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PLUTONIUM NITRATE SHIPPING INVESTIGATION

by

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Within the AEC complex there has been a long history of shipper-receiver assay differences in the transfer of plutonium nitrate solutions. Since the AEC is considering establishing plutonium nitrate as one of the chemical forms of plutonium for Commission purchase of privately produced plutonium, it is necessary that the shipper-receiver problem be resolved. The program formulated by Rocky Flats for doing this, and the results obtained to date, are discussed.

INTRODUCTION

Plutonium nitrate solution is one of the forms the AEC is considering as a medium for Commission purchase of privately produced plutonium. Within the AEC complex, however, there has been a long history of differences between the shipper-determined and receiver-determined plutonium content of plutonium nitrate solutions. In some cases, this difference has been as high as 3%. The causes for and the conditions relating to these differences have never been adequately defined. It was only logical, then, that before plutonium nitrate was used as a form for the purchase of privately produced plutonium, a thorough study should be undertaken to investigate the problems associated with the shipping of plutonium nitrate. The Commission requested just such a study in August of 1962.

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It was with this request in mind that we at Rocky Flats have undertaken a program whose object is to determine the causes for, and to eliminate if possible, the shipper-receiver differences on shipments of plutonium nitrate. It is this program, its background and the results obtained to date, that will be discussed in this report.

INFORMATION ON THE MAGNITUDE OF SHIPPER-RECEIVER DIFFERENCES

There has been a history in the AEC, as mentioned above, of differences in the plutonium content between the shipper and the receiver of plutonium nitrate solutions. Attempts have been made to determine the cause of this, but to our knowledge no generally applicable explanation has been found.

The best documented data on shipper-receiver differences available to us is information collected at Rocky Flats 7 years ago on 73 batches of plutonium shipped from Hanford to Rocky Flats. The average difference in the plutonium content of these batches was 1.35%, the shipper being high.

In contrast, more recently there has been another, though smaller, series of shipments of plutonium nitrate from Hanford. Even though these batches had been stored in the shipping containers for about 2.5 years, the shipper-receiver difference was much lower (0.29%) and the shipper was low.

In looking for a source of the shipper-receiver differences, one of the first areas of suspicion is the sampling procedure. The design of the sampling procedure used at Rocky Flats for the Hanford material permitted obtaining a measure of the precision of the total sampling procedure, which includes both the sampling and the analytical determination, as well as a measure of the precision of the analytical determination only. The relative standard deviation for the total sampling procedure was $\pm 0.61\%$ while the relative standard deviation for the analytical determination only was $\pm 0.51\%$. This indicates that the total sampling and concentration measurement procedures contribute only a small uncertainty to the total observed shipper-receiver difference of 1.35% ($t = \frac{1.35}{0.61} \sqrt{73} = 18.9$).

Information about the accuracy of the analytical methods used for plutonium analyses is required when the sampling procedures are being evaluated. The most direct way to measure this accuracy is to analyze standards. But at the time this work was being done, there were no accepted analytical standards for plutonium. The most efficient substitute for such standards are exchange samples. In this procedure, each laboratory analyzes the same sample. Under ideal conditions, if any of the laboratories introduce bias, it will be detected. Such a sample exchange was undertaken with the

transfer of frozen plutonium nitrate solutions to three laboratories. The samples were frozen to minimize possible radiation-induced decomposition of the solution. Three groups of five frozen nitrate samples each were analyzed at two of these laboratories and one group of five frozen samples at all three laboratories.

The sources of plutonium nitrate for the sample exchange program were about equally divided between process material and standard material. The standard material was prepared at Rocky Flats by dissolving a weighed amount of analyzed plutonium metal in hydrochloric acid and fuming with nitric acid.

The data on all the sample exchange results are given in Tables 1, 2, and 3. In the bias data, Table 3, note that the difference between the mean values for Laboratories A and B for all 20 samples exchanged is only 0.07 milligrams per gram or 0.05%. This difference is not statistically significant at the 95% confidence level. This, in itself, is particularly interesting because the analytical methods for plutonium analysis used at the two laboratories were independent. Laboratory B used zinc amalgam reduction with standardization against sodium oxalate, while Laboratory A used titanium(III) reduction and standardization against iron. Laboratory C, however, used an X-ray absorption method for their plutonium analysis.

