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ANALYTICAL CHEMISTRY DIVISION

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STATISTICAL QUALITY CONTROL REPORT

October, 1951.

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STATISTICAL QUALITY CONTROL REPORT

OCTOBER, 1951

INTRODUCTION

The distribution of the 1055 control determinations made during October is presented in ^{tabular form} ~~Table I~~ under the following headings, General Ionic Laboratory, HR Control Laboratory, and X-10 Analytical Laboratories.

The ratio of the sample determinations to the control determinations is being omitted this month because there is reason to believe that it does not give a true picture of the number of determinations that are being made in the laboratories which are participating in the control program.

Table I
Summary of Control Determinations
October

<u>Laboratory</u>	<u>Material</u>	<u>Determination</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	97	327
	" "	U	l-ascorbic acid	148	
	" "	V	Hydrogen peroxide	36	
	Bartow clay	U	Fluorimetric	47	
HR Control	Synthetic solutions	U	Jones-Reductor	92	228
	" "	Fe	α - α' dipyradyl	36	
	" "	Ni	Dimethyl glyoxime	27	
	" "	Cr	Diphenyl carbazide	63	
	" "	Mn	Periodate	10	
X-10 (3550) X-10 (3019)	Synthetic solutions	U	Fluorimetric	84	500
	" "	U	Thiocyanate	138	
	" "	U	Fluorimetric	96	
	" "	U	Thiocyanate	182	
GRAND TOTAL					1055

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GENERAL IONIC ANALYSES LABORATORY

The control program for this laboratory was accelerated in October, increasing the number of control determinations to 327 as compared to 100 in September. This was believed to be necessary to determine the effect of certain modifications that had been made in the methods being used.

Uranium (Fluorimetric)

In September, 20 uranium determinations were made for four test solutions, using two fluorimetric procedures, with the result that it was not possible to reach any conclusion as to the accuracy and precision of the test results being obtained. However, by increasing the number of control determinations to 96, during the month of October, the accuracy and precision of the test results obtained by the two fluorimetric procedures could be ascertained.

The two fluorimetric procedures used are designated as "FD" (direct plating of the control solution) and "FE" (extraction of the uranium with TBP prior to the plating and fluxing operations).

In all cases, the precision, expressed as the limit of error of one analysis at a 95 percent probability level, of the "FE" series of test results was better, the average L.E. for the "FD" series being 37 percent as compared to 22 percent for the "FE" series. The accuracy for both series was satisfactory since $B \pm C.I.$ in every case included zero, the average $B \pm C.I.$ for the "FD" series being -2 ± 17 as compared to $+5 \pm 9$ for the "FE" series. (See Table II and Figures 1 and 2.)

Table II
General Ionic Analysis Laboratory
Uranium-Fluorimetric Method
October

Code No.	Method	Number of Results N*	Uranium, γ /ml				Precision L.E.	Accuracy B + C.I.
			Known Y	Average $\bar{X}$	Standard Deviation S	Confidence Interval C.I.		
F-400	FD	6	17.0	16.4	2.4	2.5	37	-4 + 13
	FE	6		17.6	1.5	1.6	21	+3 + 9
F-500	FD	5	6.8	6.7	1.1	1.1	46	-1 + 25
	FE	5		6.7	0.4	0.4	16	-1 + 7
F-600	FD	7	3.4	3.5	0.5	0.5	35	+3 + 14
	FE	5		3.6	0.3	0.3	23	+6 + 8
F-700	FD	7	1.7	1.6	0.2	0.2	30	-6 + 13
	FE	7		1.9	0.2	0.2	26	+11 + 11

*One result = average of two determinations
FD = Direct plated
FE = Extracted with TBP prior to plating

Uranium (Colorimetric)

Uranium solutions tested for control purposes by the l-ascorbic acid method were processed by three procedures. Series "CD" were taken to perchloric fumes prior to the addition of the chromogenic reagent, but were not extracted; series "CE" were extracted with diethyl ether in the continuous extractor and processed in the usual way; series "FE" were extracted with TBP and the uranium content determined by the fluorimetric method.

