JUL 10 1978

MEMORANDUM: Robert B. Minogue, Director
Office of Standards Development

Clifford V. Smith, Jr., Director
Office of Nuclear Material Safety
and Safeguards

Ernest Volgenau, Director
Office of Inspection & Enforcement

FROM: Saul Levine, Director
Office of Nuclear Regulatory Research

SUBJECT: RESEARCH INFORMATION LETTER # 31 ASSAY OF STANDARD REFERENCE MATERIAL (SRM) 950b

31

Introduction

This memorandum transmits the results of a completed phaseof research on the assay determination of uranium in Standard Reference Material (SRM) 950b, which is part of a continuing NRC research activity entitled "Measurements and Standards for Nuclear Materials Safeguards." This study was performed by the National Bureau of Standards (NBS), for the Office of Nuclear Regulatory Research (RES) in response to a research request (SD-77-3) from the Office of Standards Development identifying a need to improve the quality of measurements made on special nuclear material for control and accounting purposes.

The purpose of this phase of the study was to develop and certify a uranium oxide, U_3O_8 assay standard to replace the virtually depleted SRM 950a. The new replacement calibration standard, designated as uranium assay standard SRM 950b, was certified through a cooperative effort of NBS and New Brunswick Laboratory (NBL) using both the modified Davies-Gray method and coulometry.

The research results indicate that the newly developed SRM 950b calibration standard has a certified value of 99.97 $\pm$ 0.02 percent uranium oxide (U_3O_8).

Results

The results of the first phase of a series of SRMs to be developed under this research task have been completed. Tables I and II summarize the resulting quantitative data that have been generated.

Additional efforts in the area indicated are continuing. The aim is to develop, test and certify a set of uranium oxide (U_3O_8) assay SRMs and the associated set of Nuclear Safeguards SRMs for nondestructive assay (NDA) use. The first set to be developed will cover the low enriched spectrum ranging from 0.7 percent to 5.0 percent. Additional sets of low enriched standards will be developed over the next two years followed by the production of standards for high enriched calibrations. Research Information Letters (RIL's) will be prepared for distribution as each SRM standard or series of standards are developed, tested and certified.

The results of this work have been exposed to expert review through extensive collaboration with knowledgeable individuals in both private and government facilities and through numerous technical meetings (e.g., ASTM, ANSI, INMM, international information exchanges). SAFER's Measurements and Standards Research Review Group concluded that the work was sufficiently mature and technically sound that this Research Information Letter be prepared.[1] While the exact impact of this work on current licensing practices has not been identified, it is felt that there are immediate applications involving the verification of licensee inventory measurement data by NRC regional inspectors.

Since the issuance of SRM 950a in early 1960, essential information about the use of calibration standards has been placed directly on the new certificates (See Enclosures II and III). These results can best be utilized in estimating the uncertainty associated with "Material Unaccounted For" (MUF) determination and other pertinent accountability measurements. The stated uncertainty associated with the certified value gives the limit of the random error and the estimated upper limit of conceivable systematic errors, including material variability.

RES concludes that this phase of ongoing research activity has achieved most of its initial objectives and that these findings will continue to be evaluated and disseminated as new SRMs become available in the later stages of the program.

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[1] Minutes of the SAFER Measurement & Standard Review Group Meeting, May 4, 1978, Washington, D. C., issued June 16, 1978.

Discussion

SRM 950b is a high purity natural uranium standard intended to provide a reference material of known uranium content. The certified value for this material is 99.969 ± 0.020 percent uranium oxide (U_3O_8) and is based on the material being ignited at a temperature of 800°C for one hour in an open crucible in a muffle furnace and cooled in a desiccator. It is critical that the material be freshly ignited in the prescribed manner to obtain accurate assay results.

SRM 950b is a good example that the certification of a reissue SRM does not always proceed in a smooth manner. Despite the fact that both SRM 950a and b are materials of relatively high purity, there are some substantial differences between the two. For SRM 950a, an ignition temperature of 900°C for one hour was found to be satisfactory and gave reproducible uranium assay values. For SRM 950b, an ignition temperature of 900°C for one hour gave ignition loss variations of up to 0.05 percent depending on the rate of cooling after ignition. An ignition temperature of 800°C for SRM 950b gave reproducible ignition losses to within 0.005 percent irrespective of cooling rates or even if the ignition temperature was in error by as much as ±50°C. The titrimetric assay of SRM at NBS also showed that the type of furnace used for ignition could influence the assay value by a small but statistically significant amount. As a result, the certificate for SRM 950b states that the ignition is to be performed in a muffle furnace at 800°C for one hour (Enclosure III).

The original NBS assay of SRM 950b was performed using a coulometric technique and the assay of this material at New Brunswick Laboratory (NBL) used a titrimetric procedure. The results of the two analyses differed by more than 0.03 percent. Investigations of both the coulometric and titrimetric methods resulted in several modifications being made to the coulometric method which accounted for this difference. The certificate for SRM 950b lists an uncertainty of ± 0.02 percent which reflects both a small interlaboratory uncertainty and some imprecision noted for the coulometric method.

Recommendations

The above results and discussion are offered for user office consideration for application to an identified regulatory need. The primary significance of the work described is to improve the standardization and calibration capability of both NRC field inspectors and the nuclear industry as a whole. RES believes that the reported results are likely to have significant near-term impact on current SD guides that will address the implementation of 10 CFR 70.57, Licensees Measurement Control Plans.

SRM 950b is available to NRC regional inspectors, NRC contractors, DOE contractors, licensees and foreign governments that have entered an agreement in cooperation with the U. S. Government concerning the civil uses of atomic energy.

