ESADA FUEL FABRICATION DEVELOPMENT PROGRAM

TERMINAL REPORT

VOLUME V

Process Analysis – Chemical, Metallographic, and Statistical

PART I

CHEMICAL AND METALLOGRAPHIC ANALYSES

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PART I

CHEMICAL AND METALLOGRAPHIC ANALYSES

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ABSTRACT

This report describes the procedures, techniques, and equipment utilized for the metallographic and chemical analysis of uranium carbide. The purpose of the analyses was to verify the control of the manufacturing processes, and to attest to the conformance of the product to specification.

I. INTRODUCTION

This report discusses and describes the analyses which were conducted in order to ultimately qualify both UC melt stock and cast UC slugs. Details of the sampling plan, and statements pertaining to the statistical evaluation of the experimental data, are covered. The following chemical and metallographic analyses are described in this report:

a) Determination of total uranium

b) Determination of total carbon — chemical

c) Determination of equivalent carbon — metallographic

d) Determination of oxygen

e) Determination of nitrogen

f) Determination of U^{235} enrichment

g) Determination of trace impurities

h) Determination of oxygen in sodium

II. OBJECTIVES AND DESCRIPTION OF ANALYTICAL EFFORT

Compositional control of the uranium carbide product, throughout its production and fabrication into fuel elements, is necessary, to insure a product devoid of those nuclear poisons and other impurities which might adversely affect the performance of the material as a nuclear reactor fuel; also, to insure consistent, predictable behavior during fabrication (e. g. , oxygen-accelerated erosion of graphite electrodes during arc melting). The objective of the analytical effort, coupled with the specified sampling plan, was to demonstrate to an acceptable, economically feasible, statistical confidence level, that the product indeed conformed to specifications designed to assure reliable in-pile performance.

Uranium carbide melt stock, for the preparation of cast slugs, was either procured from a commercial supplier or prepared in house, as described in Volume II. As-received material (viz, uranium metal, uranium dioxide, or uranium carbide) was analyzed for uranium, minor and trace constituents, oxygen or carbon, and uranium-235 enrichment. Cast slugs were similarly analyzed.

In the fabrication of cast slugs into completed fuel rods, metallic sodium is used as a thermal bond in the fuel-cladding annulus. Analysis of sodium for oxide content was performed.

III. SUMMARY

Table I provides a summary of the procedures used for the analyses conducted. Details of the analytical procedures, and descriptions of the equipment, are contained in the appendixes. Metallographic and chemical examinations of the manufactured product were able to verify process control and conformance of the product to specifications.

TABLE I

SUMMARY OF ANALYTICAL PROCEDURES

Analysis	Procedure
Uranium	Ceric sulfate titration, ferroin indicator, visual end point
Total carbon	Combustion — collection of CO_2 on Ascarite, gravimetric
Equivalent carbon	Metallography
Oxygen in uranium carbide	Vacuum fusion, platinum bath, manometric readout; Inert gas fusion, conductimetric readout
Nitrogen	Kjeldahl analysis, colorimetry using Nessler's reagent
U^{235} enrichment	Gamma-ray spectrometry
Trace impurities	Emission spectrography, dc arc, carrier distillation
Tungsten	Spectrophotometric, dithiol in isoamyl acetate
Oxygen in sodium	Mercury amalgamation

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APPENDIX A
DETERMINATION OF TOTAL URANIUM

I. DISCUSSION

The method is based upon the oxidation of U^{IV} to U^{VI}, by means of standard ceric sulfate reagent. Acid solution of uranium is passed through a lead reductor to reduce uranium to a mixture of U^{III} and U^{IV}. The uranium in this mixture is air oxidized to U^{IV}, which is then titrated with standard ceric sulfate using a ferroin indicator. Corrections must be applied to the required milliequivalents of ceric sulfate for the contributions of the blank and of iron. The equivalent weight of uranium must be adjusted for enrichment.

II. PROCEDURE

    a) Dissolve 0.5 g uranium carbide in water. Slight heating may be required to initiate the reaction. When the reaction has subsided and sample has crumbled, add 5 ml concentrated nitric acid and heat to near dryness.

    b) Add 5 ml concentrated HNO_3 and 5 ml concentrated $HClO_4$; evaporate to dense white fumes, then to near dryness.

    c) Cool sample and take up in 20 ml concentrated HCl and 80 ml H_2O. Mix solution and pass through a lead reductor into a receiving flask.

    d) Wash reductor with 80 ml 1 $\underline{N}$ HCl.

    e) Add 1 drop 85% H_3PO_4 and 1 ml 0.001 $\underline{M}$ ferroin indicator to solution in flask.

    f) Titrate with ceric sulfate until color begins to lighten.

    g) Add 2 drops H_3PO_4.

    h) Continue titration until color changes from red-orange to yellow-green.

III. CALCULATION

Weight percent uranium

$$= \frac{\text{m}\ell \text{ ceric sulfate (corrected for blank + iron)}}{\text{milliequivalent weight of U (corrected for enrichment)}}$$

$$\text{x} \frac{\text{N of ceric sulfate}}{\text{sample weight}} \text{ x } 100$$

IV. STANDARDIZATION

The analyses may be verified by analyzing, in the same manner, samples of U_3O_8 of composition certified by the United States National Bureau of Standards (Standard No. 950a - 99.94% U_3O_8).

III. CALCULATION (Corrected)

$$\text{Weight percent uranium} = \frac{V \times N \times E}{W} \text{ x } 100$$

where:

V = mℓ ceric sulfate
(corrected for blank and iron)

N = normality of ceric sulfate

E = milliequivalent weight of U
(corrected for enrichment) (mg/meg)
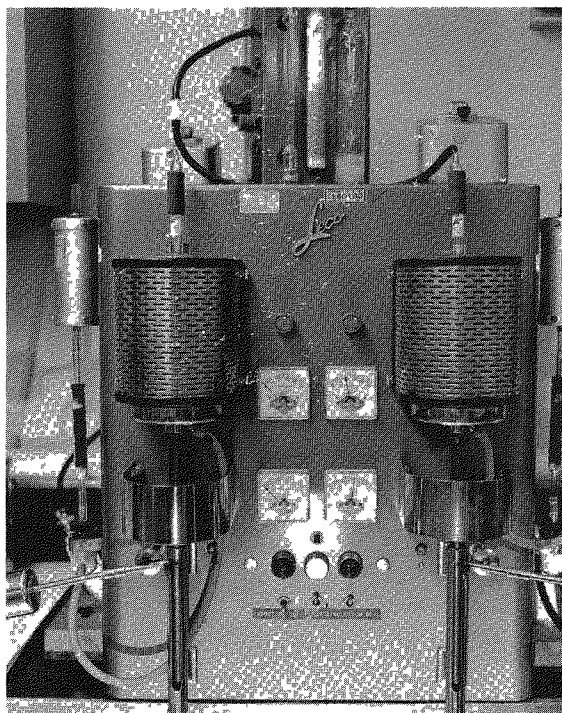
W = sample weight (mg)

APPENDIX B
DETERMINATION OF TOTAL CARBON – CHEMICAL

I. DISCUSSION

This method consists of burning the sample in a stream of oxygen, and determining the weight of generated carbon dioxide which is collected in an Ascarite absorption tube.

II. PROCEDURE

a) Weigh, to nearest 0.1 mg, approximately 400 mg of uranium carbide into a ceramic crucible.

b) Add one scoop of iron chip and 1/3 scoop of tin as accelerators.

c) Place crucible on pedestal of induction furnace (see Figure 1 for equipment layout); and, in a stream of oxygen (750 ml/min), burn the sample for 7 min.

7610-1830

Figure 1. Apparatus for Total
Carbon Analysis

d) Record, as mg CO_2, the weight increase of the absorption bulb, corrected for the blank.

III. CALCULATION

$$\text{Weight percent carbon} = \frac{27.29(\text{mg } CO_2)}{\text{sample weight(mg)}}$$

IV. STANDARDIZATION

Performance of the equipment, and quantitative recovery of the CO_2, is verified by the use of United States National Bureau of Standards Chemical Standard No. 4i (3.26% carbon in cast iron).

APPENDIX C
DETERMINATION OF EQUIVALENT CARBON – METALLOGRAPHIC

I. DISCUSSION

The metallographic method for determination of relative amounts of free uranium or UC_2 phases entailed metallographic examination and comparison with a set of previously prepared standards. The standards (Figure 2) were developed by selecting photomicrographs representative of uranium carbide of known chemical carbon contents.

A primary advantage of the metallographic method for determination of equivalent carbon was that of economics. Another equally important attribute was from a technical viewpoint: metallographic examination and analyses revealed inhomogeneties within a heat, or within a given sample, that may have been masked by chemical analyses which average an entire sample. For example, a sample near stoichiometric UC composition (4.8 wt % C) may show metallographic evidence of localized UC_2 platelets, even though the average chemical composition of the sample is ≤ 4.8 wt %. Previous work indicates that the presence of UC_2 platelets inhibits fuel-cladding compatibility.

## II. PROCEDURE

A. Specimen Preparation

The 0.5-in. diameter by ~0.75-in. long fuel slug specimens were clamped in an automatic polisher (Figure 3) in batches of ten, and worked through numbers 180, 230, 400, and 600 grit abrasive papers, using kerosene as a lubricant. Following this; a chemical polish, using a solution of 10% oxalic acid and Linde B (Al_2O_3 abrasive) on a polishing wheel, was performed. Finally, using equal parts of acetic acid, nitric acid, and water, the samples were etched sufficiently to clearly delineate the structure. The samples were thoroughly rinsed with fresh alcohol and dried with an air blast after each processing step. Water was not used during preparation, except as indicated in the etching solution.

