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# NOBLE GAS ATMOSPHERIC MONITORING AT REPROCESSING FACILITIES

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## Abstract

Monitoring of stable noble gas (Kr, Xe) isotopic abundances at reprocessing plant stacks appears to be able to yield information on the burnup and type of the fuel being processed. To estimate the size of these signals, model calculations of the production of stable Kr, Xe nuclides in reactor fuel and the subsequent dilution of these nuclides in the plant stack are carried out for two case studies: reprocessing of PWR fuel with a burnup of 35 GWd/tU, and reprocessing of CANDU fuel with a burnup of 1 GWd/tU. For each case, a maximum-likelihood analysis is used to determine the fuel burnup and type from the isotopic data.

## 1. Introduction

The discovery in Iraq after the Gulf War of the existence of a large clandestine nuclear-weapon program has led to an across-the-board international effort, dubbed Programme 93+2, to improve the effectiveness and efficiency of International Atomic Energy Agency (IAEA) safeguards /1-3/. Programme 93+2 has raised the prospect of the first major changes in the technical methods by which the Agency may apply safeguards in nonweapon states parties to the NPT since the conclusion and implementation of NPT safeguards agreements in the late 1970s. As discussed below, one particularly significant potential change is the introduction of environmental monitoring (EM) techniques as an adjunct to traditional safeguards methods.

One of the more interesting and timely problems to which the new methods called for in Programme 93+2 might be applied is that of large-scale reprocessing facilities devoted to civil uses. Several such facilities have either come on-line in recent years or are projected to do so in the near future. In 1990, the UP-3 plant at La Hague in France commenced operations, and has a design annual throughput of 800 tonnes heavy metal /4/, which could contain up to

8000 kg plutonium.* In 1993, the Thermal Oxide Reprocessing Plant (THORP) in Great Britain came on line and is ramping up towards its design annual throughput of some 1200 tonnes uranium, or an annual plutonium separation rate of about 12000 kg /5/. Japan is also a pacesetter in this area. Its Tokai Reprocessing Plant (TRP), which is currently operating, has a design throughput of 90 tonnes uranium per year, or, equivalently, about 900 kg plutonium annually. Furthermore, the Rokkasho Reprocessing Plant (RRP), now under construction and scheduled to commence operations in 2000, will have an annual throughput of 800 tonnes uranium, or a plutonium separation rate of about 8000 kg /6/. Plants of this size have hitherto only been found in the weapon states, where they are not required to come under IAEA safeguards.** Safeguarding these civil facilities adequately will present a challenge to IAEA safeguards /7/, and environmental monitoring could play a useful role in meeting that challenge.

As we discuss below, one EM technique that could be widely applicable to safeguarded reprocessing facilities is the monitoring of atmospheric noble gas isotopic abundances in the facility's stack effluents. The objective of this and related EM techniques in this context is to complement current safeguards techniques by increasing the transparency of the facility's operations and by providing a consistency check on the process data inferred from more traditional methods of material accountancy. Although for our analysis we do not assume any particularly intimate access to the facility, we do assume that it is possible to obtain stack samples of the plant's effluent. This is relatively unintrusive in comparison to the access required in the normal course of safeguards implementation.

The purpose of this paper is to outline the noble gas technique in the context of safeguarding declared facilities and to illustrate some of the process information that may be attainable through its use. We do not address the very difficult problem of locating clandestine nuclear facilities. Despite this, we believe that the general techniques and approach discussed here will have broad applicability to the field of EM and will be in some degree relevant to all EM problems.

In what follows, we first begin with a brief discussion of

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* At typical burnups, light-water reactor (LWR) fuel contains about 10 kg Pu per tonne uranium.

**THORP and the UP3 plant at La Hague, as civil nuclear facilities, come under European Atomic Energy Community (EURATOM) safeguards. Military stocks in France and Britain or the other weapon states currently do not come under any form of international safeguards.

noble gas atmospheric monitoring in general terms. Then we pass to the technical considerations that comprise the heart of this study. Finally, we offer some concluding reflections on the possible inclusion of this technique in the IAEA's safeguards toolkit.