From the data on the plutonium nitrate exchange, it is evident that there is better agreement between the chemical methods at Laboratories A and B than there is between these methods and the physical method used at Laboratory C.

There was another interlaboratory check of the analytical assay methods for plutonium underway at about the same time as the exchange program just discussed. It involved metallic plutonium, however, rather than plutonium nitrate. The results on this program are given in Table 4. Comparing this data with the bias data for plutonium nitrate in Table 3, it is obvious that the general agreement between laboratories is better on metal than on nitrate solutions.

This discussion of the shipper-receiver experience between Hanford and Rocky Flats and the investigation of the sampling and analytical procedures, summarizes the program carried out at Rocky Flats to investigate the shipper-receiver problem. It indicated that the magnitude of the shipper-receiver difference during the period of the study was greater than any of the uncertainties or inaccuracies in the Rocky Flats procedures.

There have been two other programs at Rocky Flats involving the transfer of plutonium nitrate that should be mentioned. Information obtained from them has to be considered in attempting to obtain an understanding of the causes for shipper-receiver differences.

Table 1
Plutonium Nitrate Exchange
Mean Results

<u>Source of Samples</u>	<u>Site of Analysis</u>	<u>Mean Value, mg/ml</u>
Four groups of five (12 proc., 8 std.)	A	135.50
	B	135.43
Four groups of two (8 std. only)	A	157.03
	B	157.35
One group of five (3 proc., 2 std.)	A	145.20
	B	145.76
	C	147.52

Table 2
Plutonium Nitrate Exchange
Precision Data

<u>Source of Samples</u>	<u>Sites</u>	<u>SD *, mg/ml</u>
Four groups of five (12 proc., 8 std.)	A-B	±0.93
Four groups of two (8 std. only)	SV-A	±0.45
	SV-B	±0.55
One group of five (3 proc., 2 std.)	A-C	±1.63
	B-C	±1.82
	A-B	±0.58

*Calculated from difference of results between two laboratories on same sample or between a laboratory and the standard value.

Table 3
Plutonium Nitrate Exchange
Bias Data

<u>Source of Samples</u>	<u>Sites</u>	<u>Diff. Between Mean Values</u>		<u>Diff. Sign. at 95% CL?</u>
		<u>mg/ml</u>	<u>%</u>	
Four groups of five (12 proc., 8 std.)	A-B	0.07	0.05	No
Four groups of two (8 std. only)	SV-A	0.64	0.41	Yes
	SV-B	0.35	0.22	No
	A-B	-0.29	-0.18	No
One group of five (3 proc., 2 std.)	A-C	-2.32	-1.60	Yes
	B-C	-1.76	-1.19	No
	A-B	-0.56	-0.38	No

Table 4

Plutonium Metal Exchange
Bias Data

<u>No. of Samples</u>	<u>Sites</u>	<u>Average Diff., % Pu</u>
30	A-B	0.09
10	A-C	0.08

The first of these programs involved the transfer of two samples of plutonium nitrate received at Rocky Flats from Hanford back to Hanford in Hanford shipping containers. The initial mean shipper-receiver difference (Hanford being the shipper) was 3.3%, the shipper being high. When this same material was returned to Hanford (Rocky Flats being the shipper), the mean shipper-receiver difference was 0.4%, the shipper being high. Note that in both cases the shipper is high, but the size of the difference is distinctly different.

The other program that should be mentioned involved the shipment of plutonium nitrate solutions to Rocky Flats from Oak Ridge. On 25 batches there was an average shipper-receiver difference of 0.1% per batch, the receiver (Rocky Flats) being lower than the shipper (Oak Ridge). A single frozen plutonium nitrate solution was run by both laboratories at the time of these shipments. The results were 42.97 and 42.94 milligrams plutonium per gram sample for Rocky Flats and Oak Ridge, respectively. It should be noted that the Oak Ridge material differed from that received from Hanford in that it contained sulfamic acid which kept the plutonium in the trivalent state.

