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INVESTIGATION OF SPECTROCHEMICAL SOLUTION-METHODS OF ANALYSIS

The Use of Designed Experiments and Statistical Methods of Analysis in the Interpretation of Data

J. A. Norris
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ORNL-2927
Chemistry - General

Contract No. W-7405-eng-26

Analytical Chemistry Division

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DATE ISSUED

APR 25 1960

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ABSTRACT

During a period of 12 months, 46 systems for introducing a liquid sample into the spark-gap of a spectrograph were studied by means of eight designed experiments. Such factors as types and sources of electrodes, signal-to-noise ratios, number of exposures per electrode, et cetera, were included in this investigation. Statistical techniques were used to evaluate the 30,000 measurements that were secured in these investigations. As a result of this work, the electronic system of the spectrograph was modified to provide for an automatic compensating system and optimum conditions for introducing a liquid into the spark-gap were tentatively established for the rotating-disc electrode system.

INVESTIGATION OF SPECTROCHEMICAL SOLUTION-METHODS OF ANALYSIS*

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INTRODUCTION

There are numerous advantages in using solution-methods for the spectrochemical analysis of many types of materials; specifically, standards are easily prepared, the addition of an internal standard can be controlled more precisely, concentration ranges can be extracted or adjusted for greater sensitivity, etc. The solution-method combined with the speed, range and versatility of a photoelectric spectrometer, therefore, results in a rapid and economical system for analyzing a wide variety of materials. With such a system, experiments which require a mass of data can be performed in a short period of time. Then, by utilizing electronic computing equipment to evaluate these data, improvements in spectrographic techniques, based on the results of such experiments, can be made and tested without delay.

Combining this system of spectrochemical analysis, solution-methods and a photoelectric spectrometer, with the availability of electronic computing equipment, eight experiments were performed and evaluated to determine the most precise method of introducing solutions into a high voltage spark. This report concerns the design of these experiments, the analysis and interpretation of

* Presented at the Eighth Annual Spectroscopy Seminar, Gainesville, Florida, January 6, 7 and 8, 1960.

the data, the conclusions that were reached and the improvements that were made as a result of these experiments.

EXPERIMENTAL

Basically, the purpose of this investigation is to determine the most precise method for introducing a solution into the spark-gap of a spectrograph. As an adjunct to this, it was expected that any other critical sources of variability would be identified so that optimum conditions for this type of spectrographic analysis could be established. In order to provide a basis of comparison therefore, mixtures of rare earths, similar to samples that are analyzed in this laboratory by a solution technique,[1] were selected for this investigation. In all, eight experiments were performed using test materials that contained a mixture of the rare earths, with strontium as an internal standard, in a 50 per cent HCl solution.

While certain factors were changed from one experiment to another, the general experimental conditions given below remained the same for all eight experiments:

Instrumentation:

Spectrograph - Paschen-Runge mounted 21-ft. grating spectrograph using 1P28 and 1P21 photomultiplier tubes for recording the intensity of the spectral line.

Electronics - The electronic system is a modified Baird-Atomic Direct Reader with 16 recording channels and two internal standard channels. The recording system uses either 8 clocks or 16 channels of tape read-out.

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1. J. A. Norris and C. E. Pepper, "Quantitative Spectrochemical Analysis of Rare-Earth Mixtures," Anal. Chem., 24, 1399 (1952).

Instrumentation (Cont'd)

Source - A National Spectrographic Laboratories Spec-Power-unit high voltage spark circuit (air-gap type), 13,000 volts, 2 breaks/half cycle and an average current of 6-7 rf amps.

Exposure - All exposures are made to a constant voltage (30 V) of the internal standard capacitor where an automatic sensing device actuates the electronic read-out system.

Analytical Lines:

	Element	Wavelength	Order	Photomultiplier
1.	Y	3710	2	1P28
2.	La	4333	2	1P21
3.	Ce	4186	2	1P28
4.	Pr	4222	2	1P21
5.	Nd	4303	2	1P21
6.	Sm	4424	2	1P21
7.	Eu	3971	2	1P21
8.	Gd	3646	2	1P28
9.	Tb	3676	1	1P28
10.	Dy	3944	2	1P28
11.	Ho	3891	2	1P28
12.	Er	3906	2	1P28
13.	Tm	3131	1	1P28
14.	Yb	3694	1	1P28
15.	Lu	2615	1	1P28
16.	Th	4019	2	1P28
17.	Sr	4077	2	1P28

All lines above 4000A using 1P28 tubes have glass filters at the slit to remove low order interferences.

Data Reduction:

Clock readings are converted to concentrations by means of previously prepared calibration curves. Tape readings are converted to concentrations by means of a standard Baird data reduction calculator.

The factors that were varied during these investigations are tabulated, by experiment, in Table I.

While other investigators have studied solution-methods of spectrochemical analysis, they were primarily concerned with sensitivity studies[2] which is of secondary interest here. The results of this study are interpreted in terms of precision and the matter of sensitivity is given little consideration.

In the following sections, the results for the eight experiments are described in terms of each individual series of tests and the conclusions reached at each stage are discussed.

DISCUSSION OF EXPERIMENTS

Experiment No. 1 (2400 numbers)

In this first experiment two variables were investigated; namely,

1. The reproducibility of four different types of porous-cup electrodes and a spark-in-spray system, and,
2. The influence of the signal/noise ratio.

A solution that contained the eight elements, yttrium, gadolinium, lanthanum, cerium, praesodymium, neodymium, samarium, and europium, plus strontium as an internal standard, was used in this study. The concentration of the eight constituents was adjusted to give a high signal to noise ratio, $\sim$4 to 1, for four elements and a low one, $\sim$1 to 1, for the remaining four. The data were collected by making 6 exposures for 10 electrodes of each of the five electrode-systems. In this way, 300 values were obtained for each of the eight elements to give a total of 2400 numbers. A tabulation of these data is given in the appendix.

Basically, this first investigation was not planned in accordance with

2. William K. Baer and Edwin S. Hodge, "Spectrochemical Analysis of Solutions," Paper No. 116 presented at Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 2-6, 1959.