## 2. Noble gas monitoring

Although there are many particular ways in which EM might be applied to safeguards, they all share a common general approach. In all cases, the essential problem of EM is to identify and measure disturbances in the environment that are specifically due to nuclear activities and to use these measurements to ensure there are no inconsistencies with peaceful-use declarations, or with information obtained through other safeguards methods, thereby increasing confidence and transparency.

In this vein, the first task in EM is to identify a useful set of signals. Useful in this context means signals that are (1) directly related to a facility's activities, (2) strong enough to measurably perturb the environmental background, and (3) useful in determining process parameters of safeguards interest. Clearly the choice of an appropriate set of signals will depend critically on the parameters one is interested in determining. In general, no one set of signals will be able to yield answers to all possible questions of interest.

For the specific case of reprocessing plants, two important questions are the following: What is the burnup of the fuel that is being reprocessed? And what type of reactor did it come from? The first is critical in differentiating between the reprocessing of power reactor fuel, which is typically run to fairly high burnups (on the order of 35 GWd/tU* or more), and the reprocessing of weapon production fuel, which usually has a burnup on the order of 1 GWd/tU or less. The second question is helpful in addressing the question of whether natural uranium fuel has been substituted for low-enriched fuel by an operator in contravention of declared operations.

It is important to realize that this does not exhaust the list of items of safeguards interest. In particular, an environmental determination of the burnup and fuel type does not yield the total plutonium inventory, which may be obtained by traditional material accountancy. The objective of EM in this context, as mentioned above, is not to replace other safeguards methods but rather to provide additional transparency and consistency checks on information

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* Throughout this paper, reactor fuel burnup is measured in terms of this unit, which is 1000 megawatt days per metric tonne uranium.

obtained through other means, and thereby to contribute to the overall safeguards objective of obtaining an accurate picture of the facility's operations.

A potentially useful set of signals for addressing the two questions of burnup and fuel type is comprised of the relative abundances of the stable krypton and xenon isotopes produced as fission products during the operation of nuclear reactors. These signals have two great advantages: they are directly related to the number of fissions that have taken place in the fuel while it was in an operating reactor, and, because of their chemical inertness, they are undisturbed by the complex chemistry of reprocessing and are emitted freely during the dissolution process. Moreover, the relative isotopic abundances of nonradioactive isotopes are unaffected by the amount of time elapsed between the removal of the fuel from the reactor and the dissolution of the fuel during reprocessing.*

Previous studies in the area of noble gas monitoring have in the main centered around Kr-85, due to its very low background. Global surveys of the distribution of Kr-85 in the atmosphere have been made for many years /8/. The present analysis, however, systematically integrates the different specializations necessary in using stable noble gas isotopic abundance signals as a transparency measure in an international cooperative context. It is also unique in considering non-radioactive noble gas isotopes in addition to Kr-85.

Although, in contrast to Kr-85, the natural backgrounds of the stable noble gas isotopes are relatively high, calculations outlined below suggest that the plant-induced shift in the isotopic abundances should still be distinguishable by high-precision mass spectrometric analysis of atmospheric samples taken from the stack. A complete isotopic analysis of such samples offers the possibility of multiple determinations of the fuel burnup and type, which is not possible by analyzing Kr-85 alone.

Hudson /9/ and Aregbe *et al.* /10/ have also considered the question of the stable noble gas signals arising from reprocessing, but they have not considered the important question of back-calculating fuel parameters of interest from the measured isotopic ratios. This report addresses this issue.

## 3. The choice of signals

Among all the possible krypton and xenon isotopes, only a subset are actually produced as fission products. For krypton, the fissiogenic isotopes with fission

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* We implicitly assume that no equipment to trap noble gases has been installed in the facility. This is in keeping with current practice, and, in principle, could be checked by other means.

yields greater than $2.5 \cdot 10^{-6}$ percent* and half lives greater than one day are 82 (s), 83 (s), 84 (s), 85, and 86 (s). In this list, stable isotopes are followed by (s); the rest are radioactive. Similarly, the fissiogenic xenon isotopes with fission yields greater than $2.5 \cdot 10^{-6}$ percent are 129 (s), 130 (s), 131 (s), 132 (s), 133, 134 (s), 135, 136 (s).** Other isotopes, e.g., Xe-127, are not produced in reactors and are therefore not useful for safeguards.

