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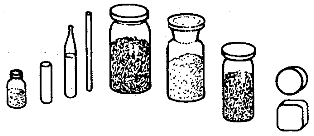

Standard Reference Materials:

ANALYSIS OF URANIUM CONCENTRATES AT THE NATIONAL BUREAU OF STANDARDS

U.S. Department of Commerce

National Bureau of Standards

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Standard Reference Materials:

Analysis of Uranium Concentrates at the National Bureau of Standards

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Institute for Materials Research
National Bureau of Standards
Washington, D.C.

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PREFACE

Within the framework of the NBS Institute for Materials Research the area of standard reference materials is a broad and important one, including the preparation, characterization and distribution of a wide variety of materials in such diverse fields as metallurgy, polymers and inorganic materials. In carrying out such a program there is much interaction with representatives of industry and science, beginning with discussions as to which primary standard materials will do most to advance technology, the furnishing of materials and fabrication of samples, and the characterization and certification of the materials by cooperative efforts. The many groups participating in a standards program are very interested in detailed information on specific aspects of the program -- but to date there has been no publication outlet for such written discussions.

To meet this need, NBS Miscellaneous Publication 260 has been reserved for a series of papers in the general area of "standard reference materials". This series will present the results of studies and investigations undertaken within the Institute for Materials Research with emphasis on the preparation and characterization of standard reference materials. This subject-oriented series will provide a means for rapid dissemination of this detailed information and we hope will stimulate the use of standard reference materials in science and industry.

W. Wayne Meinke, Chief
Office of Standard Reference Materials

OTHER NBS PUBLICATIONS IN THIS SERIES

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STANDARD REFERENCE MATERIALS:
ANALYSIS OF URANIUM CONCENTRATES AT THE NATIONAL BUREAU OF STANDARDS

M. S. Richmond

Institute for Materials Research
National Bureau of Standards

ABSTRACT

NBS experiences with the problems of assaying uranium concentrates are described. Umpire determinations of uranium were performed on several thousands of ore concentrates from world-wide sources. Contributions were made to the resolution of the sampling base line problem. Also, it was demonstrated that the standard U_3O_8, NBS No. 950a, provides the over-all standard necessary for precise assay of uranium materials. A comprehensive analytical procedure applicable to all types of uranium concentrates is presented.

Key words: analytical procedure, assay, ore concentrates, sampling base line, standard U_3O_8, umpire determinations, uranium concentrates.

1. INTRODUCTION

The development of atomic energy for military purposes opened a new era in the analysis of uranium materials. In a general history of the development of the first atomic bomb, Smyth [1] has noted the analytical contributions between 1939-42 by C. J. Rodden and others at the National Bureau of Standards. By 1943, this Bureau had established a separate section headed by Rodden to handle uranium analytical problems. The section rapidly expanded to a level of about 20 employees concentrating on development and control activities through the war years.

The breakdown in 1946 of international negotiations for the control of atomic weapons was followed by a renewed urgent military demand for uranium. Between 1949 and 1959 the expenditures of the U. S. Atomic Energy Commission for the production of uranium concentrates increased some 30-fold to more than $600 million per year.

As the AEC sought production from every available source, domestic and foreign, there was a rapidly expanding analytical load. However, most commercial and industrial laboratories had little experience in analyzing uranium materials, and many of the analytical methods developed or improved during the war were classified or not available for publication. This situation led to the establishment of new AEC laboratories including the New Brunswick Laboratory (NBL) at New Brunswick, N. J. NBL was to carry on the control activities and special problems that Rodden's group had handled at NBS; consequently most of that group transferred to the AEC when NBL opened in April 1949.

However, uranium procurement was still largely from foreign sources, and the foreign contracts with AEC provided for umpire determinations to be made at NBS. At the request of the AEC, this Bureau has continued both foreign and domestic umpire work through June 30, 1965. NBS has also conducted special studies leading to a better understanding and control of some of the sampling and analysis problems of uranium concentrates.

The foreign phase of the umpire work has involved laboratories representing Belgian, South African, Canadian, Australian, or Portuguese producers and one or more of the U. S. A.E.C. laboratories at Fernald (NLO), Weldon Spring (MCW), Paducah (GCD), or New Brunswick (NBL).* The domestic work mainly involved 22 Colorado Plateau producers and the AEC laboratories at Grand Junction (LPI) and Weldon Spring (MCW). NLO's direct connection with the domestic uranium umpire work was limited to a few samples of by-product concentrates derived from phosphate materials and sampled at Fernald. Altogether, NBS was called upon to assay concentrates from more than 50 different mills including about 29 in the western United States and 14 in Canada.

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* Except for NBL, the abbreviation identifies the contractor operating the laboratory, as follows: (NLO) National Lead Company of Ohio, (MCW) Mallinckrodt Chemical Works, (GCD) General Chemical Division of Allied Chemical, and (LPI) Lucius Pitkin, Inc.

Each lot of concentrate was officially weighed and sampled at one of the central processing facilities. The official samples, representing a lot weight of 4,000 to 60,000 pounds, were assayed for uranium by the AEC (at the processing facility) and by the seller (at his mill, usually). If the two assays agreed with the preset splitting limit*, the average of the two assays was the basis of settlement. The splitting limit was 0.3 percent U_3O_8, or more, in the early fifties, but has been reduced to 0.2 percent U_3O_8 in recent contracts. When the splitting limit was exceeded, a reserved sample was sent to NBS for umpire analysis. This generally occurred in the case of 10 to 20 percent of the lots, but in 1953-54 serious difficulties in the analysis of South African concentrates resulted in the majority of the purchased lots requiring umpire analysis.

During fiscal years 1953-57, the number of umpire requests ranged between 170 and 300 per year. The later rapid development of new sources of uranium production led to about 500 umpire requests in fiscal year 1958, and 900 in 1959. AEC procurement of uranium reached a peak of around 35,000 tons of U_3O_8 in fiscal year 1960, but by then the major sampling problem had been solved and the requests for umpire analyses had dropped back to about 500 per year.

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* The splitting limit is the maximum allowable difference between two assays.

Now the need for an uranium umpire program at NBS is obviated. Sampling and assay problems are better understood, generally reliable sampling procedures have been developed, the black oxide standard reference material, NBS No. 950a, has been accepted as a satisfactory uranium assay standard, and the AEC's foreign contracts are nearing expiration. Consequently a close-out of the program is underway, and this publication has been prepared to set down a comprehensive and detailed account of the program at NBS as a guide for the use of future umpires and other groups analyzing uranium.

2. THE PROBLEM OF SAMPLING WEIGHT BASE LINE

A. Basis of Choice

The primary problem in the assay of uranium concentrates was the establishment of a reliable sampling weight base line. The normal commercial practice of drying to constant weight is very unsatisfactory for the complex salts in uranium chemical concentrates. These materials usually contain 40 to 80 percent uranium, and assorted impurities, including vanadium, iron, arsenic, molybdenum, copper, and thorium in varying amounts. They may also contain considerable amounts of ammonia, magnesium, sodium, calcium, sulfate, phosphate, and/or halogens, depending on the production process. The impurities differ not only from mill to mill but from time to time at a given mill, e.g., lot moisture may range from 0.00% to 10%, sodium from 0.1 to 9%, and sulfate from 0.1 to 13%.

For these hydrated concentrates, the so-called "drying-to-constant-weight" basis actually varies according to the moisture content of the ambient atmospheres under which measurements are made. At NBS the moisture content of laboratory atmosphere ranges widely, e.g., between 0.002 and 0.010 g H_2O/g dry air in November 1953 and between 0.008 and 0.018 in August 1953. Equally large variations probably occur at Fernald, Weldon Spring, New Brunswick, South Africa, and at some of the mills in the western United States. At Grand Junction, on the other hand, the normally dry atmosphere shows relatively little variation. Since contract settlements depended on the agreement of assays performed under these variable conditions, there was a need for a sampling procedure that did not require drying to constant weight.

B. Historical Review.

The existence of a drying problem was noted in 1950 in connection with an African concentrate known as MgX, containing about 30 percent uranium; NBL observed that results for "loss-on-drying" were more constant when obtained in a constant humidity room instead of the usual laboratory, and also that dried MgX seemed to pick up water from desiccants other than magnesium perchlorate. However, the full scope of the problem was not recognized for several years.

The extent of the correlation between assay results and laboratory atmospheric conditions was most readily apparent to the umpire. Each AEC (processing plant) laboratory handled only certain types of materials, assayed large numbers of samples, and tended to assay samples soon after their preparation and with the minimum of natural climate variation. On the other hand, the umpire performed relatively few assays, received samples from all problem areas, and performed its analyses from weeks to months after the bottling of the samples.

By 1951 NBS was correlating the erratic interlaboratory biases reported by AEC statisticians with probable differences in laboratory atmospheric conditions. Producers, vendors, and samplers were still prone to attribute interlaboratory disagreements to assaying or sampling practices of "the other party," and to propose evaluation of assay comparisons by means of standard samples of uranium concentrates. NBS, however, emphasized that the specification of drying conditions was a primary problem that must be solved before the standard samples could be established. In 1951 NBS studied the effect of "dry" air (passed over indicating silica gel) on the rate and extent of loss at 110 °C for MgX material. The loss values were increased as much as two percent of the sample weight when the ambient air in the oven was replaced with drier air. Also, reproducibility was much better and the time required for reaching relative equilibrium was reduced from a highly variable number of days to one overnight drying interval. The dry-air basis seemed adequate for interlaboratory assay comparisons, but the sampling plants wanted an easier way of getting the official lot weight on the same basis as the assay samples.

In 1953 T. W. Steele of the Government Metallurgical Laboratory in Johannesburg, South Africa, investigated the effect of calcining temperature on the stability of uranium precipitates and explained the results in terms of the hygroscopic nature of UO_3 formed when the bulk product was calcined in trays at 500 °C [2]. Subsequently, Calcined Products (Pty.) Ltd. handled the drying problem by splitting a portion from the 500-°C-calcined, bulk sample; further calcining the split portion to 900 °C; and having all assays made on the 900 °C-calcined portion.

In 1952 NBL and NLO had begun investigating the use of a mixer-blender for preparing official samples of MgX material. Their studies indicated that the blended material might be bottled, sealed, and stored without changing in assay, and by 1954 NLO was blending entire lots and packaging samples for assay on an "as is" basis. Rodden [3] reported at Geneva in 1955 that the mixer-blender method had "been used with some success". However, subsequent experience showed that the base line weight difficulties were far from ended.

With increasing use of the blender method, bottle sealing troubles became evident. Several years elapsed before the closure problem was resolved and satisfactory sealing procedures were established. In the meantime, NLO intensively investigated the drying behavior of a wide variety of concentrates to determine the minimum amount of control required to yield reproducible moisture-loss values. Some of the NLO results have been published by Valent and Gessiness [4].

C. NBS Studies.

Between 1956 and 1959, NBS investigated the sampling base line problem from three directions. The study of the closure problem for INX material (an African concentrate assayed on the "as is" basis) is described below with additional details in Appendix A. The interlaboratory standards program of 1958, coordinated by the AEC Grand Junction Office, is described in Appendix B. The special drying studies of a few samples of two domestic by-product materials, IMCC* uranous fluoride concentrate and Blockson phosphate, are summarized below and briefly described in Appendixes C and D.

The INX material containing about 60 percent uranium and 10 percent water, was packaged in 30- to 40-g units in conventional glass bottles closed with hard plastic screw caps and plastic tape covered with sealing wax. The analyst received triplicate units from a lot and was requested to remove the so-called "seal", immediately weigh the sample, dissolve the entire sample and analyze an aliquot. However, at NBS 1- to 2-g samples from each of two bottles were analyzed and, if the results agreed within 0.2 percent, the third bottle was reserved unopened. Assay agreement was satisfactory within bottles, but often poor between bottles as illustrated in table 1, and very bad between laboratories as illustrated in table 2. NBS averaged 0.70 percent U_3O_8 higher than the AEC values for the 12 lots listed in table 2.

INX material appeared to be finer than 200 mesh; but the vendor stated there was significant agglomeration due to the high moisture content, and found up to twice as much moisture in coarse agglomerates as in the finer portion. The vendor insisted the assay disagreement was a segregation problem and complained because NBS continued to use 1- to 2-g samples. However, NBS had checked its results with enough 10-g samples to

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* International Minerals and Chemical Corporation.

Table 1. Contrast of "between bottle" and "within bottle" agreement, as shown by NBS individual assay results, for six bottles of two INX lots sealed 2-6-57.

Bottle Storage			Sample		Percent U_3O_8	
NBS No.	Months Stored	Date Opened	Weight (g)	Aliq. No.	Assay	Difference
6-A	3-	4-25	1.48[a]	1	64.42	0.00
				2	(64.48)[c]	(.06)
			1.59[b]	1	64.42	.00
6-B[d]	3-	4-25	1.53[a]	1	64.93	.51
				2	(64.99)	(.57)
			1.52[b,e]	1	64.98	.56
6-C[d]	4	6-4	1.50[a,f]	1	64.75	.33
			1.47[b,g]	1	64.76	.34
7-A	3-	4-25	1.51[a]	1	66.67	0.00
				2	(66.70)	(.03)
			1.48[b]	1	66.65	- .02
7-B	3-	4-25	1.47[a]	1	66.21	- .46
				2	(66.27)	(- .40)
			1.61[b,e]	1	66.26	- .41
7-C	4	6-4	1.51[a,f]	1	66.47	- .20
			1.52[b,g]	1	66.41	- .26

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[a] Analyzed by chemist H except for reduction and titration by chemist R.

[b] Analyzed by chemist R.

[c] Parentheses indicate values not corrected for minor volume changes (~0.05 ml).

[d] Very poorly sealed; the tape was not smooth and only partially covered by wax.

[e] Had extra treatment with cupferron.

[f] Had extra treatment with HF.

[g] Had extra treatment with HF, cupferron, and $HClO_4$.

Table 2. Interlaboratory disagreement of assay results for 12 INX lots bottled between September 1956 and March 1957.

Storage of NBS Bottles[a]				Percent U_3O_8			
NBS No.	Date Sealed	Months Stored	Date Opened	Assay AEC	Difference from AEC[b]		
					Vendor	NBS	Accepted
1	9-29	5+	3-4	71.29[c]	-0.33	0.41	0.00
2	10-1	5+	3-4	71.45	- .43	.44	.00
3	11-28	5-	4-25	62.44	+ .53	.82	.53
4	2-5	3-	4-25	60.81	+ .60	.47	.47
5	2-5	3-	4-25	63.00	+ .79	.68	.68
6	2-6	3- 4	4-25 6-4	63.91	+ .40	.80	.40
7	2-6	3- 4	4-25 6-4	65.48	+1.42	.96	.96
8	2-7	3-	4-25	69.31	- .36	.71	.00
9	3-1	3	6-4	71.87	+1.84	1.16	1.16
10	3-1	3	6-4	72.26	+3.10	.74	.74
11	3-1	2-	4-26	70.14	+ .64	.50	.50
12	3-4	3	6-4	70.31	-1.10	.69	.00
Average		3+			+0.59	+0.70	+0.45

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[a] Includes storage by AEC before exchange of AEC-vendor results, plus storage by NBS due to a backlog of work. AEC assays (at the sampling plant) normally were made a day or two after sealing; and vendor assays, some days or weeks later.

[b] The contract specified acceptance of the middle assay value for umpired samples.

[c] Underlined values were accepted.

be convinced that segregation was not the major problem, and was investigating the dependability of bottle closures. By March 1957 NBS demonstrated there could be a significant exchange of moisture between the sample and the bottle caps, especially those containing paper sub-liners.

As detailed in Appendix A, six bottles were marked and carefully cleaned (inside and/or outside as appropriate) before their base weights were obtained. The controls (No. 1 and 2) had been emptied of sample and were kept loosely-closed except during extra weighings of bottles and caps. Bottles No. 3, 4, 5, and 6 each contained INX material and were left closed as received. Bottles No. 1, 3, and 5 were stored over "saturated NH_4NO_3" in a closed container*, and bottles No. 2, 4, and 6 were stored in a desiccator freshly charged with Anhydrone at the start of the experiment.

Observed weight changes are summarized in figures 1 and 2. The results for the loosely-closed, empty bottles, No. 1 and 2, indicated that (1) within three months a <u>dry</u> cap could absorb at least 0.35 g of water from the moist atmosphere in equilibrium with 40 g of INX material, (2) the absorption by the cap continued for months but at a gradually decreasing rate, and (3) the initial rate of this change could be great enough to cause significant assay differences even within the first two days after the sample was bottled.

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*The atmosphere in equilibrium with saturated NH_4NO_3 at 25°C contains about 0.012g H_2O/g dry air (equivalent to 60% relative humidity at 25°C).