The average limit of error of one analysis (L.E., percent) and the average accuracy ($B \pm C.I.$, percent) are given below for four of the five solutions tested; the fifth solution was omitted because of insufficient data.

Series Designation	L.E. (Average)	B $\pm$ C.I. (Average)
		Percent
CD	5	-4 $\pm$ 2
CE	8	-4 $\pm$ 4
FE	12	+3 $\pm$ 6

The accuracy of the test results for series "CD" and "CE" is not satisfactory and the precision of series "CE" could be improved. In contrast to series "CD" and "CE", the accuracy and precision of the "FE" series test results are good.

In Table III and Figures 3 and 4, the data obtained during October are given.

Table III
General Ionic Analyses Laboratory
Uranium - l-ascorbic Acid Method
October

Code No.	Method	Number of Results N*	Uranium, mg/ml				Precision L.E.	Accuracy B + C.I.
			Known Y	Average $\bar{X}$	Standard Deviation S	Confidence Interval C.I.		
C-100	CD	4	0.341	0.328	0.005	0.005	3	-3.9 + 1.4
	CE	4		0.326	0.005	0.008	5	-4.8 + 2.4
	FE	6		0.330	0.020	0.021	15	+2.5 + 6.0
C-300	CD	2	1.02	0.970	*	*	*	*
	CE	2		0.930	*	*	*	*
	FE	7		1.27	0.26	0.24	50	+20 + 19
C-400	CD	6	0.170	0.164	0.002	0.002	3	-3.5 + 1.3
	CE	6		0.170	0.008	0.008	12	0 + 4.3
	FE	8		0.182	0.012	0.010	15	+6.6 + 5.6
C-500	CD	6	0.612	0.593	0.006	0.006	3	-3.1 + 1.8
	CE	3		0.585	0.008	0.020	6	-4.6 + 3.4
	FE	6		0.607	0.030	0.031	12	+0.8 + 5.4
C-600	CD	4	1.70	1.63	0.045	0.072	9	-4.3 + 4.4
	CE	4		1.57	0.053	0.084	10	-8.2 + 5.3
	FE	6		1.73	0.099	0.104	15	+1.7 + 6.0

*One result - average of two determinations

CD = Direct color development

CE = Extracted with diethyl ether prior to color development

FE = Extracted with TBP and the uranium content determined by the fluorimetric method

Vanadium (Colorimetric)

The precision of the vanadium test results obtained by the hydrogen peroxide method is comparable to that obtained in previous months, but a trend toward low results is developing with the result that the accuracy is not as good as that observed during September. However, since the number of samples being tested for vanadium has decreased to the point that it is doubtful whether this program will be extended beyond this month, the trend toward low values does not warrant any remedial action at this time. (See Table IV and Figure 5.)

Bartow Clay Leaches

The two Bartow clay leach solutions designated BC1N (nitric acid leach) and BC1S (sulfuric acid leach) have been processed by three fluorimetric procedures during this period. The uranium concentration was obtained in series FD-100 by direct plating 100% of the solution onto the gold plate before fluxing; in series FD-10, by direct plating 10% of the leach solutions onto the gold plate and processing in the usual way; and in series FE by extracting with TBP prior to the plating and fluxing operations.

Since the results for both series FD-100 and FD-10 are lower than the uranium value determined for series FE, it is obvious that some constituent of the leach solution is causing quenching.

Inasmuch as the precision for series FD-100 and FE test results is of the order of 20-25 percent, it might be possible to direct plate solutions of this type by preparing calibration curves to correct for the effect of quenching. (See Table V and Figure 6.)