Kr-82, Xe-129, and Xe-130 can also be deleted from the list. Their cumulative fission yields are suppressed because they are shielded in fission-product $\beta$ decay chains by very long-lived isotopes: Se-82 ($1.4 \cdot 10^{20}$ yr), I-129 ($1.57 \cdot 10^{7}$ yr), and Te-130 ($2.5 \cdot 10^{21}$ yr), respectively. Therefore, they too are not produced in significant quantities in reactors.

With all these considerations, the list of safeguards-usable isotopes is thinned to: Kr-83, 84, 85, and 86; and Xe-131, 132, 134, and 136. All are stable except Kr-85.

Table I contains the Evaluated Nuclear Data File recommended values for the U-235 thermal fission yields of the relevant krypton and xenon isotopes /11/. It illustrates that the compositions of fissiogenic krypton and xenon differ markedly from the background compositions of atmospheric krypton and xenon, another useful characteristic from a safeguards point of view. In particular, the shift toward the heavier isotopes in the fission process implies that they should be much more abundant in an environmental sample than the lighter isotopes.

## 4. Technical analysis

The basic technical issues are the following: to model how the plant krypton and xenon signals are diluted in the atmospheric background; to demonstrate how meas urements of krypton and xenon ratios in the plant's stack can yield safeguards-relevant information; and to calculate the effects of measurement uncertainty in distinguishing the signal from the background.

Throughout this analysis, it will be assumed that the isotopic ratios are measured by taking macroscopic samples in the stack of a reprocessing facility and then measuring the krypton and xenon isotopic abundances in these samples in a high-precision mass spectrometer. Aregbe *et al.*[1] at the Institute for Reference Materials and Measurements in Belgium have recently reported krypton and xenon abundance ratio measurements with relative precisions

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* On the usual scale of 0 to 200 percent used in this field, because each binary fission results in two fission fragments.

**These data are taken from the 14th edition of the *Chart of the Nuclides* (San Jose, CA: General Electric, 1989).

(relative standard deviations) of a few parts in $10^5$. This precision will be assumed here.

It will also be assumed that, at the same time a sample is taken from the plant stack, a background sample is also taken and measured to establish the local krypton and xenon background, so that it may be accurately subtracted.

**Table I**
**ENDF/B-VI Fission Yields and Relative Isotopic Distributions[a]**

| Isotope | Percent Cumulative Fission Yield (thermal) | Relative Isotopic Distribution rom Fission Process (%) | Atmospheric Isotopic Abundance /19/ (%) |
|---|---|---|---|
| Kr-78 | — | — | 0.35 |
| Kr-80 | — | — | 2.25 |
| Kr-82 | 5.47E-05 | — | 11.6 |
| Kr-83 | 0.536 | 14.2 | 11.5 |
| Kr-84 | 1.00 | 26.5 | 57.0 |
| Kr-85 | 0.283 | 7.48 | — |
| Kr-86 | 1.97 | 51.9 | 17.3 |
| | | | |
| Xe-124 | — | — | 0.1 |
| Xe-126 | — | — | 0.090 |
| Xe-128 | — | — | 1.91 |
| Xe-129 | — | — | 26.4 |
| Xe-130 | — | — | 4.1 |
| Xe-131 | 2.89 | 13.2 | 21.2 |
| Xe-132 | 4.31 | 19.7 | 26.9 |
| Xe-134 | 7.87 | 35.9 | 10.4 |
| Xe-136 | 6.31 | 28.8 | 8.9 |

## Outline of the analysis

The analysis contained in this study falls naturally into two main parts that we shall dub the "forward" problem and the "inverse" problem. Both components revolve around the basic equation for the isotopic abundance of the *j*th isotope of, say, xenon:

$$A\left({}^{j}Xe\right) = \frac{\left[{}^{j}Xe\right]_{BG} + DQ_{j}(B)}{\sum\left[{}^{k}Xe\right]_{BG} + D\sum Q_{k}(B)}. \quad (1)$$