Storage for any appreciable time was under vacuum. All applicable safety regulations pertaining to uses of chemicals and radioactive materials were observed.
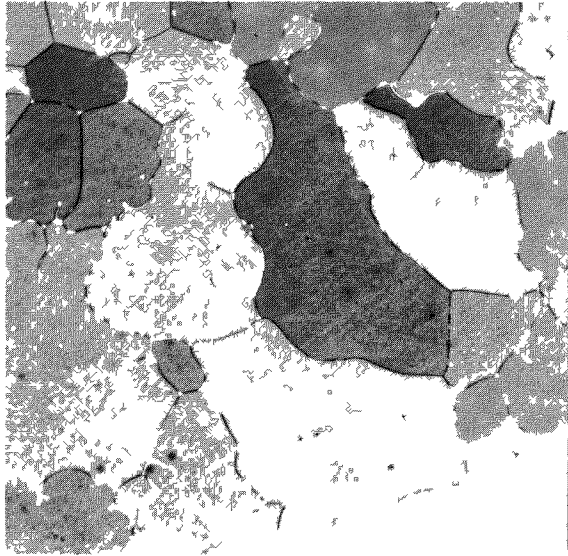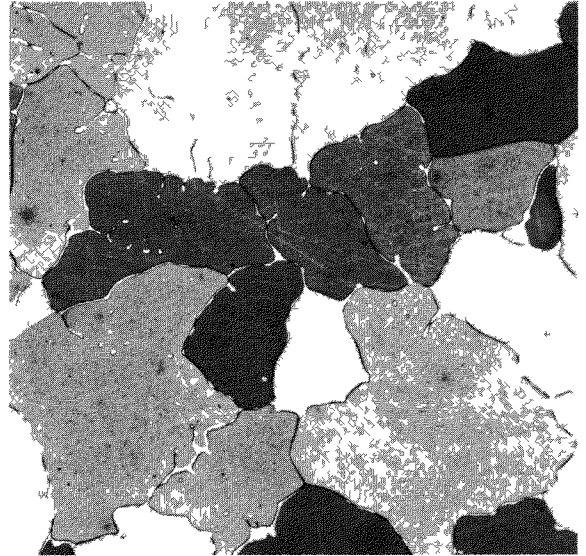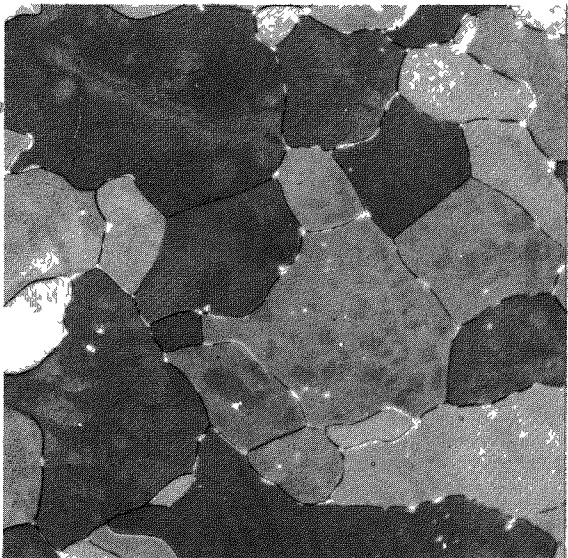
a. 4.4 wt % C

100X
2478-3-1
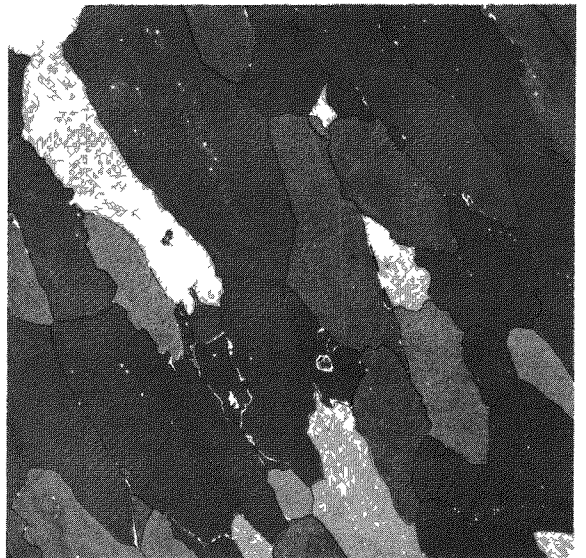

b. 4.5 wt % C

100X
2478-4-1

c. 4.6 wt % C

100X
2478-5-1

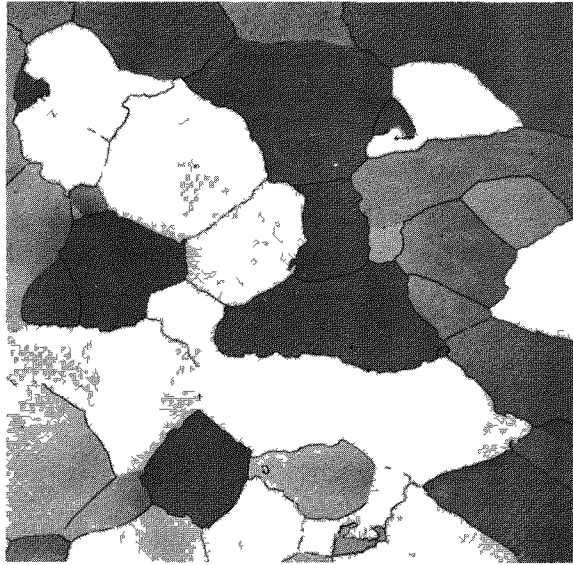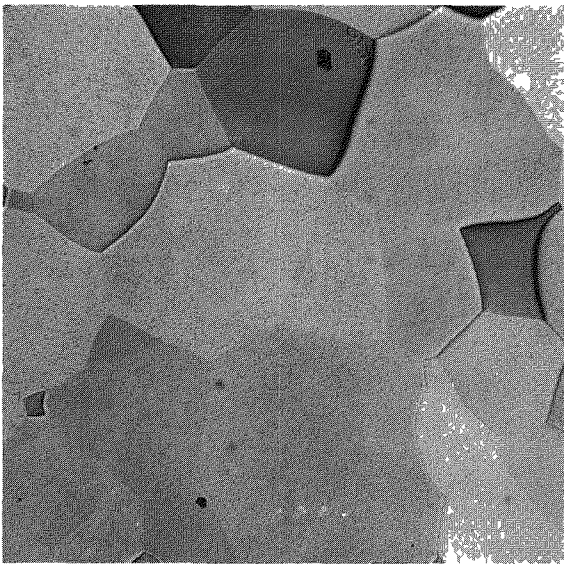d. 4.7 wt % C

100X
2478-6-1

Figure 2. Metallographic Standards for Equivalent Carbon Content
in Uranium Carbide
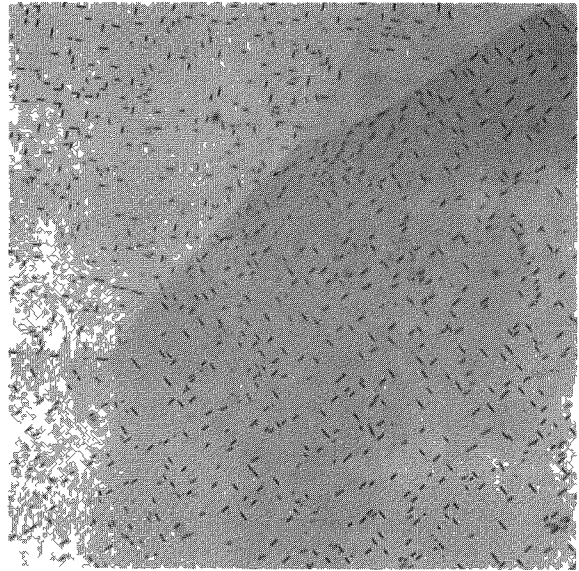
100X
2478-7-1

e.   4.8 wt % C

4126-12-1
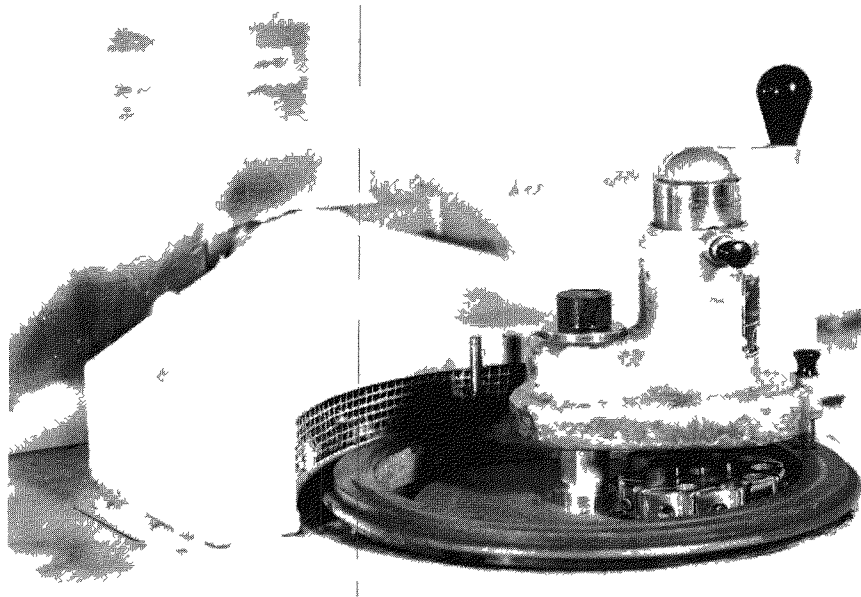

4126-12-2

1)   100X   2)   500X

f.   4.83 wt % C

Figure 2.   Metallographic Standards for Equivalent Carbon Content
in Uranium Carbide (Continued)

4126

Figure 3. Automatic Polisher for Preparing
Metallographic Samples

B.   Analytical Techniques

The individual samples were scanned under a metallurgical microscope
(at 100X magnification) such that at least one complete traverse, passing through
the geometric center of the specimen, was observed.   Samples with equivalent
carbon compositions near 4.8 wt % C, the stoichiometric composition of UC
(i. e., those revealing a single UC phase), were scanned similarly at 500X, to
determine whether any minute UC_2 platelets were present.   (See Figure 2f.)
The structures were compared with the standards (Figure 2), and the equivalent
carbon content of each sample was reported to the nearest 0.05 wt % carbon
(e. g., 4.60, 4.65, 4.70, etc).

The results were compared statistically to the melt grab sample chemical
analyses for carbon.   A regression line, as mentioned in Part II of this volume,
was determined, and showed reasonably good agreement between the two methods
of analysis.

APPENDIX D

DETERMINATION OF OXYGEN BY VACUUM FUSION

I. DISCUSSION

The principle of this method involves reacting oxygen with carbon-saturated platinum at high temperatures to produce carbon monoxide. In practice, samples are introduced into a graphite crucible containing molten platinum at approximately 2000°C. Carbon monoxide is transferred, by mercury diffusion pumping, into an analytical system where the gas may be measured manometrically or by gas chromatography.

II. PROCEDURE (See Figure 4)

a) Weigh 200 to 400 mg of uranium carbide to nearest 0.1 mg.

b) Drop sample into a graphite crucible containing platinum (ten times the sample weight) at 1950°C.

c) Pump released gases into analytical system.
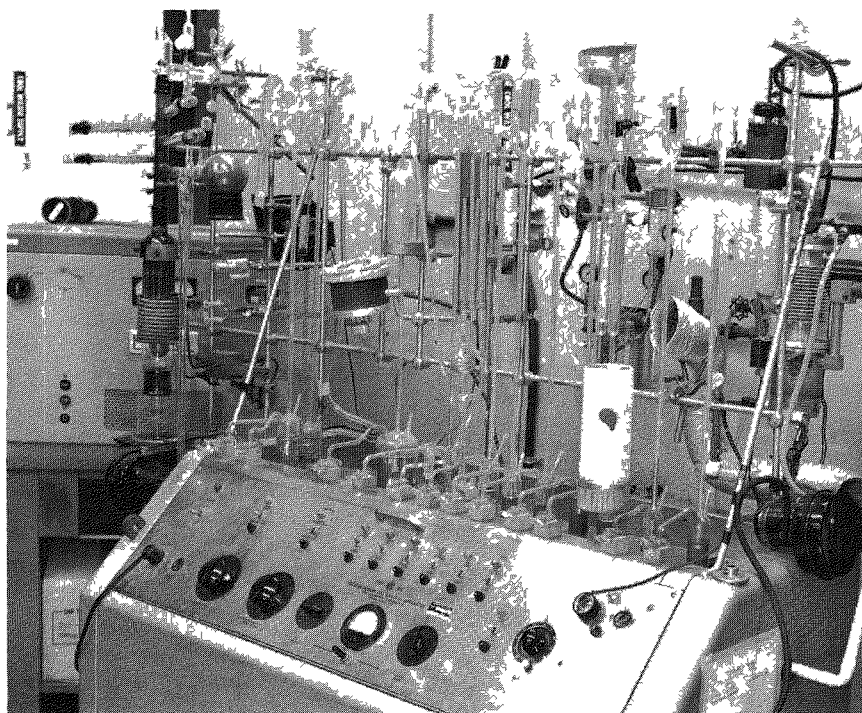
7610-1825

Figure 4. Vacuum Fusion Gas Analyzer

d) Measure total pressure of gases in McLeod gauge (P_1).

e) Circulate the gases through hot copper oxide and magnesium perchlorate, converting the hydrogen to water [which is trapped on the $Mg(ClO_4)_2$] and carbon monoxide to carbon dioxide.

f) Measure pressure (P_2). $P_1 - P_2$ = partial pressure of hydrogen.

g) Circulate gases through liquid nitrogen trap.

h) Pump off noncondensables to initial vacuum reading. Remove liquid nitrogen, allow CO_2 to expand into McLeod gauge. Measure pressure (P_3). P_3 = pressure of CO_2.