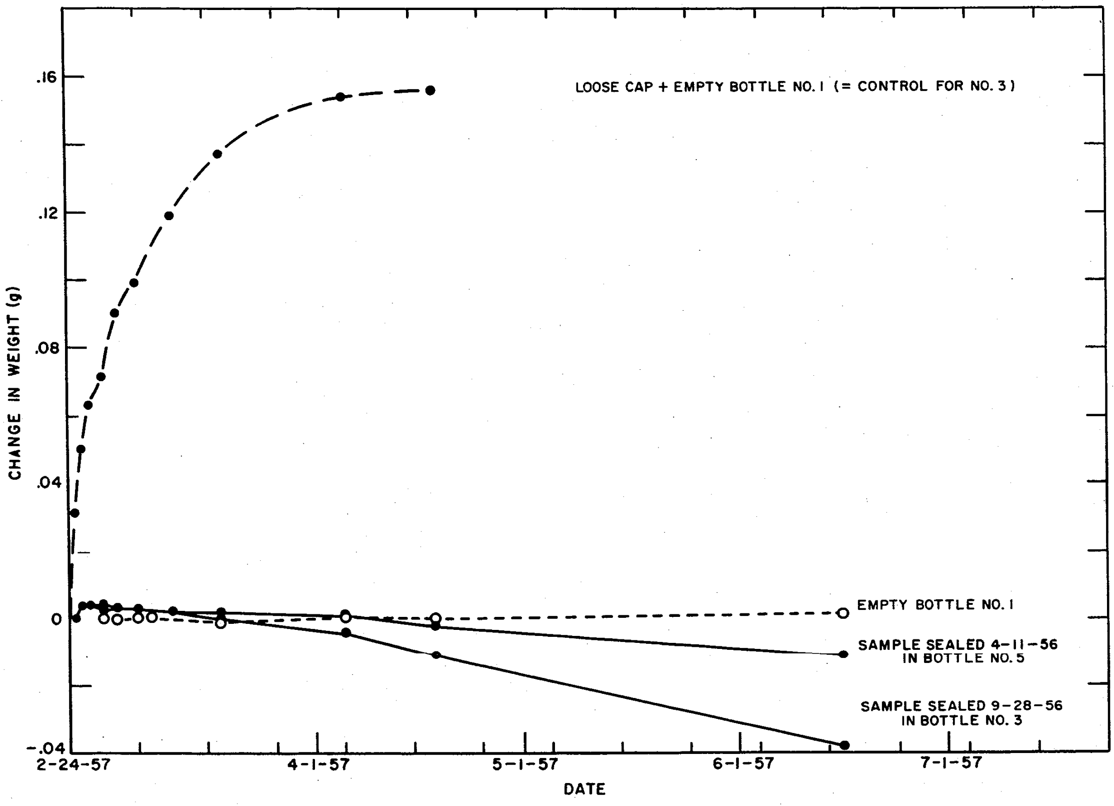

Figure 1. Change in weight of INX samples and/or caps during storage in a humid atmosphere (about 0.012 g H_2O/g dry air).

The caps were made of hard black plastic and lined with plastic or metal foil. The relative tendency of the different parts of the taped and waxed cap to lose moisture is indicated in figure 3.

Variations in closure quality were observed also, as follows: (1) there were differences in the extent to which the plastic tape around the cap was covered with sealing wax; (2) when the bottles were first opened, the caps usually were

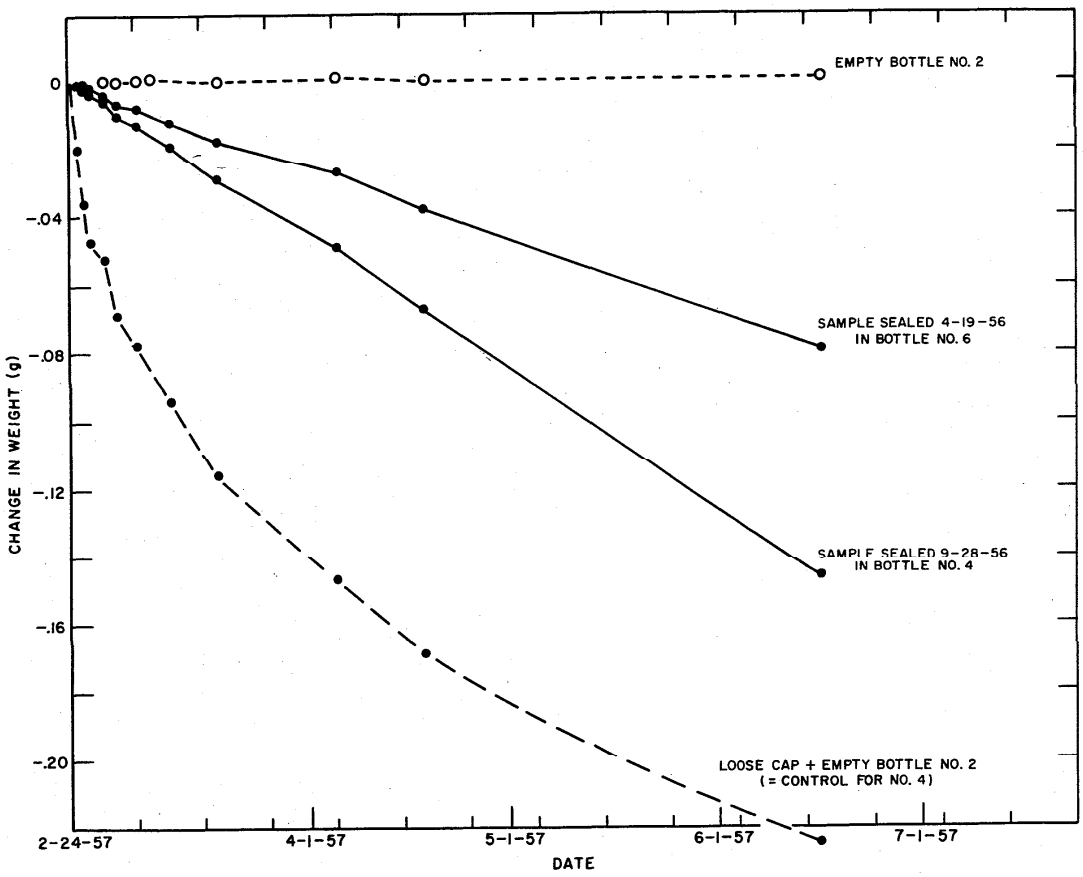

Figure 2. Change in weight of INX samples and/or caps during storage in a dry atmosphere (over Anhydrone).

easy to turn; (3) cap liners for a single lot were not identical (e.g., some were covered with metal foil and some with plastic); and (4) a little sample material was often present between the cap and the top of the bottle. The data in figures 1 and 2 indicated that the rate of leakage from the "sealed" bottles, No. 3, 5, 4, and 6 was (1) different for each bottle; (2) relatively constant for a given bottle except

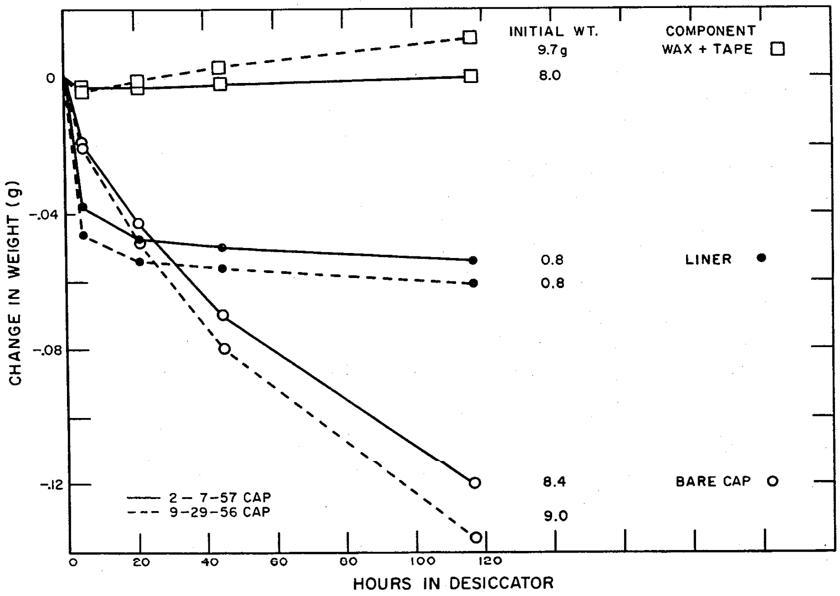

Figure 3. Change in weight of separate components of INX bottle caps during storage in a dry atmosphere (over Anhydrone). (Base weights were obtained on 6-26-57, after separating the parts and exposing them to room air for two hours.)

during the initial weeks in the humid atmosphere (i.e., after the taped and waxed cap was near equilibrium with the surrounding atmosphere); and (3) large enough to account for assay differences up to 0.3 percent in four months.

Thus, it became apparent that the original "as is" INX material was losing varying amounts of moisture by diffusion either past the closure, to the cap, or both. Since AEC assays were performed at the sampling plant, usually a day or two after the bottles were sealed and probably before the vendor received his samples, it was concluded that the AEC results should most nearly represent the true assay of the gross lot.

On this basis, the accepted values for the 12 lots listed in table 2 probably averaged 0.45 percent high. The +0.7 percent average bias of NBS in table 2 was attributed to a combination of the factors involved in the three-month average storage time: the initial dryness of the caps, the quality of the seals, and the storage conditions. The magnitude of the bias was in line with the storage time, the experimental evidence (see figures 1 and 2) that a <u>dry</u> cap could absorb water equivalent to an INX weight loss (or higher assay) of nearly one percent, and the evidence (see table 1 for results from duplicate bottles with duplicate storage history) of 0.4 to 0.5 percent U_3O_8 differences due to the different quality of seals.

The IMCC and Blockson concentrates presented more specialized aspects of the sampling base line problem. Although IMCC material containing sulfate and/or phosphate as well as fluoride, could be dried to a reproducible state at 110 °C in a controlled moist ambient atmosphere (equivalent to 60 percent relative humidity at 80°F), this hygroscopic material gained as fast as 0.3 percent per hour and up to a total of two or three percent, with subsequent loss of hydrogen fluoride during storage or drying. For each of three umpired samples, four laboratories agreed within 0.30 percent on the "as is" basis, but one of the laboratories was about one percent high on the dry basis, presumably due to faulty storage or drying (i.e., the laboratory did more than remove the moisture absorbed after the sampling plant dry weight basis was established). NBS drying tests on IMCC material are described in Appendix C.

Two lots of Blockson material gained up to two percent during ordinary "drying" and lost up to one percent when heated to the same temperature in bone-dry air. The special drying procedure and additional details of the tests on Blockson material are given in Appendix D.

D. Resolving the Base Line Problem.

The breakthrough on the closure problem began in 1956 when Lucium Pitkin, Inc., used Mason jars for bottling Anaconda material in Grand Junction. The Mason jar lids were not lined and had a thin rubber gasket that gave a good seal and thus permitted assay on the "as is" basis.

Grand Junction continued to use the so-called "dried-to-constant-weight" basis until late 1959, but actually this was more of a "vacuum canned" basis because material dried at 110 °C and immediately put into warm sample bottles in the dry, low-pressure atmosphere of Grand Junction tended to be vacuum sealed on cooling to room temperature. When such samples were heated at 110 °C at NBS they usually gained instead of losing; any gain was reported as "0.00% loss", and thus made the "dry basis" equal to the "as is" basis. NBS early noticed that many of the Grand Junction samples were received under vacuum and that on such samples good assay agreement with Grand Junction was obtained on the "as is" basis.

By the fall of 1958, after initiation of the interlaboratory standards program described in Appendix B, the Grand Junction sampling plant was deliberately "vacuum canning" its samples. The laboratory samples were put in "baby food" bottles of the press-on type; all bottles were put in the oven together for a final drying and then rapidly capped and sealed while still hot [4-b]. Also, it had become standard practice at NBS to take all assay samples of Western materials immediately after the sample bottle was first opened. As might be expected, no loss-on-drying was found unless the vacuum seal had been broken prior to sampling. Furthermore, NBS "as is" results agreed well with Grand Junction results, indicating: (1) the adequacy of the assay procedures, (2) the absence of storage and moisture factors in the Grand Junction analysis, and (3) the effectiveness of "vacuum canning" in avoiding changes due to storage conditions. Finally in late 1959 Grand Junction, with the support of NBS, eliminated the laboratory-moisture determination for Western concentrates and officially adopted the present practice of hermetically sealing analytical samples at the same time, and under the same atmospheric conditions as those under which, the sampling plant performs the moisture determination .

E. Effectiveness of Present Sampling Procedures

An evaluation of several sealing methods at MCW has been described by Nelson, Kneip, and Mohl [5]. Since 1960, the effectiveness of uranium sampling procedures has also been checked by means of the AEC General Analytical Evaluation Program. This program, coordinated by the U. S. AEC's New Brunswick Laboratory, and designed to permit the various laboratories performing analyses for the Commission to evaluate their performance, was extended to uranium concentrates after the establishment of the hermetic-seal bottling method. From 1961 to 1964, the program dealt with four types of concentrates each year. A reference or "known" sample was prepared for each of these concentrates. Once a month each cooperating laboratory received four samples, in any combination of materials, both production and disguised reference samples, so that at the end of the year there were 12 results from each laboratory on each of the 4 materials. Six of the results were on the monthly production lot samples and six on the reference samples. The only analysis made was the U_3O_8 assay on an "as received" basis. The gross weight of each sample was noted at the time of bottling and again at the time of analysis; if leakage had occurred that bottle was omitted from the study.

All results have been evaluated in annual reports by Roszkowski, Mullin, and Lanza [6]. Although true uranium values are not known for the reference materials, the results have disclosed significant differences among the laboratory averages each year, and the presence of statistically significant changes in laboratory relationships during the first two years. There was decided improvement in laboratory agreement for the third year over that of the first two years, as shown in figure 4. Interlaboratory agreement has shown little if any relation to the particular uranium concentrate analyzed; usually, if a

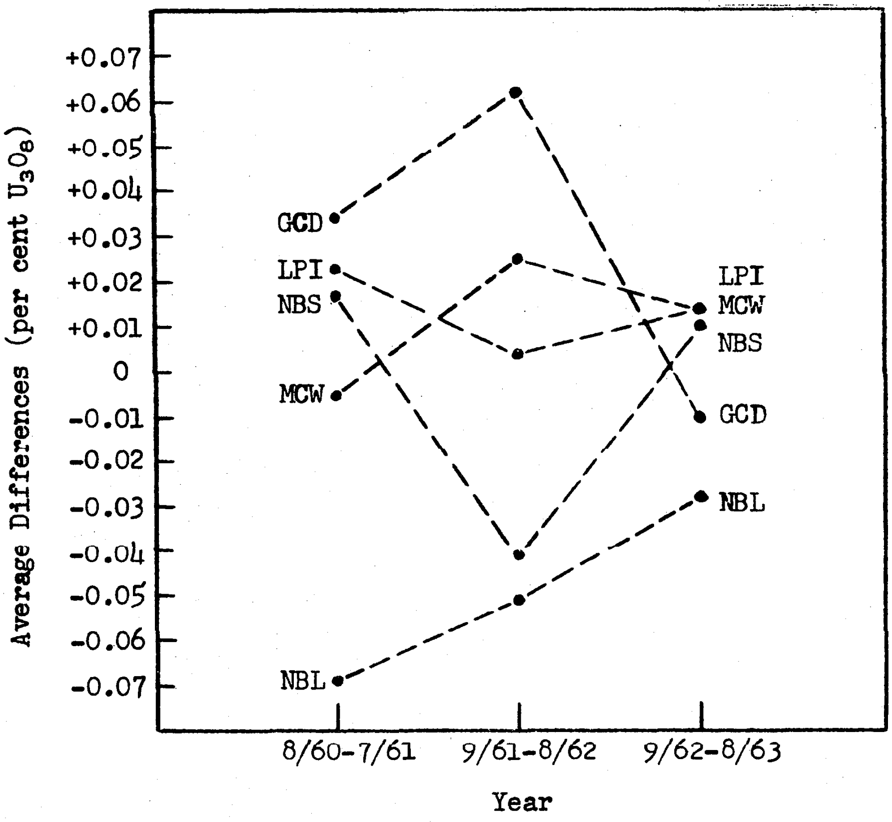

Figure 4. Relative laboratory positions and average differences from overall averages for three years. See [6], NBL-203, p. 9.

laboratory showed a bias on one material, it showed a similar bias on other materials.

