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ANALYTICAL CHEMISTRY DIVISION

Y-12 BRANCH

M. T. Kelley, Director

C. D. Susano, Associate Director

STATISTICAL QUALITY CONTROL

December, 1951, Through February, 1952

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C. D. Susano
R. L. McCutchen

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STATISTICAL QUALITY CONTROL REPORT

DECEMBER, 1951, THROUGH FEBRUARY, 1952

INTRODUCTION

In the three-month period beginning December 3, 1951, the number of control determinations being made in the General Ionic Analyses Laboratory and the HR Laboratory was decreased, pending a revision of the control program for these laboratories.

In addition to the regular uranium control programs being carried out at the X-10 laboratories, a control program was instituted for the colorimetric determination of thorium.

The distribution of the control determinations for this period is given in Table I, under the following headings: General Ionic Analyses Laboratory, HR Control Laboratory and X-10 Analytical Laboratories.

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Table I
Summary of Control Determinations
December, 1951, Through February, 1952

<u>Laboratory</u>	<u>Material</u>	<u>Determi- nation</u>	<u>Method</u>	<u>Number of Control Determinations</u>	<u>Total Number of Determinations per Laboratory</u>
General Ionic Analysis	Synthetic Solutions	U	Fluorimetric	42	108
	Synthetic Solutions	U	Colorimetric (l-ascorbic acid)	30	
	Synthetic Solutions	U	Potentiometric Titration	8	
	Synthetic Solutions	U	Gravimetric	8	
	Bartow Clay Leach	U	Fluorimetric	20	
HR Control	Uranyl Sulfate Soln.	U	Jones Reductor-Ceric Sulfate	52	113
	Uranyl Sulfate Soln.	U	Jones Reductor-Dichromate	12	
	Uranyl Sulfate Soln.	Fe	α-bipyridyl	3	
	Uranyl Sulfate Soln.	Ni	Dimethylglyoxime	21	
	Uranyl Sulfate Soln.	Cr	Diphenyl Carbazide-Bismuthate	21	
	Uranyl Sulfate Soln.	Mn	Periodate	4	
X-10 (3550)	Synthetic Solutions	U	Fluorimetric	124	490
	Synthetic Solutions	U	Colorimetric (Thiocyanate)	184	
	Synthetic Solutions	Th	Colorimetric	182	
X-10 (3019)	Synthetic Solutions	U	Fluorimetric	286	814
	Synthetic Solutions	U	Colorimetric (Thiocyanate)	528	
GRAND TOTAL					1525

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GENERAL IONIC ANALYSES LABORATORY

The determination of uranium by four different methods comprised the control program for the General Ionic Analyses Laboratory during this period. In only one series of control solutions was a natural material used; in all other cases synthetic solutions were analyzed.

Uranium - Fluorimetric Method

Uranyl nitrate solutions containing uranium in the range of 1.7-17 γ /ml were tested by two fluorimetric procedures: (1) extraction of uranium with TBP (tributyl phosphate) prior to the plating and fluxing operations; and (2) direct determination of the uranium content without extraction. The precision was found to be better by a factor of three when the extraction step was omitted. However, it should be noted that materials containing constituents that will either quench or enhance the uranium fluorescence can not be processed without the TBP extraction step, unless the extent of interference is known. A summary of the test results for this period is given in the following table:

<u>Method</u>	<u>Number of Determinations N</u>	<u>Concentration Range γ/ml</u>	<u>Standard Deviation</u>	<u>Confidence Interval</u>	<u>Limit of Error*</u>
			<u>S</u>	<u>C.I. Percent</u>	
Extracted	22	1.7-17.0	7	3	15
Not Extracted	20		3	1	5

*95 percent probability level

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Uranium - Colorimetric (1-ascorbic Acid) Method

Uranyl nitrate solutions containing uranium in the range of 0.2 to 1.7 mg/ml were tested by two colorimetric procedures: (1) extraction of uranium with diethyl ether prior to the development of color; and (2) direct development of color without extraction of the uranium. The precision of the test results obtained by the two methods differs by a factor of three, with the latter method giving better precision. Elimination of the extraction process is desirable for several reasons: (1) an analysis would require less time; (2) precision of the test results would be better; and (3) the space occupied by the extraction apparatus could be used for other purposes. However, in many types of samples, it is not possible to develop the uranium color directly with 1-ascorbic acid, due to the presence of other elements which are known to interfere with this process. In those cases, the uranium must be separated from the impurities in order to develop the uranium-ascorbic acid color. It is possible that some factor in the diethyl ether extraction process is responsible for the precision being poor, elimination of such a factor (if it does exist) should improve the precision of the method. The following table summarizes the results reported during this period:

<u>Method</u>	<u>Number of Determinations N</u>	<u>Concentration Range mg/ml</u>	<u>Standard Deviation</u>	<u>Confidence Interval</u>	<u>Limit of Error*</u>
			<u>S</u>	<u>C.I.</u> Percent	
Extracted	18	0.2-1.7	4	2	8
Not Extracted	12		1	1	3

*95 percent probability level

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Bartow Clay Leach Solutions - Fluorimetric Method

Bartow clay leach solutions containing large amounts of aluminum, phosphate and SiO_2 were tested for control purposes by the two fluorimetric procedures previously discussed. The precision of the test results obtained with and without TBP extraction is essentially the same. However, the high concentration of impurities apparently causes quenching with the result that low values are obtained for samples processed without extraction. If the extent of the quenching is a constant factor, then the direct fluorimetric method could be used by applying a suitable correction factor and thus eliminate the extraction process. The test results for this period are summarized in the following table:

Method	Number of Determinations N	Concentration Range γ/ml	Standard Deviation S	Confidence Interval C.I. Percent	Limit of Error *
Extracted	10	45-55	3	2	8
Not Extracted	10	20-25	4	3	10

*95 percent probability level

Uranium - Gravimetric and Potentiometric Titration Methods

Two uranyl sulfate solutions containing microgram amounts of iron, nickel, chromium, and manganese were prepared as routine control solutions for the HR Laboratory and as special control solutions for the General Ionic Analyses Laboratory. The uranium content of each solution was determined four times by both the gravimetric, NH_4OH precipitation, method and the potentiometric, ferric sulfate, titration method. The results obtained are summarized in the following table:

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<u>Method</u>	<u>Number of Determinations N</u>	<u>Concentration Range mg/al</u>	<u>Standard</u>	<u>Confidence</u>	<u>Limit of Error*</u>
			<u>Deviation S</u>	<u>Interval C.I. Percent</u>	
Gravimetric	8	26-43	0.4	0.3	0.9
Potential- metric	8		0.1	0.1	0.3

*95 percent probability level

These data indicate that the uranium content of uranyl sulfate solutions containing microgram amounts of impurities can be obtained with a precision of one percent or better.

HR CONTROL LABORATORY

The control program for the HR Laboratory is essentially the same as that reported in previous months. Uranyl sulfate solutions were tested for uranium and such minor constituents as iron, nickel, chromium and manganese, with the emphasis being placed on the determination of uranium, nickel and chromium.

Uranium

In November, the uranium test results were observed to be erratic, with poor precision and accuracy, a condition that had also existed during October. Since the test results reported during this two-month period seemed to indicate that some variable was being introduced that was causing this difficulty, a thorough check of the method and techniques being used was made. As a result of this investigation, it became apparent that the method and techniques were satisfactory, but that the control solutions

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were not. Since all control solutions had been carefully prepared, standardized and rechecked before being used for control purposes, the solution to the problem involved two possibilities: (1) solutions were evaporating from closed containers on standing; or (2) uranium was being introduced from some extraneous source. The latter possibility seeming improbable, a study was undertaken to determine whether or not uranyl sulfate solutions would evaporate from 2-ounce, screw-capped bottles under normal storage conditions.

Three, 2-ounce, screw-capped bottles were washed, rinsed with alcohol and dried overnight at 110° C. (usual procedure for preparing control solution sample bottles). Twenty-five ml of an uranyl sulfate control solution was pipetted into each of two of the bottles, while the third one was allowed to remain empty to serve as a counter-poise.

The two bottles containing the uranyl sulfate solution were weighed at intervals over a period of 39 days. One bottle (designated No. 1) lost about 0.5 percent, and the other (designated No. 2) about 4 percent during this period (see Figure 1). At this time the screw caps of both bottles were sealed, in so far as possible, with rubber "Okonite Tape," reweighed and stored for 21 days. During the final 21-day period, bottle No. 1 lost only 0.1 percent and bottle No. 2 lost 0.2 percent.