III. CALCULATION

$$\frac{P_3 V \text{ x temperature factor}}{\text{sample weight}} = \text{weight percent oxygen}$$

where

V = volume in which the gas is contained.

NOTE: The temperature factor includes terms for the gas constant (R), the molecular weight of the gas (atomic weight of element), as well as the temperature (°K).

IV. STANDARDIZATION

National Bureau of Standards (No. 950a) U_3O_8 may be used to verify operation of the equipment.

APPENDIX E
DETERMINATION OF OXYGEN BY INERT GAS FUSION

I. DISCUSSION

The principle of this method involves reduction of metallic oxides by carbon at elevated temperatures to yield carbon monoxide. Samples are introduced into a graphite crucible and fused at temperatures of 2400 to 2700°C. The system, having been purged with purified argon, carries the monoxide through iodine pentoxide, where carbon monoxide is converted to carbon dioxide, and into a conductivity cell filled with barium hydroxide. The change in conductivity is measured as a function of oxygen in the sample.

II. PROCEDURE (See Figure 5)

    a) Weigh a sample of 200 to 300 mg to nearest 0.1 mg.

    b) Drop sample into a graphite crucible heated to 2400°C.
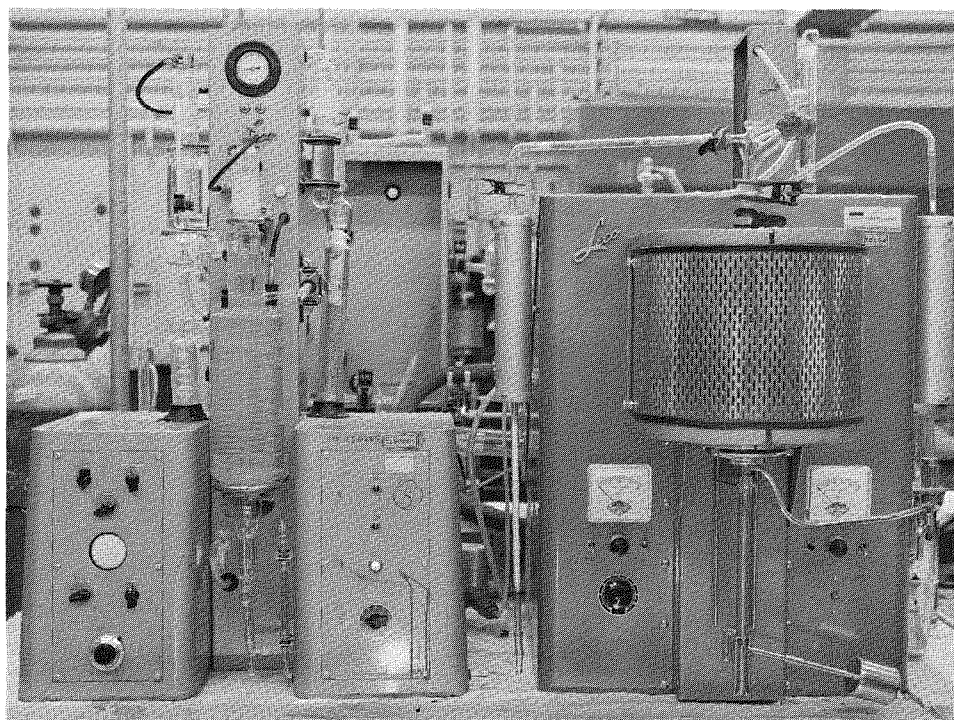
7610-1827

Figure 5. Inert Gas Fusion Oxygen Analyzer

c) Burn for 1 min, sweep with argon for an additional 4 min.

d) Balance the conductivity bridge with the potentiometer.

e) Read weight of carbon from working curve of ohms (corrected for blank) vs µg oxygen.

III. CALCULATION

$$\text{weight percent oxygen} = \frac{\text{µg oxygen}}{\text{mg sample}} \times 10^{-1}$$

IV. STANDARDIZATION

National Bureau of Standards (No. 950a) U_3O_8, Ag_2O, or potassium acid phthalate may be used to prepare standard working curves, and to verify operation of the equipment.

APPENDIX F
DETERMINATION OF NITROGEN

I. DISCUSSION

The Kjeldahl method is based upon the conversion of nitrogen to ammonia, which is distilled. Ammonia is determined colorimetrically, using Nessler's reagent and reading at 430 mµ on a spectrophotometer. Standard curves, using known quantities of nitrogen, are prepared by plotting absorbance vs mg nitrogen.

II. PROCEDURE (See Figure 6)

a) Crush sample under inert atmosphere and dissolve in 1:1 HCl with heat.

b) Transfer dissolved solution to a distillation flask and cool in crushed dry ice.
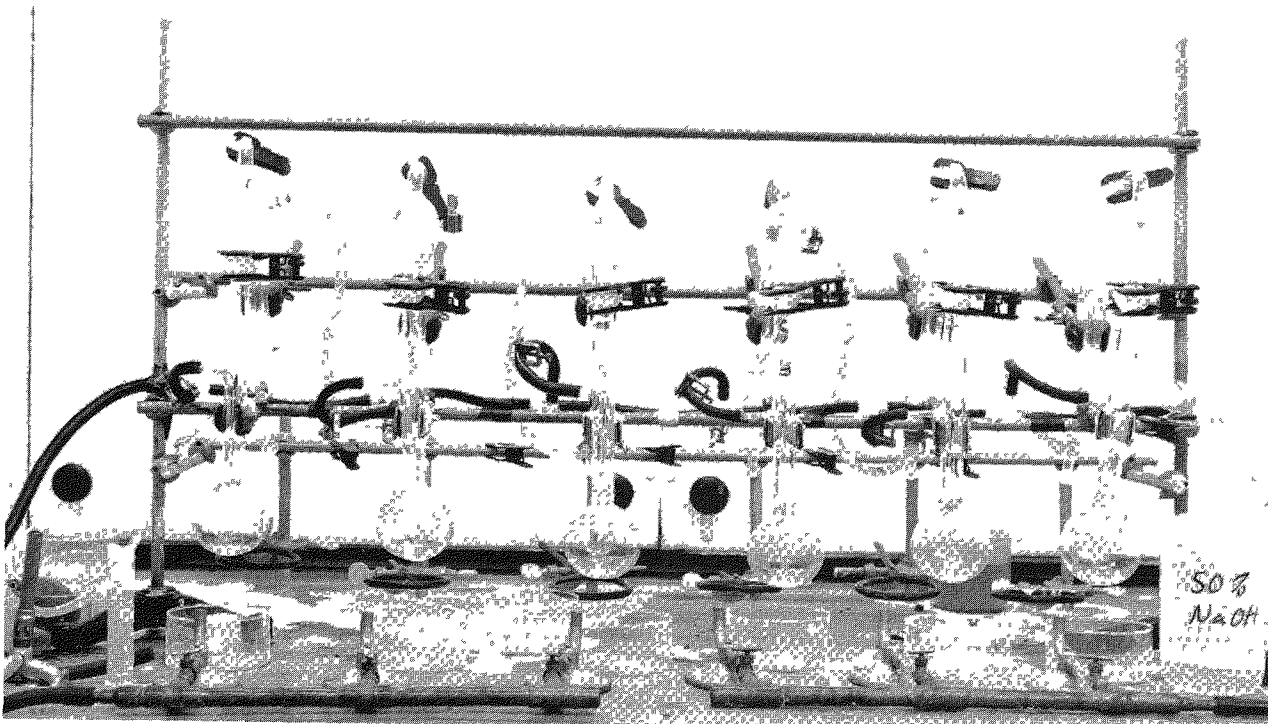
7610-1829

Figure 6. Kjeldahl Apparatus for Nitrogen Analysis

c) Add 25 mℓ of 50% NaOH (insure excess!) and rapidly connect to a condenser.

d) Under a slow helium flow, heat until 40 mℓ of distillate are collected in 0.001 $\underline{N}$ H_2SO_4.

e) Transfer distillate to a 100-mℓ volumetric flask.

f) Add 1 mℓ Nessler's reagent and dilute to mark with H_2O.

g) Develop color for 30 min.

h) Read absorbance at 430 μ in 5-cc cells.

III. CALCULATION

$$\text{weight percent nitrogen} = \frac{\text{mg nitrogen}}{\text{mg sample}} \times 100$$

APPENDIX G
## DETERMINATION OF U^{235} ENRICHMENT

I. DISCUSSION

Gamma spectrometric measurements are made of the 184-kev gamma emission from U^{235}, and are compared with the gamma intensities from National Bureau of Standards uranium isotopic standards in the approximate range of interest. Uranium unknowns and standards are separated, using ion exchange to remove daughter decay products and make all samples and standards uniform, relative to their approach to secular equilibrium.

II. PROCEDURE (See Figure 7)

a) Dissolve samples, and standards containing at least 150 mg uranium, in a minimum of 8 $\underline{N}$ HNO$_3$.

b) Evaporate to dryness and take up in 10-mℓ concentrated HCl, and repeat.

c) Transfer sample to resin column containing Dowex 1-X8 (chloride form), and wash with 100 mℓ concentrated HCl. Discard washings.

d) Elute uranium with 0.1 $\underline{N}$ HCl until eluate is clear.

e) Evaporate to dryness and ignite at 900°C for 1 hr.

f) Cool and weigh 100 ± 0.5 mg of U$_3$O$_8$ into a 1.5-cm diameter vial.

g) Add 1 mℓ 6 $\underline{N}$ HNO$_3$ to dissolve U$_3$O$_8$.

h) Gamma count standards and unknowns.

i) Read enrichment from a plot of net counts in 184 photopeak $\underline{vs}$ enrichment.