Although the reproducibility between bottles of a material has been generally good, there was a large difference in reproducibility for two reference materials studied in 1964. This is shown in figure 5, where each point represents the assay of one bottle of material. For the Climax material, the inner, solid lines represent 95 percent confidence limits for the

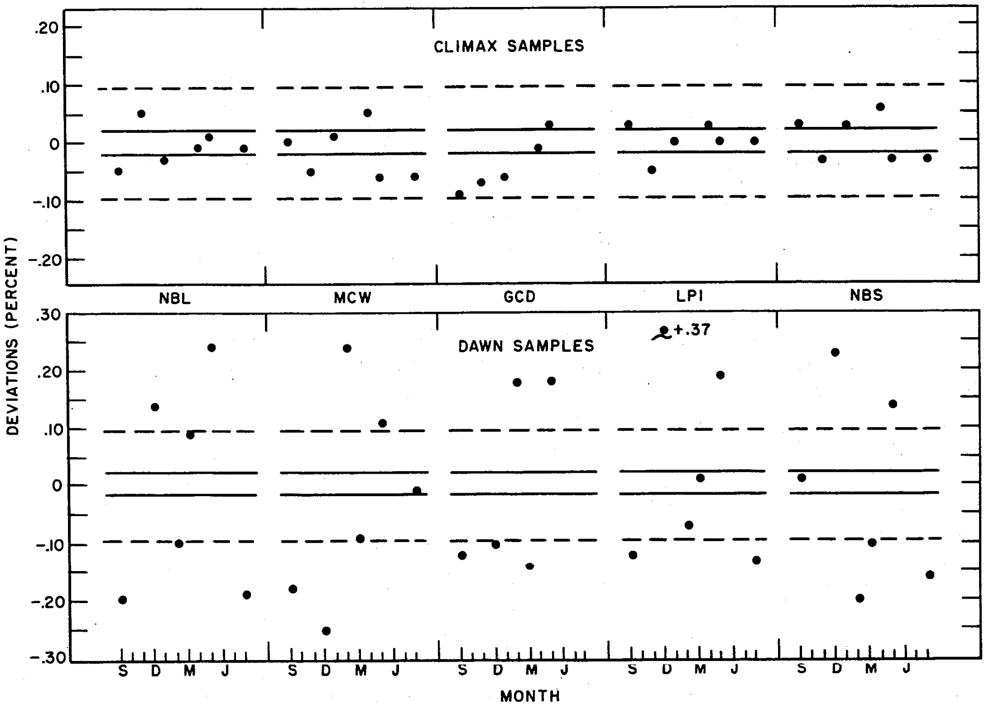

Figure 5. Deviations from average U_3O_8, for two reference materials in 1963-64.
See [6], NBL-221, pp. 28, 31.

laboratory averages, and the outer, dashed lines represent 95 percent confidence limits for a single plotted point. Bottling reliability has been greatly improved since the 1950's, but the variability of the Dawn reference material indicates that unsuspected sampling variations may still occur. This emphasizes the continued need for basing assay evaluations on a standard of known composition, such as NBS No. 950a. The effect of variations in composition on the assay can still be determined by adding approximate amounts of appropriate impurities to known amounts of uranium.

3. DEVELOPMENT OF PROCEDURES

As the umpire, NBS has received a wide variety of samples from more than 50 producers, but only spotty knowledge of the sources, production methods, and total composition of individual samples. Consequently, the assay method was chosen for its general applicability to accurately assaying relatively small numbers of samples originating from a variety of materials. This eliminated the need for varying the method with type of concentrate. One basic procedure was used for all uranium umpire samples except for a few that were either of low uranium content or of refinery grade. The basic procedure was designed for materials containing at least 50 percent uranium and having a splitting limit of 0.2 percent. It is completed with a titration of 100 to 320 mg of uranium and is described in detail in section 4. That section also includes a brief description of three modified procedures indicating the changes made to obtain higher accuracy, remove larger amounts of interferences, or determine uranium in the 10-mg range.

In the umpire method, the uranium is dissolved by treatment with mixed acids--generally nitric, hydrofluoric, and sulfuric. The hydrogen sulfide group is removed by precipitation in a diluted sulfuric acid solution (5:95). Additional interferences are removed by oxidizing the filtrate, increasing its acidity (to 1:9), treating with cupferron, and extracting with chloroform. Most organic matter is destroyed by fuming with nitric acid. Residual organic matter and nitric acid is removed by additional fumings with perchloric and sulfuric acids. The solution or a suitable aliquot is reduced in a Jones reductor containing zinc amalgamated with 10 percent by weight of mercury, and then aerated to oxidize U(III) to U(IV). Excess ferric solution is added to completely oxidize the uranium, phosphoric acid is added to complex the remaining ferric iron, and the ferrous iron resulting from oxidation of U(IV) to U(VI) is titrated visually with potassium dichromate solution that has been standardized against a standard sample of uranium oxide (U_3O_8).

This general method has been used for umpire uranium assays since the mid-forties. The chloroform extraction of cupferrates was reviewed by Furman, Mason, and Pekola [7]. The "10-percent-amalgam" reductor recommended by Grimaldi [8] for elimination of nickel interference was adopted for general use at NBS because of its stability (long life). The excellent study by Sill and Peterson [9] of a different uranium assay method provided valuable information about the analytical chemistry of uranium. Methods used for uranium assays in other laboratories have been reviewed by Rodden [3,10] and Steele and Taverner [11]. The recent review by Booman and Rein [12] is of a more general nature. The compilation by Jones [13] of selected measurement methods for product materials give details of several sampling and assay procedures that also apply to source materials.

In South Africa much use has been made of the cellulose column method; and in the United States, MCW [14] prefers to separate uranium from impurities by means of the tetrasodium salt of ethylene-diamine-tetraacetic acid (EDTA) and ammonium uranyl phosphate, reduce uranium in a lead reductor, and titrate with ceric sulfate. LPI, NBL, NLO, and GCD have used methods similar to those of NBS but varying in regard to the thioacetamide use, HCl-HBr removal of arsenic, cupferron extraction techniques, percent mercury in the Jones reductor, etc.

At NBS it has generally been more convenient to make the sulfide separation by use of hydrogen sulfide than by thioacetamide. The latter has been used successfully, however, as described in the alternate procedure based on the LPI procedure [15] and included in section 4. The analytical chemistry of thioacetamide has been reviewed by Swift and Anson [16].

We have deliberately avoided use of hydrobromic acid for volatilizing arsenic because the presence of hydrogen bromide in our laboratory appeared to cause some low results and because we failed to obtain proof that it was necessary. Rowe [17] also found no serious interference by arsenate in the volumetric determination of uranium, but his experimental conditions and requirements were somewhat different from those of the umpire method.

The precision of the basic procedure was demonstrated in 1958 in the standards program described in Appendix B. That program excluded operator differences at NBS, whereas the GAE program (section 2.E) does not. In 1963 an additional study was made of the precision of umpire assays. Thirty samples selected by the AEC were analyzed as routine umpires except that a second (i.e., extra) aliquot was titrated for most of the solutions. The analyses were performed by three analysts, and all used the same pipette, same dichromate solution, same titer, and same correction for loss in extraction. Except for two lots (No. 25 and 26), one analyst prepared one sample solution and assayed the first aliquot of it; another analyst did likewise with a second sample. Immediately after the first aliquot was removed by one analyst, a different analyst removed and assayed a second aliquot. Two aliquots each of 57 sample solutions and 15 solutions of NBS Standard No. 950a were assayed. The 15 first aliquots of standard solutions had a range of 0.11 and an estimated standard deviation of 0.03. All sample results are listed in table 3. For 12 of the 30 samples, the difference between first aliquots of two solutions exceeded 0.06 and ranged up to 0.14. Although only one sample in this study gave a difference greater than 0.03 between the average of two (first) aliquots and the average of four (first and second) aliquots, it was made a standard practice at NBS after September 1963 to titrate second aliquots of any

Table 3. Comparison of NBS individual assay values for thirty lots of three types of Colorado Plateau uranium concentrates (July - August 1963).

Lot	Individual Results (Percent U_3O_8)				Differences	
NBS	1st Aliquots		2nd Aliquots		of 1st	Gr. Ave.
No.	Soln. 1	Soln. 2	Soln. 1	Soln. 2	Aliquots	-1st Ave.
1	79.86-B[a]	79.88-S	79.90-S	79.90-B	- 0.02	+ 0.01
2	79.97-B	79.97-S	80.07-S	79.95-B	.00	+ .02
3	81.28-B	81.33-S	81.31-S	81.35-B	- .05	+ .02
4	81.09-B	81.17-S	81.18-P	81.18-B	- .08	+ .03
5	81.15-B	81.18-S	81.19-P	81.15-P	- .03	+ .01
6	81.77-B	81.78-S	81.75-P	---	- .01	- .01
7	81.55-B	81.66-S	81.64-P	81.56-P	- .11	.00
8	86.87-B	86.90-S	87.02-P	86.95-P	- .03	+ .06
9	83.70-P	83.71-S	83.78-S	83.71-P	- .01	+ .02
10	82.11-B	82.00-P	82.17-S	82.03-B	+ .11	+ .02
11	85.98-B	85.87-S	85.99-P	85.87-B	+ .11	+ .01
12	84.83-B	84.70-S	84.75-P	84.78-P	+ .13	.00
13	85.75-B	85.78-S	---	85.81-P	- .03	+ .02
14	86.09-B	86.10-S	---	86.15-P	- .01	+ .01
15	85.98-B	86.06-S	85.97-P	86.07-P	- .08	.00
16	85.45-B	85.41-S	---	85.42-P	+ .04	.00
17	85.59-P	85.66-S	85.65-S	85.58-P	- .07	.00
18	85.42-P	85.56-S	85.54-S	85.56-P	- .14	+ .03
19	85.68-P	85.72-S	85.68-S	85.64-P	- .04	- .02
20	85.14-P	85.14-S	85.15-S	85.18-P	.00	+ .01
21	85.12-P	85.14-S	85.07-B	85.19-B	- .02	.00
22	85.94-P	85.87-S	85.89-B	85.86-B	+ .07	- .01
23	86.27-P	86.23-S	86.24-B	86.23-B	+ .04	- .01
24	85.59-P	85.52-S	85.60-S	85.53-B	+ .07	.00
25	86.03-S	86.01-S	85.98-B	86.01-B	+ .02	- .01
26	87.05-B	87.00-B	87.07-S	87.00-P	+ .05	+ .01
27	86.46-B	(86.14)-S[b] 86.54-S	86.44-S	(86.21)P[b] 86.57-B	- .08	.00
28	86.90-B	86.83-S	86.86-S	86.84-B	+ .07	.00
29	86.50-B	86.48-S	86.50-S	86.44-B	+ .02	- .01
30	84.19-B	84.25-S	84.25-S	84.22-B	- .06	+ .01

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[a] Letters (B, S, and P) identify the three analysts.

[b] This value is listed because the analyst had no explanation, but it is omitted from the average because it has been a practice at this laboratory to discard such values.

duplicate umpire samples that differ by more than 0.06 percent U_3O_8 for the first aliquots. This now occurs on less than 10 percent of the samples.

For accurate results, it is necessary that: (1) the material be weighed on the "as-bottled" basis, (2) refractory uranium materials (including UO_2) not escape dissolution by floating above the area of reaction, (3) uranium be completely washed from the sulfide filter, (4) the diluted uranium solution be well-mixed before cupferron is added to it, (5) physical losses in extraction and aeration be corrected for, (6) cracked fuming flasks be promptly recognized and eliminated, and (7) volumetric calibrations and temperature differences be suitably corrected for. Of the listed sources of error, all except the first and sixth are easily checked by carrying standard U_3O_8 through one or more steps of the procedure. The possibility of over-looking a human measurement error is greatly minimized by assaying two separate and different weight portions of each sample.

The length of the procedure provides many opportunities for error, but those encountered most often are loss of uranium or incorrect physical measurements. In trying to insure recognition of any errors, we have deliberately aimed to keep errors in one direction, to minimize compensating errors. Thus, we chose to extract with a relatively large, but constant, number of portions of cupferron-chloroform (aiming to insure complete removal of extractable interferences and limit the extraction error to a loss of uranium in spray). The average loss is determined by similar extraction of known solutions, and assay results are corrected accordingly. The magnitude and reproducibility of this loss from known solutions provide one valid test of an analyst's ability to perform umpire analyses.

The rate at which aeration oxidizes uranium beyond the tetravalent state has not been significant in assays to 1 part in 1,000 of solutions containing more than 100 mg of uranium and no catalysts such as copper, molybdenum, or platinum. The presence of catalysts can be detected by extra aeration of an otherwise duplicate aliquot. Doubling or tripling the aeration time should have no effect except for the expected greater physical loss in the air stream passed through the solution. In the umpire procedure at NBS, this loss amounts to about 0.1 percent and is compensated for in the standardization, where the standard uranium solution is aerated the same as the sample. In determining the composition of standards such as NBS No. 950a, physical loss in aeration is either (1) greatly reduced by washing the escaping air stream, or (2) avoided by passing air over a moving solution.

In washing the reductor, introduction of large amounts of air is avoided, but to minimize mixing of successive wash portions, each wash portion is deliberately drained to the top of the amalgam. Introduction of small amounts of air does no harm providing the final reduced solution contains excess U(III).

The basic umpire procedure is used only for solutions containing at least 100 mg of uranium and this should give enough of the visible olive color of U(III) to persist until the reduced solution is mixed and ready for the aeration step. For less than 100 mg of uranium, the procedure is modified to control aeration time more closely.

Over the years the assay procedure has been modified as needed to keep pace with increasing reliability of the bulk sampling procedures. The present basic procedure has proved satisfactory for concentrates with splitting limits of around 0.2 percent. However, if greater assay accuracy is desired, it would be helpful to have a better understanding of the interplay of conditions such as incomplete separation of sulfides (e.g., arsenic and platinum groups), fuming temperatures and reduction with "10-percent" amalgam; to know more about the effect of vanadium and of permanganate on the cupferron extraction; and to correlate assay results with the qualitative composition of the sample.

4. PROCEDURES USED AT NBS

A. Apparatus

1. Shaking heater. NBS uses custom-made assemblies that have evolved from the suggestions of J. J. Tregoning and A. Padgett of NBL in 1951. Six 550-w, 4.8-inch-square heating units (Precision type "HA") are mounted in a row on a base sheet of 0.25-inch transite that oscillates approximately 1.5 inches 90 times a minute. The transite base is mounted on an angle iron frame provided with eight roller skate wheels which roll (four on a horizontal plane and four against two vertical planes) on two fixed angle iron guides. The shaker is driven by a 1750-rpm, 0.33-hp motor connected through a 30:1 gear reducer to the drive shaft. A transite strip, 8.5 inches wide, with a 4-inch-diameter hole over each heating unit is mounted so as to prevent the flasks from sliding off during shaking.

The latest NBS assembly has a transite apron in front and on the level of the heating units, about three inches above the transite base. A row of six receptacles is mounted on the underside of the apron and 10 inches in front of the heating units. The apron covers the wiring without stopping air circulation, provides a cooling area for sample flasks, and decreases exposure of metal framework to acid. A variac for each unit is mounted in front of and just below the shaking assembly.

The Lowe Shaker Plate, a different assembly that is used in several uranium assay laboratories, is semi-custom made by Wesco Electric Company, 411 Glenwood Avenue, Grand Junction, Colorado.

2. Bubble dispersion tip. This is made by sealing a number of fine copper wires (of about 0.18-mm diameter) radiating from a center in a definite pattern, between a cone formed on the end of a glass tube and a circular glass disk. After the glass parts are sealed together and ground to expose the ends of the wires, the wires are dissolved in warm nitric acid. A detailed description of the tip and its construction has been given by Branham and Sperling [18].

3. Titration illumination. During titration, the beaker rests on a plate of flashed opal glass supported over a standard cool white fluorescent light. The glass is opal-flashed only on the bottom surface.

B. Reagents for Basic Procedure

1. Standard potassium dichromate solution (0.027 N: 1 ml of solution equivalent to 0.0038 g of U_3O_8). Dissolve 23.0 g of potassium dichromate (A. R., Primary Standard) in 17.2 liters of water. Standardize, as directed in section C.9 against the standard black oxide, No. 950a, used on the basis of 99.94% U_3O_8 when freshly ignited in an open crucible at 900 $^{\circ}$C for one hour.

2. Phosphoric-sulfuric acid mixture. Add 600 ml of sulfuric acid (sp. gr. 1.84) to 1400 ml of phosphoric acid

(85%) and mix.

3. Indicator solution (0.01 M). Dissolve 1.35 g of sodium diphenylamine sulfonate in 500 ml of water.

4. Ferric chloride solution. Dissolve 60 g of $FeCl_3 \cdot 6H_2O$ in 1500 ml of water, filter through a coarse-porosity sintered-glass filtering funnel. Add 15 ml of diluted sulfuric acid (1:1) that has not been exposed to fumes of nitric acid. Mix.