Table IV
General Ionic Analyses Laboratory
Vanadium-Hydrogen Peroxide Method
October

Code No.	Number of Results N*	Vanadium, mg/ml			Confidence Interval C.I.	Precision	Accuracy
		Known Y	Average $\bar{X}$	Standard Deviation S		L.E. Percent	B + C.I.
V-100	6	0.276	0.271	0.009	0.009	8	-2 ± 3
V-200	6	0.690	0.681	0.012	0.013	5	-1 ± 2
V-300	6	1.38	1.33	0.030	0.031	6	-4 ± 2

*One result = the average of two determinations

Table V
General Ionic Analyses Laboratory
Bartow Clay Leach Solutions
Uranium-Fluorimetric Method
October

		Number of Results N	Uranium, γ /ml				Precision L.E.	Accuracy B $\pm$ C.I.
Code No.	Method		Known Y	Average $\bar{X}$	Standard Deviation S	Confidence Interval C.I.		
							Percent	
BC1N	FD-100	9	*	27.2	2.7	2.0	23	* +7
	FD-10	3	*	35.6	0.95	2.3	11	* +6
	FE	11	*	50.0	6.1	4.1	27	* +8
BC1S	FD-100	10	*	27.9	2.6	1.9	21	* +7
	FD-10	2	*	38.2	**	**	**	**
	FE	12	*	46.0	4.0	2.6	19	* +6

* No known value has been established for this material

**Insufficient data

BC1N -- First nitric acid leach

BC1S - First sulfuric acid leach

FD-100- Direct plating of 100 γ aliquot

FD-10 - Direct plating of 10 γ aliquot

FE - Extracted with TBP prior to plating

HR CONTROL LABORATORY

The analysis of uranyl sulfate solutions, containing uranium in the range of 30 to 50 mg/ml for such minor constituents as iron, nickel, chromium and manganese which are present as the result of the corrosion of the reactor structural material, has been the main concern of the HR Control Laboratory.

Uranium

The uranium concentrations of the uranyl sulfate solutions tested for control purposes during October were in the range of 27 to 58 mg/ml.

Twenty-seven of the 92 test results reported this month were outside the allowable limit of plus or minus one percent, or, in other words, about 30 percent of the values were "out of control."

The precision of the test results for this period is comparable to that obtained in previous months (L.E. = 2 percent) although a limit of error of 2 percent is not considered satisfactory for uranium concentrations in this range or the Jones reductor method being used. Also, the accuracy is poor with a definite positive bias being observed during most of the period. (See Table VI and Figure 7.)

Iron

The positive bias observed for the iron test results during September continued during the month of October, although the precision for both months is comparable (L.E. = 20 percent). It is evident that remedial measures must be taken to improve the accuracy of the iron test results by the α - α' dipyradyl method. (See Table VI and Figure 8.)

Table VI
HR Control Laboratory
Summary of Control Determinations
October

<u>Material</u>	<u>Constituent Determined</u>	<u>Number of Results N</u>	<u>Units</u>	<u>Known Y</u>	<u>Average $\bar{X}$</u>	<u>Standard Deviation S</u>	<u>Confidence Interval C.I.</u>	<u>Precision L.E. Percent</u>	<u>Accuracy B $\pm$ C.I.</u>	<u>Comments</u>
Uranyl Sulfate Solution (IV)	U	92	mg/ml	233.5	234.2	2.1	0.4	1.8	+0.3 $\pm$ 0.2	Positive Bias
	Fe	36	γ/ml	79	87	9	3	20	+ 9 $\pm$ 3	Positive Bias
	Ni	27	γ/ml	45	51	7	3	28	+12 $\pm$ 5	Positive Bias
	Cr	63	γ/ml	179	139	26	7	37	-30 $\pm$ 5	Negative Bias
	Mn	10	γ/ml	112	97	19	14	44	-15 $\pm$ 14	Negative Bias

Nickel

The precision and accuracy of the nickel test results are poor as compared to previous months. The precision of the September test results was 18 percent as compared to 28 percent for October, and the trend toward high results noted in September has continued during this month. (See Table VI and Figure 8.)

