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Initial Analysis of the Detectability of UO_2F_2 Aerosols Produced by UF_6 Released from Uranium Conversion Plants

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This article considers the use of wide-area environmental sampling to detect a covert centrifuge-enrichment program. It is proposed that detection may be more feasible by looking for the uranium-conversion facilities that produce the feedstock for centrifuges instead of the centrifuges directly. Aerosol particles of UO_2F_2 suspended in the atmosphere are considered as a possible signature. Source terms for a small-scale plant are coarsely estimated based on limited emissions data, atmospheric chemistry, and the thermodynamic of UF_6 release. Atmospheric dispersion modeling is used to estimate the distance at which detection could be reasonably expected. Further research is necessary before drawing conclusions on the feasibility of this method.

INTRODUCTION

Cascades of gas centrifuges used to enrich uranium in the isotope ^{235}U can make high-enriched uranium for use in nuclear weapons. For this reason, most countries have agreed to let the International Atomic Energy Agency (IAEA) monitor their centrifuge plants. However, a clandestine centrifuge plant could be very difficult to detect creating a loophole in the inspection regime. Centrifuge plants do not have distinctive characteristics or infrared signatures that would distinguish them from other industrial facilities when using overhead imaging. Further, most of the pipes in centrifuge plants operate below atmospheric pressure, so there is very little leakage of the process gas to the

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atmosphere. At present, there is no publicly known way to detect or identify a centrifuge plant at distances of more than a few kilometers.

The key to uncovering hidden centrifuge plants may lie not with the plant itself, but with its supporting facilities. The plant alone is useless without a supply of uranium-hexafluoride (UF_6) gas. If *inventory-verification safeguards* were applied to all UF_6 production facilities, and all imports of UF_6 were known, then it would be difficult for a proliferator to divert UF_6 from these monitored sources to a covert centrifuge plant. Such safeguards are already within the IAEA's purview.[1] Adding *production-verification safeguards* would make it difficult to produce extra (undeclared) UF_6 at overt facilities. In combination, these safeguards would force the proliferator to seek UF_6 on the black market, or to produce it at a covert facility. Therefore, if a covert UF_6-production facility were discovered, it would strongly suggest the existence of a clandestine enrichment effort. This article outlines one possible way to detect covert UF_6-production facilities (also called *conversion* facilities) based on their release of UF_6 to the atmosphere.

UF_6 DEGRADATION IN THE ATMOSPHERE

The detection of uranium atoms in air is not a sensitive technique for finding nuclear facilities because uranium forms about 1.7 ppm of average crustal rock and is therefore naturally present as airborne dust. Natural-background uranium and uranium released from a conversion plant also have identical isotopic compositions. It is thus necessary to consider molecular differentiation. Natural-background uranium is usually in an oxide form, whereas UF_6 is strictly anthropogenic. When UF_6 is released into the atmosphere, it reacts with water vapor to form uranyl fluoride (UO_2F_2) by the reaction $UF_6 + 2H_2O \rightarrow UO_2F_2 + 4HF$.

UO_2F_2 is an extremely stable substance. It does not thermally decompose to lower-energy U_3O_8 (or U_4O_9) at temperatures below 200–300°C.[2] Neither will UO_2F_2 react with important atmospheric species, such as ozone O_3, singlet-delta dioxygen $O_2(^1\Delta)$, excited atomic oxygen $O(^1D)$, H_2, HONO, H_2SO_4, HNO_3, SO_2, or NH_4.[3] Uranyl fluoride can form complex salts in organic bases, but these are not common in the atmosphere and even in these cases the UO_2F_2 kernel usually remains intact. All of this suggests that UO_2F_2 would be stable in the environment, but this must be experimentally verified.

Despite the chemical stability of UO_2F_2, its physical properties suggest an atmospheric lifetime short enough to neglect the possibility of an atmospheric background. At atmospheric temperatures and pressures, UO_2F_2 is a solid, so it exists as an aerosol. Large aerosols deposit by gravitational settling, and most aerosols are efficiently scavenged from the atmosphere by rain. However, fine and ultrafine aerosols can persist on time scales of 4 to 40 days, with a lifetime determined in part by their solubility in water. No experimental data appears to be available on the atmospheric lifetime of fine UO_2F_2 aerosols, but UO_2F_2 is hygroscopic and moderately soluble in water (it will form a 2.1 M solution). Depending on the exact lifetime, there may be confusion from other regional conversion plants, but the global background should approach zero. This article assumes no background confusion.