There are undoubtedly other data on shipper-receiver differences involving other sites. However, the experience at Rocky Flats is probably typical of the shipper-receiver differences experienced at these sites. This experience, combined with information that could be obtained from other sites, was the basis for developing the program for investigating the problems associated with the shipping of plutonium nitrate that will be discussed now.

DEFINITION AND ANALYSIS OF PROBLEM

To determine the possible causes of plutonium nitrate solution shipper-receiver differences, and to eliminate these differences, if possible, a single coordinated program was set up in which the administrator has complete control over both simulated shipping and simulated receiving functions. To develop this program, the problem was defined and the possible causes summarized as shown in Tables 5 through 8.

Table 5

Problem Analysis and Definition

Problem: Shipper Pu Conc. (g/g) x Shipper Weight >
Receiver Pu Conc. (g/g) x Receiver Volume x Density

Possible Direct Causes:

- I. Analytical Bias (S>R)
- II. Bulk Measurement Bias (S>R)
- III. Sampling Bias
- IV. Loss during shipment) Possible, but
- V. Bookeeping errors) unlikely.

Table 6

Problem Analysis and Definition

I. Analytical Bias (S>R) - Possible Causes

- A. Shipper's and/or receiver's methods not properly standardized.
- B. Pu in solution non-reactive because of instability resulting from shipping (e.g., colloid or polymer formation).
- C. Pu in sample non-reactive or non-homogeneous because of change after sampling but before analysis (e.g., post-precipitation).

Table 7

Problem Analysis and Definition

II. Bulk Measurement Bias (S>R) - Possible Causes

- A. Shipper's and/or receiver's bulk measurement method not properly calibrated.
- B. Incomplete transfer of plutonium from shipping to measuring container or vice versa.
- C. Inaccurate measurement of amount of "heel" or other residue in shipping container or transfer equipment.

Table 3

Problem Analysis and Definition

III. Sampling Bias - Possible Causes

- A. Inaccurate sample of shipping solution by shipper and/or receiver (e.g., contaminated sampling system).
- B. Non-homogeneity of shipping solution because of instability (e.g., polymer or precipitate "plating out" on vessel walls).

In defining the problem, the possible causes for the shipper-receiver differences were placed in three categories: analytical bias; bulk measurement bias; and sampling bias. From a more practical viewpoint, these causes could also be arranged in five more functional areas as shown in Table 9. It was from the causes as expressed in Table 9 that the following plan for investigation was developed.

Table 9

Causes of Shipper-Receiver Differences

1. Analytical method standardization error.
2. Plutonium solution instability.
3. Bulk measurement calibration error.
4. Contamination during sampling.
5. Incomplete cleanup of shipping container.

PLAN FOR INVESTIGATION

The investigation of the possible causes for the shipper-receiver differences is divided into four technical phases:

Phase 1 - Plutonium Solution Instability

The objective of this part of the program is to determine the most likely composition of plutonium nitrate shipping solutions, study the stability of these solutions and, if they are found to be chemically unstable, develop adequate analytical methods for determining their plutonium content.

Phase 2 - Bulk Measurement and Sampling

The objective of this work is to develop adequate procedures for bulk measurement, complete transfer, agitation, and sampling of the plutonium nitrate solutions. Equipment will also be set up so that these procedures can be applied to the bulk shipping solutions used for Phases 2 and 4 of this work. It is hoped that errors affecting the plutonium balance can be eliminated from these operations.

Phase 3 - Optimum Shipping Container

While a standardized shipping container may not be necessary to assure accurate transfers of plutonium nitrate solutions, there are some advantages inherent in being able to write standard bulk measurement, sampling, agitation, and transfer procedures for a specific shipping container. Therefore, work will be undertaken on the design, construction, and testing of optimum shipping containers. This requires detailed considerations of nuclear safety, health physics, shipping hazards, transfer and bulk measurement problems, and effects of container materials on solution stability.

Phase 4 - Verification of Procedures

To demonstrate the adequacy of the methods, procedures, and equipment developed in the first three phases of this investigation, an actual shipment of 6-12 shipping solutions will be made to another site for plutonium content measurement. The objective will be to prove the adequacy of all procedures recommended as a result of this program.

In the detailed planning involved in setting up the work in the program, a work flow or critical path diagram was used. It is anticipated that 18 months will be required to complete the program. The work began in February of 1963 and will be completed in August 1964.