Table I

Variable Conditions - Experiments No. 1 Through 8

Experiment No.	Electrode System Type	Electrode System No.	Composition of Test Solution	Signal/Noise Ratio	Other Conditions	Total Number of Measurements
1	Porous Cup	1	Soln. 1 - 8 rare earth elements	1/1 and 4/1	1. Porous cup electrodes (10/system) batch No. NC-86N, UCP-201, UCP-203, and UCP-1994; 6 exposures/elec.	2400
	Spray	1	4 at low conc.; 4 at high conc.			
2	Porous Cup	2	Soln. A: Low Level - Gd, Eu, Sm, Nd High Level - Y, La, Ce, Pr	1/1 4/1	1. 10 electrodes/electrode system; batch No. NC-86N 2. Helium atmosphere in 1/2 of tests	
			Soln. B: Converse of Soln. A.	1/1 and 4/1	3. 6 exposures/electrode	1920
3	Porous Cup Spray	1	Same as Experiment No. 2	1/1 and 4/1	1. 10 electrodes/electrode system; batch No. NC-86N 2. 6 exposures/electrode	1920
4.	Porous Cup Rotating-disc	11 1	Soln. C: 15 rare-earth elements + Th, each at ~100 μg/ml level	~4/1	1. 10 electrodes/batches No. C-32 (0.025) AGKSP, C-32 (0.040) AGKSP, G-58 (0.040) AGKSP, L-20 (0.040) AGKSP, NC-79N, NC-85N, NC-86N, UC-1759, UC-2101, UC-205, 29X (0.025) SPK for porous cup. 10 electrodes/batch NC, for rotating disc. 2. 4 exposures/electrode	7200
5.	Rotating-disc	5	Same as Experiment No. 4	~4/1	1. 10 electrodes/each rate of rotation; rates of 4, 8, 12, 16, 20 rpm. 2. 4 exposures/electrode	2400
6.	Rotating-disc	4	Same as Experiment 4	~4/1	1. Background compensating system installed. 2. 10 electrodes/each rate of rotation; rates of 10, 20, 30, 40 rpm. 3. 4 exposures/electrode	2560
7	Rotatiug-disc	8	Same as Experiment No. 4	~4/1	1. Rates of rotation, 10, 20, 40 rpm; electrode time 20, 25, 30, 35, 55 and 80 seconds for rotating disc system and 20 seconds porous cup. 2. 10 electrodes/system and 4 exposures/electrode. 3. Background compensating system functioning.	7040
8	Rotating-disc Wick Porous Cup	2 1 1	Soln. D: 16 rare-earth elements; high concentration level	10/1	1. Rotating-disc (40 rpm) electrodes; 1/8" thick lower X 1/8" upper and 3/16" lower upper and 3/16" X 1/8" porous cup (NC-86N). 2. 10 electrodes/system; 4 exposures/electrode. 3. Modified background compensating system installed	4800
Total		46				30,240

the concepts of statistically designed experiments. As a consequence, it was necessary to discard some of the data and to base an analysis of variance on averages in order to derive as much information as possible from these first tests. After this preliminary examination of the data, an analysis of variance and of residual variance was obtained by means of an electronic computor; an IBM-704 which was programmed for this purpose. The results for the analysis of variance are given in Table II.

Since the main effects were of primary interest in this investigation, the interactions were not considered individually. In Table II, part IA, the ratio between the variance of each of the main effects and the residual was found to be significantly greater than the theoretical value for these ratios. Therefore, the levels of each factor were considered to be different and significant sources of variability in the analysis. Since the measurements for the eight elements were different, a test of significance was expected. Furthermore, on the basis of previous experience, differences in the electrode systems, in the signal to noise ratio and in the exposures were expected. These tests then served to confirm observations that had been made in the past.

It had been noted previously that the variability for exposures 1 and 2 appeared to be greater than that observed for the other exposures. When the data were re-evaluated, omitting exposures 1 and 2, the difference in the other exposures was found to be negligible. This is shown in Table II, part IB.

Omitting exposures 1 and 2 decreased the variability of the other main effects to some extent, as shown in Table II, part II, but not to the extent that the exposure effect was reduced. From this it was concluded that exposures 1 and 2 should be omitted in subsequent tests or some provision should be made to eliminate the excessive variability in the first two exposures.

Table II

Identification of Sources of Variability in Spectrographic Analysis

Experiment No. 1

I. Analysis of Variance

Source of Variability	Degrees of Freedom D.F.	Sum of Squares Total T_{ss}	Sum of Squares Mean M_{ss}*	Variance Ratio F_e	Variance Ratio F_t (95% C.L.)	Significance**
		$\times 10^5$				
A. All Data:						
Elements (A)	6	602	100	2000	2.2	+
Electrodes (C)	4	15.3	3.8	76	2.5	+
Signal/Noise (D)	1	3479	3479	7×10^4	3.9	+
Exposures (E)	5	84.7	16.9	340	2.3	+
Interactions (IA)	283	1324	4.7	94	1.3	+
Residual (R)	120	6	0.05			
Total (T)	419	5511				
B. Exposures E_1 and E_2 Omitted:						
Elements (A)	6	406	67.7	11×10^3	2.3	+
Electrodes (C)	4	9.7	2.4	404	2.5	+
Signal/Noise (D)	1	2598	2598	4×10^5	4.0	+
Exposures (E)	3	0.4	0.14	2.3	2.7	-
Interactions (IA)	193	843	4.4	733	1.5	+
Residual (R)	72	0.4	0.006			
Total (T)	279	3857				

*M_{ss} = Variance or S^2

**$F_e > F_t$ test is significant; designated by "+"

$F_e < F_t$ test is not significant; designated by "-"