SOURCE TERMS

Albright and Barbour[4] estimate source terms for both the routine and accidental release of UF_6. Routine releases are the result of regular maintenance activities, small leaks in process piping—which, in conversion facilities, carry UF_6 above atmospheric pressure—and evaporation of residues left on discharge valves. Routine releases are typically small in magnitude and exhausted to the atmosphere through roof vents or the large bay doors typical of these facilities. In a well-designed facility, an air-handling system would keep the building at a slight negative pressure so that most of the contaminated air would pass through an air-filtration system first.

Accidents can release UF_6 in much larger quantities than occurs from routine operations. Accidents might involve the dropping and rupture of UF_6-storage cylinders, weld failures, or the shearing-off of valves. These kinds of accidents have occurred at most U.S. facilities. The UF_6 released during an accident may or may not pass through an air-filtration system, depending on where the accident occurs and the amount released. A very large release might saturate some filtration systems.

Source terms were calculated for a "reference facility" scaled to produce enough UF_6 feed for a centrifuge enrichment plant to produce annually 25 kg of 90%-enriched uranium, enough for one nuclear weapon per year. The exact amount of feedstock depends on the operational parameters of the enrichment plant. If the proliferator has limited enrichment capacity, it can use more feedstock to compensate. If the proliferator has a large amount of enrichment capacity, but is constrained by access to feedstock, then the opposite optimization can occur. Table 1 illustrates the trade-off.

Table 1: Feedstock requirements under differing constraints.

	Tailings assay (% ^{235}U)	Separative work (kg-SWU)	Feedstock (kg)
Feedstock limited (low)	0.11	7000	3700
Economic operation (med)	0.32	4700	5700
Enrichment limited (high)	0.60	3500	20,000

This article assumes that separative work is scarcer than uranium feedstock, giving 12,500 kg of natural uranium contained in UF_6 per year, and corresponding to 0.525% ^{235}U left in the depleted uranium. (Natural uranium contains 0.72% ^{235}U.)

The size of a routine release is estimated from one 1960s-era U.S. conversion facility, which leaked about 0.24 grams of uranium into the atmosphere for every kilogram of uranium in UF_6 produced. Although such an old facility is not representative of modern technology or environmental-protection standards, it may better represent the kind of facility a proliferator might build. It is not known whether this early U.S. facility was equipped with an air-filtration system. Assuming the same leakage rate, the reference facility would release 3.8 kg-UF_6 per year or about 10 grams per day.

Accidental release is less predictable. The only known case from which a crude probability estimate can be drawn is from the record of cylinder-filling accidents at the U.S.-operated Sequoyah Fuels facility.[5] Of the approximately 11,600 cylinders filled at Sequoyah, only one resulted in the complete release of the (overfilled) cylinder's contents, about 13,400 kg of UF_6. It was estimated that about half of the spill evolved into the atmosphere (based on the amount collected from the ground during clean-up). About 75% of that half was estimated to have been released during the first five minutes, with the balance over the subsequent forty minutes.

48 Y cylinders, like those used at Sequoyah, normally hold 12,000 kg of UF_6, and only about one such cylinder would be needed per year for our reference facility. If the probability of an accident depended only on the number of cylinders used, then a large release like the one at Sequoyah would occur once every 10,000 years. Accidents releasing tens or hundreds of kilograms of UF_6 due to valve or piping failures would occur somewhat more frequently. At a scaled rate, smaller accidents would occur once every 600 years. These values suggest that the detection of accidental spills is not a useful verification tool.