III. STANDARDIZATION

National Bureau of Standards has available uranium isotopic standards varying from 0.5 to 93% U^{235}.
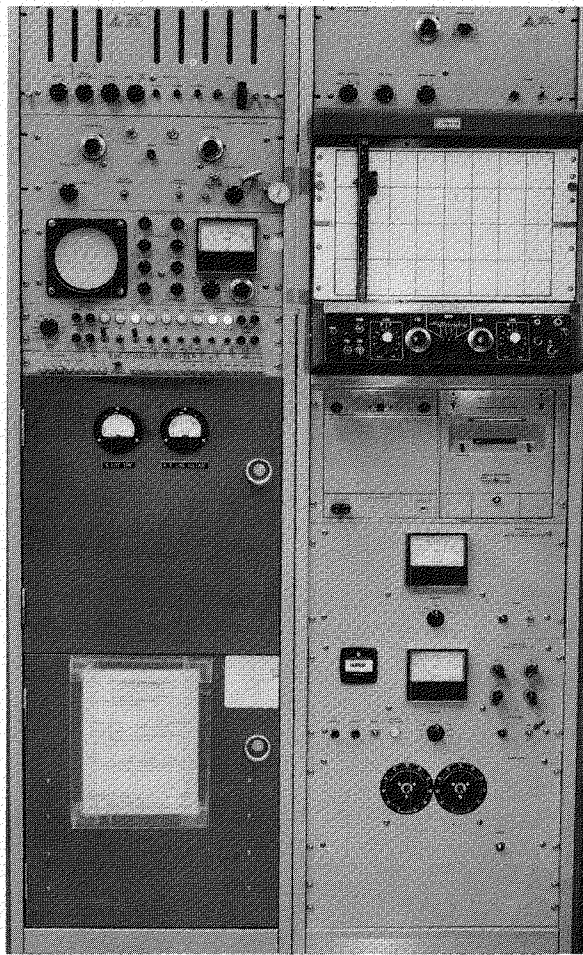
7610-1836

Figure 7. Gamma-Ray Spectrometer

APPENDIX H
DETERMINATION OF TRACE IMPURITIES – EMISSION SPECTROGRAPHY

I. DISCUSSION

Emission spectrography, utilizing carrier distillation, dc-arc technology, is used to determine the presence of trace impurities. Intensities of lines are observed, relative to those from synthetically prepared standards, to quantitate the amounts of impurities present in uranium carbide.

II. PROCEDURE (See Figure 8)

    a) Uranium carbide is fired to U_3O_8, and mixed 100:5 with AgCl:NaF (5:1) or Ga_2O_3.

    b) Load 100 mg of the mixture into a graphite spectrographic electrode.

    c) Preburn for 3 sec, then expose the film for 40 sec.

    d) Compare the standard plates with the unknown plates, to quantitate the impurity level (see Figure 9 for a typical spectrographic plate).
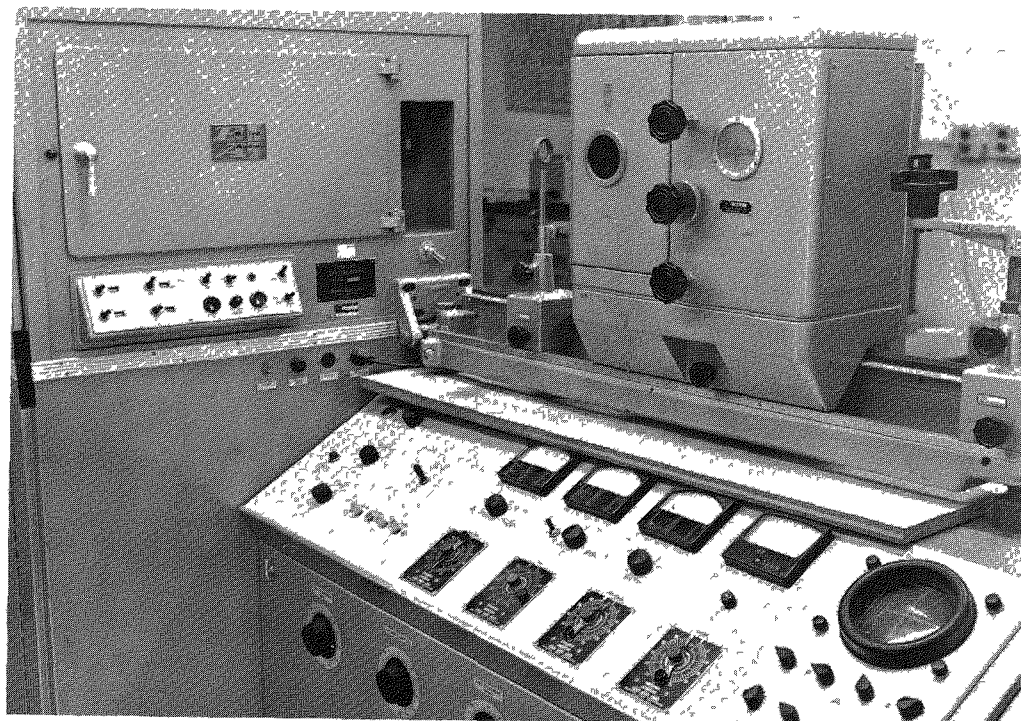
7610-1837

Figure 8.   Three-Meter Grating Spectrograph
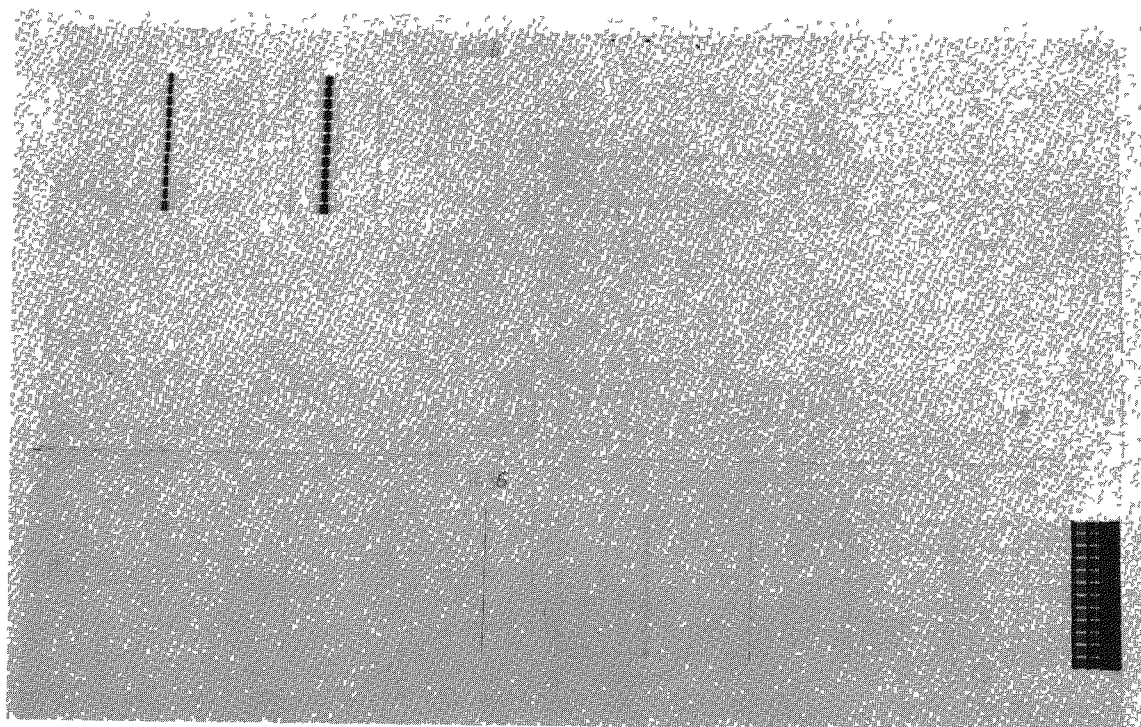
7610-1828

Figure 9.   Typical Spectrographic Plate, Showing Presence of
Impurities

APPENDIX I
DETERMINATION OF TUNGSTEN

I. DISCUSSION

The presence of trace levels of tungsten is not readily detected by emission spectrography. A method is used, in which the tungsten forms a colored complex with toluene-3,4 dithiol (dithiol), the absorbance of which is measured spectrophotometrically.

II. PROCEDURE

a) Weigh 500 to 1000 mg of sample to nearest 0.1 mg.

b) Add 15 ml 1:1 HNO_3, treat until sample is dissolved.

c) Add 15 mg Fe and 4 ml concentrated H_2SO_4.

d) Heat to dense white fumes.

e) Cool and add 5 ml $SnCl_2$ solution (10 g $SnCl_2 \cdot 2H_2O$ in 100 ml concentrated HCl).

f) Heat on boiling water bath for 4 min.

g) Add 10 ml dithiol solution (1 g in 100 ml isoamyl acetate), continue heating for 10 min with stirring.

h) Cool to room temperature and transfer to a separatory funnel, washing with isoamyl acetate.

i) Shake, allow the phases to separate. Discard the aqueous phase.

j) Wash organic phase to a dry 25-ml volumetric flask. Dilute to volume with isoamyl acetate.

k) Read the absorbance at 630 mμ in 1-cm cells, correcting for the blank.

III. CALCULATION

From a standard curve of absorbance vs μg tungsten, prepared using known quantities of tungsten, read the quantity of tungsten in the sample.

APPENDIX J
DETERMINATION OF OXYGEN IN SODIUM

I. DISCUSSION

The principle underlying this method is the insolubility of sodium oxide in mercury or sodium amalgam. In practice, the sample of sodium is reacted with mercury under inert atmosphere. Continued extraction with mercury separates the sodium from the sodium oxide. The quantity of sodium in each phase is determined, and the amount of oxide calculated.

II. PROCEDURE (See Figure 10)

a) A sample, containing 1 to 3 g sodium, is introduced into the reaction vessel and reacted with mercury.

b) After several minutes of mixing, mercury (containing sodium) is drawn off the bottom, leaving sodium oxide floating on a mercury layer.
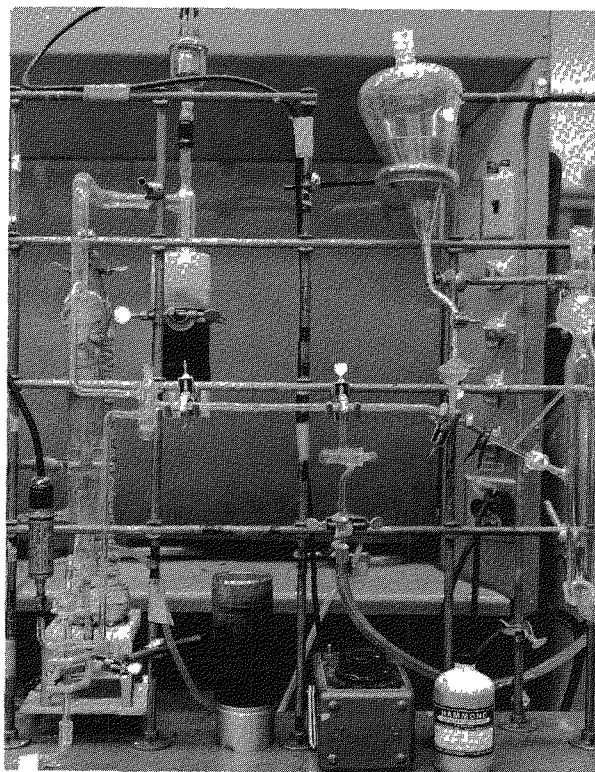
7610-1826

Figure 10. Apparatus for Oxygen-in-Sodium Analysis

c) The mercury extraction is repeated until a litmus test of the bottom layer is negative for bases.

d) The reaction vessel is drained, and washed with carbonate-free water.

e) Add the washings to mercury containing the sodium oxide.

f) React the amalgam with water.

g) Determine sodium in each solution (from e and f) by flame photometry or titration with standard HCl.