5. Cupferron solution. Dissolve 18 g of cupferron in 300 ml of ice-cold water.

6. Amalgamated zinc for 10% Jones reductor. Dissolve 70.8 g of mercuric chloride in 1200 ml of hot diluted sulfuric acid (1:99) and cool the solution to room temperature. Clean 540 g of 20-mesh zinc (low in As, Pb, and Fe) by covering with diluted sulfuric acid (5:95), stirring for about 10 seconds, rapidly decanting and rinsing three times with approximately 300-ml portions of water. Immediately after decanting off the last rinse, add the mercuric chloride solution and agitate the zinc, as by shaking in a loosely-closed bottle, vigorously for two minutes and occasionally for 10 minutes. Discard the liquid by decantation. Wash the amalgam several times with diluted sulfuric acid (5:95) and then several times with water. Cover with water, stir about two hours after amalgamation to crush the lumps formed by the fresh amalgam, and allow to stand overnight. Prepare the reductor column (about 22 mm inside diameter) by adding to the tube a plug of glass wool,

a little water and then about an inch of the amalgam at a time, gently tamping it in place with a glass rod. Wash thoroughly with diluted sulfuric acid (5:95) and with water.

C. Basic Procedure (for High-Grade Ores and Concentrates)

1. Sampling. Mix the material by rotating and shaking its container for several minutes. Carry out the appropriate procedure described below, using the grab-sampling (see below) method particularly for the materials to be reported on the "as received" basis and for very hygroscopic concentrates. If the gross weight of the bottled sample was noted on the bottle at the sampling plant, reweigh shortly before sampling in the laboratory, to determine if the "as received" basis has been maintained. Grab a total of at least four samples (usually 1.5 g each) of each lot that is to be assayed on the "as received" basis. Take all samples from underneath the surface material, and sample different regions whenever possible. Make determinations in duplicate; if more than one bottle of the material is submitted, assay one sample from each of two bottles.

(a) Grab-sampling. Immediately after breaking the "seal" of the bottle, rapidly transfer two or more samples from it to cap-style, 25 x 40-mm weighing bottles. Close each weighing bottle promptly and firmly and weigh it (to 0.1 mg) 30 to 60 minutes later. Obtain the assay sample weight by difference after pouring the sample into a narrow-mouth, 500-ml Erlenmeyer flask and weighing the emptied bottle.

Reserve the extra samples for assay rechecking as needed. Store with a tare weighing bottle but without desiccant.

(b) Direct weighing. Transfer the sample to a tared weighing pan and determine its weight, to the nearest 0.1 mg, 60 seconds after opening the container. Transfer the sample, with the aid of a small brush, into a 500-ml Erlenmeyer flask.

(c) Samples for moisture. If the analysis is to be on the dry basis, take two additional samples, taking one just before and one just after the assay samples. Transfer approximately 5 g of material to a weighed, tared, cap-style, 40 x 50-mm weighing bottle, close the weighing bottle promptly and firmly, and weigh it 30 to 60 minutes later.

2. Moisture determination. Dry the moisture samples at 110 °C for approximately 16-hour intervals. Dry the materials from different sampling plants or with widely different moisture contents separately. In general, do not dry over 12 portions together. During the first drying interval, leave the weighing bottles wide open, with their tops lying next to them, but during later intervals, leave the tops tilted on the bottles in order that the latter may be closed as soon as possible after the oven is opened. Cool seven bottles over magnesium perchlorate in an 8-inch desiccator for one hour; then open each bottle for an instant, close firmly, and leave in the desiccator for at least one hour longer before weighing. Check the weight of the tare bottle, which has been handled exactly as the sample bottles, and then weigh the samples

against the tare. Dry every sample that is put in the oven together, until the weight of each is constant or increases in the same interval but for not less than three intervals.

3. Dissolution. Proceed, as follows, with (a) or (b) depending on sample size.

(a) Small assay sample (1.5 to 2.0 g). Wash down the inside of the flask with approximately 15 ml of water and swirl to mix. Add 15 ml of diluted sulfuric acid (1:1) and about 15 ml of diluted nitric acid (1:1); for pitchblende ores, increase the nitric acid to 50 ml (1:1) and also add 20 ml of diluted hydrochloric acid (1:1). Digest at 80 to 100 °C until reaction ceases (up to one hour), swirling as needed to keep the sample dispersed. Wash down the wall with water and add up to one ml of hydrofluoric acid (48%). Place the flask on a fast heater and heat, while shaking the heater, until the sulfuric acid refluxes at least one inch up the wall of the flask; if hydrofluoric acid was added, continue heating until the sulfuric acid refluxes nearly to the neck of the flask. Remove from the heater; and when the flask is cool, wash down the inside of the flask with 145 ml of water. Cover with a beaker and digest on a steam bath for one hour, swirling once near the middle of the digestion. Examine for complete decomposition; if a significant amount of dark material persists, add one ml of perchloric acid, evaporate, refume, dilute, and digest again. Continue as directed in section C.4.

(b) Large assay sample (8 g). Wash down the inside of the flask with 25 ml of water and swirl to mix. Add 25 ml of concentrated nitric acid. Digest at 80 to 100 °C and swirl occasionally until reaction ceases (up to one hour). Cool and wash down. Cautiously add 35 ml of concentrated sulfuric acid and mix. Add about 2 ml of hydrofluoric acid. Place the flask on a fast heater and heat, while shaking the heater, until the sulfuric acid refluxes nearly to the neck of the flask. Cool. Cautiously add 200 ml (more for difficultly soluble material) of water and mix. Cover and digest on a steam bath for 30 minutes. Cool to room temperature. Filter through an 11-cm No. 40 paper into a 500-ml volumetric flask. Wash with 100 ml of diluted sulfuric acid (2:98) and several times with water. Ignite and weigh the residue. (If it amounts to 0.1 percent of the sample, test the residue for uranium as directed in section C.3c.) Dilute the filtrate to nearly 500 ml while mixing the solution by swirling. Cool it to room temperature. Dilute the solution to the mark, mix thoroughly, note the temperature and transfer a 100-ml aliquot to a 500-ml, narrow-mouth Erlenmeyer flask. Before diluting the aliquot, dry the stopper and neck of the volumetric flask and close the flask tightly so that a duplicate aliquot may be obtained later if desired. Add 50 ml of water to the 100-ml aliquot. Continue as directed in section C.4.

(c) Residue. When fluorimetric or spectrographic checking of a residue is not convenient, analyze the residue for uranium simply by decomposing it, usually with the aid of hydrofluoric acid, and then proceeding as for a reagent blank, section C.10a.

4. Treatment with hydrogen sulfide. (Carry out the work in an efficiently ventilated hood.) Heat the solution of the sample, in 150 ml of diluted sulfuric acid (5:95), to boiling. Immediately attach the flask by means of a short glass tube in a rubber stopper to a hydrogen sulfide manifold. Connect the last exit of the manifold through a trap to a regulator to maintain a pressure equivalent to 18 inches of water. Sweep out the air in the flask by gassing one sample at a time and loosening the stopper intermittently while vigorously and constantly swirling the flask for two or three minutes. Then tightly stopper the flask and repeat with successive solutions. After connecting all flasks to the manifold, cool them to ice-bath temperature. Continue the gassing and occasional swirling until the swirling does not noticeably decrease the pressure in the ice-cold flask (usually at least one hour). Close the hydrogen-sulfide-filled flasks while cold and let them stand at room temperature overnight.

Although the gassing technique described above usually insures the presence of excess hydrogen sulfide in each solution, pass hydrogen sulfide over the solutions again just before filtration, while also saturating a wash solution of diluted sulfuric acid (2:98) with the gas. Filter the sample through a No. 40 Whatman paper into a narrow-mouth, lipped, 500-ml Erlenmeyer flask. Wash with at least 100 ml of the hydrogen sulfide-sulfuric acid solution. Add 5 ml of diluted sulfuric acid (1:1) and 10 to 20 glass beads to the filtrate. Mix the solution and place the flask on a fast heater. Boil until the volume is reduced to 75 to 80 ml.

5. Extraction of cupferrates. Heat the above solution, containing 12 ml of concentrated sulfuric acid, to boiling and add dropwise a 2-percent solution of potassium permanganate until the uranium solution is pink. Cool the solution in an ice bath to a temperature of 5 °C. Transfer the solution quantitatively to a 300-ml separatory funnel containing a few drops of chloroform; use water for washing the flask and diluting the solution to 100 ml. Swirl to mix. If the pink color has faded, add 1 or 2 drops of 2-percent potassium permanganate to make it pink again.

Add 25 ml of an ice-cold, 6-percent cupferron solution, mix by swirling the mixture for 5 seconds, and allow to stand for a few moments. Add 25 ml of ice-cold chloroform and shake vigorously for 15 seconds. Carefully release the pressure through the stopcock. Each time the funnel is returned to the upright position make sure that a drop of aqueous layer is not trapped next to the stopcock. Then loosen the stopper and wash it and the top of the funnel with a little chloroform.

Allow the funnel and contents to stand until the layers have separated completely, but not long enough for the chloroform layer to start bubbling and giving a curdy, light-colored precipitate. Drain off most of the chloroform layer and repeat the extraction with chloroform.

Add permanganate to make the solution pink again. Add 10 ml more of cupferron solution and extract twice more with 25-ml portions of chloroform.

Add another drop or two of permanganate, a third portion of cupferron (usually 10 ml), and extract with three more 25-ml portions of chloroform. The third portion of cupferron should give a white precipitate; its chloroform extract should be pale blue-greenish with no brownish tinge even after short standing; and the last chloroform layer should be colorless. Before draining the last extract, wash the outside of the funnel stem with chloroform. If colored extract has dried on the inside of the stem, wash it out with diluted sulfuric acid; this usually is necessary for the large stems (9-mm inside diameter).

Drain the aqueous layer from the separatory funnel back into the lipped, 500-ml Erlenmeyer flask, washing out the separatory funnel at least three times with water. Add 15 ml of concentrated nitric acid, 15 ml* of diluted sulfuric acid (1:1), and swirl to mix.

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[*] If the solution contains less than 380 mg of U_3O_8, omit this sulfuric acid.

6. Fuming. Swirl again to mix well. Boil the solution until sulfuric acid refluxes to the neck of the flask. After the solution has cooled, wash down the inside of the flask with at least 15 ml of water. Add 1 ml of perchloric acid (70%). Again boil until the sulfuric acid refluxes into the neck of the flask. Repeat the cooling, washing down, and fuming, twice more. After the fourth fuming, cool the solution, add about 100 ml of water, and heat to dissolve all soluble salts. Wash down the inside of the flask immediately after the last heating. After the solution has cooled, transfer it to a 200-ml volumetric flask* and dilute nearly to volume while mixing by swirling. Allow the solution to come to room temperature.

7. Aliquoting and reduction. Dilute the solution exactly to the mark and mix thoroughly. Record the room temperature. Remove a 50-ml aliquot and transfer it to a 250-ml beaker; the aliquot should contain at least 100 mg of uranium. Add 2-percent potassium permanganate, usually one drop, until the uranium solution is pink. Heat the solution just to boiling; then cool it, in a water bath, to room temperature. Immediately before each group of reductions, wash the reductor several times with diluted sulfuric acid (5:95), then with water. Reduce an extra aliquot of the first sample;

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* If the solution contains less than 380 mg of U_3O_8, do not transfer it to a volumetric flask. Instead, adjust the volume to 90 ml, oxidize with permanganate, heat to boiling, cool, and reduce as in section C.7.

then reduce the test aliquots. Make each reduction by passing through the reductor in the following order: about 20 ml of diluted sulfuric acid (5:95), the uranium solution, 110 ml of diluted sulfuric acid (5:95) in three portions, and finally 110 ml of water in three portions. Carry out the reduction in three to four minutes.

8. Aeration and titration. Transfer the reduced solution to a 600-ml beaker. Aerate with a stream of fine bubbles of washed air* for 15 minutes, adjusting the rate of aeration so as to change the brownish solution into a clear green one in about 5 minutes. Carefully wash the cover glass, aerator, and beaker wall. Add 20 ml** of 4-percent ferric chloride solution, stir, wait one minute, and add 15 to 16 ml of phosphoric-sulfuric acid mixture and 0.35 ml of diphenylamine sulfonate indicator (stir after each addition). Titrate the solution with 0.027 N potassium dichromate solution (added from a calibrated 100-ml bulb buret) until the maximum purple color is obtained. Record the room temperature at the time of titration.

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* Pass the air at a rate of about 300 ml/min through cotton and glass wool, a rotameter, a coarse frit under two inches of sulfuric acid, a coarse frit under one inch of water, an empty gas-washing bottle, and the Branham-Sperling bubble-dispersion tube with its tip near the bottom of the sample solution. All connections are made with cleaned, pure gum rubber tubing.

** To high-uranium solutions (equivalent to about 95 ml of dichromate) add 30 ml (instead of 20) of 4-percent ferric chloride solution, and 23 ml (instead of 15) of phosphoric-sulfuric acid mixture.

Make corrections and calculate the uranium content from the net volume and titer of the dichromate as directed in section C.10.

9. Standardization -- titer of dichromate. Transfer about 15 g of standard black oxide to a platinum crucible. Ignite in the open crucible in an electric muffle at 900°C for one hour. Cool over magnesium perchlorate in a desiccator; crush and stir the oxide briefly; and rapidly transfer 1.500-g portions to each of four small weighing bottles, closing each weighing bottle immediately and firmly. Weigh accurately 15 to 20 minutes later. Remove at least three samples for each standardization, as follows: Pour the sample into a lipped, 500-ml Erlenmeyer flask and obtain the sample weight by difference after correcting for any change in the tare weight. Wash down the inside of the flask with 15 ml diluted H_2SO_4 (1:1). Add 10 to 15 ml of diluted nitric acid (1:1). Digest at 80 to 100 °C until **reaction ceases.** Wash down the wall with 25 ml of diluted H_2SO_4 (1:1) and continue as directed in sections C.6, C.7, and C.8.

10. Calculation and selection of assay values.

(a) Titration corrections. Determine the corrections needed to convert all observed dichromate volumes to volumes at 25 °C (from a chemistry handbook table of changes in water volume with temperature).

Since the indicator does not give an end point in a blank solution, determine the indicator correction indirectly as the difference between the titration values of two 50-ml aliquots of a uranium solution when one aliquot is titrated as a single solution and the other aliquot is divided and titrated as two solutions. From 0.2 to 0.3 ml of dichromate is required for the indicator.

Determine the correction for other reagents by carrying a blank solution through sections C.3, C.4, C.5, and C.6, combining a 50-ml aliquot of the blank with one of two duplicate aliquots of a uranium solution, then reducing and titrating the two uranium aliquots alike. The reagent correction, or difference between the two titrations, has been small enough to be omitted at NBS.

Calibrate the buret and volumetric flasks, and provide corrections if needed.

(b) $\underline{U_3O_8 \text{ in sample}}$. Obtain the net volumes of dichromate by applying temperature, indicator, other reagent and glassware corrections found as directed in section C.10a to each dichromate volume observed in sections C.8 and C.9. Using the net volumes, and ignited No. 950a, designated as "R", on the 99.94% U_3O_8 basis, the following calculations apply.

$$\%U_3O_8 \text{ as rec'd} = \frac{(\text{net ml of } K_2Cr_2O_7 \text{ for sample aliquot})FA'}{(\text{grams of total sample})} \times 100$$

$$\%U_3O_8\text{, dry basis} = \frac{\%U_3O_8 \text{ as rec'd}}{100\% - (\% \text{ loss on drying})} \times 100$$

where:

"As received" applies only if no leakage occurred between receipt and analysis,

$$A' = \frac{\text{volume before aliquoting in section C.3b}}{\text{volume of aliquot in section C.3b}},$$

$$F = \frac{TA}{B},$$

$$T = \frac{0.9994 \times (\text{grams of R in aliquot from section C.9})}{(\text{net ml of } K_2Cr_2O_7 \text{ for R aliquot from section C.9})},$$

(R = ignited NBS Standard Reference material No. 950a)

$$A = \frac{(\text{volume before aliquoting in section C.7})}{(\text{volume of aliquot in section C.7})},$$

$$B = \frac{(\text{net ml of } K_2Cr_2O_7/\text{gram of R from sections C.1-8})}{(\text{net ml of } K_2Cr_2O_7/\text{gram of R from section C.9})},$$

The factor "B" is applied to correct for a rather consistent loss obtained in carrying samples of ignited standard black oxide through the entire assay procedure. Usually one such standard is run with each five umpire samples. The value for "B" is the average for a considerable number of such runs and now is greater than 0.999 at NBS. It should be determined by each analyst.

(c) U_3O_8 reported. Report the average of one aliquot each from two separate solutions providing the two values agree within 0.06%. Otherwise, report the average of two aliquots each from two separate solutions providing the range of the four values is not greater than 0.15%, or the average of one aliquot each of three or more separate solutions providing the range of the three or more values is not greater than 0.2%.

D. Alternate Procedure Using Thioacetamide

Follow the basic procedure except modify sections C.3 and C.4 as follows:

C.3-alternate -- Dissolution before thioacetamide use.

(a) Small assay sample (1.5 to 2.0 g). Wash down the inside of the flask with approximately 15 ml of water and swirl to mix. Add 24 ml of diluted sulfuric acid (1:1) and about 15 ml of diluted nitric acid (1:1). Digest at 80 to 100 °C until reaction ceases (up to one hour), swirling as needed to keep the sample dispersed. Wash down the wall with water and add up to one ml of hydrofluoric acid (48%). Place the flask on a fast heater and heat, while shaking the heater, until the sulfuric acid refluxes nearly to the neck of the flask. Remove from the heater; and when the flask is cool, wash down the inside of the flask with 90 ml of water. Continue as directed in section C.4-alternate.