From a qualitative perspective, however, accidents are more interesting. Accidents are usually the result of imperfect handling procedures, so they should be more frequent for inexperienced plant operators. That said, even if accidents were to occur with ten times the stated frequency, accidents would still be too improbable on the time scales of interest-no more than once every sixty years. It may, however, be unreasonable to scale accident rates with a plant's output, especially by factors of more than one thousand. The qualitative and true statement that "most U.S. facilities have experienced cylinder accident" suggests that an accident is likely to occur early on, and irrespective of the plant's size. This article concludes that realistic estimates for the probability of an accident cannot be obtained from the available data, but an accident is still considered as one of the possible scenarios.

Other accident history, although devoid of frequency data, are useful in estimating the probable size and conditions of accidental release. For example, a weld rupture in a small cylinder at the Manhattan Engineering District Pilot Plant released an estimated 123 kg of uranium contained in UF_6 over a period of 17 seconds. A spill of UF_6 liquid at the Comurhex plant in France is reported to have released about 330 kg of uranium into the atmosphere over a period of about 10 to 15 minutes.[6]

In sum, the authors consider routine operations to be the only reliable source of UF_6 effluent. For our reference facility, this occurs at 3.8 kg-UF_6/yr. It is assumed that the nature of this release (as described later) is such that it occurs without regard to the operating hours of the plant, giving a steady-state source term of 120 μg/s. The authors also model an accidental unfiltered release of 200 kg of UF_6 liquid over a period of 10 minutes.

UF6 RELEASE DYNAMICS AND AEROSOLIZATION

The fraction of the release that is suspended into the atmosphere and the size of the aerosol particles depend on the release scenario. Solid residues of UF_6 and UO_2F_2 left on the surfaces of valves may slowly sublimate into gaseous effluents and be seen as a continuous routine-release. These vapors would have particle sizes of only one or so molecules and the authors treat them in the gas limit.

UF_6 released in gaseous form—as might occur from a leak in process piping—results in a superheated vapor and no solid form is immediately produced. When the vapor cools, it nucleates into an aerosol.[7] As a general rule, aerosols produced from gas result in particles with diameters of 10^{-3} to 10^{-2} μm. These ultrafine aerosols then coagulate to 0.1–1 μm sizes, depending on the frequency of particle collision, which in turn depends on the local concentration of the effluent. A study of UF_6 gas released into moist air found that puffs produced aerosol particles between 0.05–0.08 μm, and that at "low concentrations" further coagulation was negligible.[8] Air filters analyzed after the Sequoyah Nuclear Fuels accidents were reported to contain UO_2F_2 particles in the 0.4–2.5 μm range, with a peak between 1.27 and 1.59 μm.[9] An experiment by Pickerell[10] to study UO_2F_2 formation found spheroids of 0.3–0.6 μm, which aged to 1–2 μm. Another experiment conducted at the Portsmouth Gaseous Diffusion Plant found particles in the 1.1–1.4 μm range.[11]

It is assumed that small gas leaks with minimal coagulation contribute to routine release, and that the resulting particles are in the experimentally determined size-range for low concentrations (0.05–0.08 μm), with an upper bound equal to the sizes of early-formation particles found by Pickerell (0.3–0.6 μm). For accidental release, particles were assumed to be in the peak range found on the Sequoyah Nuclear Fuels air-filters after their accident (1.27–1.59 μm). UF_6 released in liquid form—as might occur during a cylinder-filling accident similar to those described for the Sequoyah, Comurhex, and Manhat-