III. CALCULATION

The value obtained for sodium in solution from (f) is the sample size. The sodium in solution from (e) is from the oxide.

$$\text{ppm oxygen} = \frac{\mu g \text{ of sodium in (e)}}{g \text{ of sodium in (f)}} \times \frac{8}{23}$$

PART II

STATISTICAL ANALYSES

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ABSTRACT

The uranium carbide program for ESADA established quantitive reliability levels for the measurement methods used for determining critical chemical constituents, and the actual values of these constituents. It also employed statistical techniques to evaluate chemical and metallographic analytical data, and to assure conformity of the end product with the pertinent specifications.

I. INTRODUCTION

In August of 1961, a program of statistical analyses was started, to evaluate factors affecting the quality of uranium carbide. This program encompassed: (a) a statistical analysis of test data from experimental heats of uranium carbide melt stock and from cast slugs, and (b) statistical design of test series to evaluate processing parameters relative to the conformance of the end products with the specifications. This was a continuing effort, which terminated with the issuance of final specifications defining the requirements for uranium carbide melt stock and for cast uranium carbide fuel slugs.

II. OBJECTIVE

The objective of the statistical analyses was to determine quantative reliability and confidence levels which would assure the production of high quality UC melt stock and cast slugs.

III. SUMMARY

Statistical analyses, to determine the reliability of measurement methods for critical variable factors, such as carbon, oxygen, and uranium levels, constituted a major portion of the UC reliability program. Some of these studies are listed in the following sections.

A. CARBON

Experimental test series were designed, to determine the variation of carbon content in the melt stock. As a result, determination of the average carbon content of the melt stock was established at the 95% confidence level. Control charts for the carbon content of the UC fuel slugs were utilized to aid in controlling the variation of (1) duplicate or repeated chemical analyses (precision), and (2) the analyses of the standard (accuracy).

Correlation studies, between the carbon content of chemically analyzed grab or header samples from the UC melt and the carbon content of a series of randomly selected samples from slugs of that melt, showed a high degree of correlation at the 95% confidence level. The results of these analyses provided a basis for determining whether to sample and analyze the slugs from the heat or to recycle the heat. It also aided in determining the charge for the succeeding heat.

Numerous statistical test series and analyses were made, to evaluate uranium carbide homogeneity during processing. Due to the importance of maintaining the carbon content of the cast slugs within specified limits, test series results were also statistically analyzed, using carbon content data obtained by metallographic examination of the slug structure. Correlation, regression studies, and statistical significance tests were utilized to evaluate factors that could affect the product, especially the amount and variation of the carbon content. The use of vendor-supplied melt stock to produce UC cast slugs was also analyzed, as to its effect on the process and the final yield. Data from all cast fuel slug melts, as well as feed stock processing, were statistically analyzed. These analyses served as a basis for determining: (1) the reliability growth in the processing of uranium carbide, and (2) that the slugs produced from an individual melt were homogeneous.

Sampling plans, incorporated into the final specifications, insure a high degree of reliability and confidence that the product will be within the specification requirements.

B. OXYGEN

A series of statistically designed experiments was developed and utilized in establishing a maximum oxygen content of 500 ppm in the UC melt stock. This provided adequate melting characteristics for the casting operation.

Statistical techniques were also utilized, to evaluate the precision of the chemical analyses for O_2 contents in UC melt stock and slugs. This resulted in improved sampling techniques and the purchase of new analytical equipment. These changes yielded improved oxygen analyses, with lower variation, which were more consistent with the theorized oxygen levels of the cast UC slugs.

C. URANIUM

A statistically designed test series was developed, to evaluate the reliability of various procedures for determining uranium in uranium carbide. The results of the test series indicated the two most reliable analytical methods.

IV. DISCUSSION

Statistical techniques were utilized to formulate test series and evaluate test data relative to the processing of both UC feed stock and cast fuel slugs. Their purpose was: (a) to determine the content and variability of the critical parameters (carbon, oxygen, and uranium), (b) to isolate the cause of variability, and (c) to provide acceptance testing procedures for the assurance that the fuel material produced had the desired reliability and quality level.

The variability of the carbon content within a heat was the most complex problem, from a reliability standpoint. The major difficulties involved were isolation of the degree of carbon variation due to the process, the sampling technique, and the method of analysis. This applied to both the melt stock and the cast fuel slugs.

A. PRECISION OF THE ANALYSIS

In August 1961, statistical evaluations of the precision (repeatability) of duplicate chemical analyses for carbon content of UC ·slugs indicated an average standard deviation of 0.075 wt % C. This variation was much higher than could be tolerated by specification requirements. As a consequence of this evaluation, control charts were utilized in the laboratory, and changes were made in the selection and preparation of the sample for analysis.

Figure 11, covering the period from October 1 through November 16, 1962, illustrates the improvement resulting from these techniques, showing an average standard deviation of 0.043 wt % C. Subsequent evaluations indicate that the precision remained at approximately 0.04 wt %. It must be realized that the results shown for the precision of duplicate analyses also include any variation that may be present in the samples used for the duplicate analyses. Statistical evaluation of the precision obtained, using metallographic analysis for carbon content, indicates an average standard deviation of 0.019 wt % C. However, a regression study of metallographic precision vs carbon content indicates that, at a 4.8 wt % carbon level, the precision improves to 0.008 wt % C for the standard deviation. In summary, these evaluations have indicated that, at the higher levels of carbon content, the precision obtained by metallographic analyses is superior to that obtained by chemical analyses.
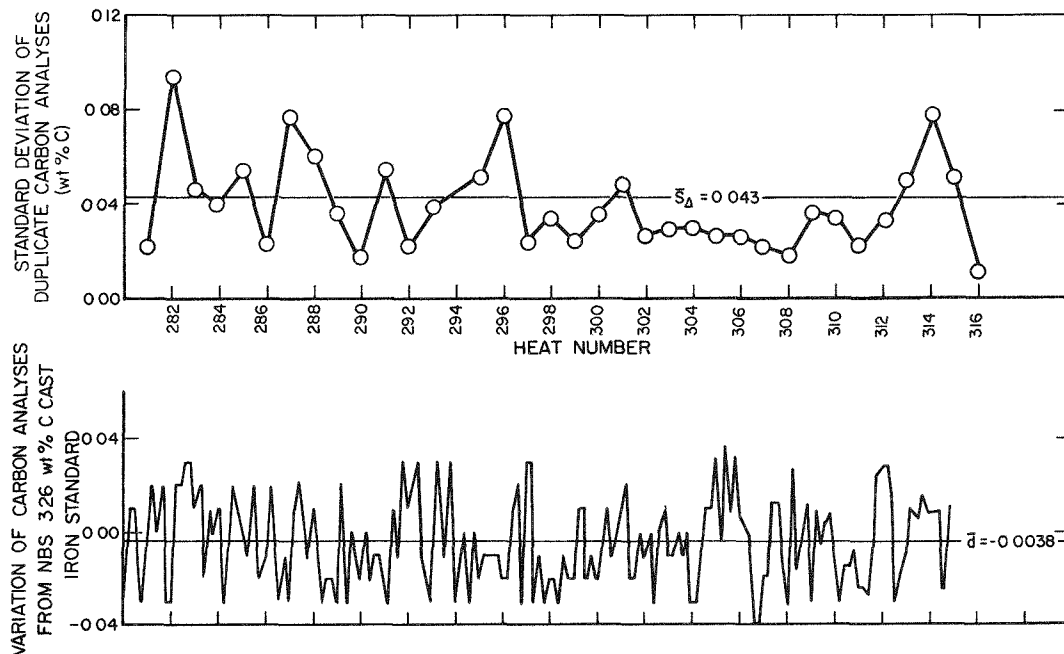
Figure 11. Carbon Analyses — Heats 281 through 316

B. ACCURACY OF THE ANALYSIS

The accuracy obtained in the determination of the carbon content of UC slugs was measured, using a 3.26 wt % carbon, cast iron NBS standard as a reference material. The average difference between the actual carbon analyses and the certified value of the NBS carbon standard was a negative 0.0038 wt % carbon (Figure 11). This type of chart has been in continuous use, during the ESADA program, in order to maintain a constant check on the accuracy of the analytical method used in determining the carbon content of the UC slugs.

C. HOMOGENEITY OF THE CARBON CONTENT

A series of statistically designed experiments was made, to determine the homogeneity of the slugs within a heat. Results, over the past year, have shown that the slugs are very homogeneous. A recent demonstration of this homogeneity, with its evaluation, is cited in the following experimental test series.

Slugs from ESADA Heats 370, 371, and 372 were used for the test series. Two to six chemical analyses, and one metallographic inspection, were made

at four difference positions on each of seven randomly selected slugs from each of the three heats.

The analysis of variance technique was used on the chemical and metallographic data, to determine the significant contributions to the variation in the data. Results of this analysis indicated that there was no significant variation, at the 95% confidence level, between slugs and within slugs (between positions), when compared to the analytical error. Therefore, the main contributors to the variation in the data were heat-to-heat variation and analytical error variation.

Since the heats were of varying compositions, we expected the heat-to-heat variation to be significant; thus, we were not concerned with the magnitude of this variation, since we know its cause, and that it is probably independent of the homogeneity within a heat (slug-to-slug, and within-slug variation).

Conclusions drawn from the statistical analyses are:

1) Slugs are homogeneous, to the extent that analytical error makes any nonhomogeneity.

2) Metallographic inspection is much more precise than chemical analyses, in the 4.5 to 4.8 wt % C range.

3) All results in this report are applicable only to the high side of the equivalent carbon specification, since the three heats analyzed were all very close to stoichiometric material. The averages of the three heats were 4.692, 4.563, and 4.633 wt % C by chemistry, and 4.795, 4.750, and 4.789 wt % C by metallography.

4) It should also be noted that, even though the slugs appeared to be homogeneous, the results from inspecting sampled slugs still contained the analytical errors. Thus, acceptance sampling procedures must be utilized, in order to meet any requirement imposed on the process.

D. CORRELATION STUDY ON THE CARBON CONTENT OF THE HEADER SAMPLE

A correlation and regression study was performed on data from ESADA Casting Heats 281 through 368, to determine the relationship between the average of the carbon determinations obtained from a sample of the header from a

heat and the average of the carbon analyses obtained from the sampled fuel slugs in the heat. This study showed a correlation coefficient between these two variables of 0.968. This correlation coefficient is significant, at the 99% confidence level; thus, it can be assumed that there is a strong relationship between these two variables. The regression study shows a regression line of Y = 0.241 + 0.950 (X), where "Y", the dependent variable, is the average of the carbon analyses obtained from the sampled fuel slugs from the heat, and "X", the independent variable, is the average of the carbon determinations obtained from a sample from the header.