Table II

II. Comparison of Variances After Omission of Exposure E_1 and E_2

Source of Variability	Degrees of Freedom		Mean Sum of Squares		Variance Ratio		
	$D.F_1$	$D.F_2$	M_{ss} (1)	M_{ss} (2)	F_e	F_t (95% C.L.)	Sign.
Elements (A)	6	6	100	67.7	1.5	4.3	-
Electrodes (C)	4	4	3.8	2.4	1.6	6.4	-
Signal/Noise (D)	1	1	3479	2598	1.3	161	-
Exposures (E)	5	3	16.9	0.14	120	9	+
Interactions (IA)	283	193	4.7	4.4	1	1.3	-
Residuals (R)	120	72	0.05	0.006	8.3	1.5	+
Totals (T)	419	279	13.2	13.8	1	1.2	

III. Residual Variance* Relative to the Source and Type of Electrodes

Electrode System		Residual Variance	
Source	Type	All Data (N = 84)	E_1 and E_2 Omitted (N = 56)
		($\times 10^5$)	
NC-86N	Porous Cup	2.16	2.04
	Spray	2.88	2.92
UCP-203	Porous Cup	3.34	3.19
UCP-1994	Porous Cup	3.40	3.30
UCP-201	Porous Cup	4.05	3.60

*Residual Variance (S_r^2):

S_r^2 = Total sum-of-squares - (Sum-of-Squares of the main effects);

i.e., for Table II, Part A,

$S_r^2 = 5511 - (602 + 15.3 + 3479 + 84.7) = \underline{\underline{1330}}$

In Table II, part III, the residual variance or experimental error attributable to the different types of electrodes is given for all data and for the data when exposures 1 and 2 are omitted. From this compilation, it appeared that the spray system, or the porous-cup system with electrodes from lot NC-86N, was somewhat better than the other systems tested because the residual variance was less for these two systems. Additional tests will be required to establish the validity of these observations.

Experiment 1A (840 numbers)

As indicated previously, the analysis of variance presented in Table II is based on averages. Consequently, when it was noted that the residual variances for the electrode systems involving a spark-in-spray method and the porous cup technique (electrode lot 86N) were somewhat less than those for the other systems, all the data, instead of averages, for these two systems were re-evaluated.

While these data were evaluated by means of an analysis of variance, the results merely confirmed the significance of the main effects as sources of variability in this procedure. At this point, the statistical evaluation of these data were carried one step further by comparing the variability within and between the electrodes for the two types of systems. This comparison is presented in Table III.

From this analysis of the data, it was noted that the variability between the electrodes for the two systems as well as that within the electrodes was not significantly different.

It was then decided that additional tests were required to definitely establish the superiority of one system over the other.

Table III

Comparison of the Variability Within and Between Electrodes for Two Types of Electrode Systems

Electrode System Source	Type	Degrees of Freedom D.F.	Variance M_{ss} S^2	Ratio F_e	F_t	Significance **
A. Within Electrodes:						
NC-86N	Porous-Cup	5	13.2	4.7	5.0	-
	Spray	5	2.8			
B. Between Electrodes:						
NC-86N	Porous-Cup	9	17.4	1.5	3.2	-
	Spray	9	11.4			

*95% probability level

** "+" = significant difference

"-" = no significant difference

Experiment No. 2 (1920 Numbers)

Experiment No. 2 was designed to test the effect of a partial helium atmosphere in a porous-cup electrode system and to evaluate the contribution of different signal-to-noise ratios to the total variability of this type of spectrochemical procedure.

Since the signal-to-noise ratio is dependent on the quantity of a constituent present, two solutions, each containing the eight elements, Gd, Eu, Sm, Nd, Pn, Ce, La and Y, were prepared. In one solution, designated as A, the concentration of Gd, Eu, Sm and Nd was adjusted to give a low signal-to-noise ratio of about 1 to 1 while the quantity of the other four elements was adjusted to give a ratio of about 4 to 1. These quantities and ratios were reversed in the second solution, designated as solution B.

In order to obtain a partial helium atmosphere, when the sample is being excited in the spark, a hole was placed in the lower electrode and helium was introduced, through this hole, into the spark-gap.[3] Since the results of the previous tests had indicated that the variability of the porous-cup electrodes was less for lot NC-86N, electrodes from this lot were used in these tests. In all, 40 electrodes were used; 10 electrodes per solution per electrode system. Again, six exposures per electrode were made a total of 1920 results was secured in this experiment. A tabulation of these data are given in the appendix.

When these data were evaluated by means of an analysis of variance, see Table IV, the results were similar to those given in Table II for Experiment No. 1. In this case, however, omitting exposures 1 and 2 did

[3] C. Feldman, "Spark Exposures in a Helium Atmosphere Without the Use of a Chamber," Anal. Chem. Ann. Prog. Rep. Dec. 31, 1958, ORNL-2662, p. 76.

not change the residual (R) variance. This is not necessarily a significant observation, but is merely an indication that the main effects being studied, or some effect that is directly related to these factors, are the critical variables in this method of analysis. Otherwise, a change in the residual would be expected.

Table IV

Identification of Sources of Variability

In Spectrographic Analysis

Experiment No. 2

I. Analysis of Variance

Source of Variability	Degree of Freedom D.F.	Sum of Squares Total T_{ss} X 10^3	Sum of Squares Mean M_{ss} X 10^3	Variance Ratio F_e	Variance Ratio F_t 95% C.L.	Significance
A. ALL DATA:						
Elements(A)	7	3530	504	13×10^3	2.0	+
Electrodes(C)	1	117	117	3×10^3	3.9	+
Signal/Noise(D)	1	3474	3474	87×10^3	3.9	+
Exposure(E)	5	11	2.2	50	2.2	+
Interactions(IA)	277	471	1.7	43	1.2	+
Residual(R)	1728	63	0.04			
Total (T)	1919	7666	3.99			
B. EXPOSURES 1 and 2 OMITTED:						
Elements(A)	7	2375	339	8×10^3	2.0	+
Electrodes(C)	1	68	68	2×10^3	3.9	+
Signal/Noise(D)	1	2360	2360	59×10^3	3.9	+
Exposure(E)	3	1	0.3	8	2.6	+
Interaction(IA)	115	305	2.7	68	1.3	+
Residual(R)	1152	40	0.04			
Total (T)	1279	5149	4.03			

Table IV (Cont'd.)