In this formula, the bracketed isotopes denote concentrations of that isotope measured in, say, atoms/m$^3$. The subscript $BG$ indicates the atmospheric background concentrations of each isotope. The parameter $D$ represents the effect of atmospheric dilution and has the dimensions of s/m$^3$, i.e., of a concentration divided by an emission rate; $B$ is the burnup of the fuel given in GWd/tU; the $Q_j(B)$ are the plant source terms, measured in, e.g., moles/s; and the term $DQ_j$ is the plant component of the total concentration of isotope $j$. The sums in the denominator range over all the stable xenon isotopes with either a background component or a plant component or both.

The two main parameters, $D$ and $B$, that we are interested in estimating from the isotopic data deserve special comment. We have not assumed any particular model or form for $D$, but only that the diluted plant term is proportional to the source term. This guarantees that $D$ only enters in a linear fashion. Furthermore, while $D$ depends implicitly on the operational conditions under which the stack sample is taken, it is the same for each isotope. The $Q_j$ are functions of the burnup, $B$, which vary from one reactor type to another, and can be computed using the ORIGEN2 code /13/ or other, more sophisticated, transport and decay codes /14-16/.

The above equation indicates that the abundance of any isotope will approach its background value as the plant production rate goes to zero, as it should. Moreover, if a ratio of two isotopes is desired instead of their relative abundances, the ratio can be obtained from the above formula by dividing the abundances of the two isotopes.

The forward problem consists of using models to derive a theoretical form for the source terms under reasonable reprocessing scenarios. These theoretical expressions will then be used in estimating the burnup from the isotopic data. If desired, these expressions may also be used to estimate the diluted isotopic abundances under various conditions to see whether they differ substantially from the background.

The inverse problem, however, is qualitatively different. As mentioned above, we assume that two different measurements are made simultaneously: one in the stack to measure the abundances of the noble gas isotopes and another outside the stack to measure the local background abundances. The objective then, given these experimental values of the stack abundances and the backgrounds, is to estimate the best values for the dilution factor and the fuel burnup, in essence inverting the basic abundance (or ratio) equation.

## Two case studies

In order to illustrate the noble gas concept, we will explore two test simulations of practical importance: the first concerns the reprocessing of PWR power fuel at a typical power-production burnup of 35 GWd/tU; the second the reprocessing of CANDU fuel at a burnup of 1 GWd/tU. The first case involves a burnup that is a standard value for civilian power production. The second involves a burnup that could be consistent with a military application.

The strategy followed in each case will be to generate simulated isotopic data, and then to show how these data may be used in estimating process parameters of interest.

Although technical information about almost all reprocessing plants is tightly held, for either national security or industrial proprietary reasons, there is one reprocessing plant, no longer in operation, about which operational information can be obtained. This is the Plutonium-Uranium Extraction (PUREX) Plant located at the Hanford Site in Washington State /17/. Details about the operating parameters, throughputs, flows, etc., have been declassified over the past several years and are now generally available. Table II contains the plant parameters needed for the modeling purposes in this study.

With these parameters, ORIGEN2 calculations of krypton and xenon production in reactors, and some order-of-magnitude assumptions about the effect of dilution, we can now conduct the two experimental simulations. It should be emphasized that the "data" generated below are model data; they are *not* experimental data.

**Table II**
**Model Reprocessing Facility Parameters**

| Fuel Throughput (tonnes/hr) | Stack Height (m) | Stack Inner Diameter (m) | Exit Temperature (K) | Exit Velocity (m/s) |
|---|---|---|---|---|
| 1.25 | 50 | 2 | 313 | 20 |

## Outline of the forward problem

The purpose of this section is merely to outline the elements of the forward problem, i.e., to generate simulated data we will need to illustrate the basic method. The more interesting results are those of the inverse problem and will be given in the next section.

Let us begin with the background krypton and xenon concentrations we will use. The background krypton and xenon concentrations can be estimated from the atmospheric isotopic abundances of krypton and xenon given in the literature /18/ and the sea-level number density of the US standard atmosphere, $2.43 \cdot 10^{19}$ particles/cm$^3$. The results of this calculation are given in Table III. Note that the typical backgrounds for the fissiogenic krypton isotopes are about two orders of magnitude greater than for the fissiogenic xenon isotopes.