Chromium

The chromium test results obtained by the diphenyl carbizide method are erratic with the same trend toward low results that was observed during September. The method consists of oxidation with ~~KMnO₄~~^{KMnO₄} at a pH of 1 and then boiling with HCl to remove the permanganate color, the addition of the chromogenic reagent (diphenyl carbazide), and the determination of the optical density by means of a Beckman "B" using 1 cm cells. In view of the known volatility of chromium in the presence of chlorides, it would appear that low and erratic test results could be expected, thus indicating the necessity for modifying the method to eliminate this obvious source of error. (See Table VI and Figure 9.)

Manganese

The accuracy and precision of the manganese test results are poor; however, some improvement is noted when the September and October test results are compared. Although the concentration of manganese is in the range of 2 to 11 γ /ml, this should be sufficient manganese to give better precision and accuracy than is being obtained inasmuch as the periodate method is very sensitive to small amounts of manganese. (See Table VI and Figure 9.) This is probably a matter of technique rather than an inadequate method.

X-10 ANALYTICAL LABORATORIES

Five hundred uranium determinations were made by the Analytical Chemistry Division at the X-10 Site during October. One hundred and eighty of the determinations were processed by the fluorimetric method while the remainder were tested by means of the colorimetric method (thiocyanate method).

Uranium (Fluorimetric)

The accuracy and precision of test results obtained in Laboratories 3019 and 3550 continue to be good with no significant bias existing during this period, although the test results for series C-1 (7.0 γ /ml) Building 3019 and series FX-500 (6.8 γ /ml) Bldg. 3550 are showing a trend toward low results.

The average precision and accuracy for both laboratories are given below:

	Precision L.E. (Average)	Accuracy B $\pm$ C.I. (Average)
	Percent	
Building 3550	7	-0.8 $\pm$ 1.5
Building 3019	8	-0.5 $\pm$ 2.8

(See Table VII and Figures 10, 11 and 12.)

Uranium (Colorimetric)

The precision of the colorimetric uranium test results reported by Laboratory 3550 continues to be slightly better than that for Laboratory 3019, but the precision of both laboratories is satisfactory.

The average precision and accuracy for both laboratories is given below:

Table VII
X-10 Analytical Laboratories
Uranium Determination
October

Part I - Fluorimetric Method

Code No.	Bldg.	Number of Results N*	Uranium, γ /ml				Precision L.E.	Accuracy B $\pm$ C.I.	Comments
			Known Y	Average $\bar{X}$	Standard Deviation S	Confidence Interval C.I.			
FX-200	3550	21	3.4	3.4	0.13	0.06	8	0 $\pm$ 2	
	3019	8		3.4	0.12	0.10	9	0 $\pm$ 3.0	
FX-500	3550	21	6.8	6.7	0.17	0.08	5	-2 $\pm$ 1	Negative Bias
	3019	4		6.8	0.19	0.30	9	0 $\pm$ 5	
C-1	3019	36	7.0	6.9	0.19	0.07	6	-1.4 $\pm$ 0.9	Negative Bias

Part II - Colorimetric Method

Code No.	Bldg.	Number of Results N*	Uranium, γ /ml				Precision L.E.	Accuracy B $\pm$ C.I.	Comments
			Known Y	Average $\bar{X}$	Standard Deviation S	Confidence Interval C.I.			
CX-100	3550	8	341	343	2.4	2.0	1.7	+0.6 $\pm$ 0.6	
	3019	4		340	2.1	3.4	2.0	-0.3 $\pm$ 1.0	
CX-200	3550	23	384	381	2.6	1.1	1.4	-0.8 $\pm$ 0.3	Negative Bias
CX-500	3550	15	682	680	4.8	2.7	1.6	-0.3 $\pm$ 0.4	
A-1	3019	41	650	658	6.8	2.2	2.1	+1.2 $\pm$ 0.3	Positive Bias
Milligrams/ml									
CX-600	3550	23	273	274	2.1	0.9	1.5	+0.3 $\pm$ 0.3	
	3019	5		273	1.6	2.0	1.6	0 $\pm$ 0.7	
B-1	3019	41	253	254	3.6	1.1	2.5	+0.4 $\pm$ 0.3	