II. Comparison of M_{ss} of Main Effects After Omission of Exposures 1 and 2

Source of Variability	Degrees of Freedom $D.F_1$	$D.F_2$	Mean Sum-of-Squares $M_{ss}^{(1)}$	$M_{ss}^{(2)}$	Variance Ratio F_e	F_t	Significance
			$\times 10^3$			95% C.L.	
Elements(A)	7	7	504	309	1.5	3.8	-
Electrodes(C)	1	1	117	68	1.7	161	-
Signal/Noise(D)	1	1	3473	2360	1.5	161	-
Exposures(E)	5	3	2	0.3	6.7	9	-
Interactions(IA)	277	115	471	305	1.5	1.3	+
Residuals(R)	1728	1152	0.04	0.04	1.0	1.0	
Total (T)	1919	1279	3.99	4.03	≤ 1	1.0	

To complete the analysis of these data, the variability within and between electrodes for the two electrode systems and for the two signal-to-noise ratios were compared.

While a noticeable decrease in the variability within-electrodes was observed for the second electrode system, porous-cup in a helium atmosphere, the variance between the electrodes for the two systems was essentially the same; see Table V, Part I, Sections A.

Table V

Comparison of the Variability Within and Between Electrodes

I. Electrode Systems

Electrode System	Degrees of Freedom D.F.	Variance M_{ss} S^2	Ratio F_e	Ratio F_t 95% C.L.	Significance
A. Between					
1. Within electrodes:					
Porous-Cup	5	15.2	2.8	5.1	-
Porous-Cup + Helium	5	5.4			
2. Between electrodes:					
Porous-Cup	9	18.2	1.0	3.2	-
Porous-Cup + Helium	9	17.7			
B. Within					
Porous-Cup					
Between elec.	9	18.2	1.2	1.6	-
Within elec.	5	15.2			
Porous-Cup + Helium					
Between elec.	9	17.7	3.3	4.8	-
	5	5.4			

Table V (Cont'd.)

II. Signal-to-Noise Ratios

Signal-to-Noise Ratio	Degrees Of Freedom D.F.	Variance M_{ss} S^2	Ratio F_e	Ratio F_t 95% C.L.	Significance
A. Between					
1. Within electrodes					
1:1	5	14.5	2.4	5.1	-
4:1	5	6.1			
2. Between electrodes					
1:1	9	29.8	1.4	3.2	-
4:1	9	41.9			
B. Within					
1:1					
Between Electrodes	9	29.8	2.1	4.8	-
Within Electrodes	5	14.5			
4:1					
Between Electrodes	9	41.9	6.9	4.8	+
Within Electrodes	5	6.1			

In both systems, however, the variance between electrodes is greater than that within electrodes; see Table V, Part I, Section B.

It was concluded from this that the introduction of helium does not improve the overall precision of this method.

When a similar comparison was made for the two signal-to-noise ratios, see Table V, Part II, it was found that the variance between electrodes for the two ratios was different and in all cases was greater than the corresponding variability within-electrodes. This difference in the between-electrode variability, however, may not be real because the average concentration of the 8 elements at the high signal-to-noise ratio is greater,

by a factor of nearly 2, than the concentration of these same constituents at lower signal-to-noise ratio of 1/1. The variability within the electrodes, however, is independent of this concentration effect and consequently is more effective in estimating the significance of differences in the two signal-to-noise ratios. As was expected, less variability was observed for the higher signal-to-noise ratio.

Experiments 1a and 2 Combined

At this point, the data for Experiments 1a and 2 were combined in order to compare the two porous-cup electrode systems with the spark-in-spray technique for introducing a sample into the spark-gap. This comparison of the electrode systems is presented in Table VI.

Table VI

Comparison of Electrode Systems

Experiments 1a and 2

Electrode System Source	Type	Experiment Number	Number of Meas. N	Relative Range* R (%)	Variance (S^2) Within	Between
	Spray	1a	420	6	3	11
NC-86N	Porous Cup + Helium	2	960	10	8	18
NC-86N	Porous Cup	1a	420	7	13	17
		2	960	8	14	18
		1a + 2	1380	8	14	18

* R(%) = (Range x 100)/average.

The results of this comparison confirm the observations made previously; namely, that the range and variance is less for the spark-in-spray system than for the other systems tested. In all cases, however, the variance within the electrodes was less than that between the electrodes.

Experiment No. 3 (1920)

As indicated previously, certain compromises were necessary in order to evaluate the data derived from Experiment No. 1. Since the spark-in-spray system was included in that investigation, but not in Experiment No. 2, this third experiment was designed to provide data for a more reliable comparison of the porous-cup and the spark-in-spray systems.

Except for the substitution of the spark-in-spray for the porous-cup-in-helium system, the basic design and conditions of Experiment No. 2 were repeated in this third investigation. A tabulation of these data are given in the appendix.

An analysis of variance was made, and as had been anticipated, the variability of the data decreased when exposures 1 and 2 were omitted. This, of course, merely confirmed previous observations. When the variance between- and within-electrodes for the two electrode systems were compared, however, the omission of exposures 1 and 2 became a critical factor in establishing the superiority of one system over the other. This situation is shown in Table VII.

Table VII

Comparison of Electrode Variability for a Spark-in-Spray and a Porous-Cup System

Electrode System	Number of Measurements N	Relative Range* R (%)	Variance (S^2) Within S^2_W	Variance (S^2) Between S^2_B
A. ALL DATA:				
Porous-Cup	960	8	11	39
Spark-in-Spray	960	5	20	16
B. EXPOSURE 1 AND 2 OMITTED:				
Porous-Cup	640	8	2	44
Spark-in-Spray	640	5	3	14

* R (%) = (Range x 100)/Average

While the variance between electrodes was significantly less for the spark-in-spray system when all data were included in the analysis, the variability within-electrodes was less for the porous-cup system. After exposures 1 and 2 were omitted, however, the variability within-electrodes was found to be essentially the same for both systems. Under these circumstances, the spark-in-spray system was considered to be superior to the porous-cup method for introducing the sample into the spark-gap.