(b) Large assay sample (8 g). Wash down the inside of the flask with about 25 ml of water and swirl to mix. Add 25 ml of concentrated nitric acid. Digest at 80 to 100 °C and swirl occasionally until reaction ceases (up to one hour). Cool and wash down. Cautiously add 35 ml of concentrated sulfuric acid and mix. Add about 2 ml of hydrofluoric acid. Place the flask on a fast heater and heat, while shaking the heater, until the sulfuric acid refluxes nearly to the neck of the flask. Cool. Cautiously add 200 ml (more for difficultly soluble material) of water and mix. Cover and digest on a steam bath for 30 minutes. Cool to room temperature. Filter through a 11-cm No. 40 paper into a 500-ml volumetric flask. Wash with 100 ml of diluted sulfuric acid (2:98) and several times with water. Ignite and weigh the residue. (If it amounts to 0.1 percent of the sample, test the residue for uranium as directed in the basic procedure, section C.3c.) Dilute the filtrate to nearly 500 ml while mixing the solution by swirling. Cool it to room temperature. Dilute the solution to the mark, mix thoroughly, note the temperature, and transfer a 100-ml aliquot to a 500-ml Erlenmeyer flask. Before diluting the aliquot, dry the stopper and neck of the volumetric flask and close the flask tightly, so that a duplicate aliquot may be obtained later if desired. To the 100-ml aliquot, add 9 ml of diluted sulfuric acid (1:1). Continue as directed in section C.4-alternate.

C.4-alternate -- Treatment with thioacetamide. Add a few glass beads and boil gently to dissolve soluble salts. Cool slightly, add a small portion of potassium bisulfite, and boil to remove sulfur dioxide. Dilute to 100 ml, bring to a boil, and continue to boil gently while adding 8* to 10 ml of 2 percent thioacetamide in 2-ml portions. Continue to boil gently to coagulate the precipitate. Remove and filter while hot through an 11-cm No. 40 paper into a 500-ml lipped Erlenmeyer

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* Use less than 8 ml if amount of impurities is very small.

flask. Wash thoroughly with cold water (to obtain at least 200 ml of filtrate). Add glass beads. Boil the filtrate until the hydrogen sulfide is removed, or until the volume reaches 90 ml. Add a small portion of ammonium persulfate, and continue to boil until the volume is 75 to 80 ml. Proceed with the extraction of cupferrates as in the basic procedure, section C.5.

E. Modification for Portuguese Concentrate (about 10 percent Uranium)

Follow the basic procedure with the following changes:

1. Assay on the dry basis; use 6-g samples for assay.

2. After proceeding through basic procedure sections C.3b and C.4, boil down to 60 ml and add 2 percent potassium permanganate dropwise until the uranium solution is pink. Chill, transfer to a separatory funnel, and dilute to 80 ml. Treat with 40 ml of cupferron and extract with 60 ml of chloroform, then 25 ml of chloroform; followed by 15 ml of cupferron and three 25-ml portions of chloroform; then 10 ml of cupferron and three 25-ml portions of chloroform.

3. In section C.5, omit the addition of sulfuric acid after extraction.

4. Follow section C.6 as footnoted.

5. In section C.10b, because of the modified aliquoting procedure, use "T" instead of "F" and calculate as follows:

$$\%U_3O_8 \text{ as rec'd} = \frac{(\text{net ml of } K_2Cr_2O_7 \text{ for sample aliquot})TA'}{(\text{grams of total sample})B} \times 100$$

F. Modification for Refined Orange Oxide

The summary below indicates how the basic procedure was extended to visual indicator titration of solutions containing about five grams of uranium. Although subsequent studies of high-accuracy analyses of uranium standards have suggested even further modifications, particularly in regard to controlling the acidity in step 2, using a still smaller reductor, preventing physical loss during aeration, determining the U(III)-U(IV) end point and measuring the reagent blank, the details of those studies are beyond the scope of this paper. The following method has given adequate results for material having an 0.1-percent splitting limit and not requiring separations.

1. Follow the basic grab-sampling procedure except take samples weighing about 6 g. Weigh by difference of the closed weighing bottle before and after transferring the sample to a 500-ml Erlenmeyer flask.

2. Add 30 ml of perchloric acid and heat over a medium hot plate with care to prevent boiling and to control the amount of acid lost by evaporation. Try to avoid swirling any solid up on the flask wall. Be sure the sample is completely dissolved; examine closely.

3. Dilute the above solution, containing about 25 ml of perchloric acid, to approximately 100 ml. Mix. Cool to room temperature.

4. Use a small Jones reductor, with a 10x150-mm column of zinc amalgamated with two-percent mercury; and collect the

reduced solution in a 750-ml Erlenmeyer flask. Clean the reductor by washing with about 200 ml of diluted sulfuric acid (5:95) and then with water. Reduce the samples by passing through the reductor in the following order: about 20 ml of diluted sulfuric (5:95), the uranium solution, 200 ml of diluted sulfuric acid in four portions, and finally 100 ml of water in three portions. Allow each wash to drain to the top of the amalgam before the next wash is added. Decrease the flow rate of the uranium solution to insure sufficient reduction for some U(III) to persist until aeration. During the washing with acid, return to the normal flow rate, to minimize gas entrapment and possibly poor removal of uranium from the reductor.

5. Stir with a "cooled"* magnetic stirrer while aerating for one-half hour. Use a spray trap made, for example, by passing the bubbler tube through a stemless funnel recessed into the flask, adding a few beads to the funnel and squirting diluted sulfuric acid (5:95) into the funnel and around the neck of the flask. After aeration, wash down the walls of the funnel with diluted sulfuric acid (5:95) and transfer the solution to an 800-ml beaker. During aeration the color of the sample changes from dark green to olive green and finally to transparent green.

6. Add the calculated amount of accurately-weighed potassium dichromate (NBS Standard No. 136b) to oxidize 99 percent of the uranium. Stir for one minute after complete solution.

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* The transfer of an appreciable amount of heat from the stirrer to the solution is avoided by placing a wet cloth or a water bath between the stirrer and the flask.

7. Add 20 ml of 4-percent ferric chloride solution, stir for two minutes, add 23 ml of phosphoric-sulfuric acid mixture, and stir to mix. Add 1.00 ml of 0.003 M indicator and titrate as in the basic procedure except over a 200-w light bulb and from a 25-ml buret.

8. Apply the vacuo correction to the weight of dichromate used in step 6. Add to the dichromate used in step 7 and convert to uranium.

G. Modification for Solutions Containing about 10 mg of Uranium

Use the basic procedure with the following exceptions:

1. Prepare modified reagents as follows:

(a) Standard potassium dichromate solution (0.01 N). Transfer 1 g of potassium dichromate (NBS Standard No. 136b) weighed to 0.1 mg, to a 2-liter volumetric flask, dissolve in water, dilute to the mark at room temperature, and mix thoroughly.

(b) Stock uranium solution (4 mg U_3O_8/ml and 0.04 ml H_2SO_4/ml). Prepare as in the basic procedure, section C.9, except use 2.00 g of ignited standard U_3O_8 and dilute with water to 500 ml (in a volumetric flask, at room temperature). Record the dilution temperature, and mix well.

(c) Dilute uranium solution (0.2 mg U_3O_8/ml and 0.01 ml H_2SO_4/ml). Transfer a 50-ml aliquot of modified reagent (b) to a 1-liter volumetric flask. Add some water and 8 ml of sulfuric acid. Swirl to mix. Cool to room temperature, dilute to the mark with water, and mix.

(d) *Sodium diphenylamine sulfonate indicator solution*, 0.002 *M*. Dilute one volume of the 0.01 *M* solution (from basic procedure) with four volumes of water.

(e) Jones reductor. Prepare as in the basic procedure but use only one-third as much amalgam, making a 10x150-mm column of ten-percent amalgam.

2. Use glassware reserved for this level of uranium, or freshly cleaned for this purpose.

3. After dissolving and separating the uranium from interferences, including easily oxidized organic matter, fume the uranium solution, containing about 12.5 ml of sulfuric acid, as in the basic procedure, section C.6, except make the fourth fuming on titration day. Use extra care during each fuming of solutions that precipitate and tend to bump. Watch constantly. When precipitation begins, immediately remove the flasks from heat, cool slightly, and fume at a slower rate until sulfuric acid refluxes to about one inch, then increase the heat and finish fuming.

4. Before the fourth fuming add a 50-ml aliquot of modified reagent (c) to each sample containing less than 5 mg of uranium.

5. Also prepare "direct control" samples as follows: Into each of three lipped 500-ml Erlenmeyer flasks, pipette 50.0 ml of modified reagent (c). To each of two of the flasks, add a second 50-ml aliquot of modified reagent (c), and label "20 mg". Label the other one "10 mg". To the "10 mg" flask, add 12 ml of sulfuric acid; and to each of the "20 mg" flasks, add 11.5 ml of sulfuric acid. Add a few beads, boil down, and fume once.

6. After the fourth fuming of the samples and one fuming of the "direct controls", dilute each solution with 80 ml of water. Mark the level, boil to dissolve any salts, and redilute to the mark. If insoluble salts persist, dilute to about 120 ml and boil down to the mark.

7. Oxidize the solution with 2-percent potassium permanganate (heat to boiling) and cool to room temperature. Make sure the solutions are diluted to the mark or slightly higher, and mixed after dilution.

8. Use the small reductor (freshly washed with diluted sulfuric acid) and reduce in the following order:

- one "20 mg" direct control
- one "10 mg" direct control
- all sample solutions (not over 11)
- one "20 mg" direct control

Avoid draining solutions below the top of the amalgam. For small amounts of uranium, it is more important to limit the entrance of air into the reductor than to get sharp separations of successive washes. Make all reductions. Then proceed promptly with step 9, and titrate the solutions in the same order that they were reduced.

9. Aerate for 12 minutes*. Add 15 ml of the filtered ferric chloride reagent, 15 ml of phosphoric-sulfuric acid mixture, and 1.0 ml of 0.002 M indicator (stir after each addition). Titrate with 0.01 N $K_2Cr_2O_7$ (added from a 25-ml buret) until the maximum purple color is obtained. Make corrections and calculate the uranium content from the net volume and titer of the dichromate. Use the "direct control" results for judging whether there was significant air oxidation of the dilute solutions (and for calculating appropriate corrections if required).

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* The length of time is not critical; it is important that all solutions in the group be aerated alike.

5. SUMMARY

Between 1949 and 1964 the National Bureau of Standards performed umpire analyses of several thousands of uranium concentrate samples resulting from the uranium procurement program of the U. S. Atomic Energy Commission. These represented more than 50 producers located in widely scattered areas of the world. All samples were analyzed by one standard assay method, including dissolution with acids, removal of interferences by sulfide precipitation and chloroform-cupferrate extraction, reduction in a Jones reductor, and titration with potassium dichromate. A basic procedure applicable to all types of material was developed and standardized by means of known amounts of uranium provided by NBS standard reference material No. 950a. The primary problem in the assays was the establishment of a reliable sampling weight base line. NBS conducted studies that contributed to a better understanding and control of this problem, and the later replacement of the usual "drying-to-constant-weight" basis with the "as received" basis. A comprehensive account is given of NBS experiences in connection with the identification and the solving of uranium concentrate assay problems.

6. APPENDIXES

APPENDIX A

Details of INX Studies

Bottles No. 1 and 2 were filled from different lots at Fernald sampling plant on 9-28-56, opened at NBS on 1-24-57, emptied on 2-22-57, cleaned and treated alike until the base weights were obtained on 2-24-57. Their interiors were carefully dry-cleaned with Kimwipe tissue and their exteriors were cleaned by scraping off the labels, using damp tissue to remove all glue and loose material, and finally drying with dry Kimwipes.

Bottles No. 3, 4, 5, and 6 were four unopened reserve bottles sealed at Fernald in 1956 on 9-28, 9-28, 4-11, and 4-19, respectively, and included two (No. 3 and 4) filled from the same lots as No. 1 and 2. The closures of No. 3, 4, 5, and 6 were not disturbed, but the exteriors were cleaned like No. 1 and 2. All six of the cleaned, marked bottles were stored together in the laboratory atmosphere for 44 hours just before their base weights were obtained.

During the first month, the NH_4NO_3-H_2O mixture (under bottles No. 1, 3, and 5) was stirred magnetically as needed to maintain approximate saturation. Due to fluctuations in room temperature, the surface of the NH_4NO_3 solution was less than saturated during the latter months of the experiment.

The relative tendency of the different parts of the taped and waxed cap to lose moisture was determined as follows: On 6-26-57 one bottle (No. C) each from two lots bottled on 9-29-56 and 2-7-57 were carefully opened and the cover of each was separated into three portions: sealing wax and tape, cap liner, and bare cap. No solvents were used, and the six test portions were left exposed to the room air for two hours before the base weights were taken. Then the test portions were stored in the same desiccator used for the earlier dry-air storage experiment. Losses of weight were observed as shown in figure 3 of the text.

APPENDIX B

GRAND JUNCTION URANIUM CONCENTRATE STANDARDS PROGRAM OF 1958

Summary

Because of the high backlog of uranium umpire requests in 1958, a means was sought to qualify private laboratories to act as umpire assayers. Representatives of Grand Junction AEC Office, of its Sampling Plant, and of NBS decided that each interested laboratory should be furnished a suite of standard samples upon which the average assay and confidence limits had been accurately determined; the laboratory would be considered acceptable if it were able to assay each standard sample within the established confidence limits. Subsequently, Lucius Pitkin, Inc., carefully prepared 100 pulps each of seven different materials, representing the various types of uranium concentrate produced on the Colorado Plateau. Two pulps each of three of the materials were submitted to each of the five laboratories (LPI, MCW, NBL, NLO, and NBS) then analyzing uranium concentrates for the USAEC. Each laboratory analyzed each of its six pulps in duplicate by each of the four methods proposed for establishing the sampling base line, as follows: the "as is" basis, regular drying at 110 °C, controlled atmosphere drying at 110 °C, and ignition at 900 °C.

The results indicated that only the "as is" method was a reliable basis at that time, and even for it, more detailed specifications of sampling conditions and procedures were needed to obtain confidence limits suitable for standard samples. There was some evidence that some of the "as is" results were biased by moisture pickup during sampling.

The specification for the "as is" method was simply to weigh out duplicate samples as quickly as possible. However, NBS did all of its sampling for this study in a dry box to insure both that all of its samples were started on one reproducible basis and that its "as is" basis was not biased by the high humidity of summer in Washington. An outline of the NBS sampling and analysis procedure given below was furnished to the other laboratories before the standards were sampled, but in this program (1958), each laboratory had considerable latitude in deciding what sampling details to observe. The following information is given as background for possible future studies.

GJOO Procedure for Preparation of the Standards

(a) Combine the dried, 115-mesh sample rejects on hand from each mill (Anaconda, Durango, etc.).

(b) Mix this combined quantity (approximately 35 lbs) for seven hours in a Y-blender equipped with an intensifier bar.

(c) Remove the mixed material from the blender and place promptly in stainless steel drying pans and dry in a forced draft oven for 48 hours at a constant temperature of 110°C.

(d) At the end of the drying period, two or three people should transfer as rapidly as possible approximately equal portions of the concentrate from each pan into predried Mason sample jars with Kerr lids (approximately 100 grams per jar, 120 pulps per material type).

(e) The half-pint Mason jars and Kerr lids should then be placed in an oven and dried for 24 hours at a temperature of 110°C, removed, capped, and sealed immediately while hot.

Specifications of Analytical Methods for the Program

(a) "As is" Method - Weigh out duplicate samples as quickly as possible and assay by the usual procedure.

(b) "Regular" Method - Weigh out two more samples for determination of moisture in the usual way. Dry these samples at 110°C at room atmospheric conditions, but keep a record of the temperature and relative humidity during the weighing and drying operations. Report any losses and gains in weights, and correct the assay sample weights for any moisture losses. Consider gains as zero loss, but record and report separately.

(c) "Special Drying" Method - Repeat Method No. (b) except perform all weighing and drying of the moisture samples under controlled humidity conditions of not greater than 10% relative humidity (i.e., 0.936 grains H_2O/cubic foot of air at 75 °F)*.

(d) "Ignition" Method - Weigh out two more samples and heat slowly in a muffle furnace to an ignition temperature of 900 °C ± 25 °C and hold for a period of one hour. Weigh the ignited sample and record the loss on ignition; then assay the ignited sample.

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* This is equivalent to <0.002 g H_2O/g dry air.