A similar correlation and regression study was also performed on data from 29 ESADA heats (369 through 398). The analyses showed results very similar to those previously reported. Figure 12 shows the relationship between the two variables, the calculated regression line, and 99% confidence limits about the line of regression. The correlation coefficient for this data was 0.934, which is also significant at the 99% confidence level, and indicates a very strong relationship between the variables. This demonstrates that a very accurate prediction for the average of the carbon analyses for a given heat can continuously be made from the average of the carbon analyses of a sample from the
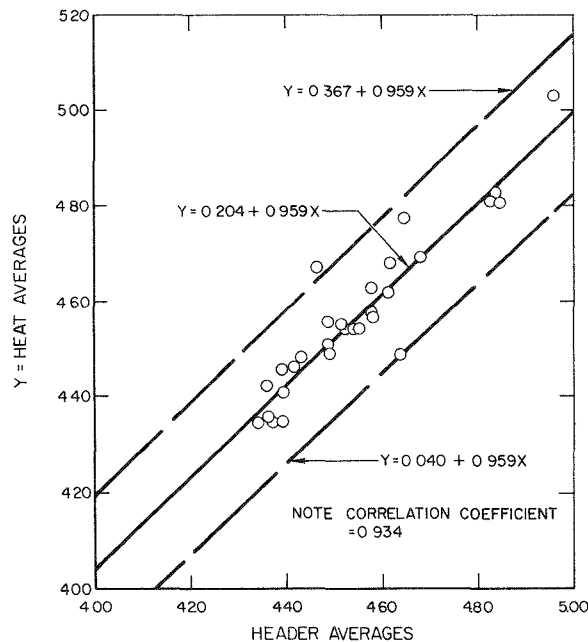

Figure 12. Correlation Analysis of
Header Averages vs
Heat Averages

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header. The results of these analyses provided a basis for determining whether to sample and analyze the slugs from the heat or to recycle the heat. It also aided in determining the charge for the succeeding heat.

E. VARIATION OF CARBON CONTENT FROM HEAT TO HEAT

Several studies were made to isolate factors contributing to the heat-to-heat variation in carbon content. These studies included:

1. Electrode Effect

Various statistical analyses and tests were made, to determine the effect of electrode type on the amount of electrode carbon erosion. These analyses and tests are based upon data from Heats 281 through 368, which used a melting current of 9,000 amp.

Table II is a tabulation of the electrode type, average electrode erosion, estimated standard deviation of electrode erosion, and the number of heats evaluated which used the particular type of electrode.

TABLE II

ELECTRODE DATA

Electrode Description*	Graphite	Average Electrode Erosion (wt % C)	Estimated Standard Deviation (wt % C)	Number of Heats Using Electrode Type
6-in. long	ATJ	187.0	101.0	23
7-in. long	ATJ	117.5	12.8	4
Tapered 5-in.	ATJ	123.0	34.5	27
ZrC Impregnated 6-in.	ATJ	116.5	21.2	13
ZrC Impregnated 6-in.	AUC	119.0	17.2	5

*A detailed description of the individual electrodes is available in Volume III of this report.

The statistical evaluation showed that the variation in the amount of electrode erosion observed when the 6-in. ATJ graphite electrode was used was significantly greater, at both the 95 and 99% confidence levels, than the variation observed in the other electrodes. There was no significant difference, at the 90% confidence level, in the variation of electrode erosion between the other electrodes.

2. Furnace Charge Effect

A statistical study was made to determine the effect of furnace charge on the carbon content variation. This study was made, utilizing data from Casting Heats 168 to 368. However, for the purposes of illustrating the results of this study, only charts from Heats 281 to 368 were included in this report.

Figure 13 shows the heat-to-heat variation of the carbon content, in heats charged with melt stock, recycle, uranium, and skull. The overall average of the carbon analyses for these heats is 4.472 wt %C, with an overall average standard deviation of 0.047 wt % C.

Heats 350 to 368, which had the same type of charge specified in the preceeding paragraph, were from the Phase I Pilot Production Run. The overall average carbon content for the heats in this run was 4.464 wt % C, with an average standard deviation of 0.048 wt % C.

Figure 14 shows the heat-to-heat variation of the carbon content in heats charged with recycled scrap uranium and skull. The overall average carbon content for these heats was 4.630 wt % C, with an overall average standard deviation of 0.074 wt % C. It should be noted that Heats 313, 314, 317, 318, 321, 335, 336, 337, 341, and 343 each contained five or more kilograms of fines.

Figure 15 shows the heat-to-heat variation of the carbon content, in heats charged with melt stock and skull. The overall average carbon content for these heats was 4.821 wt % C, with an overall average standard deviation of 0.054 wt % C.

Figure 16 shows the heat-to-heat variation of the carbon content, in heats charged with melt stock, uranium, and skull. The overall average carbon content for these heats was 4.646 wt % C, with an overall average standard deviation of 0.051 wt % C.
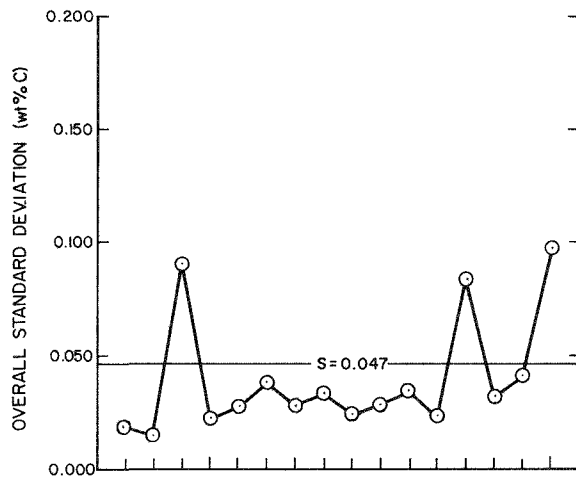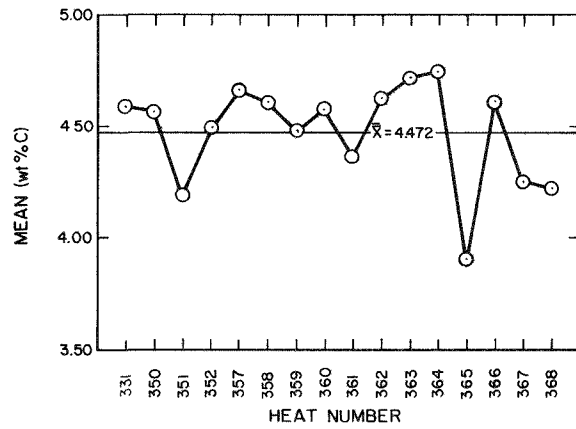
Figure 13. Mean and Standard
Deviation of Carbon Analyses —
Slug Heats 331 through 368

It can be observed, from the preceeding evaluations and the referenced figures, that the type of furnace charge does not appear to have a significant effect on the within-heat (casting) carbon variation.

F. VARIATION OF CARBON CONTENT

The following paragraphs outline the variation of the carbon content during Phase I of the development and pilot production program for the fabrication of ESADA UC fuel slugs.
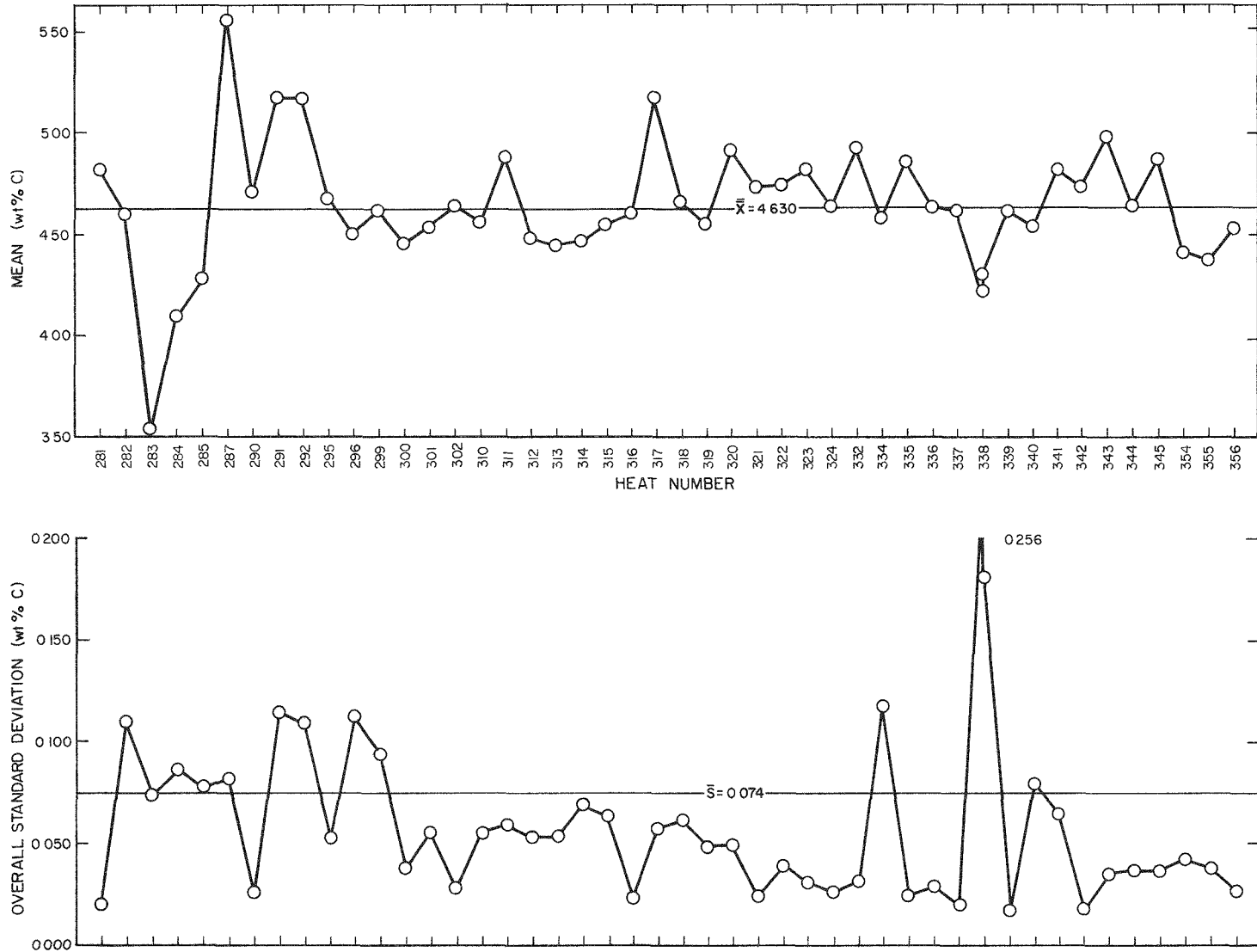
Figure 14. Mean and Standard Deviation of Carbon Analyses — Slug Heats 281 through 356
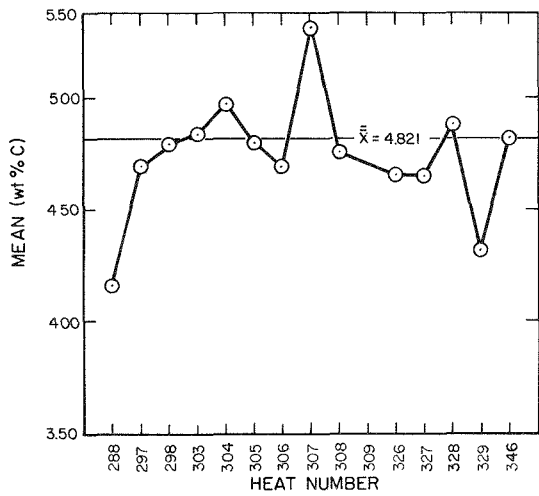
Figure 15. Mean and Standard Deviation of Carbon Analyses — Slug Heats 288 through 346
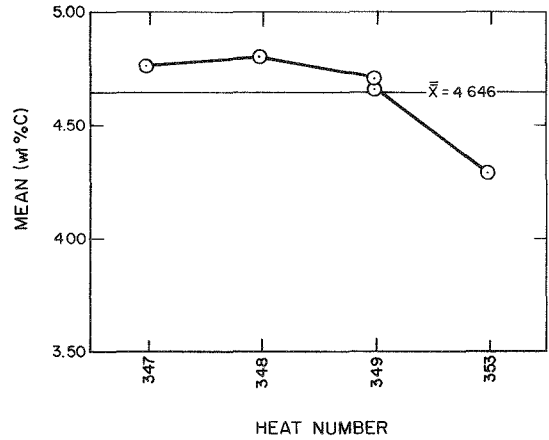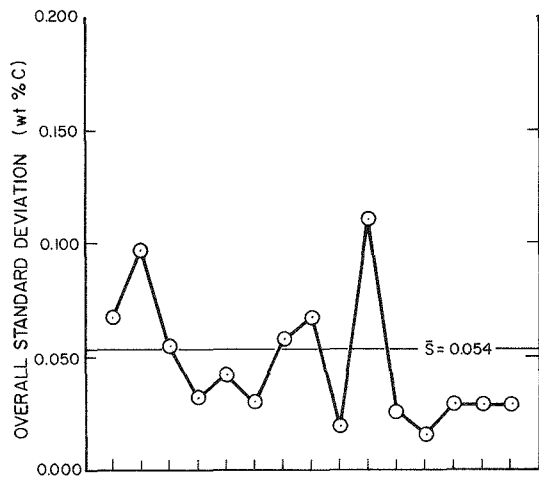