At the end of the 60-day period covered by this study, it was obvious that the 2-ounce, screw-capped bottles were the source of the erratic results being obtained in the HR Control Laboratory.

The standard procedure for control solutions at this time is to prepare only a week's supply at any one time, and seal the screw caps with "Okonite Tape." All control solutions analyzed during December,

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January and February were prepared and handled in this manner.

The precision and accuracy of the uranium results obtained by the Jones Reductor-Ceric Sulfate Method during this period were very good, indicating that the new procedure for preparing and handling the control solutions is satisfactory.

During the latter part of February, a method to eliminate the aeration step of the Jones Reductor-Ceric sulfate procedure was put into operation in the laboratory. The new method involved the use of phosphoric acid instead of sulfuric acid during the reduction process, and titration with potassium dichromate using barium diphenyl amine sulfonate as the indicator in place of the ceric sulfate used in the Jones Reductor-Ceric Sulfate Method. The first results obtained by this method were high, but this was corrected and it is anticipated that the results by this new method will be as satisfactory as those obtained by the ceric sulfate method. The following table gives a summary of the results obtained during this 3-month period for both methods (see Figure 2).

<u>Method</u>	<u>No. of Detns. N</u>	<u>Conc. Range mg/ml</u>	<u>Std. Dev. S</u>	<u>Conf. Int. C.I. Percent</u>	<u>Limit of Error*</u>	<u>Bias</u>
Jones-Reductor Ceric Sulfate	52	26-43	0.7	0.2	1.3	None
Jones-Reductor Dichromate	12		1.1	0.7	2.4	Positive

*95 percent probability level

267-10

Nickel - Dimethyl Glyoxime Method

Both the precision and accuracy of the nickel test results improved during this period. In November, the limit of error of one analysis (95 percent probability level) was 20 percent; whereas in this period, it is only 15 percent. The positive bias observed earlier has been corrected and at the present time no bias exists. The results for this period are given in Table II and Figure 3.

Chromium - Diphenyl Carbazide - Bismuthate Method

The precision and accuracy of the chromium test results during the first part of December were good, but since that time the results have been erratic and during February a definite negative bias was known to exist. A correction factor has been recommended which should correct this negative bias. The over-all precision for the period is much poorer than for November when a limit of error of one analysis (95 percent probability level) of 8 percent was obtained. (See Table II and Figure 4.)

Table II

Nickel and Chromium

December, 1951, through February, 1952

<u>Constituent Determined</u>	<u>No. of Detns. N</u>	<u>Conc. Range γ/ml</u>	<u>Std. Dev. S</u>	<u>Conf. Int. C.I. Percent</u>	<u>Limit of Error*</u>	<u>Bias</u>
Ni	21	12-60	7	3	15	None
Cr	21	7-36	10	5	20	Negative

*95 percent probability level

267-11

Iron and Manganese - Colorimetric Methods

Since only three iron results and four manganese values were reported during this 3-month period, it is not possible to reach any conclusion regarding the accuracy and precision of the iron and manganese test results.

X-10 ANALYTICAL LABORATORIES

During the past three months, the analysis of materials for thorium by the Analytical Chemistry Division at the X-10 Site has become of major importance. Consequently, a control program for the colorimetric determination of thorium was instituted. This program was in addition to the two uranium programs already in operation.

Uranium - Fluorimetric Method

The uranium test results reported by Laboratory 3019 for solutions of series F-1 (3.0 γ /ml) and E-1 (2.5 mg/ml) were somewhat erratic, with a definite positive bias being observed for series F-1 test results. The precision of the test results reported by Laboratory 3550 for series F-1 was good and was somewhat improved over that noted for November. The results reported by both laboratories are summarized in the following table. (See Figures 5, 6 and 7.)

<u>Laboratory</u>	<u>Number of Determinations N</u>	<u>Concentration Range γ/ml</u>	<u>Average Precision</u>	<u>Average Accuracy</u>	<u>Bias</u>
			<u>L.E.*</u>	<u>B $\pm$ C.I.</u>	
			<u>Percent</u>		
3550	62	3.0	7	0 $\pm$ 1	None
3019	143	2.5-7.0	11	-0.4 $\pm$ 2	None

*95 percent probability level

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Uranium - Colorimetric (Thiocyanate) Method

The precision of the uranium test results reported by both Laboratories 3550 and 3019 were equally good, with a limit of error of 2 percent being observed for the 3-month period covered by this report. A negative bias was noted for series D-1, (598 γ /ml) results reported by Laboratory 3550; and for series B-1, (253 mg/ml) results reported by Laboratory 3019. (See Figures 8, 9 and 10.)