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	<u>Precision</u> <u>L. E. (Average)</u>	<u>Accuracy</u> <u>B ± C.I. (Average)</u>
	<u>Percent</u>	
Building 3550	1.5	-0.1 ± 0.4
Building 3019	2.0	+0.3 ± 0.6

In only two cases was a trend toward high or low values noted.

Test results for series CX-200 (384 γ /ml), Building 3550, were exhibiting a trend toward low results and for series A-1 (650 γ /ml), Building 3019, a trend toward high values was observed. (See Table VII and Figures 13, 14, 15 and 16.)

87 557
2158 18

Fig. 2
URANIUM CONTROL PROGRAM
Fluorescent Method
9933-2 Laboratory

Fig. 3
General Isotope Analysis Laboratory
Uranium---1-ascorbic Acid Method

Series: C-100, Uranium, 0.541 mg./ml.

Series: C-500, Uranium, 0.612 mg./ml.

Date of Analysis

• Direct Method
• TSP Scheduled

Fig. 4
URANIUM CONTROL PROGRAM
 Colorimetric Method
 9953-2 Laboratory

Series: C-400, Uranium, 0.17 mg./ml.

Series: C-400, Uranium, 1.70 mg./ml.

Fig. 5
 VANADIUM CONTROL PROGRAM
 Hydrogen-peroxide Method
 9933-B Laboratory

Fig. 8
Barlow Clay Control Program
STSS-2 Laboratory
LEACH SOLUTIONS
Uranium----Fluorimetric Method

Fig 7
WRE CONTROL PROGRAM
Uranium — Jones Reductor Method

Fig. 8
HAE CONTROL PROGRAM
Iron and Nickel
Colorimetric Methods

Fig. 28-9
 HERE CONTROL PROGRAM
 Chromium and Manganese
 Colorimetric Methods

Fig. 10
URANIUM CONTROL PROGRAM (X-10)
Fluorimetric Method
Bldg. 3019

Series FX-200, Uranium, 3.41 μ /ml.

Series FX-500, Uranium, 6.82 μ /ml.

Date of Analysis

Deviation From Known Value
 (Percent)

2139 27

Fig. 11
URANIUM CONTROL PROGRAM (X-10)
Fluorimetric Method

Bldg. 5550

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Fig. 12
URANIUM CONTROL PROGRAM (X-10)
Fluorimetric Method
Bldg. 3019

Date of Analysis

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Fig. 15
URANIUM CONTROL PROGRAM (X-10)
Colorimetric Method
 Bldg. 3850

Series: CX-200, Uranium, 384 γ /ml.

Series: CX-600, Uranium, 682 γ /ml.

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Fig. 14
URANIUM CONTROL PROGRAM (X-10)
Colorimetric Method
 Bldg. 3019
 Series: CX-100, Uranium, 341 μ /ml.

Series: CX-500, Uranium, 682 μ /ml.

Date of Analysis

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Fig. 15
URANIUM CONTROL PROGRAM (X-10)
Colorimetric Method

Series: OX-600, Uranium, 273 mg./ml.

Bldg. 3550

DEVIATION FROM KNOWN VALUE
 (Percent)

Bldg. 3019

2139 32

Fig. 16
URANIUM CONTROL PROGRAM (X-10)
Colorimetric Method

Bldg. 3019

Series A-1, Uranium, 650 μ /ml.

Series B-1, Uranium, 253 μ /ml.

Date of Analysis

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END