Figure 16. Mean and Standard Deviation of Carbon Analyses — Slug Heats 347 through 353
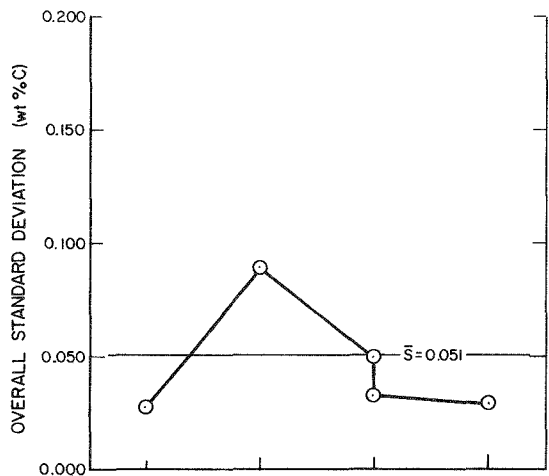
Figure 17 is a graphical presentation of the average and standard deviation of the carbon content for heats produced during the latter part of the program. The results plotted on Figure 17 are based on data generated from Military Standard-414 sampling plan for the indicated heats.

Figure 18 is the same type of chart as Figure 17. However, it indicates the results obtained during the pilot production run of Phase I. Here again, the data were generated from a MIL-STD sampling plan for the indicated heats.

During the development phase, the average mean carbon value was 4.584 wt %, with an average standard deviation of 0.045 wt %; while, during the pilot production run of Phase I, the average mean carbon value was 4.568 wt %, and the average standard deviation was 0.038 wt %.

1. Oxygen Content

A statistically designed test series was developed, to determine the critical amount of oxygen that could be tolerated in the furnace charge of the UC melt. The results of this study indicated the maximum amount of oxygen that could be tolerated, if the degree or variation of the electrode carbon erosion were to be held at a very low level.

A running statistical evaluation was performed upon the oxygen contents of the UC fuel slug heats. Figure 19, illustrating the results of these analyses on Heats 288 through 368, is included as an example of these evaluations. It should be noted that, starting with Heat 302, a revision was made in the methods of analyzing for oxygen. This revision entailed an improved sampling technique, new analytical equipment, and a new analytical technique. The revision resulted in improved and lower oxygen analyses, with lower variation, which were more consistent with the theorized oxygen level in the UC fuel slugs.

2. Uranium Content

A statistical study was made to determine the accuracy and precision of various analytical methods for determining uranium content. These evaluations were made, using a uranium solution containing 52.04 g uranium per liter.
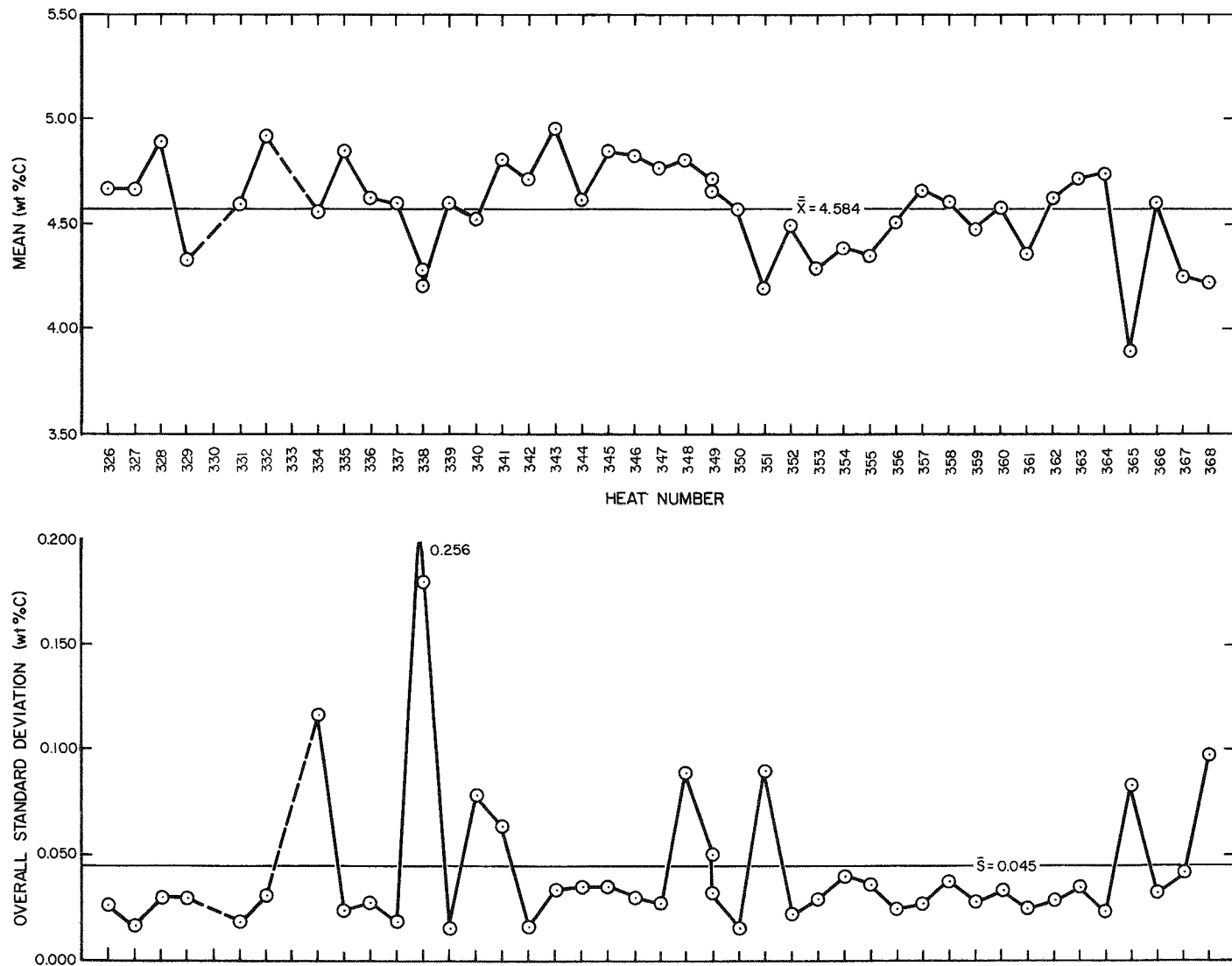
Figure 17. Mean and Standard Deviation of Carbon Analyses — Slug Heats 326 through 368
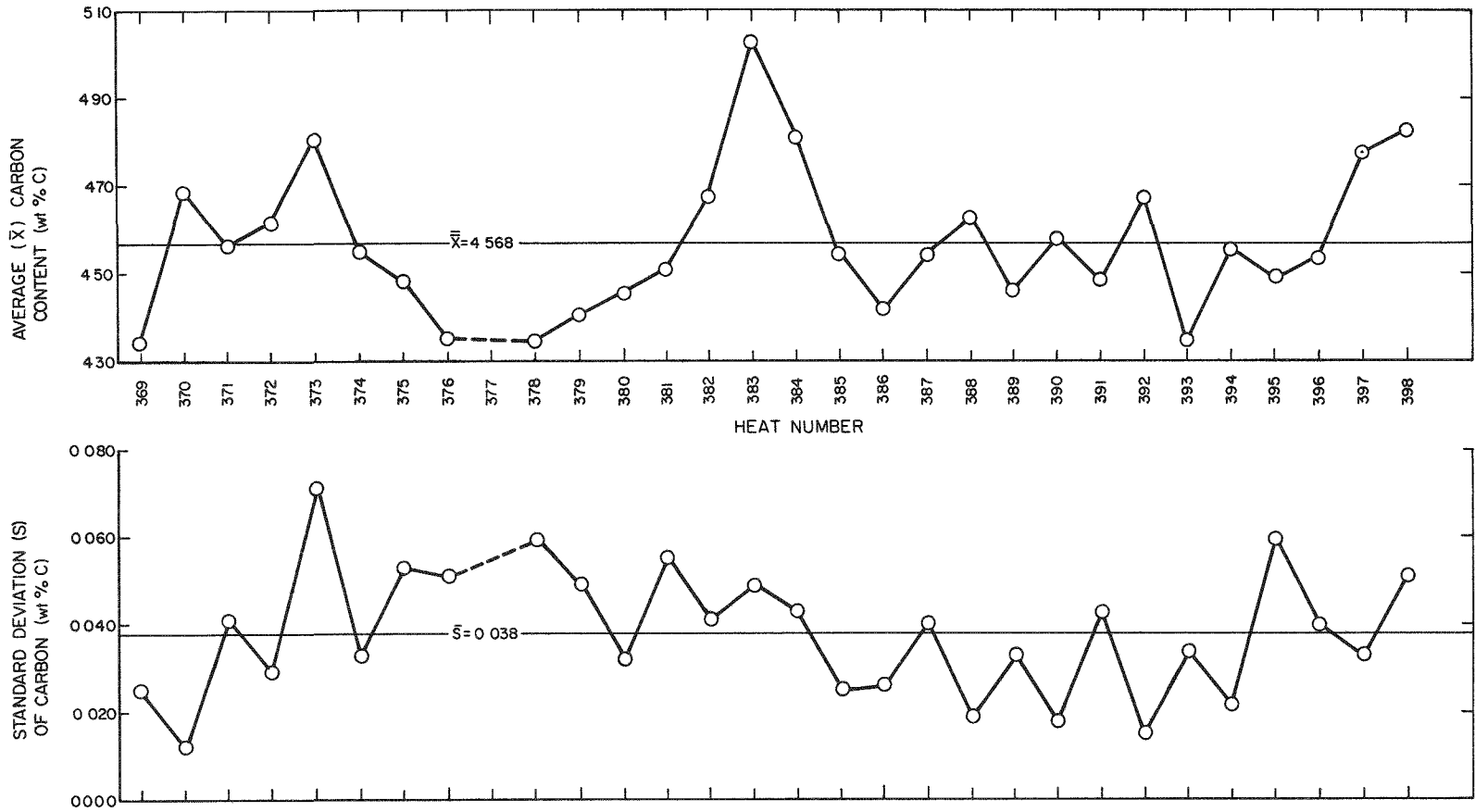
Figure 18. Mean and Standard Deviation of Carbon Analyses — Slug Heats 369 through 398 (Phase I)
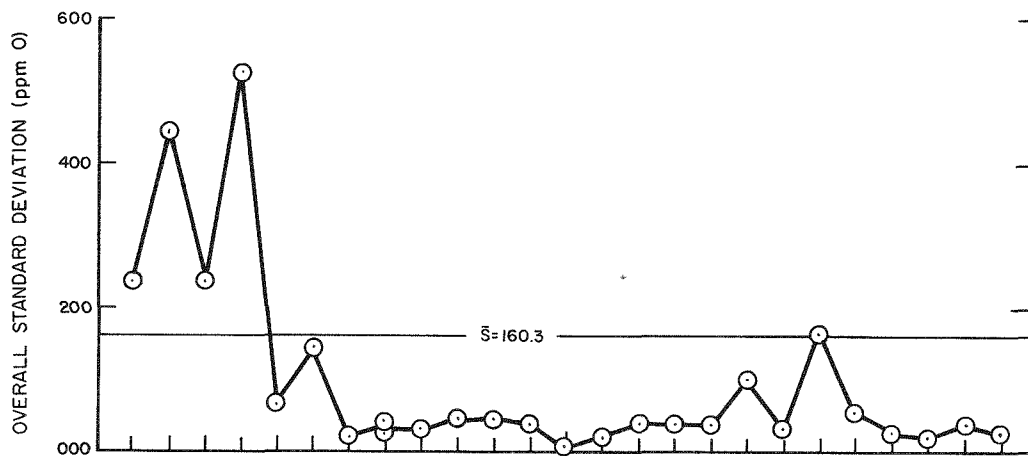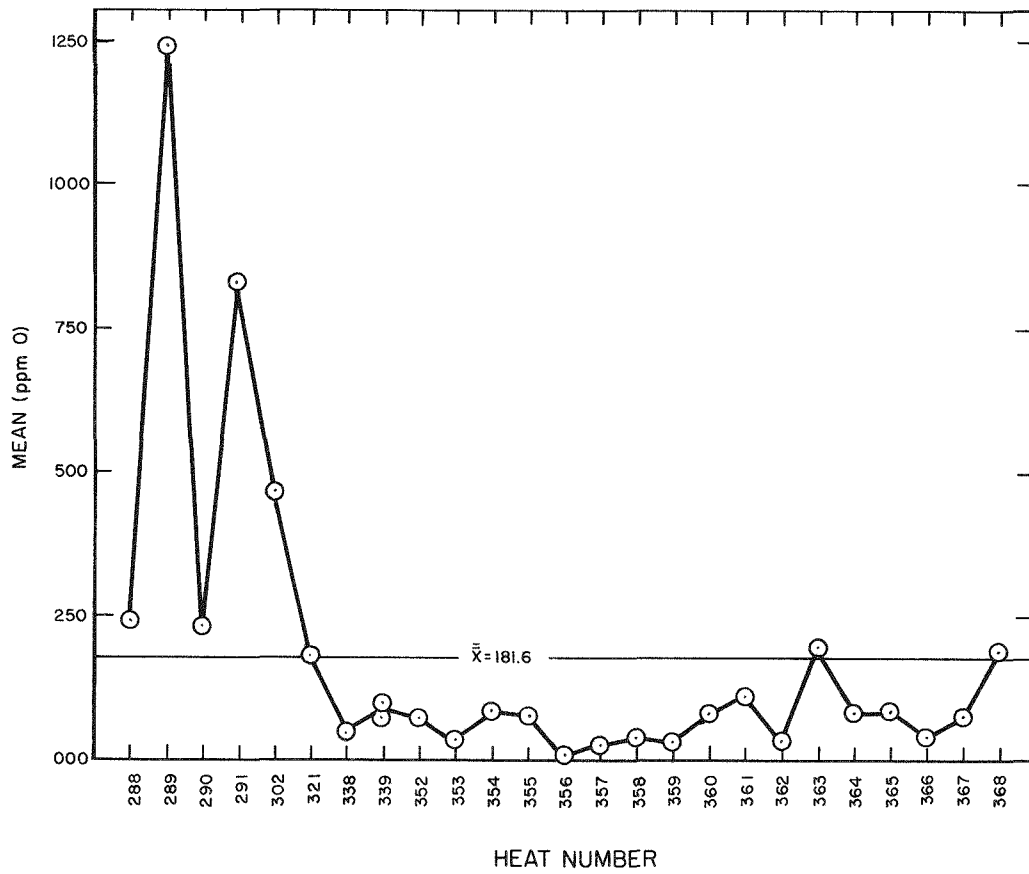
Figure 19. Mean and Standard Deviation of Oxygen Analyses —
Slug Heats 288 through 368