Experiment No. 4 (7200 Numbers)

Because of certain undesirable characteristics of the spark-in-spray system for introducing liquid samples into the spark-gap and the realization that the electrodes were a critical source of variability in this spectrochemical method, a fourth experiment was planned to evaluate the relative merits of 11 types of porous-cup systems plus one other method that involved a rotating-disc.

In this experiment, four, rather than six, exposures/electrodes were made for 10 electrodes/systems. Since a test solution that contained 15 of

the rare-earth elements, at concentration levels of ~100 μg/ml, was used in this experiment, 600 values/system were obtained. A tabulation of the 12 sets of 600 values (7200 numbers in all) is given in the appendix.

Since this study was concerned with only one variable, the electrode systems, an analysis of variance was considered unnecessary. Instead, these 12 systems were evaluated on the basis of the average range and variance for each set of 10 electrodes. A comparison of the 12 systems, on the basis of these characteristics, is given in Table VIII and is shown graphically in Fig. 1.

As shown in Table VIII, the variance associated with the rotating -disc system is less than that noted for 9 of the 11 systems in which the porous-cup technique was used. Furthermore, when the range of the results is considered as a function of the time required to reach a constant potential, see Fig. 1, it is apparent that the rotating-disc system is relatively insensitive to this time factor. This same factor, however, is a significant source of variability in all the porous-cup systems.

Having tentatively established the superiority of the rotating-disc system over the porous-cup technique, further tests were planned to determine the optimum conditions for this system.

Table VIII

Comparison of Ranges and Variances for 12 Electrode Systems

Electrode System	Average* Range R	Average* Variance S^2	Relative Dispersion **
Porous-Cup: NC-85N	16	28	1.0
" : 29 x (0.025)SPK	16	38	1.3
Rotating-Disc: NC	26	71	2.5
Porous-Cup: C-32 (0.040)AGKSP	24	83	2.9
" : NC-79N	30	110	3.8
" : NC-86N	28	127	4.4
" : L-20 (0.040)AGKSP	30	127	4.4
" : UC-2101	28	140	4.9
" : UC-2105	34	160	5.6
" : G-58 (0.040)AGKSP	37	182	6.3
" : UC-1759	42	185	6.4
" : C-32 (0.025)AGKSP	96	2870	100

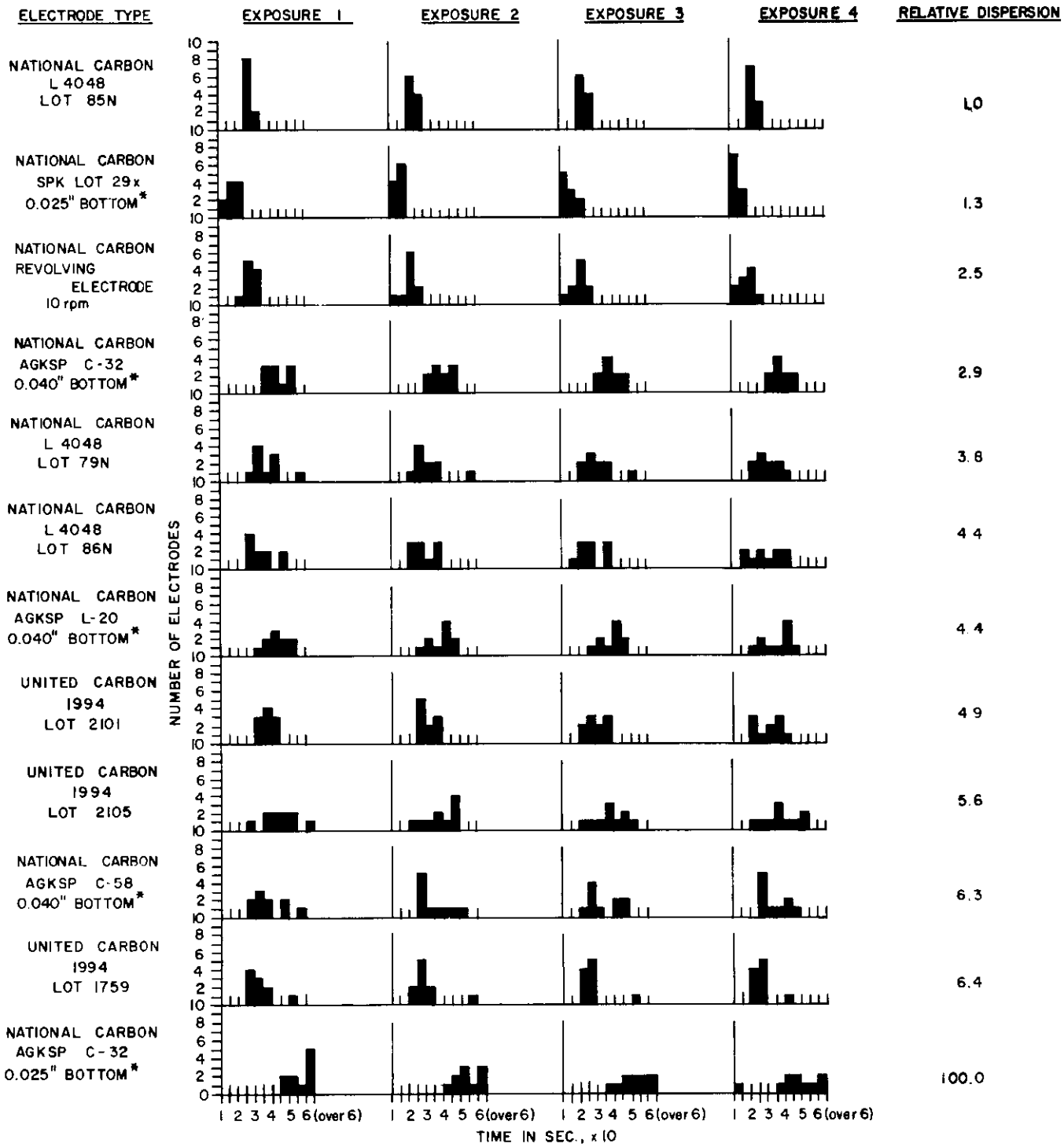
* For 10 electrodes

** Variance of each system relative to NC-85N, porous-cup system.

Experiment No. 5 (2400 Numbers)

Having decided, on the basis of the results of Experiment No. 4, that the rotating-disc system for introducing a liquid sample into a spark-gap warranted further study, a fifth experiment was designed to investigate the optimum rate-of-rotation for this system. Measurements for the test solution, used in Experiment No. 4, were made at five rates, 4, 8, 12, 16 and 20 revolutions per minute (rpm). Again, four exposures for each of 10 electrodes were obtained for each system, or in this case, for each rate-of-rotation.

