several years.

Samples of water, soil, and vegetation were taken and analyzed using analytical techniques having sensitivities several orders of magnitude higher than those needed for environmental monitoring. The samples were taken from several areas at defined distances from the plant site. The primary sample source was evergreen foliage from pine trees in the area. The results from approximately 120 pine needle samples are summarized in Table 3.

Table 3. Typical pine needle sample results

Distance from plant site (arbitrary unit)	Isotopic abundance (at. %)		
	^{234}U	^{235}U	^{236}U
1	0.033	3.952	0.0080
2	0.016	1.756	0.0071
4	0.0091	1.184	0.0040
8	0.0072	0.913	0.0018
12	0.0060	0.775	0.0038
16	0.0054	0.743	0.0014

Samples were taken at defined distances from the plant site until the uranium isotopic abundances in the samples were not significantly different from that of natural uranium. The results indicate that uranium enrichment activities can be detected at some distance from the plant site. The distance in Table 3 is given in arbitrary units. The actual distance of detection would be dependent on many factors (e.g., uranium release rates, processing capacity, and weather conditions) and would be different for other facilities and site conditions. The isotopic results do indicate, without doubt, that enriched uranium activities can be detected by analysis of bulk samples taken some distance from the plant site.

Results for water samples are shown in Table 4. The upstream and downstream samples were taken from a large river which flows by the site. Enriched uranium processing activities could be detected in both the upstream and downstream samples.

Table 4. Water samples outside plant property

Sample location	Distance from plant site (arbitrary unit)	Isotopic abundance (at. %)		
		^{234}U	^{235}U	^{236}U
Upstream	2	0.0062	0.730	0.0003
Downstream	12	0.0070	0.868	0.0009

The results presented above represent what may be typical of a large gaseous diffusion uranium enrichment facility which has been in operation for a number of years. A smaller facility with similar operations would probably release less uranium to the environment. Extrapolation of the data to a small facility that has been in operation only a short time or to a facility based on a different technology has not been undertaken.

During this study, standards from the U.S. National Institute of Standards and Technology (NIST-1575 pine needle standards) were analyzed for quality assurance purposes. The uranium concentration in this standard is certified as 20 ± 4 ppb. The average of 25 analyses of NIST-1575 over a period of several months was 19.1 ± 0.6 ppb. The precision of $^{235}U/^{238}U$ ratios is about ± 0.5% for this sample size, and the ^{235}U abundance values can be determined to about ± 0.01 at. % for standard materials containing natural uranium.

CONCLUSIONS AND RECOMMENDATIONS

Analyses of samples taken in the vicinity of a large gaseous diffusion uranium enrichment facility for uranium isotopic content have indicated that enrichment facilities using gaseous UF_6 can be detected unambiguously outside the plant boundary. At enriched uranium processing facilities, some enriched uranium will inevitably be released to the environment: the uranium isotopic abundances will be altered sufficiently to be noticeable using sensitive analytical techniques. Extrapolation of these results to other types of uranium processing activities would be unreliable. Additional data from other facilities are needed to reach conclusions concerning the probability of detecting small facilities producing or processing HEU.

The sampling techniques reported are simple, and minimal inspection resources would be required to implement an environmental sampling program. Analysis of the samples would require "clean room" facilities, sophisticated analytical techniques, and high-sensitivity mass spectrometers to achieve optimum results.

A working group should be convened involving member states with enriched uranium processing facilities to evaluate the possibilities of using environmental sampling as an additional safeguards tool for use by the IAEA. The group could (1) review the data currently available from member state enriched uranium processing facilities, (2) determine needs for additional data from selected facilities, (3) coordinate collection and analysis of samples for additional data if required, and (4) provide the IAEA with recommendations for actions concerning implementation of environmental sampling techniques for detection of undeclared enriched uranium processing activities.

SUGGESTED READING LIST

Adriano, D. C., J. E. Pinder III, K. W. McLeod, J. C. Corey, and A. L. Boni, "Plutonium Contents and Fluxes in a Soybean Crop Ecosystem Near a Nuclear Fuel Chemical Separations Facility," *J. Environ. Qual.* 11(3):506 (1982).

Bondietti, E. A., F. O. Hoffman, and I. L. Larsen, "Air-to-Vegetation Transfer Rates of Natural Submicron Aerosols," *J. Environ. Radioact.* 1(1):5 (1984).

Carter, J. A., R. L. Walker, D. H. Smith, and W. H. Christie, "Isotope Dilution Resin Bead Mass Spectrometry—An Ultratrace Technique for Measuring Nuclides in Three-Mile Island Water," *J. Environ. Anal. Chem.* 8:241 (1980).

Cataldo, D. A., T. R. Garland, R. E. Windung, and J. M. Thomas, "Foliar Absorption of Transuranic Elements: Influence of Physiochemical Form and Environmental Factors," *J. Environ. Qual.* 9(3):364 (1980).

Donohue, D. L., and R. Zeisler, "Behind the Scenes: Scientific Analysis of Samples from Nuclear Inspections in Iraq," *IAEA Bulletin* 34(1):25 (1992).

Harbottle, G., R. Miller, and E. V. Sayre, "Pine Needles as Sensors of Atmospheric Pollution," *Environ. Monit. and Assess.* 2(3):27 (1982).

Hartmann, G., and K. Bachman, "Pu and Other Trace Elements in/on Plants," *J. Environ. Radioact.* 8(1):21 (1988).

Koranda, J. J., and W. L. Robison, "Accumulation of Radionuclides by Plants as a Monitor System," *Environ. Health Persp.* 27:165 (1978).

Polomski, J., H. Fluhler, and P. Blaser, "Accumulation of Airborne Fluoride in Soils," *J. Environ. Qual.* 11(3):457 (1982).

Smith, D. H., R. L. Walker, and J. A. Carter, "Sampling and Analysis of Radioactive Solutions," *Anal. Chem.* 54:827A (1982).

DATE
FILMED
8/20/93

END