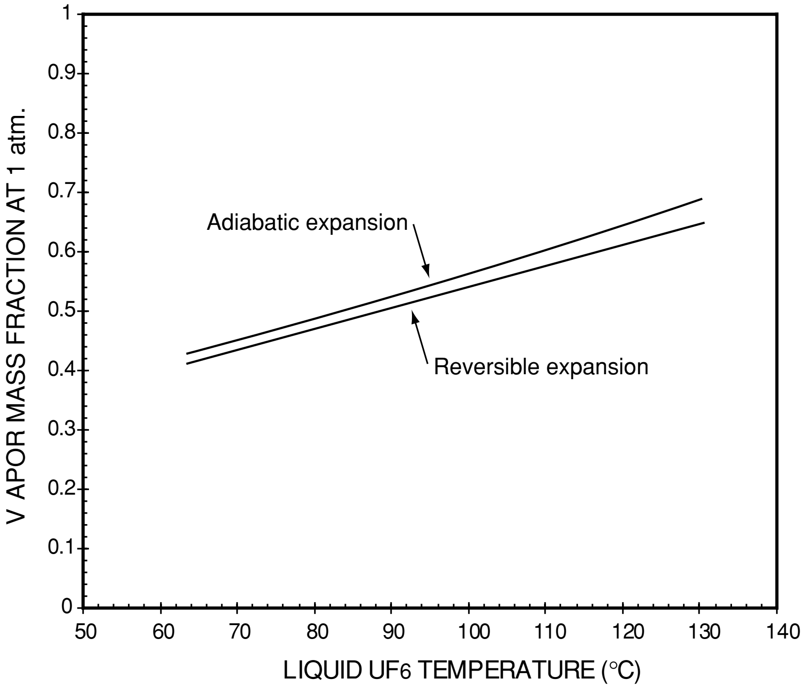

Figure 1: Vapor mass fraction produced in the release of UF_6 liquid to 1 atm.

tan Engineering District plants—would flash into mixture of solid and vapor upon decompression to atmospheric pressure. The mass fraction of UF_6 partitioned into vapor and solid forms can be bounded thermodynamically.[13] If expansion is assumed to be reversible (i.e., isentropic), a lower bound on the vapor fraction is estimated, because vapor formation is an entropy-increasing process. If the expansion is assumed to be adiabatic, an upper bound on the vapor fraction is estimated, as no energy is lost to the environment. Methods of determining the maximum entropy and enthalpy of a UF_6 release are described in Williams.[14] The mass fractions are bound as shown in Figure 1.

Note that the upper and lower bounds are closely matched, and that about 50% would be released into a gas form. Assuming that the solidified fraction falls rapidly to the ground and none is suspended into the air, then the thermodynamic estimate agrees with reports from the Sequoyah accident, in which about 50% of the release was collected from the ground. The vapor portion will eventually condense into an aerosol in a fashion identical to that described for the gas release.

TRANSPORT

Atmospheric transport was modeled using HYSPLIT 4.7[15] and historic 3-hour 80-km Eta/EDAS meteorology from NOAA's National Center for Environmental

Prediction. Ground-level concentrations were integrated on a 12-hour basis and isopleths drawn for each integration period. The plots chosen for reproduction here are of approximately the 70th percentile: about 70% were less favorable and 30% were more favorable in terms of the extent of the isopleths.

Given the generality of this model, the authors are only interested in order-of-magnitude values for the airborne concentration of UO_2F_2, and the general shape and size of the plumes over a generically flat terrain. The plume was thus released from Abilene Municipal Airport in central Texas (32.413N -99.679E) during the early days of January 2003. There are no major weather events on record during this period, except for one instance of high winds.

Deposition by sedimentation is not important for the ultrafine aerosols of routine release. Their deposition velocity, as given by the Stokes-Cunningham equation, is extremely small $\approx$0.0002 cm/s. For the larger aerosols of accidental release, the sedimentation velocity is still less than 0.05 cm/s. Rather, deposition is dominated by impaction and diffusion onto surfaces, which depend strongly on the terrain and turbidity of transport. A generic deposition velocity of 0.1 cm/s was chosen based on deposition velocities used for other fine inert aerosols. The model was also computed using a deposition velocity of 1 cm/s as a sensitivity test.

Routine release involved the continuous release of 0.378 g/hr of UO_2F_2 (equivalent to 0.432 g/hr of UF_6). Figure 2 shows the twelve-hour-averaged concentration for January 18, sixteen days after the beginning of the continuous release. The only major weather event between the initiation of the release and the results shown was a 4-hour period of high winds (40–55 km/h) on the evening of January 15. Isopleths reaching 200–400 km from the release point typically had concentrations of 10^{-7} to 10^{-9} μg/m^3, dropping into the 10^{-8} to 10^{-9} range when the deposition velocity was increased to 1 cm/s. Isopleths on the scale of 500–1000 km were typically 10^{-9} μg/m^3 or less in concentration, dropping into the 10^{-9} to 10^{-10} range for the higher deposition rate.