Procedure for Sampling and Analyzing USAEC Standard Concentrates Nos. "D," "E," and "F" at NBS, as Revised 8-4-58

Sample one material per week, grabbing all 32 samples from the two bottles in a dry box at a single sitting, as detailed below in steps (1) through (7). Reserve half of the samples, designated A' through H-2', for rechecks or extra data as needed. Assay only four samples (two as is and two after ignition) from each bottle, and use the loss-on-drying values to calculate the other assay values. Have any given operation performed by a single analyst for all standard samples.

(1) Place in the dry box the two bottles of sample (with sealing wax removed); two unweighed, glass-stoppered, 40x50-mm weighing bottles; 16 weighed 40x50-mm weighing bottles, plus four tares (two for dry-air and two for regular drying); 16 weighed 25x40-mm weighing bottles, plus two tares; a Scoopula; a small brush; a small fast balance (30-g capacity, for estimating 1.5 g); weights; forceps; wiping tissues; and an 8x10-inch pan.

(2) Flush the box overnight with a slow stream of air dried by passing through magnesium perchlorate.

(3) Mix the samples.

(4) Open and line up the weighing bottles and tares for a set of eight samples, A through H:

A	for regular loss	5 to 10 g
B	for dry air loss	5 to 10 g
C	for "as is" assay	1.4 to 1.6 g

d	for ignition loss and assay	1.4 to 1.6 g
e	for ignition loss and assay	1.4 to 1.6 g
f	for "as is" assay	1.4 to 1.6 g
G	for dry air loss	5 to 10 g
H	for regular loss	5 to 10 g

(5) Break the seal on one bottle of sample Immediately pour at least 50 g into an unweighed bottle, stopper it firmly, and reserve for the duplicate, *A'* through *H'*, set. From the remainder, grab the *A* through *H* set (in 5 to 10 minutes). Stopper each weighing bottle immediately after the sample is put in it, and handle the tare bottle like a sample bottle.

(6) Open and line up the weighing bottles for a second set of eight samples, and grab the *A'* through *H'* set from the reserved portion.

(7) Repeat steps (5) and (6) with the second bottle of sample for sets *A2* through *H2* and *A2'* through *H2'*.

(8) Sort the 38 weighing bottles into four groups as follows:

A, *H*, *A2*, *H2*, and tare *N*;
B, *G*, *B2*, *G2*, and tare *D*;
c, *d*, *e*, *f*, *c2*, *d2*, *e2*, *f2*, and tare *s*;
all reserve samples and tares.

Rapidly transfer the weighing bottles from the dry box to desiccators freshly charged with magnesium perchlorate; use a separate desiccator for each group. Wait 30 minutes. Then weigh initially in the following order:

tare N, A, A2, tare D, B, B2, G, G2, H, H2, tare N (to dry);
tare s, c, c2, f, f2, (to run for "as is assay);
tare s, d, d2, e, e2, tare s (to ignite and assay);
tare s', c', c2', f', f2', d', d2', e', e2', tare s' (to reserve)
tare N', A', A2', tare D', B', B2', G', G2', H', H2', tare N' (to reserve).

Have a second analyst repeat the whole series of weighing.

(9) Allow A, A2, B, B2, and tare N to stand in room air for one hour. Reweigh to determine if the material gains significantly in closed weighing bottles.

(10) Pour the c, c2, f, and f2 samples into 500-ml Erlenmeyer flasks, and the d, d2, e, and e2 samples into Coors No. 0 porcelain crucibles previously ignited and weighed with a tare crucible. Close each weighing bottle immediately after emptying, and handle the tare weighing bottle in the same manner as the others.

(11) Wait 30 minutes and weigh the empty weighing bottles as in step (8).

(12) Dry A, A2, H, H2, and tare N together (in normal air).

(13) Dry B, B2, G, G2, and tare D together (in dry air) as follows: Heat the samples at 110°C in a small oven (3.7-liter capacity and designed for vacuum drying but used as a normal pressure oven) through which air from a drying train is circulated at a rate of 200 to 250 ml per minute. [The drying train consists of two 32-mm-diameter columns containing a total of

about 200 g of magnesium perchlorate, preceded by three similar columns containing about 400 g of indicating silica gel. The silica gel is replaced as often as necessary to prevent *any* visible color change (from deep blue to either light blue or pink) in the column next to the magnesium perchlorate. The silica gel is regenerated by drying alone in an oven at 110 °C.] Close the weighing bottles rapidly before removal from the oven. Cool over fresh magnesium perchlorate. After one hour, loosen each cap momentarily (to equalize pressure) and reclose firmly. Leave another hour; then weigh.

(14) Ignite *d*, *d2*, *e*, *e2*, and the tare together, heating them from 25°C to 900°C in four hours and then igniting at 900 °C for one hour. Cover the hot crucibles and cool only two in each desiccator. Uncover just before weighing, and weigh as rapidly as possible after opening the desiccator.

(15) Transfer the ignited samples to 500-ml Erlenmeyer flasks, by pouring out the bulk, dissolving the remainder with diluted HNO_3 (and HCl if needed), and finally washing with water. Assay with the *c*, *c2*, *f*, and *f2* samples. (Note whether material reacts with the crucible glaze.)

(16) Ignite two reserve samples, *d'* and *e2'*, as in step 14 except repeat the ignition for 1-hour periods until constant weight is obtained.

NBS Results

The results in tables 2, 3, and 4 are values for samples obtained as described above*. The additional results in tables 1 and 5 involve several experimental variations.

There is some uncertainty about the values for bottles I and II of "D" because of the sampling in helium. However, in two respects, the "as is" assay and the dry-air loss, there is good agreement of the original results for bottles I and II, in table 1, with those for bottles III and IV, in table 2. The later samples, _i_, _j_, and _k_, listed in table 5 and taken one hour to 11 days after removal of bottles D.I, D.II, and D.III from the dry box, showed changes of 0.05 to 0.70 in the "as is" assay.

For each of the standards, all of the original samples showed good reproducibility on the "as is" basis, whether the samples were assayed directly or after ignition. Also, each pair of duplicate ignited samples listed in tables 1, 2, 3, and 4 agreed on the ignited basis.

Equally good agreement was not obtained for all recheck assays on the ignited-for-one-hour basis listed in table 5. The results of tests 1, 4, and 6 (table 5) indicate that it may be necessary to ignite the samples at 900 °C for two or three hours in order to obtain constant weight. Furthermore,

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*M. S. Richmond did all sampling and initial weighing, i.e., through step 9. J. R. Baldwin checked the initial weighings and made all assays and loss determinations.

Table 1. NBS initial results for standard concentrate "D", Bottles I and II (sampled in helium on 7-21[a]; titrated on 7-30-58).

Bottle	Sample	% U_3O_8 on "As is" basis[b]		% Loss at 900°C	% Change at 110°C Dry air	Regular[c]
D.I	A	-	-	-	-	+0.33
	B	-	-	-	-0.56	-
	c	83.26	-	-	-	-
	d	-	83.31	8.37	-	-
	e	-	83.30	8.47	-	-
	f'	83.30	-	-	-	-
	G	-	-	-	-0.52	-
	H	-	-	-	-	+0.32
D.II	A	-	-	-	-	+0.32
	B	-	-	-	-0.55	-
	c	83.26	-	-	-	-
	d	-	83.29	8.45	-	-
	e	-	83.31	8.44	-	-
	f	83.33	-	-	-	-
	G	-	-	-	-0.51	-
	H	-	-	-	-	+0.33
Average of 2 determinations						
D.I		83.28	83.30	8.42	-0.54	+0.32
D.II		83.30	83.30	8.44	-0.53	+0.32
Average of 4 determinations						
D.I, D.II		83.29	83.30	8.43	-0.54	+0.32

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[a] The initial weights of the weighing bottles plus samples were not constant due to exchange of helium and air through the ground joint of the weighing bottle. Results in table 1 are based on weights obtained after storing the weighing bottles plus samples in a desiccator for about 20 hours; the desiccator was opened and closed a number of times during the first 3 hours

[b] Although d and e samples were ignited before assay, all results were calculated from the "as is" weights of the samples. The c, f, and f' samples were assayed directly.

[c] Value is for the minimum gain, obtained on 7-30, when the relative humidity was 59% at a temperature of 77°F (equivalent to 5.9 grains H_2O/cubic foot of air, or 0.012 g H_2O/g dry air).

Table 2. NBS initial results for standard concentrate "D", Bottles III and IV (sampled in dry air on 9-5; titrated on 9-12-58).

Bottle	Sample	% U_3O_8 on "As is" basis[a]		% Loss at 900°C	% Change at 110°C Dry Air	Regular[b]
D.III	A	-	-	-	-	+0.14
	B	-	-	-	-0.54	-
	c	83.23	-	-	-	-
	d	-	83.24	8.39	-	-
	e	-	83.25	8.35	-	-
	f	83.22	-	-	-	-
	G	-	-	-	-0.53	-
	H	-	-	-	-	+0.15
D.IV	A	-	-	-	-	+0.14
	B	-	-	-	-0.51	-
	c	83.31	-	-	-	-
	d	-	83.19	8.34	-	-
	e	-	83.21	8.33	-	-
	f	83.20	-	-	-	-
	G	-	-	-	-0.53	-
	H	-	-	-	-	+0.13
Average of 2 determinations						
D.III		83.22	83.24	8.37	-0.54	+0.14
D.IV		83.26	83.20	8.34	-0.52	+0.14
Average of 4 determinations						
D.III, D.IV		83.24	83.22	8.35	-0.53[c]	+0.14

---

[a] Although the d and e samples were ignited before assay, all results were calculated from the "as is" weights of the samples. The c and f samples were assayed directly.

[b] Value is for the minimum gain, obtained on 9-8, when the relative humidity was 48% at a temperature of 76°F (equivalent to 4.6 grains H_2O/cubic foot of air, or 0.009^{+}g H_2O/g dry air).

[c] Two reserved samples gave loss values of 0.6 in 15 hours or 0.7 in 32 hours when dried in the bone-dry air described in Appendix D.

Table 3. NBS initial results for standard concentrate "E" (sampled in dry air on 8-8; titrated on 8-15-58).

Bottle	Sample	% U_3O_8 on "As is" basis[a]		% Loss at 900°C	% Change at 110°C	
					Dry air	Regular[b]
E.I	A	-	-	-	-	+0.02
	B	-	-	-	-0.02	-
	c	78.42	-	-	-	-
	d	-	78.48	1.11	-	-
	e	-	78.48	1.10	-	-
	f	78.43	-	-	-	-
	G	-	-	-	-0.02	-
	H	-	-	-	-	+0.02
E.II	A	-	-	-	-	+0.02
	B	-	-	-	-0.02	-
	c	78.44	-	-	-	-
	d	-	78.44	1.07	-	-
	e	-	78.48	1.12	-	-
	f	78.44	-	-	-	-
	G	-	-	-	-0.02	-
	H	-	-	-	-	+0.02
Average of 2 determinations						
E.I		78.42	78.48	1.10	-0.02	+0.02
E.II		78.44	78.46	1.10	-0.02	+0.02
Average of 4 determinations						
E.I, E.II		78.43	78.47	1.10	-0.02	+0.02

---

[a] Although the d and e samples were ignited before assay, all results were calculated from the "as is" weights of the samples. The c and f samples were assayed directly.

[b] Value is for the minimum gain, obtained on 8-9, when the relative humidity was 46% at a temperature of 79°F (equivalent to 4.8 grains H_2O/cubic foot of air, or 0.010 g H_2O/g dry air).

Table 4. NBS initial results for standard concentrate "F" (sampled in dry air on 8-20; titrated on 8-28-58).

Bottle	Sample	% U_3O_8 on "As is" basis[a]		% Loss at 900°C	% Change at 110°C	
					Dry air	Regular[b]
F.I	A	-	-	-	-	+0.03
	B	-	-	-	-0.05	-
	c	85.53	-	-	-	-
	d	-	85.64	1.00	-	-
	e	-	85.65	0.98	-	-
	f	85.65	-	-	-	-
	G	-	-	-	-0.06	-
	H	-	-	-	-	+0.03
F.II	A	-	-	-	-	+0.04
	B	-	-	-	-0.06	-
	c	85.59	-	-	-	-
	d	-	85.62	0.95	-	-
	e'	-	85.66	0.86	-	-
	f	85.65	-	-	-	-
	G'	-	-	-	-0.06	-
	H	-	-	-	-	+0.03
Average of 2 determinations						
F.I		85.59	85.64	0.99	-0.06	+0.03
F.II		85.62	85.64	0.90	-0.06	+0.03
Average of 4 determinations						
F.I, F.II		85.60	85.64	0.95	-0.06	+0.03

---

[a] Although the *d*, *e*, and *e'* samples were ignited before assay, all results were calculated from the "as is" weights of the samples. The *c* and *f* samples were assayed directly.

[b] Value is for the minimum gain, obtained on 8-28, when the relative humidity was 58% at a temperature of 75°F (equivalent to 5.5 grains H_2O/cubic foot of air, or 0.011-g H_2O/g dry air).

Table 5. NBS recheck and initial average results.

Test No.	Bottle Sample	Date Ignited	% Loss at 900°C			% U_3O_8[a]	
			1 hr.	2 hr.	3 hr.	"As-is"	Ignited
IA	D.I,D.II	7-23-58	8.43[b]	--	--	83.30[c]	90.97
1	D.II.e'	8-4,5,9	8.57	8.66	8.68	83.26[d]	91.06
	D.I.d'	8-4,5,9	8.60	8.65	8.66	--	--
2	D.I.i	7-23	8.59	--	--	82.98[c,e]	90.78
	D.I.j	---	--	--	--	82.87[c,e]	--
	D.II.i	---	--	--	--	82.96[c,e]	--
	D.II.j	---	8.58	--	--	82.99[c,e]	90.78
3	D.I.k	8-5	9.05	--	--	82.97[f]	91.22
	D.II.k	8-5	9.47	--	--	82.54[f]	91.17
IA	D.III,D.IV	9-6	8.35	--	--	83.23[g]	90.81
4	D.III.d'	9-8,9,10	8.35	8.61	8.64	--	--
	D.IV.d'	9-8,9,10	8.25	8.59	8.62	--	--
5	D.III.i	---	--	--	--	83.20[g,h]	--
	D.III.j	---	--	--	--	83.15[g,h]	--
	D.III.f'	---	--	--	--	83.20[i]	--
IA	F.I,F.II	8-23	0.95	--	--	85.62	86.44
6	F.I.d'	9-6,9,10	0.65	0.89	0.94	--	--
	F.II.d'	9-6,9,10	0.62	0.89	0.96	--	--

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[a] The "as-is" assay was calculated from the as-sampled weight and the ignited assay from the ignited-one-hour-at-900°C weight.

[b] Initial averages (from tables 1, 2 or 4) are underlined.

[c] Titrated on 7-30-58.

[d] Titrated on 8-15.

[e] Sampled two days after removal of D.I and D.II from the dry box.

[f] Sampled 11 days after removal of D.I. and D.II from the dry box; and titrated on 8-8.

[g] Titrated on 9-12.

[h] Sampled one hour after removal of D.III from the dry box.

[i] Titrated 1-15-59.

since the samples used in test 1 were duplicates of (and sampled at the same time as) the initial samples of D.I and D.II and agreed with them on the "as is" assay basis, the three-hour loss values in test 1 compared with the initial average one-hour loss for D.I and D.II suggest that all one-hour ignition losses obtained on 7-23 may be about 0.25 percent below constant weight. If so, the ignited-to-constant-weight-based assay for original samples of D.I and D.II is 91.21 percent, and for the later samples i and j of D.I and D.II may be 91.03 percent. Similarly, the results of Tests 4 and 6 indicate that all one-hour ignition losses obtained on 9-6 may be about 0.3 percent below constant weight and that the ignited-to-constant-weight-based assay for D.III and D.IV is 91.09 percent. On the other hand, comparison of the initial average loss value for F.I and F.II with the results in Test 6 for other original samples indicates that constant weight was sometimes reached in one hour. If that occurred in Test 3, then all NBS values for "D" on an ignited-to-constant-weight basis would fall between 91.03 and 91.22 percent. Some of the difference in NBS one-hour ignition loss values may be due to the variations that occurred in manually changing the furnace rheostat in the four hours before the temperature reached 900 °C.

The only evidence found of material reacting with the glaze of the porcelain crucibles was an 0.5 mg gain in the weight of each crucible used for igniting 1.5 g of either Standard "E" or another Vitro sample. There was no visible stain, and no significant difference in the "as is" basis values for samples whether assayed directly or after ignition.

Tare corrections were made, and all weighing bottles for A through H samples were stored in desiccators. The i, j, and k analysis samples were taken in room air and not put in desiccators; i.e., they were sampled exactly like umpire samples except for the delay between first opening the bottle and sampling the material.

All A, B, G, and H samples were heated at 110°C for a five-hour interval followed by two approximately 16-hour intervals. The A and H samples were heated simultaneously with the B and G samples. The time required for obtaining the minimum weight in normal air varied from 5 to 38 hours. In dry air, "D" material lost 0.16 percent in the first five hours.