SUMMARY OF WORK TO DATE

Phase 1 - Plutonium Solution Instability

A literature survey of possible causes for plutonium nitrate solution instability was made⁽¹⁻⁸⁾. The two most probable causes of solution instability are the formation of plutonium(IV) polymer and the formation of insoluble plutonium compounds with a number of anions.

The rate of formation of the polymer is a function of the plutonium(IV) concentration, temperature, acid concentration, electrolyte concentration, complexing agent concentration, etc. The polymer is not in equilibrium with the monomer. Depolymerization can be a very slow process. Guidelines for handling the nitrate to prevent formation of the polymers might be as follows: (a) never let the acid concentration get below 0.3 to 0.5 normal and (b) never dilute plutonium(IV) solutions with water, always with acid.

Although plutonium(IV) can form insoluble compounds with a number of inorganic anions, these anions are seldom present in plutonium nitrate solutions prepared by current production techniques. Organic compounds resulting from degradation of anion exchange resins can also precipitate plutonium, but, by careful selection of resins and operating conditions, degradation can be minimized.

An experiment has been set up to study the factors that would most likely affect solution stability. These factors and the levels at which they were investigated were determined from available information on processes used in the production of the plutonium nitrate solutions. These factors and their levels are shown in Table 10.

Table 10

Study of Plutonium Nitrate Solution Stability

<u>Factor</u>	<u>Level</u>	
	<u>Low</u>	<u>High</u>
HNO ₃ conc.	2N	5N
Pu conc.	50 g/l	215 g/l
Impurity conc.*	None added	Max. added
Temperature	Ambient	Cycled **

* Impurities added - Fe, Cr, Ni, Sulfate.

** This cycle is to simulate a cross-country shipment.

Phase 2 - Bulk Measurement and Sampling

Bulk measurement and sampling have to be considered in the design of a shipping container. Nuclear safety and the size of the container, for instance, have to be compatible with the accurate and precise bulk measurement and sampling of the plutonium nitrate solution within the container. The people responsible for the measurement aspect of this investigation are working closely, therefore, with those who are concerned with the shipping container design.

Some preliminary investigative work is underway in which plutonium nitrate solutions are being stored in small plastic bottles under varying conditions of agitation and temperature. The quantity of plutonium put in these bottles was initially measured on both a weight and volume basis. When, after storage, the solutions are removed and the plutonium content redetermined, an estimate of measurement errors will be available. This information can be applied to the work with the large shipping containers.

Phase 3 - Optimum Shipping Containers

Two container designs have been developed. One design is for a relatively small container (3-10 liters) and the other for a large container (15-100 liters).

Both designs are basically a container within a container. In the smaller one, the inside container is a plastic bottle with a diameter of 11.5 cm inside a stainless steel pressure vessel. This bottle can be removed from the pressure vessel for measuring and transfer of the plutonium solution. The outside container is a drum (diameter of 22 inches) whose height is governed by the size of the plastic bottle inside. For a plastic bottle containing 3 liters, the height of the outside container is that of a standard 55-gallon drum - 34 inches. Between the inside (pressure vessel) and outside containers, there is the necessary shielding materials

(cadmium and wood) to make the total container meet AEC Class I shipping container requirements, i.e., nuclearly safe in any number and in any arrangement even after involvement in a serious accident.

The large container consists of a 2-inch diameter pipe wound on a 4-foot diameter coil. The volume of this container can be varied by changing the number of coils. Fifteen turns give a 100-liter volume while 2.5 turns will give approximately a 15-liter volume. This coil of pipe is set in epoxy resin and this is surrounded with the necessary cadmium and wood to give a nuclear safe container to meet Class I shipping requirements. The total container has a diameter of 72 inches and a height of 52 inches for the 15-liter version and the same diameter but a height of 80 inches for the 100-liter version.

Each of these designs has specific advantages which, if either is finally recommended, depend on whether a batch tank can be sampled or whether each individual shipping container must be sampled. It also depends on further experience with prototypes of the tanks themselves to see what measuring, sampling, and construction problems develop.

Phase 4 - Verification of Procedures

This work will be the last undertaken in this program and it has not yet been started.

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