A sample ORIGEN2 calculation yields another interesting point. The fissiogenic Kr, Xe inventories for 3.5 percent enriched, pressurized-water reactor (PWR) fuel are given in Table IV. Note that the xenon concentrations are about an order of magnitude larger than the krypton concentrations. Together with the facts mentioned above, this implies that xenon signal to background ratios should be substantially higher than those for krypton (with the exception of Kr-85). In view of this, we will henceforth concentrate on xenon, although our approach can be easily generalized to include krypton.

Fissiogenic krypton and xenon inventories for varying burnups can also be calculated with ORIGEN2. It is convenient in both the forward and the inverse problem to use analytic forms of the inventory curves obtained by fitting the ORIGEN2 results to quadratic functions of the burnup. With

**Table III**
**Background Atmospheric Kr, Xe Concentrations**

| Isotope | Concentration (atoms/m$^3$) |
|---|---|
| Kr-78 | 9.61E16 |
| Kr-80 | 6.25E17 |
| Kr-82 | 3.19E18 |
| Kr-83 | 3.18E18 |
| Kr-84 | 1.58E19 |
| Kr-86 | 4.82E18 |
| Xe-124 | 2.01E15 |
| Xe-126 | 1.88E15 |
| Xe-128 | 4.06E16 |
| Xe-129 | 5.59E17 |
| Xe-130 | 8.60E16 |
| Xe-131 | 4.49E17 |
| Xe-132 | 5.68E17 |
| Xe-134 | 2.21E17 |
| Xe-136 | 1.87E17 |

**Table IV**
**Kr, Xe Inventories in 3.5%, 35 GWd/tU, PWR Fuel**

| Isotope | Concentration (g/tU) |
|---|---|
| Kr-83 | 43.65 |
| Kr-84 | 121.8 |
| Kr-85 | 25.77 |
| Kr-86 | 204.5 |
| Xe-131 | 441.9 |
| Xe-132 | 1137 |
| Xe-134 | 1558 |
| Xe-136 | 2466 |

these functions, and the plant throughput, it is possible to calculate the plant emission rates needed in equation (1) for various reactor types and burnups of spent fuel. It will be assumed below that such rates are given in moles/s of the individual isotopes.

As discussed above, we can take dilution into account by introducing a multiplicative dilution factor, *D*. Although estimating this factor might be approached in various ways, it is sufficient for our purposes to give a simple order-of-magnitude estimate. In generating the simulated data for the two test cases, we will use an approximate value of $D = 10^{-5}$ s/m$^3$. This gives a typical value of the type of dilution that might be seen in a stack sample. In any event, it is a relatively simple matter to redo the simulation with a different value for the dilution, if so desired.

One further point should be mentioned. The complicated denominator in equation (1) can be eliminated by considering isotopic ratios rather than abundances, particularly if we use as a reference isotope one that is not produced in reactors, e.g., Xe-129. Of course, using ratios with respect to Xe-129 is completely equivalent to using abundances. This is particularly convenient from the point of view of a mass spectrometric analysis because Xe-129 is the most abundant isotope that is not fissiogenic, and thus is well measured.

Case 1 simulated isotopic ratios. The “true” background ratios with respect to Xe-129 can be calculated by dividing the appropriate concentrations in Table III. To make for a more realistic simulation, we assume that the simulated background ratios are normally distributed about these “true” values with a relative standard deviation of $10^{-5}$, and then we draw the simulated values randomly from this distribution. This has the effect of introducing some gaussian noise into the simulation. The resulting simulated values are given in Table V.

Notice that we are assuming that the ratio can be measured to about five significant figures. This is consistent with the part or so in

$10^5$ precision currently obtainable in state-of-the-art noble gas mass spectrometry /10,12/. At any rate, the difference between the diluted and the background ratios can be seen in the first few significant figures, as evident in Tables V and VI.