Interlaboratory Evaluation

The results from all five laboratories were analyzed statistically by Dr. W. J. Youden of NBS. He found that the data did not properly qualify for establishment of confidence limits by application of statistical formulas and expressed the feeling that these data should be evaluated by a scrutiny of the individual results. This is provided in the following detailed statistical analysis by Dr. Youden supplemented by the notes based on laboratory observations.

In figure 1, Dr. Youden has compared the five laboratories by plotting their deviations from average assays (tabulated in Dr. Youden's table 2); the deviations of "as is" assays are plotted against those of "regular drying" assays. The No. 3 and No. 5 laboratories had high results; the No. 2, low; and the No. 4, erratic, with reference to the average for all five laboratories. Since the points tend to lie along a 45° line, it was concluded that both methods showed the same bias. Actually, this apparent similarity was due to (1) the gains observed during "regular drying" being considered as zero loss, and (2) the samples being prepared in a dry climate and vacuum-sealed while hot, a method that prevented the occurrence of any significant loss during regular drying.

ANALYSIS OF DATA ON THE URANIUM CONCENTRATE STANDARD SAMPLE PROGRAM*

The average difference between duplicates

(a)	Run by same analyst on same bottle	0.057
(b)	Run by same analyst on different bottles	0.064
(c)	Run by different analysts (same lab) same bottle	0.061

(Somewhat over 100 pairs of duplicates for each case.)

I conclude that there is no difference between bottles and that analysts in the same laboratory check each other.

Some of the data was discarded so that four determinations were taken for each sample, by each method, for each laboratory. The ranges for these four determinations are shown in table 1.

There are 15 such ranges for each method and the average ranges were

	Avg range for four
For "as is" sample	0.109
For "regular method"	0.104
For "special drying"	0.094
Avg for all 45 ranges	0.103

I conclude that the reproducibility is the same for all three methods.

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* Written by W. J. Youden, March 6, 1959, except for footnotes regarding laboratory observations.

Table 1. Statistical analysis of ranges for 45 sets of four determinations (for three samples, by three methods of base line establishment, in five laboratories).

Lab. No.	As is sample			Regular method			Special drying			Laboratory average
	D	E	F	D	E	F	D	E	F	
1	.12	.07	.05	.22	.03	.14	.27	.03	.06	.11
2	.07	.10	.11	.05	.06	.10	.06	.02	.04	.07
3	.11	.02	.12	.11	.02	.12	.10	.02	.13	.08
4	.19	.29	.09	.16	.23	.04	.09	.07	.20	.15
5	.13	.13	.04	.07	.13	.09	.08	.15	.09	.10
Method average			.109			.104			.094	.103

Sample average	
D	.122
E	.091
F	.095

Average range for sample of 4 = 2.059 σ

Estimate of σ = 0.05

There are fifteen ranges that can be averaged for each sample:

	Avg range for four
Sample D	0.122
Sample E	0.091
Sample F	0.095

There is no* reason to expect greater ranges for one sample than another.

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* This is based on the analysis of only the assay results. From the results for % change at 110 °C, in tables 1-4, it can be seen that sample D varied more than the other samples with atmospheric moisture changes. (Laboratory observation)

There are nine ranges from each laboratory and the average range for each laboratory follows:

Laboratory	Avg range for four
No. 1	0.11
No. 2	0.07
No. 3*	0.08
No. 4	0.15
No. 5	0.10

There is a two-fold spread between 0.07 and 0.15 which is large enough to suggest a real difference between laboratories. The data suggest that the largest range, 0.15, is a bit out of line. Mere reproducibility is only one aspect of the problem, perhaps the minor one.

Table 2 shows the averages for the same four determinations used to get the ranges shown in table 1. The row of averages is our first interest. Clearly there is no difference between the results with the "as is" and "regular" methods**. The special drying does have an effect, and this depends, as would be expected, upon the sample. The largest effect appears for sample D, and here the laboratories show pronounced disagreement. Laboratories No. 4 and No. 5 run sharply higher than the others on the special drying in the case of sample D.

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[*] NBS.

[**] This is because the "regular" method gave gains (except for a few small losses in Colorado), and the gains (of up to 0.25) were considered zero loss. (Laboratory observation)

Table 2. Averages of the 45 sets of four determinations; deviations from interlaboratory averages; and laboratory average discrepancy.

	Sample D			Sample E			Sample F			
Lab. No.	As is sample	Reg. method	Spec. drying	As is sample	Reg. method	Spec. drying	As is sample	Reg. method	Spec. drying	
1	83.12	83.18	83.43	78.39	78.39	78.40	85.42	85.45	85.46	
2	83.07	82.92	83.68	78.22	78.18	78.28	85.29	85.28	85.47	
3	83.24	83.24	83.68	78.43	78.43	78.45	85.60	85.60	85.65	
4	82.90	83.10[a]	84.29	78.40	78.36	78.42	85.43	85.52	85.59	
5	83.30	83.27	84.44	78.41	78.39	78.45	85.57	85.55	85.66	
Average	83.13	83.14	83.90	78.37	78.35	78.40	85.46	85.48	85.57	
				Deviations from above averages						Average Discrepancy
1	-.01	+.04	(-.47)[b]	+.02	+.04	.00	-.04	-.03	-.11	-.01
2	-.06	-.22	(-.22)[b]	-.15	-.17	-.12	-.17	-.20	-.10	-.15
3	+.11	+.10	(-.22)[b]	+.06	+.08	+.05	+.14	+.12	+.08	+.09
4	-.23	-.04	(+.39)[b]	+.03	+.01	+.02	-.03	+.04	+.02	-.02
5	+.17	+.13	(+.54)[b]	+.04	+.04	+.05	+.11	+.07	+.09	+.09

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[a] This value is for samples that showed no loss-on-drying. It should not be 0.2 higher than the "as-is" value unless the "regular" samples were taken before the "as-is" samples and the material absorbed moisture between the two samplings. (Laboratory observation)

[b] Omit from average discrepancy.

The deviations for each laboratory from the average of all the laboratories is also shown (in both table 2 and figure 1). These deviations are particularly instructive, especially when the "sample D - special drying" set are set aside. Note that No. 2, the laboratory with the smallest range (0.07) is

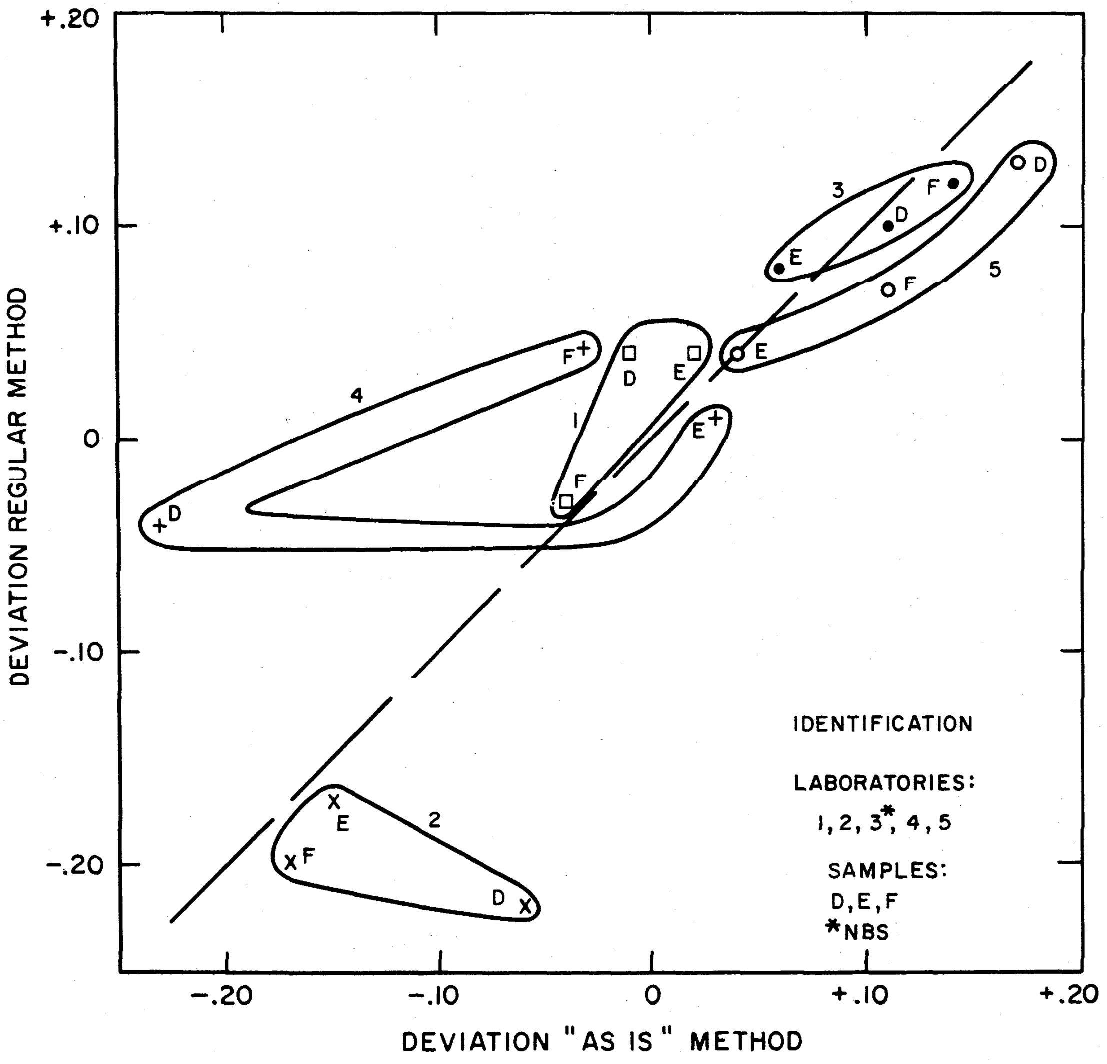

Figure 1. Graphical diagnosis showing groupings of deviations by laboratories.

consistently low[*]. Indeed the average amount low is 0.15 and represents a serious bias either for this laboratory or the others. Laboratories No. 3 and No. 5 are consistently high, the deviations all being positive. Note that these averages of +0.09 and -0.15 are far in excess of what would be expected considering the reproducibility as revealed by the average range. The average range for a sample of four is 2.059σ. The average range, 0.103, divided by 2.059, gives 0.05 as an estimate of the standard deviation of a single determination, considering only reproducibility within a laboratory.

Each laboratory is represented by 9x4 or 36 determinations in table 2. The laboratory average would have a standard deviation of $0.05 / \sqrt{36}$ or about 0.01. Clearly the scatter of the laboratory averages, as revealed by the deviations:

No. 1	-0.01
No. 2	-0.15
No. 3	+0.09
No. 4	-0.02
No. 5	+0.09

demonstrates beyond question the existence of substantial laboratory biases. It is not the role of statistics to single out the laboratory with the smallest bias. The data suffice

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[*] This appeared to be due in part, at least, to a pickup of moisture during sampling, as evidenced by loss-on-drying values that did not agree with known climate variables. (Laboratory observation)

to detect a difference between biases of

$$\frac{0.05}{\sqrt{36}} \cdot \sqrt{2} \times 2 = 0.03$$

The spread here is from +0.09 to -0.15 or 0.24.

In summary we find, as usual, that differences in precision from laboratory to laboratory are minor and quite unimportant. The methods agree very closely because each laboratory apparently carries over into each method the same bias. There are pronounced differences between laboratories in these biases and the problem really resolves into one of finding out who is right. If the laboratories all run the same standard sample and adjust their results on unknowns by whatever discrepancies they find on the standard sample, the laboratories will be brought into agreement. If a sample of known content is used, we can decide which laboratory has the least bias - pending that, no one knows.

Anyone impressed by a majority vote would pick No. 1, No. 3, and No. 5 to establish a consensus. These three laboratories do consistent work as revealed by the three samples, and yield a general average with which each of three laboratories agree quite well.

W. J. Youden
March 6, 1959

APPENDIX C

Summary of Drying Tests on IMCC Material at NBS

Three samples of Florida green salt material, representing IMCC Lots 4, 5, and 6, were received at NBS on 10-24-56. Each bottle was completely sealed with wax. Immediately after the seals were broken on 10-28-56, eight samples of each lot were rapidly transferred to weighing bottles. The latter were all closed within 4 minutes after the sample bottles were first opened, and were weighed within the next hour. The No. 1, 2, 7, and 8 samples, weighing 7 to 10 g each (in 3- to 7-mm deep layers) were in 40- x 50-mm weighing bottles; the other samples, weighing approximately 1.5 g each, were in 25- x 40-mm weighing bottles.

The No. 1 and 7 samples were dried under usual Washington laboratory conditions, with the moisture of the ambient autumn air varying from 0.010 to 0.003 g H_2O/g dry air.* The No. 2 and 8 samples were dried in a specially conditioned room with the moisture of the ambient air maintained at approximately 0.013 g/g (or 80°F and "60" percent relative humidity) to simulate a Florida atmosphere. The No. 3 and 5 samples were assayed. The No. 4 and 6 samples were stored in closed weighing bottles (but not in a desiccator) in the laboratory for 39 days, and then were used to test experimental procedures before application of the latter to the No. 1 and 2 samples. Figure 1 shows

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* The wet and dry bulb temperatures were obtained at the end of each drying interval with a Weather Bureau sling psychrometer, and the measurements were converted to g of moisture per g of dry air with the aid of a psychrometric chart.

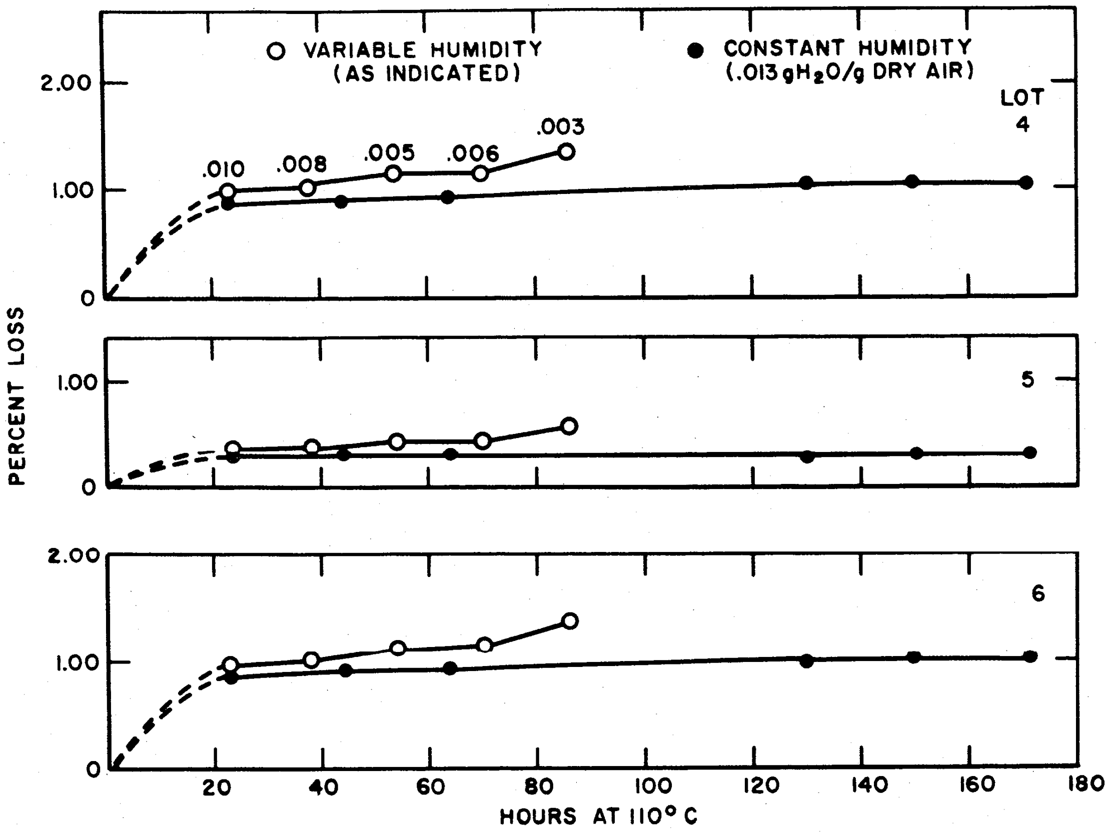

Figure 1. NBS results for drying IMCC material in room air.

the variations in loss results due to varying the moisture of the ambient air from 0.013 to 0.003 g/g.