Accidental release assumed that half of a 200 kg of UF_6 spill was suspended as 1.3 μm particles and released over a period of ten minutes. Figure 3 shows isopleths for the sixth day after the pulse release. No weather events interfere with the movement of the plume during the simulation time, but a wind change blew the south-moving plume back over the release point. In other simulations, the plume can be seen moving more or less unidirectionally over the continent. Concentrations of 10^{-3} μg/m^3 or better were found in the 400–800 km range. Lower concentrations approaching those shown in the routine-release plot easily exceeded 1000 km in range.

DETECTION

It was assumed that confusion emanated from a natural background of UO_2F_2 or nearby conversion plant. This eliminated the statistical calculation normally

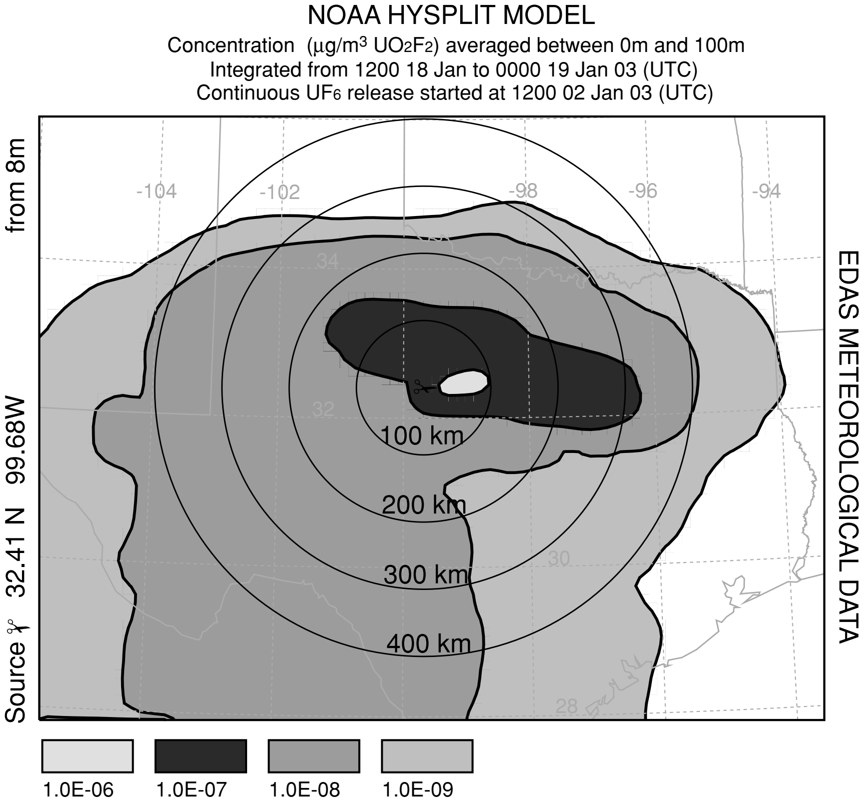

Figure 2: Isopleths for routine-release. UO_2F_2 concentration in μg/m^3.

required to make statements about positive detection. The minimum detectable concentration is then set only by the sample-collection efficiency and sensitivity of the assay method.

The IAEA has considered collecting aerosols using automated forced-air filtration.[16] The larger aerosols from an accident-type release (1.1–1.4 μm) would attach to the filter by impaction, whereas the finer aerosols of continuous releases (0.05–0.6 μm) would be collected by Brownian diffusion of particles onto the filter medium. Filter performance generally decreases in the 0.1 to 0.4 μm range, where both effects are in play but neither is dominant.[17] Nonetheless, there are established methods for filtering the entire spectrum of aerosol sizes. Standardized High-Efficiency-Particulate (HEPA) filters must remove 99.97% of 0.3 μm particles, which is approximately the most difficult aerosol size to capture.[18] Thus, it is unlikely that filter performance would lower the minimum-detectable concentration by an order of magnitude.