FIGURE 1. VARIATION OF EXPOSURE TIME FOR ELEVEN TYPES OF POROUS-CUP ELECTRODES AND ONE REVOLVING DISC ELECTRODE.



$$\text{RELATIVE DISPERSION} = \frac{\text{OBSERVED VARIANCE OF ELECTRODE SYSTEM}}{\text{OBSERVED VARIANCE OF ELECTRODE SYSTEM LOT 85N}}$$

*FABRICATED LOCALLY

Since this study was of an exploratory and preliminary nature, it was decided that a partial or incomplete design of the experiment would be used. Therefore, measurements were obtained for only 12 of the 15 elements in the test solution for each rate-of-rotation. This design yielded 2400 measurements which were evaluated by relating the average range to the rate-of-rotation. A complete tabulation of these data is given in the appendix.

When the average ranges for 10 electrodes were compared for the different rates-of-revolution, see Table IX, the smallest range, and, therefore, the least variability, was noted for a rate of 20 rpm.

Table IX

Range of Measurements as a Function of the Rate-of-Rotation in the Rotating-Disc System

Rate of Rotation rpm	Average Range R
4	38
8	37
12	31
16	25
20	18

The average time required to reach a certain potential was found to be relatively independent of the rate-of-rotation, see Table X, but the ranges of the electrode-times for the groups of 10 electrodes apparently is related to the rate at which the disc revolves.

Table X

Ranges and Averages of the Time Required for 10 Electrodes to Reach a Given Potential

Rate-of-Rotation rpm	Time (seconds) Average	Range
4	21	15
8	20	18
12	19	18
16	20	6
20	19	8

This latter observation serves to confirm the decrease in the variability of measurements as the rate-of-rotation increases and, also, the time-effect relative to the electrodes themselves. Further tests will be made to evaluate the effect of higher rates-of-rotation.

Experiment No. 6 (2560 Numbers)

At the time the data for Experiment No. 5 were being evaluated, it became apparent that the signal/noise ratio was a critical factor in the rotating-disc system, and that it would be difficult to establish optimum conditions for this system until some provision was made to eliminate or minimize this source of variability. Before further studies were made, therefore, a modification in the electronic system was designed to automatically compensate for this noise (background) effect. Then a sixth series of tests was undertaken to evaluate the effectiveness of this background compensating-system and to study the effect of higher rates-of-revolution on the variability of the measurements.

In this sixth experiment, four exposures/each of 10 electrodes for four rates-of-revolution, 10, 20, 30, and 40 rpm, were made. Two sets of measurements were obtained, simultaneously, for 8 elements without a background correction and for another 8 elements with the background compensating

system in operation, using the test solution of Experiment 4. In addition, one series of tests was made at 20 rpm in which the internal standard was also corrected for background (noise). The measurements for Experiment No. 6, a total of 2540, are tabulated in the appendix.

When these data were evaluated, the results were disappointing. As shown in Table XI, the average range decreased as the rate of rotation increased, but there was little difference between the ranges for the uncorrected measurements and those which were obtained with the background compensating-system in operation.

Table XI

Comparison of Ranges Relative to Rates-of-Rotation with and Without a Background Correction

Rate-of-Rotation rpm	Average Range		
	Uncorrected	Corrected	
		Elements	Internal Standard
10	26	30	
20	19	25	27
30	16	26	
40	18	14	

When an analysis of variance was made, however, it was found that the experimental error for the corrected set of data was significantly less than that for the uncorrected measurements; see Table XII.

Table XII

Variance Analysis for Corrected and Uncorrected Sets of Data

Source	Degrees of Freedom D.F.	Total Sum of Squares T_{ss}	Mean Sum of Squares $M_{ss}(S^2)$	Variance Ratio F_e	F_t 95% P.L.	Significance
		X 10^2				
A. UNCORRECTED DATA:						
Elements(A)	7	1300	186	116	2.0	+
Exposures(E)	3	163	54	34	2.6	+
Rate-of-Rotation(C)	3	192	64	40	2.6	+
Exp. Error (R_e)	1266	2008	1.6			
Total (T)	1279	3663				
B. CORRECTED DATA:						
Elements(A)	7	33,440	4777	3980	2.0	+
Exposures(E)	3	25	8	7	2.6	+
Rates-of-Rotation(C)	3	3,011	1004	836	2.6	+
Exp. Error (R_e)	1266	1541	1.2			
Total (T)	1279	38,018				

$F_e = Re_1/Re_2 = 1.6/1.2 = 1.3$

$*F_t = 1.1$ ($D.F_1 = D.F_2 = 1266$; 95% Probability Level)

This observation plus the fact that the total variability of the corrected set of data was greater by a factor of 10^2, led to the conclusion that some factor, other than those being considered, must be affecting the second set of measurements. Since the time required for an electrode to reach a given potential had been recognized previously as a potential source of variability in this procedure, the electrode-times for these data were examined. It was found that the average time required for an electrode to reach a given potential appeared to be related to the rate at which the disc rotated; see Table XIII.