**Table V**
**Case 1 and 2 Background Ratios**

| Isotopic Ratio | Simulated Data |
|---|---|
| 131/129 | 0.80322 |
| 132/129 | 1.0161 |
| 134/129 | 0.39535 |
| 136/129 | 0.33452 |

**Table VI**
**Case 1 Stack Ratios**

| Isotopic Ratio | Simulated Data |
|---|---|
| 131/129 | 0.81670 |
| 132/129 | 1.0507 |
| 134/129 | 0.44222 |
| 136/129 | 0.40759 |

The stack ratios can be arrived at in a similar way. The model result is assumed to be the "true" value, and then some gaussian noise is added in. The results are given in Table VI.

Case 2 simulated ratios. The background ratios for Case 2 are the same as for Case 1. The stack ratios can be generated in the same way as for Case 1. The results are given in Table VII. As expected, these stack ratios are much closer to the background values because of the low burnup of the fuel in this scenario.

**Table VII**
**Case 2 Stack Ratios**

| Isotopic Ratio | Simulated Data |
|---|---|
| 131/129 | 0.80369 |
| 132/129 | 1.0168 |
| 134/129 | 0.39671 |
| 136/129 | 0.33680 |

## Results for the inverse problem

Given these model results in lieu of experimental data, how can we then extract from the isotopic data parameters of interest, such as the fuel burnup and the reactor type?

Preliminaries. If we define $R_j$ as the ratio of the $j$th isotope of xenon to Xe-129, then equation (1) becomes:

$$R_j = \frac{\left[{}^{j}Xe\right]_{BG} + DQ_j(B)}{\left[{}^{129}Xe\right]_{BG}} = R_j^0 + \frac{DQ_j(B)}{\left[{}^{129}Xe\right]_{BG}}, \quad (2)$$

or, equivalently,

$$R_j - R_j^0 \equiv \Delta R_j = \frac{DQ_j(B)}{\left[{}^{129}Xe\right]_{BG}} \equiv dQ_j'(B), \qquad (3)$$

where the background 129 concentration, a constant, has been absorbed into a redefined dilution factor, which is given explicitly by:

$$d = \left(\frac{Dr}{3600}\right)\frac{N_A}{\left[{}^{129}Xe\right]_{BG}}, \qquad (4)$$

where $D$ is the previously defined dilution factor; $r$ is the plant throughput in tonnes/h; the factor 3600 converts from hours to seconds; and $N_A$ is Avogadro's number. All the factors contributing to the plant signal that are non-isotope-specific have been absorbed into this definition. All the isotope-specific terms have been included in the redefined production function, $Q_j'(B)$. This includes the isotopic weight because the ORIGEN2-generated functions yield isotopic concentrations in g/tU, and therefore need to be divided by the isotopic weight to convert them to moles of the isotope. The *Chart of the Nuclides* lists these weights conveniently /19/. For our test cases, $D = 10^{-5}$ s/m$^3$ and $r = 1.25$ t/h, which yields $d = 0.004$.

Equation (3) demonstrates that determining the dilution factor and the burnup from the measured ratios and backgrounds depends critically on establishing experimentally that there is a nonzero difference between the ratio in the stack and the background ratio. How well the subtraction of two numbers that are relatively close together can be done in turn depends on the precision with which atmospheric noble gas isotopic ratios can be measured. As mentioned above, we are assuming mass spectrometer precisions of about 1 part in $10^5$.

The maximum-likelihood method. Equation (3) depends explicitly on $d$, the dilution, and on $B$, the fuel burnup. Given the simulated data for the four fissiogenic xenon ratios, we can invert these four equations to obtain an estimate of $d$ and $B$ using the maximum-likelihood method. Useful discussions of this method can be found in Mathews and Walker /20/ and the notes by Orear /21/. In general, we have $N$ experimentally measured quantities, $x_i$, each with a corresponding experimental uncertainty, usually given as a standard deviation, $\sigma_i$. These results are obtained in principle by making repeated measurements of each quantity, thereby establishing experimental probability distributions for each $x_i$. We will assume that these probability distributions are normal.