If we assume that the sampling system collects all suspended particles, then the relevant concentration is not the airborne values given above, but the

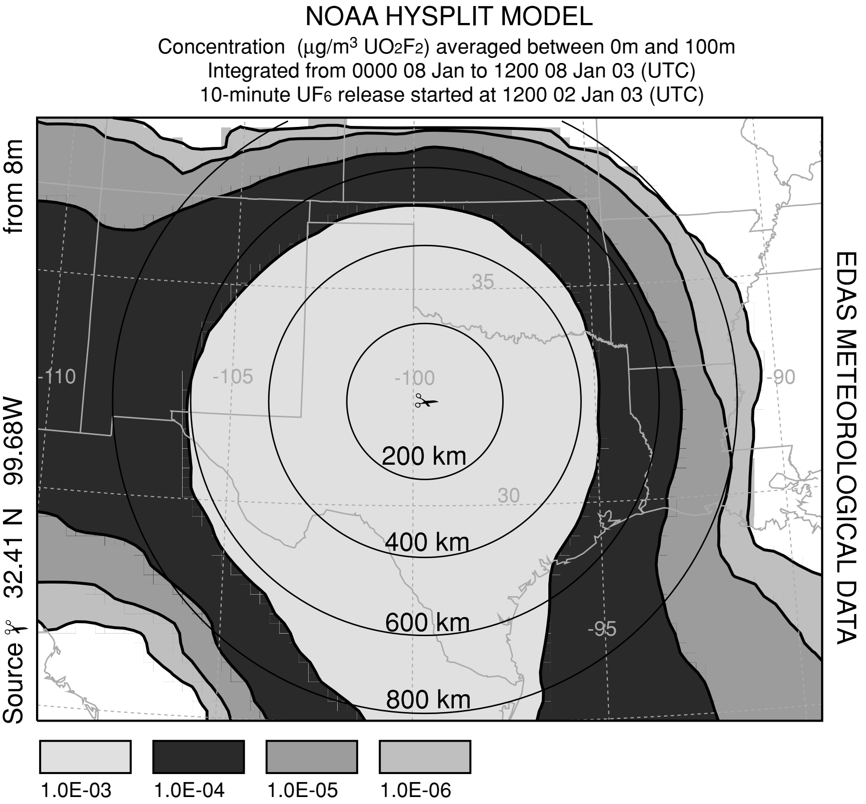

Figure 3: Isopleths for accident-release. UO_2F_2 concentration in μg/m^3. Note that both concentration and geographic scales have changed from Figure 2.

mass fraction of UO_2F_2 in the total collected aerosols. Typical aerosol loadings are 100 μg/m^3 in large cities and 4 μg/m^3 in non-arid rural areas. Deserts can have aerosol counts in excess of 1000 μg/m^3.[19] For an urban airborne-solid concentration, 10^{-7} μg/m^3 corresponds to 1 ppb of total-suspended solids, which for routine release is achieved at distances of about 200–300 km. A 0.1 ppb sensitivity would be required for distances greater than 400 km.

Many analytical methods used in atmospheric sampling can achieve 1 to 0.1 pbb sensitivity, and sometimes better. However, it was not possible to identify one method that would certainly work for UO_2F_2 in highly dilute, highly heterogeneous samples. One possible method may be fluorescence. Fluoro complexes of uranyl in acidic aqueous solutions are among the most luminescent uranyl species known.[20] UO_2F_2 is excited by light between 330 and 472 nm, and emits at 521 nm. Another detection technique may be matrix-assisted laser desorption ionization, which can gently ionize particles without breaking molecular bonds, enabling molecular mass spectroscopy.

CONCLUSION

It may be possible to use UO_2F_2 aerosols to detect routine releases from clandestine conversion facilities if three assumptions are correct: 1) The source term estimate is reasonable. The data used here is based on data from a single facility. 2) Regional conversion plants do not produce a background of UO_2F_2. 3) A suitably sensitive assay method can be developed.

Detection of accidental releases would be easier as the source term could be up to five orders of magnitude larger than routine release. The greatest uncertainty with accident-based detection is that it relies on rare events that might never happen at a clandestine facility.

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