a. Analytical Test Results

1) Ceric Sulfate Method of Determining Uranium

The average of the uranium determinations obtained, using the Ceric Sulfate Volumetric Method, was 51.976 g uranium, with a standard deviation of 0.061 g uranium. The 95% confidence limits about this average range from 51.932 to 52.020 g uranium. The best estimate of the precision of this method is 0.061 g uranium. A test shows that the average of the ten determinations obtained, using the Ceric Sulfate Volumetric Method, was significantly unequal, at the 95% probability level, to the expected average of 52.04 g uranium. Thus, it can be assumed that the method is negatively biased. The best estimate of this bias is -0.064 g uranium; 95% confidence limits about this bias range from -0.108 to -0.020 g uranium.

2) Potassium Dichromate Volumetric Method of Determining Uranium

The average of the uranium determinations obtained, using the Potassium Dichromate Volumetric Method, was 52.017 g uranium, with a standard deviation of 0.027 g uranium. The 95% confidence limits about this average range from 51.998 to 52.036 g uranium. The best estimate of the precision of this method is 0.027 g uranium. A test shows that the average of the ten determinations obtained, using the Potassium Dichromate Volumetric Method, was significantly unequal, at the 95% probability level, to the expected average of 52.04 g uranium. It can therefore be assumed that the method is negatively biased. The best estimate of this bias is -0.023 g uranium; 95% confidence limits about this bias range from -0.042 to -0.004 g uranium.

3) Ceric Sulfate Potentiometric Method of Determining Uranium

The average of the uranium determinations, using this method, was 51.654 g uranium, with a standard deviation of 0.008 g uranium. The 95% confidence limits about this average range from 51.648 to 51.660 g uranium. The best estimate of the precision of this method is 0.008 g uranium. A test shows that the average of the ten determinations obtained, using the Ceric Sulfate Potentiometric Method, was significantly unequal to the expected average of 52.04 g uranium. It therefore can be assumed that the method is negatively biased. The best estimate of this bias is -0.386 g uranium; 95% confidence limits about this bias range from -0.380 to -0.392 g uranium.

4) <u>Potassium Dichromate Potentiometric Method of Determining Uranium</u>

The average of the uranium determinations, using this method, was 52.065 g uranium, with a standard deviation of 0.076 g uranium. The 95% confidence limits about this average range from 52.009 to 52.119 g uranium. The best estimate of the precision of this method is 0.076 g uranium. A test indicated that the average of the ten determinations obtained, using the Potassium Dichromate Potentiometric Method, could not be proved unequal, at the 95% probability level, to the expected average of 52.04 g uranium. It can therefore be assumed, based on the test data, that this method of determining uranium is unbiased.

b. Relative Precision Between Test Methods

The Ceric Sulfate Potentiometric Method shows the best precision. The variance of this method is significantly less (at the 95% probability level) than the variances of either the Ceric Sulfate Volumetric Method or the Potassium Dichromate Potentiometric Method.

There is no significant difference between the variances of the Ceric Sulfate Volumetric and the Potassium Dichromate Potentiometric Methods of determining uranium. However, the Potassium Dichromate Potentiometric Method apparently has the worst precision of the four methods tested.

c. Relative Accuracy Between Test Methods

The Potassium Dichromate Potentiometric Method of determining uranium can be assumed to be unbiased.

The Ceric Sulfate Potentiometric Method of determining uranium has a significantly greater bias, at the 99% probability level, than either the Ceric Sulfate or the Potassium Dichromate Volumetric Methods of determining uranium.

There is no significant difference, at the 95% probability level, between the biases of the Ceric Sulfate and the Potassium Dichromate Volumetric Methods of determining uranium.

G. ACCEPTANCE SAMPLING PLANS

1. Carbon Content

a. Feed Stock

Determination of the carbon content in UC melt stock was attempted, by use of variable sampling procedures for MIL-STD 414, using various AQL's (acceptable quality level). This procedure was rejecting heats which contained an average carbon content very near the specification limits with a high standard deviation between samples. Since the amount and variation of the carbon present in the melt stock material was not critical to the melt process, and since the charge to be melted could be adjusted, only an accurate knowledge of the average amount of carbon in the melt stock was required for the sampling plan. It was then decided to use a plan for acceptance and rejection criteria, for each lot of melt stock, which provided 95% confidence that the true value of the average carbon content of any given lot did not differ by more than 0.04 wt % from the calculated average value. The details for the utilization of this plan are included in Atomics International Specification 7518-S71840 (Uranium Monocarbide for Melting Stock).

b. Cast UC Slugs

Acceptance criterion for the carbon content of the as-cast slug heats was originally based on variable sampling procedures selected from MIL-STD 414, considering heat size, sample size, and an acceptable quality level. This procedure also rejected heats of material which possessed a high average carbon content with a large standard deviation among samples. Since it was felt that the best quality material (very near stoichiometric) was being rejected, the sampling procedures were revised to incorporate sampling by attributes, using predetermined metallographic standards. The details for utilization of this plan are included in Atomics International Specification NB0117-101 (Fuel Slugs, As-Cast Uranium Carbide).

2. Isotopic and Impurity Content

The degree of sampling for isotopic and impurity content was not based on a formal MIL-STD sampling procedure, as statistical evaluations indicated that this would not improve the reliability. The degree of sampling indicated in AI Specification NB0177-101 (Fuel Slugs, As-Cast Uranium Carbide) for these two items provided the necessary assurance that they meet acceptance criteria.

REFERENCES

1. MIL-STD-105 "Sampling Procedures and Tables for Inspection by Attributes for Per Cent Defective"

2. MIL-STD-114 "Sampling Procedures and Tables for Inspection by Variables for Per Cent Defective"

3. Atomics International Specification NB-0177-101 "Fuel Slugs, As-Cast Uranium Carbide"

4. Atomics International Specification 7518-S-71840 "Uranium Monocarbide for Melting Stock"