The control determinations reported during this period are summarized in the following table:

<u>Laboratory</u>	<u>Number of Determinations N</u>	<u>Concentration Range</u>	<u>Precision Limit of Error*</u>	<u>Accuracy B $\pm$ C.I.</u>	<u>Bias</u>
		(γ /ml)			
3550	61	598	2	-0.5 $\pm$ 0.3	Negative
3019	155	598-650	2	+0.2 $\pm$ 0.3	None
		(mg/ml)			
3550	31	273	2	0 $\pm$ 0.4	None
3019	109	251	2	-0.8 $\pm$ 0.2	Negative

*95 percent probability level

Thorium - Colorimetric Method⁽¹⁾

The thorium concentration of three control solutions was determined by Laboratory 3550, using 1-(o-arsonophenylazo)-2-naphthol-3-6-disulfonic acid as the chromogenic reagent. A definite positive bias was noted for the results reported for series Th-2 (100.4 mg/ml) and Th-3 (84.6 mg/ml)

(1) Thomason, P. F., Perry, M. A., and Byerly, W. M., Anal. Chem., 21, 1239 (1949).

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although no bias was observed for results for series Th-1 (53 γ /ml). The precision of the test results for series Th-1 and Th-2 was found to be four percent (expressed as the limit of error of one analysis at a 95 percent probability level), and 2 percent for series Th-3. The results for this period are summarized in the following table. (See Figure 11.)

Code No.	No. of Dups. N	Thorium, ng/ml		Std. Dev. S	Conf. Int. C.I.	Precision Limit of Error*	Accuracy B $\pm$ C.I.	Bias
		Known Y	Average $\bar{X}$					
Th-1	46	0.053	0.053	0.001	0.004	11	0 $\pm$ 6	None
Th-2	25	100.4	102.1	2	0.8	4	+1.6 $\pm$ 0.7	Positive
Th-3	20	84.6	85.1	1	0.4	2	+0.6 $\pm$ 0.5	Positive

*95 percent probability level

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APPENDIX

267.15

Fig.1
RATE OF EVAPORATION OF URANYL SULFATE SOLUTIONS
FROM SCREEN-CAPPED BOTTLE UNDER NORMAL STORAGE
CONDITIONS

916916

Fig. 2
H. R. CONTROL LABORATORY

URANIUM---JONES-REDUCTOR METHOD

Fig. 3

HR Control Laboratory

IRON AND NICKEL---COLORIMETRIC METHODS

Iron

Concentration Range - 6-52 μ /ml.

Fig. 4

HR Control Laboratory
CHROMIUM AND MANGANESE
Colorimetric Methods

Fig. 5
X-10 ANALYTICAL LABORATORY

Bldg. 3550

URANIUM---FLUORIMETRIC METHOD

Series: F-1, Uranium, 3.0 /ml.

DEVIATION FROM KNOWN VALUE
 (Percent)

10
8
6
4
2
0
-2
-4
-6
-8
-10

Date of Analysis

26792

Series: F-1, Uranium, 3.0⁸/ml.

26.7.21

Fig. 7
X-10 ANALYTICAL LABORATORY
Bldg. 8019
URANIUM---COLORIMETRIC METHOD
Series D-1, Uranium, 598 μ /ml

URANIUM---FLUORIMETRIC METHOD
Series D-1, Uranium, 7.0 μ /ml.

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Fig. 8
 I-10 ANALYTICAL LABORATORY
 Bldg. 5550
 URANIUM---COLORIMETRIC METHOD
 Series: D-1, Uranium, 598^u/ml.

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Fig. 9
X-10 Analytical Laboratory
Bldg. 5019

URANIUM---COLORIMETRIC METHOD

Series: A-1, Uranium, 650 μ /ml.

Series: B-1, Uranium, 255 mg./ml

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Fig. 10
X-10 ANALYTICAL LABORATORY

Bldg. 3019

URANIUM---COLORIMETRIC METHOD

Series: A-1, Uranium, 650 Y/ml.

Series: B-1, Uranium, 253 mg/ml

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Fig. 21
 3-10 ANALYTICAL LABORATORY
 Bldg. 3450
 THORIUM—COLOIMETRIC METHOD

END