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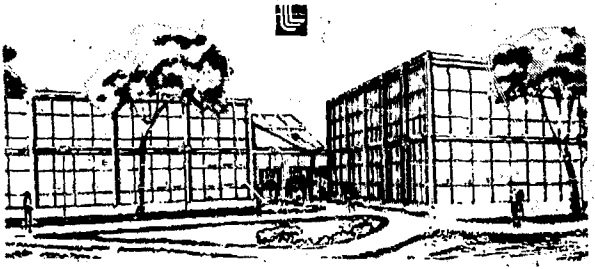

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ACCOUNTABILITY METHODS FOR PLUTONIUM AND URANIUM: THE NRC MANUALS

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ABSTRACT

Four manuals containing methods for the accountability of plutonium nitrate solutions, plutonium dioxide, uranium dioxide and mixed uranium-plutonium oxide have been prepared by us and issued by the U.S. Nuclear Regulatory Commission. A similar manual on methods for the accountability of uranium and plutonium in reprocessing plant dissolver solutions is now in preparation. In the present paper, we discuss the contents of the previously issued manuals and give a preview of the manual now being prepared.

INTRODUCTION

During the past four years, we have been engaged in a program to write and publish accountability manuals for special nuclear materials (SNM), under the auspices of the U.S. Nuclear Regulatory Commission (NRC). The manuals contain SNM accountability procedures that were selected for their reliability and ease of performance in an operating plant. Methods were chosen after a survey of current plant practices, an in-depth review of the literature, and numerous consultations with recognized experts. In the course of writing these manuals, we visited many laboratories, to talk with the staff regarding the accountability methods they use and the problems and pitfalls that they have encountered. We have tried to incorporate as much of this practical experience as possible in our discussion of the accountability methods. The draft of each manual was reviewed by scientists at several industrial and government laboratories as well as at NRC. We carefully considered their detailed comments in the preparation of the final manuscript for publication.

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The purpose of this paper is to make you aware of the existence of these manuals and to tell you of their contents and some of their unique features. We hope that you will use these manuals to help you in the solution of your accountability problems. Although the manuals were written primarily to meet the needs of chemists and managers at fuel fabrication and spent-fuel reprocessing facilities, we feel that anyone who must sample and analyze plutonium or uranium compounds by destructive methods will find them of value. The consideration of non-destructive methods of analysis was beyond the scope of our assignment.

PUBLISHED MANUALS

The four manuals that have been published to date and their availability are listed in Table 1. An additional manual on the accountability of reprocessing plant dissolver solutions is now in preparation.

Each of the published manuals was written to be self-contained, so there is some duplication of material from one manual to another. In those cases where there is duplication it is probably best to consult the Mixed Oxide manual as giving the latest and most definitive information. We have tried to write the manuals so that the user would rarely need to refer to other literature. However, each chapter of each manual is well documented, for those who may desire additional information.

Their Contents

We shall now briefly discuss the contents of the four published manuals, emphasizing any special and unique features.

Sampling

The chapters on sampling contain discussions of some important general sampling procedures and specific properties of the material that bear on the sampling process. In the case of plutonium nitrate solutions, for instance, methods of checking for homogeneity and presence of polymer are suggested. We next give an approach to answering the important question: "How many samples should one take?", based on the permissible variance of the plutonium or uranium factor. Recommended sampling procedures and examples of sampling plans for solutions, powders, pellets

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and scrap are given. We know of at least one situation at a nuclear fuel plant where the methods suggested in one of the sampling chapters were directly applied without modification. The chapter on sampling of PuO_2 is being considered by ASTM Committee C26.06 as the basis for a standard.

Sample Handling

These chapters discuss subsampling and preparation of laboratory samples, containers, handling of the material and pertinent properties.

Dissolution

Dissolution methods that are appropriate for each material are described. The most complete description of techniques for plutonium-oxide-containing materials is given in the Mixed Oxide manual. Discussed are acid dissolutions, fusions, and a combination of the two. The sealed-reflux dissolution system developed by Dahlby et al.[1] at Los Alamos is described in detail.