The RES contact for any further clarification or evaluation of these results is Dr. R. L. Shepard of the Operational Support Branch.

Original Signed by
Saul Levine

Saul Levine, Director
Office of Nuclear Regulatory Research

Enclosures: (3)
1. Two Tables
2. Certificate - Standard Reference Material 950a
3. NBS Certificate - Standard Reference Material 950b

DIST:
Central File
Circ
Chrono
R. L. Shepard Rdg
H. M. Hawkins
J. S. Durst
F. Arsenault
C. P. Jupiter
R. M. Scroggins
S. Levine

RES

C. P. Jupiter
6/ /78

RES:SAFER	RES:SAFER	RES:SAFER	RES:SAFER	RES:SAFER	RES:DIR
427-4387 RLShepard:akb	HMHawkins	JSDurst	FArsenault	RMScroggins	SLevine
6/ /78	6/ /78	6/ /78	6/ /78	6/ /78	6/ /78

ENCLOSURE 1

Table 1. Uranium Assay Results

SRM*	No. of Assays	Measured Concentration of U_3O_8 in Sample (%)	σ, Value of Standard Error (%)
960	14	99.971	0.005
950a	4[a]	99.938	0.003
950b	8[a]	99.969	0.006
950b[b]	16	99.967	0.016
950b[c]	6	99.958	0.022

[a] Ignition in muffle furnace.
[b] Determined by NBL.
[c] Determined by coulometry.
* Standard reference material.

Table 2. Comparison of Certified Values of Uranium Assay SRMs

SRM*	Certified Value of Measured Concentration (%)
960	99.975 ±0.017
950a	99.93[a] ±0.02
950b	99.97 ±0.02

*Standard reference material.
[a] Corrected for change in atomic weight of chromium.

U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
L. M. Branscomb, Director

ENCLOSURE II

Certificate

STANDARD REFERENCE MATERIAL 950a

Uranium Oxide (U_3O_8)

Uranium Oxide (U_3O_8) . . . . . 99.94 percent

This sample consists of normal uranium in the form of oxide, U_3O_8. It is intended to provide a material of known uranium content. The indicated value is based on material heated at 900 °C for one hour in an open crucible and cooled in a desiccator. The material should be freshly ignited as used.

The assay is based on high-purity normal uranium metal (dingot) using National Bureau of Standards Standard Potassium Dichromate 136a as the transfer reagent. The atomic weights used in the calculation are: uranium, 238.03, oxygen, 15.9994. It is estimated that the uncertainty in the assay does not exceed 0.02 percent.

Total impurities as determined by spectrographic analysis are less than 50 ppm. The difference between the assay and calculated purity is considered to represent deviations from the nominal stoichiometric composition.

Washington, D. C. 20234
December 1, 1961
(reprinted October 27, 1969)

Harry C. Allen, Jr., Chief
Division of Analytical and
Inorganic Chemistry

U.S. Department of Commerce
Juanita M. Kreps
Secretary

National Bureau of Standards
Ernest Ambler, Director

ENCLOSURE III

National Bureau of Standards Certificate

Standard Reference Material 950b

Uranium Oxide (U_3O_8)

(In Cooperation with the Department of Energy, New Brunswick Laboratory, Argonne, Illinois)

This material consists of normal uranium in the form of oxide, U_3O_8. It is intended to provide a reference material of known uranium content.

CERTIFIED VALUE

Uranium Oxide (U_3O_8). . . . 99.968 ± 0.020 percent

The stated uncertainty of ±0.020 percent associated with the certified value is the linear sum of 0.0076 percent, which is the limit of the random error of the assay measurements at the 99 percent confidence level (2.807 S_m, where S_m is the standard error of the mean with n = 24), and 0.012 percent, the estimated upper limit of conceivable systematic errors including material variability. The above certified value is based on material heated at 800 °C for one hour in an open crucible in a muffle furnace and cooled in a desiccator. *It is important that the material be freshly ignited in this manner to obtain accurate results.*

The total impurities as determined by spectrochemical analysis are estimated to be less than 50 μg/g. The determined iron content is ~3 μg/g and the determined vanadium content is ~ 1 μg/g. The assay of this material is based on the use of NBS Potassium Dichromate (SRM 136c), as the oxidizing agent as described in the NBL titrimetric method for the precise assay of uranium metal.[1,2] The assay values obtained are compatible with those obtained from the assay of NBS Uranium Metal, (SRM 960) and NBS Uranium Oxide, (SRM 950a). The certified value for this lot of uranium oxide has also been confirmed using a coulometric procedure.

The atomic weights used in the calculations are: uranium, 238.029, and oxygen, 15.9994.

This material was prepared under contract with the National Lead Company of Ohio, Cincinnati, Ohio. Assay of the material was performed by N. M. Trahey of the New Brunswick Laboratory, Argonne, Illinois and J. R. Moody and W. Koch of the NBS Analytical Chemistry Division. Iron and vanadium were measured by B. I. Diamondstone and S. A. Wicks of the NBS Analytical Chemistry Division.

Overall direction and coordination of the technical measurements leading to the certification were performed under the chairmanship of I. L. Barnes.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W. P. Reed.

Washington, D.C. 20234
March 1, 1978

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

Ignition of Material Before Use

To assay accurately, this material must be ignited in an open crucible in a muffle furnace at 800 °C for one hour and cooled in a desiccator just prior to use. The ignition temperature, 800 °C, was determined to be essential for this specific lot of material.

References

1. A. R. Eberle and M. W. Lerner, NBL Annual Progress Report, No. 258, July 1969 - June 1970, pp 5-9.
2. A. R. Eberle and M. W. Lerner, NBL Annual Progress Report, No. 262, July 1970 - June 1971, pp. 5-16.