Suppose also that we have a theoretical expression, $y_i$, for each $x_i$, that depends on $m$ parameters $(a_1,\ldots,a_m)$, i.e., $y_i = y_i(a_1,a_2,\ldots,a_m)$. The parameters $a$ are what we want to determine. Each choice of parameters yields a different theory, and since these parameters are in general continuous variables, there are in general an infinite number of theories. We want to find the theory, or choice of parameters, that best fits the measured data.

This can be accomplished by defining the nonnegative function

$$\chi^2(a_1,a_2,\ldots,a_m) \equiv \sum_1^N \frac{(x_i - y_i)^2}{\sigma_i^2}. \qquad (5)$$

The function $\chi^2$ defines a complicated surface in the $m$-dimensional parameter space. The maximum-likelihood estimates of the parameters are located at the global minimum of this surface. In general, there will be several local minima as well, so care and physical judgment must be used in ensuring that the minimum one is inspecting is actually the global minimum.

In what follows, the minimization problem will be handled with the symbolic mathematics program *Mathematica*®/22/.

In the case of "good statistics," the function $\chi^2$ will be fairly sharply peaked about the minimum. In this case, the uncertainties in the maximum-likelihood estimates can be calculated by differentiating $\chi^2$ /21/. Similarly, the goodness-of-fit of the estimate can be evaluated using the well-known chi-square test for $N - m = 4$ (the number of isotopes) – 2 (the number of parameters) = 2 degrees of freedom /21/.

Case 1 fit results. With these numbers, we are now able to compute the $\chi^2$, which we can then use to find the maximum-likelihood estimates $(\hat{d},\hat{B})$. The errors in these predictions, $(\Delta d,\Delta B)$, can also be calculated from standard formulas /21/. The results to fitting to a PWR are given in Table VIII. The results for BWR and CANDU fits are given in Tables IX and X.

**Table VIII**
**Case 1 PWR Fit Results**

| | |
|---|---|
| $\hat{\chi}^2$ | 0.7 |
| $\hat{d} \pm \Delta d$ | 0.004 ± 6E-06 |
| $\hat{B} \pm \Delta B$ | 35.00 ± 0.05 |
| $P_2(\chi^2 > \hat{\chi}^2)$ | 0.72 |

**Table IX**
**Case 1 BWR Fit Results**

| | |
|---|---|
| $\hat{\chi}^2$ | 26000 |
| $\hat{d} \pm \Delta d$ | 0.004 ± 2E-06 |
| $\hat{B} \pm \Delta B$ | 34.23 ± 0.02 |
| $P_2(\chi^2 > \hat{\chi}^2)$ | 0 |

**Table X**
**Case 1 CANDU Fit Results**

| | |
|---|---|
| $\hat{\chi}^2$ | 68000 |
| $\hat{d} \pm \Delta d$ | 58<br>unphysical errors |
| $\hat{B} \pm \Delta B$ | 0.0023<br>unphysical errors |
| $P_2(\chi^2 > \hat{\chi}^2)$ | 0 |

In Table X, the notation "unphysical errors" refers to a breakdown in the approximations used in deriving the standard error equations. However, this is not particularly important because the chi-square test for the CANDU shows that it does not fit the data well at all.

Inspection of these results indicates the PWR equations provide the best fit to the simulated data and give an accurate prediction of the dilution factor and burnup. A discussion of these results and how they might differ when analyzing real data is given below.

Case 2 fit results. The results of the minimization procedure are shown in Tables XI to XIII. The CANDU results clearly fit the data most accurately, as they should, and provide reasonably good predictions of the burnup and factor.