In order to determine how much the loss values could be increased by reducing the moisture content of the air, the No. 1, 2, and 4 samples were later dried in a smaller oven (3.7-liter capacity) through which air from a silica gel-Anhydrone drying train was blown in at a rate of 200 to 250 ml per minute. As shown in figure 2, (1) loss values increased as much as 0.8 percent over the previous ones (figure 1), (2) constant weights were not reached in 160 hours, but (3) large

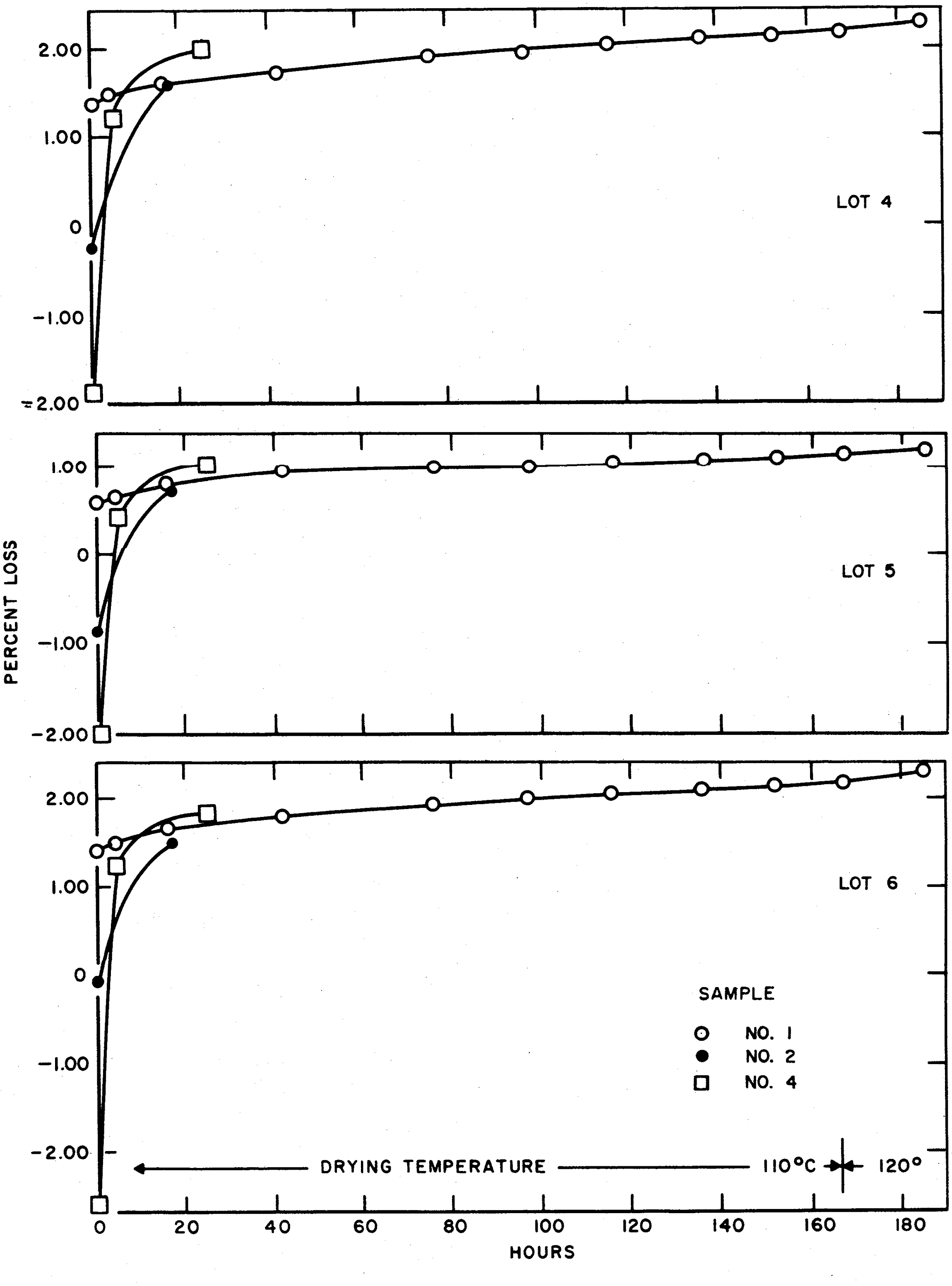

Figure 2. NBS results for drying pre-treated IMCC material in "dry" air.

amounts of moisture absorbed during exposure of the No. 2 and 4 samples to room atmospheres were removed rapidly (within 24 hours).

Observations were made on the absorption of moisture by samples that were kept at room temperature under various atmospheres. In closed weighing bottles, gains were negligible in 19 hours for the dried No. 1 and 2 samples during storage in air containing 0.003 g H_2O/g dry air, but amounted to about 1 percent within 40 days for the "as is" No. 4 and 6 samples during storage in air containing 0.004 to 0.013 g H_2O/g dry air. In open weighing bottles in air containing 0.013 g H_2O/g dry air, the No. 1, 2, and 4 samples of each lot gained as fast as 0.3 percent per hour and up to a total of 2 or 3 percent.

Finally, after redrying the No. 2 and 4 samples, the No. 1, 2, and 4 samples were heated at 110°C in a controlled, humid atmosphere obtained by passing air containing approximately 0.013 g H_2O/g dry air through the small (3.7-liter) oven at a rate of 130 to 220 ml/minute.* The results are shown in figure 3. All samples came to constant weight within 5 hours, and both wetter (No. 1) and drier (No. 2 and 4) samples approached the same equilibrium values. For the No. 2 samples, the final weights were the same as those (figure 1) originally obtained by drying in a gravity-convection Iso-Temp oven in a room with

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* Before entering the oven, the air was equilibrated with a saturated NH_4NO_3 - H_2O mixture at 24 to 28 °C. The same results were obtained by simply passing the air over the mixture as by bubbling it through a series of saturated NH_4NO_3 solutions.

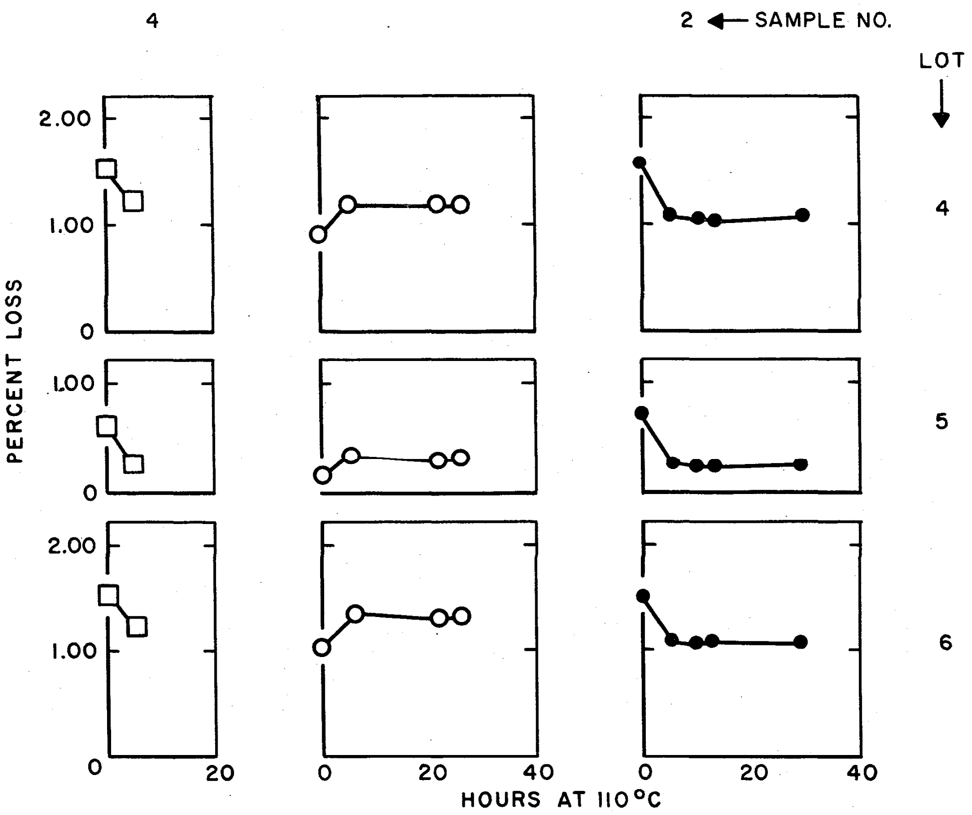

Figure 3. NBS results for heating pre-treated IMCC material in humid air (about 0.013 g H_2O/g dry air).

a controlled atmosphere (0.013 g H_2O/g air). The final loss values for the No. 1 and 4 samples were similar to those for the No. 2 samples even though the former may have undergone physical changes during the prolonged dry air treatment of the No. 1 samples and the prolonged "wetting" of the No. 4's (the wetting caused etching of the weighing bottles).*

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* In the case of Lot 5, etching was observed only with the samples that were allowed to absorb considerable moisture (No. 4 and 6 samples). But for Lots 4 and 6, even the drier samples (No. 1, 2, 7 and 8) eventually produced interference rings in their weighing bottles. Lot 6 gave the most etching and Lot 4 gave almost as much.

The results shown in figures 1 and 3 indicate that IMCC material was readily dried to a reproducible state in an atmosphere containing about 0.013 g H_2O/g dry air.

On the basis of this study and the interlaboratory comparison of IMCC, NBL, and NBS results for Lots 4, 5, and 6, it was suggested in 1957 that for IMCC material:

(1) All analytical samples be taken and weighed promptly after the initial opening of the sealed bottle.

(2) Loss determinations be made on approximately 10-g samples in weighing bottles 40 mm in diameter.

(3) All laboratories determine losses under the same atmospheric moisture conditions (e.g., 0.011 to 0.014 g H_2O/g dry air).

(4) The samples be dried at 110°C in the laboratories for only two short (4-or 5-hour) intervals, since the purpose of the drying in the laboratory was to remove only the moisture absorbed after the sampling plant dry-weight basis had been established. One drying interval probably would suffice if a mechanical-convection type oven were used, but two drying periods might be needed with a gravity-convection oven.

(5) Any samples bottled at the sampling plant in humid weather be examined for possible side effects, because of the likelihood of hydrogen fluoride liberation during storage.

APPENDIX D

Summary of NBS Drying Studies of Four Lots of Blockson Uranium Concentrates

Because of the extremely hygroscopic nature of Blockson uranium phosphate material, these studies were made in 1959 at NBS to determine the amount and rate of loss at 110 °C of the Blockson material in bone-dry air and to identify the variables to be controlled in order to obtain reproducible results.

Description of Drying Train for Obtaining Bone-Dry Air

Compressed air was passed at a rate of 1.0 to 1.5 liters per minute through a drying train arranged as follows:

(1) Column of absorbent cotton

(2) Two or more columns of indicating silica gel, reactivated by heating at 110 °C to 180 °C. The first column contained about 150 g of silica gel and was reactivated daily. No color change was observed in the second column .

(3) Trap

(4) T-tube dipping in mercury. The tube containing the mercury was supported in an extra container and loosely covered so as to prevent accidental scattering of mercury.

(5) Trap

(6) Shepherd trap immersed in a dry-ice-acetone slurry (about -77°C) contained in a four-liter Dewar tube. The Shepherd trap was the concentrating sampler described by

M. Shepherd et al*. The main tube was 260 mm high and 40 mm in diameter. The glass wool filter was 60 mm high and about 3 mm thick. In the set-up for uranium concentrate studies, air entered the outside tube and left through the center.

(7) Glass connecting tube, 9 mm in diameter and 60 cm long.

(8) Rotameter tube (Brooks Tru-Taper Tube Size 2-15-3, with stainless steel float).

(9) Glass and saran connecting tubes.

(10) Oven, 3.7-liter capacity, with an all-metal, hermetic lining and an entry port loosely covered with a piece of metal to disperse the entering air stream. The oven was designed for vacuum drying, but in this case was used at atmospheric pressure with air escaping only around the door, which was held in place by springs. (Slight additional pressure on the door decreased the rotameter reading momentarily.) There were no rubber or plastic connections between the Shepherd trap and the oven.

General Procedure

(a) Sampling. The material was grab-sampled as described in the basic procedure given in the text, sections 4.C.1a and 4.C.1c.

(b) Drying. From two to five weighing bottles, including a tare, were placed in the dry air oven together. The caps were tilted on the bottles during drying and all of the bottles

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* Shepherd, M., Rock, S. M., Howard, R., Stormes, J., Anal. Chem. 23, 1431-33 (1951).

were closed as rapidly as possible after the oven was opened. Then all of the bottles were transferred to a 160-mm desiccator freshly charged with magnesium perchlorate or phosphorus pentoxide. After cooling for one hour, each cap was loosened for an instant and closed firmly. The closed bottles were left in the desiccator for at least an additional half-hour before weighing, against the tare.

Experimental and Results

(a) Study No. I. Initial tests were made on Lots 11-58 and 12-58 as follows:

(1) The drying was repeated until less than 0.05 percent loss was obtained in each of two 20-hour intervals. The maximum loss was obtained after a total of 72 hours.

(2) Then the dry ice (in part 6 of the drying train) was omitted for two drying intervals. This resulted in a gain of 0.07 percent when the silica gel was reactivated at 110°C, and a return to the maximum loss when the silica gel was reactivated at 170°C in a relatively dry ambient atmosphere.

(b) Study No. II. Supplementary tests were made on Lots 2-59 and 3-59. When the bottles were first opened on 8-28-59, the materials were grab-sampled as usual, except that a total of seven samples from each lot were taken as follows: The first two and last two samples (No. A, B, F, and G) of each lot weighed 4.5 to 7.2 g and the middle three samples (No. c, d, and e) weighed approximately 1.5 g each. The following precautions regarding drying were observed. The silica gel in the first drying column was replaced daily; it was reactivated by heating overnight at approximately 175°C. One dry-air apparatus was used for all dry-air tests. The Shepherd trap was left in the train even when the trap was not cooled; but before use at room temperature, it was flushed with dry air enough to insure that its interior was dry. Whenever the air flow was discontinued, as during the replacing and cooling of silica gel, the exit of the Shepherd trap was closed. Except in test 5, all dry-air samples were heated in groups of two or three and cooled in covered weighing bottles beside a fresh portion (three inches in diameter) of phosphorus pentoxide in a 160-mm desiccator. Seven tests were made as follows:

(1) One sample (A or B) of each lot was heated for three intervals totaling 70 hours, in silica-gel-dried air.

(2) After test 1 was completed, the duplicate samples (A or B) were heated in silica-gel- plus cold-trap-dried air for three intervals totaling 68 hours.

(3) While samples A and B were heated in dry air, samples F were heated in normal air for seven intervals totaling 148 hours.

(4) Samples e were stored in a covered plastic box at room temperature for 2 weeks.

(5) Samples e and F of both lots were heated together in silica-gel-dried air for 14 hours.

(6) Samples e, F, and G of Lot 2-59 were heated in silica-gel-dried air for four intervals totaling 91 hours.

(7) Samples e, F, and G of Lot 3-59 were heated together in silica-gel-dried air for 4 intervals totaling 93 hours. The samples in test 7 were heated every other night and those in test 6 were heated on the alternate nights.

The results are summarized in table 1. The duplicate results obtained for the A and B samples (tests 1 and 2) and later confirmed with the G samples (tests 6 and 7) showed that the cold trap can be omitted when the air, containing up to

Table 1. Changes in weight of Blockson samples during heating at 110 °C in varied atmospheres, and during storage.

Conditions			Percent Change in Weight					
			Lot 2-59 Sample			Lot 3-59 Sample		
Test No.	Air Treatment	Time (hr)	"A"[a]	F	e	"A"[a]	F	e
1	Silica gel[b]	70	-0.62[c]			-0.88[c]		
2	Cold trap[b]	68	-0.63[c]			-0.85[c]		
3	Untreated[b] Untreated[b]	131 148		+1.77[c] +1.60			+1.96[c] +1.85	
4	None	330		-[d]	+2.7[c]		-	+2.4[c]
5	Silica gel[b]	14		+0.18	+0.3		-0.14	-0.3
6	Silica gel[b] Silica gel[b]	73 91	-0.66[c] -0.67	-0.43 -0.48	-0.7$_1$ -0.7$_3$		-	-
7	Silica gel[b] Silica gel[b]	61 93				-0.89[c] -0.94	-0.72 -0.82	-0.9$_4$ -0.9$_8$

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[a] This column includes results for A, B, and G samples: A was used for tests 1 or 2; B, for the other; and G, for 6 or 7.

[b] Followed by heating at 110 °C, for one or more overnight intervals.

[c] Result is for initial test of this sample.

[d] Dash indicates omission of sample from test.

0.015 g H_2O/g dry air (62 percent relative humidity at 83 °F) is dried with silica gel reactivated at 175°C.

Increasing the sample depth by 6 mm or opening the weighing bottle for 1 minute in normal air containing 0.011 g H_2O/g dry air appeared to decrease the loss by less than 0.1 percent.

Comparison of results for e, F, and G samples indicate that samples heated at 110 °C in normal air absorb moisture that is more difficult to remove than that absorbed at room temperature. However, the difference was less than 0.3 percent after 73 hours in dry air, and appeared to slowly decrease with additional drying. It seems plausible that the alternate heating and cooling of the F samples in normal air (for 7 intervals) would cause the ambient water vapor to penetrate more deeply into the sample particles and thus make it more difficult to remove.

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