Assay Methods

Detailed discussions and procedures are given for the following assay methods:

For Uranium

Titrimetric determination
- Davies and Gray/New Brunswick Laboratory modification[2,3]
- Zinc amalgam reduction - dichromate oxidation[4]

Controlled-potential coulometry[5]
Gravimetric determination as U_3O_8

For Plutonium

Controlled-potential coulometry
Amperometry with Fe(II) as titrant[6]

All four uranium methods are useful in the analysis of high-purity material. In the presence of plutonium, such as in mixed oxide, the Davies & Gray/NBL method and controlled-potential coulometry can be used without prior separation. The discussions of these two methods are quite

Atomic abundance values of NBS isotopic standards are commonly corrected for the β-decay of ^{241}Pu to ^{241}Am. Marsh et al.[β] have recently pointed out that the effects of the radioactive decay of ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{242}Pu to their uranium daughters can exceed that of ^{241}Pu decay, depending on the plutonium isotopic distribution of the material. Our mixed oxide manual details the steps to take in correcting isotopic abundance values for the decay of all plutonium isotopes.

Error Analysis

The concepts of limit of error, random and systematic errors, and bias are discussed. Procedures for experimental estimation of error components and calculation of limit of error are given.

CURRENT EFFORT

An additional manual covering "Methods for the Accountability of Reprocessing Plant Solutions" is now being prepared. We have found it more difficult to get information for this manual, since commercial reprocessing experience with LWR fuels in the United States has been limited, and we were not permitted to travel abroad. We have obtained first-hand information from non-commercial reprocessors and from past and future commercial reprocessing operations in this country. We have consulted the literature for available information on reprocessing operations in Europe.

Several special topics must be considered in the preparation of this manual. These include: accountability tank calibration and volume measurement; homogenization of the dissolver solution; remote sampling and handling of samples; determination of SNM content of hulls; isotope dilution techniques; and separation of SNM from fission products and other actinides.

Proposed Contents of the Manual

At the present time, we plan to include the following major topics in the manual. We shall concern ourselves only with the input solution and the waste streams in the separation process, but not with the product solutions, to which the published manuals are applicable.

Volume Measurement and Calibration of Tanks

This chapter will include descriptions of the dip-tube pneumatic bubbler system, density measurements with the Mettler/Paar instrument, and calibration of the input accountability tank.

Sampling

We shall discuss methods for obtaining a homogeneous solution, and establishing sparging and recirculation times. Suggestions will be given on the number of samples and the quantity of solution per sample to be taken. Subsampling and dilution, using remote pipettors and shielded facilities, will be described.

Assay and Isotopic Analysis of Uranium and Plutonium

Isotope dilution mass spectrometry will be the principal technique discussed. X-ray fluorescence as an assay method may also be included, if we are able to obtain more evidence of successful use of the technique in reprocessing plants.

Determination of Plutonium and Uranium in Wastes

For plutonium, selective extraction into thenoyltrifluoroacetone in xylene, followed by alpha counting of the organic phase will be used. For uranium, fluorimetric analysis will be used for low concentrations and spectrophotometry for higher concentrations. We are evaluating several color-forming agents that have been used for uranium, for this application. The determination of plutonium and uranium in leached hulls and in miscellaneous solid waste will be discussed.

Error Analysis

In this chapter, a statistical discussion of the errors involved in volume determination, sampling, assay and isotopic analysis will be given. Propagation of errors will be treated and examples will be given to show how one may calculate the limit of error in the quantity of uranium and plutonium present in a tank of dissolver solution.

ACKNOWLEDGEMENTS

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Table 1. Manuals Prepared to Date for NRC

"METHODS FOR THE ACCOUNTABILITY OF --

PLUTONIUM NITRATE SOLUTIONS"	(WASH-1282)[a]
PLUTONIUM DIOXIDE"	(WASH-1335)[a]
URANIUM DIOXIDE"	(NUREG-75/010)[b]
MIXED OXIDE"	(NUREG-0256)[b]

[a]Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402

[b]Available from National Technical Information Service, Springfield, Virginia 22161.

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