Table XIII

Rate-of-Rotation and the Average Time Required for Electrodes to Reach a Given Potential

Rate-of-Rotation rpm	Time (Average) Seconds
10	16
20	19
30	21
40	29

Even though the variability of the corrected data is greater, the actual effect of the compensating system is to remove the non-linear characteristics of the usual analytical curve, see Figure 2. Furthermore, it was concluded that the elimination of the background effect had made it possible to definitely identify electrode-time as a critical factor in this spectrochemical procedure. Until the background compensating-system was installed, the criticality of the electrode-time was obscured and could not be isolated as a main effect. At this point, it was decided that additional tests at various electrode-times and possibly for higher rates-of-rotation were necessary to establish the optimum operating conditions for the rotating-disc system for introducing a solution into the spark-gap.

Experiment No. 7 (7040 Numbers)

In the previous experiment, greater variability than had been anticipated was observed when measurements were obtained with the background (noise) compensating-system in operation. Part of this variability was attributed to a malfunctioning electrometer in the system and to the effect of an electrode-time factor. The nearly-theoretical characteristics of the linear analytical curves, however, would justify the use of this system even if some loss in precision was experienced. The purpose of this seventh series of tests, therefore, was to confirm these observations and to investigate

the effect of the electrode-time factor at different rates-of-revolution for the rotating-disc system.

The basic conditions for this seventh experiment were the same as those for Experiment No. 6 with the rates-of-revolution being changed to 10, 20 and 40 rpm. The electrode-time factors for each rate are listed in Table XIV. The source of the 7040 measurements that were made in this experiment is shown in Table XIV, also. These data are tabulated in the appendix.

Table XIV

Conditions and Source of Data for Experiment No. 7

Electrode System	Rate-of-Rotation rpm	Electrode-Time Seconds	Exposures	Electrodes	Elements	Condition*	Measurements Total	
			Number					
Rotating-Disc	10	20	4	10	8	2	640	
	10	30	4	10	8	2	640	
	10	30	4	10	8	2	640	
	10	35	4	10	8	2	640	
	20	80	4	10	8	2	640	
	40	25	4	10	8	2	640	
	40	55	4	10	8	2	640	
	40	80	4	10	8	2	640	5120
Porous-Cup:								
NC-85N		20	4	10	8	2	640	
NC-86N		20	4	10	8	2	640	
UC-2101		20	4	10	8	2	640	1920
								7040

* Conditions = Uncorrected and corrected.

In addition, tests were made with porous-cup electrodes from three sources; see Table XIV.

In previous experiments, the average range of measurements for 10 electrodes was used as a convenient method for expressing and comparing the precision or variability of different sets of data. While this term was simply referred to as the range, in those cases, it could have been desig-

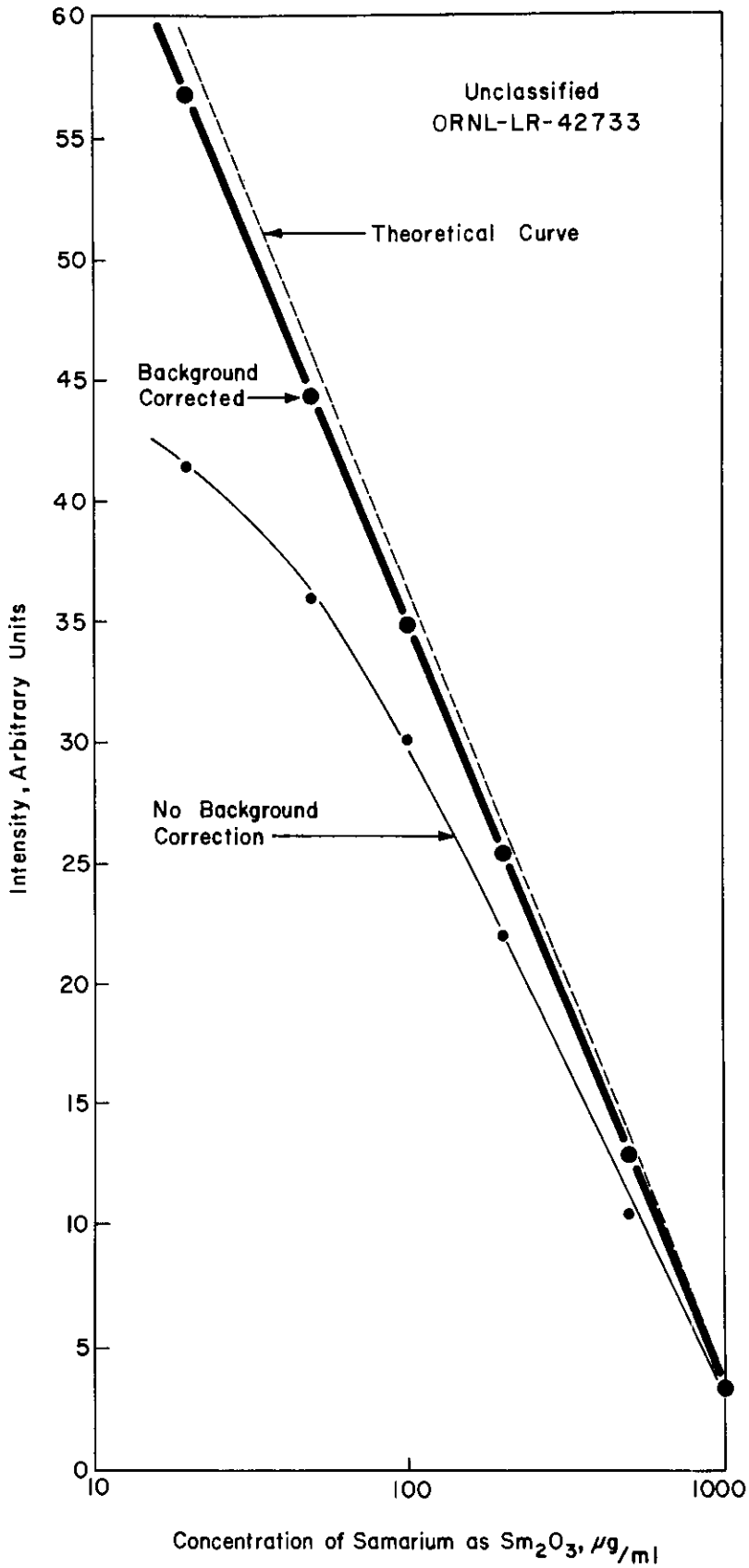


FIGURE 2 ANALYTICAL CURVE FOR SAMARIUM

nated as the "range-between" or the "between-range". This distinction is being made because the data for Experiment No. 7 was evaluated by means of a "Range-Analysis" in which a term "within-ranges" or "ranges-within" is used in addition to the term, "between-range".