**Table XI**
**Case 2 PWR Fit Results**

| | |
|---|---|
| $\hat{\chi}^2$ | 640 |
| $\hat{d} \pm \Delta d$ | 0.0003 ± 2E-05 |
| $\hat{B} \pm \Delta B$ | 17 ± 1.5 |
| $P_2(\chi^2 > \hat{\chi}^2)$ | 0 |

**Table XII**
**Case 2 BWR Fit Results**

| | |
|---|---|
| $\hat{\chi}^2$ | 920 |
| $\hat{d} \pm \Delta d$ | 0.0002 ± 2E-04 |
| $\hat{B} \pm \Delta B$ | 19 ± 1.4 |
| $P_2(\chi^2 > \hat{\chi}^2)$ | 0 |

**Table XIII**
**Case 2 CANDU Fit Results**

| | |
|---|---|
| $\hat{\chi}^2$ | 8E-06 |
| $\hat{d} \pm \Delta d$ [a] | 0.004, 0.002 |
| $\hat{B} \pm \Delta B$ | 1.0, 0.5<br>$B \leq 2.0$ with 95% confidence |
| $P_2(\chi^2 > \hat{\chi}^2)$ | 1 |

[a] Due to the lower burnup in this case, the minimization procedure does not yield a symmetric error in the parameter fit. Therefore, we do not use the ± notation, but rather give the best value and standard deviation. In the case of the burnup, a 95 percent upper confidence limit is also given.

Discussion of the fit results. The above fit results, while they do indicate how one might go about analyzing actual data, should not be taken too literally. The high accuracy of the PWR fit in Case 1 is due to two factors: (1) as mentioned above, the high measurement precision and (2) the fact that the simulated data themselves were generated using the ORIGEN2 production functions. In a sense, we merely "closed the circle" by finding the correct burnup and fuel type.

The analysis of real data will undoubtedly differ from that of the simulated data due to systematic errors in the ORIGEN2 code (or in whatever code one uses to generate the theoretical formulas that the $\chi^2$ function uses to compare with the experimental results). The ORIGEN2 code has been compared to experimental data on noble gas isotopic ratios and has been shown to be accurate to about 10 percent /23/. The estimate for the burnup should therefore be expected to have about this uncertainty even in the best of cases. Other factors such as variability of noble gas production across the reactor core and variability in irradiation histories may also contribute somewhat to divergences between the data and the theoretical formulas. However, even with an uncertainty of 10 percent, the burnup prediction is still highly useful in distinguishing high burnup from low burnup fuel. If lower uncertainty in the burnup prediction is required for some reason, more accurate modeling of the fuel irradiation may be necessary, but perhaps not sufficient.

These considerations apply equally to the Case 2 simulation.

The Case 2 results have some additional interesting features due to the low burnup. Although the $\chi^2$ is anomalously low, indicating a suspiciously good fit (due to the same considerations discussed above in Case 1), the errors in the burnup predictions are much higher (about 50 percent) than in Case 1. The main reason for this is due to the fact that we are in the low burnup regime, and in this regime, the quadratic term in the production functions is much smaller than in the high burnup case. But if the production function is essentially linear, then, rather than entering as separate variables, $d$ and $B$ enter effectively as the single variable $dB$. The fit procedure then attempts to find the best value of this composite variable.

This predominance of the linear term over the quadratic term in Case 2 is the main reason for the high errors in the burnup estimate. In this case it is only possible to give an upper limit for the burnup prediction. But this is still sufficient to determine that material with a potential military application is being reprocessed.

## 5. Conclusions

With the high measurement precisions currently attainable with sophisticated mass spectrometers, itappears the maximum-likelihood procedure shows promise for determining the correct reactor type, burnup, and dilution factor, for both high and low burnups. These results strongly indicate that the idea of using atmospheric noble gas samples at reprocessing plants for international safeguards purposes is technically feasible.

Furthermore, this problem has several features in common with all EM problems: the selection of an appropriate set of signals; the acquisition of data; and the use of the data to estimate parameters of interest. In this sense, noble gas monitoring serves as a prototypical EM problem.

It is also important to connect the technical analysis presented here with the policy framework in which it is embedded. Recalling the recent developments in international safeguards mentioned earlier, it appears that the noble gas monitoring technique could be a candidate for inclusion in the suite of environmental monitoring technologies the Agency is considering for implementation under Programme 93+2. The method is relatively unintrusive, thereby helping to alleviate concerns from some nonnuclear-weapon states that the improvements of safeguards under 93+2 would be unacceptably burdensome. Whether it will progress to the point where it becomes a standard component of the IAEA's safeguards toolkit, however, depends on many technological, political, and economic factors and remains to be seen.

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