The between-range is an estimate of the total variability of the data and the within-range is a measure of the experimental error or the minimum variability of the system under consideration.

The average between-range for each set of corrected or uncorrected data, in this experiment, is based on 32 individual ranges of measurements between 10 electrodes for the eight elements, (4 ranges/element), while the average within-range is computed from 80 individual ranges of measurements between the four exposures per electrode for the eight elements (10 ranges/element). The effect of elements is not considered in these computations.

In Table XV the within- and between-ranges are given for each of the 11 sets of data. In general, the within-range is about half of the between-range for both the corrected and uncorrected data. From the results given in Table XV, it was noted that the between-range was somewhat less for the corrected data when the rate-of-rotation, regardless of the electrode-time, was 40 rpm. In all cases, the between range was greater for the corrected data in the Porous-Cup system.

From this evaluation, it was concluded that the optimum rate-of-revolution for the rotating-disc system is 40 rpm and that any electrode-time, above 30 seconds, can be used.

Table XV

Comparison of Ranges for Corrected and Uncorrected Data Experiment No. 7

Electrode System	Rate-of-Rotation rpm	Electrode-Time Sec.	Average Range - $\bar{\bar{R}}$ Within Uncorr.	Within Corr.	Between Uncorr.	Between Corr.
Rotating-Disc	10	20	12	7	21	30
	10	30	10	6	17	20
	10	30	10	8	16	18
	10	35	11	9	13	12
	20	80	10	10	17	19
	40	25	15	6	20	14
	40	55	11	11	22	14
	40	80	18	10	19	15
Porous-Cup:						
UC-2101	--	20	12	13	18	22
NC-85N	--	20	10	13	19	34
NC-86N	--	20	11	10	23	30

Experiment No. 8 (4800 Numbers)

In both Experiments No. 6 and 7, some instability in the background compensating-system, which was attributed to malfunctioning of certain of the electronic components, was noted. This condition was corrected and an eighth experiment was undertaken to determine the effectiveness of this modified electronic system.

Measurements for 15 rare-earth elements were obtained, without any background correction and with the background compensating-system in operation for a "wick", a porous-cup, and for two rotating-disc systems. Again, four exposures for each of ten electrodes/systems were used. The source of the 4800 measurements, obtained in this experiment, is shown in Table XVI; these 4800 individual measurements are tabulated in the Appendix.

Table XVI

Source of Data Obtained in Experiment 8

Electrode System	Number of Exposures	Electrodes	Elements	Conditions*	Measurements Total No.
Rotating-Disc (40 rpm)					
1/8 - 1/8	4	10	15	2	1200
3/16 - 1/8	4	10	15	2	1200
"Wick"	4	10	15	2	1200
Porous-Cup: NC-86N	4	10	15	2	1200
					4800

* Conditions = Background corrected and uncorrected.

These data were evaluated by comparing the average within- and between-ranges for the corrected and uncorrected measurements. This comparison is presented in Table XVII.

Table XVII

Comparison of Average Within- and Between-Ranges for the Corrected and Uncorrected Data of Experiment No. 8

Electrode System	Average Ranges*			
	Within		Between	
	Uncorrected	Corrected	Uncorrected	Corrected
Rotating-Disc (40 rpm)				
1/8 - 1/8	7	4	15	7
3/16 - 1/8	6	8	10	7
Average	7	6	13	7
"Wick"	11	12	18	17
Porous-Cup: NC-86N	12	13	17	16

* On a relative basis (100 $R/\overline{X}$)

From these comparisons, it was apparent that the within- and between-ranges for the rotating-disc electrode system is less than either the "wick" or the "porous-cup" methods. Furthermore, the variability of the corrected data, as estimated from the ranges, is less for this system. On the basis of these observations it was concluded that the background compensating-component of the electronic system is functioning properly and that, under these circumstances, the rotating-disc, at a rate of 40 rpm, yields measurements with a high degree of reliability when electrodes with a thickness of either 1/8 or 3/16 in. (.200) are used in this spectrochemical method of analysis.

SUMMARY

Recognizing that the reliability of spectrographic measurements, obtained by means of a solution-method of spectrochemical analysis, was dependent on the precision of the method used to introduce a liquid into the high voltage spark of a spectrograph, 46 systems were investigated over a period of 12 months, to establish the optimum conditions for this operation. The conditions and systems studied are summarized in Table I.

Each experiment, which involved from 2000 to 7000 measurements, was based on a statistical analysis of the data obtained in the preceding experiment. In all, 8 series of tests were carried out and over 30,000 measurements were evaluated.

In this manner, a spark-in-spray system, different types of porous-cup electrodes and a "wick" system were eliminated from further consideration; the superiority of a rotating-disc system was established and optimum conditions for this system were determined; and, the noise affect of the signal-to-noise ratio was eliminated by modifying the electronic system of a spectrograph to provide for an automatic background compensating-system.

The primary purpose of this investigation was fulfilled when the rotating-disc system was established as a precise method for introducing a liquid into the spark-gap of a spectrograph. The design and installation of an automatic background (noise) compensating-system, however, represents another major achievement that can be attributed to this work. As a result of this innovation, stable analytical curves, with nearly theoretical characteristics, are being obtained.

APPENDIX

The original data on which the conclusions outlined herein are based, consists of nearly 30,000 test results or more than 160 pages. Because of the magnitude of these data, they were not appended to this report. Those persons who are interested in these data may, however, obtain a copy by contacting J. A. Norris, P. O. Box Y, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

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