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THE DIFFERENTIAL SPECTROPHOTOMETRIC DETERMINATION
OF PLUTONIUM USING THE CARY MODEL 16 SPECTROPHOTOMETER

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ABSTRACT

The application of a high-precision Cary Model 16 spectrophotometer to the differential spectrophotometric determination of plutonium(III) was investigated. The absorbances of plutonium(III) solutions were measured against colored glass filters at 560 nanometers. Selection of various instrument parameters and the determination of the best reference filter for the highest precision are discussed. Two sets of calibration points were analyzed. The absorbance for each set was measured once a day for three days. A statistical comparison between the three readings, the three least squares curves, and the two sets of calibration points are discussed. The standard deviation of the average reading about the line was ± 0.0028 g/liter plutonium in the 11 to 15 g/liter plutonium range. Detailed procedures for standard preparation from plutonium nitrate and for operation of the Cary Model 16 are included. The advantages and disadvantages of the equipment and method are discussed and further experiments suggested.

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INTRODUCTION

Highly accurate and precise plutonium analyses are required for support of Nuclear Safeguards programs and for plutonium accountability of nuclear processing plants. Plutonium assay methods using titrimetric or coulometric techniques are useful for product analyses where plutonium concentrations are high and impurities are low. The precision of these methods is usually about $\pm 0.1\%$; however they require a large amount of time and are difficult to keep under control. Therefore they do not lend themselves to the analyses of a large number of samples. The application of a differential spectrophotometric method to the analysis of plutonium was described by Phillips^[1,2] as early as 1958. Winkle^[3] and Brunner^[4] modified this initial procedure by using colored glass filters as the reference standards. A revised procedure^[5] used at Windscale by the United Kingdom Atomic Energy Authority has a measured precision of $\pm 0.2\%$ based on over 100 determinations. Even though precisions^[3] of $\pm 0.05\%$ have been claimed, in actual practice $\pm 0.50\%$ would be a more reasonable figure. All the studies in the past have been done with spectrophotometers that were designed for numerous tasks and not necessarily high precision. The purpose of this study was to evaluate the Cary Model 16 Spectrophotometer as a high-precision spectrophotometer for the analysis of plutonium.

SUMMARY AND CONCLUSIONS

The differential spectrophotometric method for plutonium described by Winkle^[3] and Brunner^[4] using colored glass filters as references was used for the evaluation of the Cary 16 spectrophotometer. Plutonium standards were prepared by reducing weighed aliquots of a pure plutonium nitrate solution with hydroxylamine hydrochloride in calibrated 25-ml volumetric flasks. Optimum instrument parameters such as instrument sensitivity and slit width were chosen according to Cary Instruments recommendations.^[6,7,8] The optimum reference optical density or concentration of plutonium was determined to be about 18.16 g/liter Pu by the method recommended by Hiskey.^[9] This value is considerably higher for the Cary 16 than the values reported by Brunner, Phillips, and Winkle. This is probably due to the high-intensity light source of the Cary 16 which allows higher optical density measurements. The positive effect of reducing the relative error as the absorbance of the reference increases has been described by Hiskey and coworkers.^[10,11] In order to use the Cary 16 for this high a reference plutonium concentration, it would be necessary to have two glass filters of equal thickness to give almost the same absorbance readings (3.0 A) as the 18.16 g/liter plutonium so that the instrument could be properly balanced in the dual-beam mode. Unfortunately the highest matched pair of filters available had absorbances, when measured against air, of only 1.81 A which corresponds to about 10.9 g/liter plutonium. For expediency it was decided to go ahead and evaluate the method using the two filters with 1.8119 and 1.8145 absorbances versus air. Two calibration curves were prepared and the data for the two curves were statistically evaluated for individual variances and between curve variances. The

reading error for the absorbances observed in the first calibration was ± 0.000389 A or ± 0.0026 g/liter in the 11 to 15 g/liter Pu range. When the two calibrations were compared, no significant differences existed. The observed standard deviation of the average of three readings about the combined calibration line was ± 0.000424 A or ± 0.0028 g/liter Pu. This is $\approx 0.03\%$ at the 11 g/liter Pu level. Since this standard deviation is based only on calibration data it cannot necessarily be extrapolated to mean that this is the standard deviation for the method. When data were analyzed from reading the absorbance of three glass filters against a fourth glass filter over a period of six months, the reading error was found to be two to three times that of the calibration (0.000389 A). If this is assumed to be representative of the long-term error, then the precision for the Pu analysis would be approximately $\pm 0.05\%$.

The Cary 16 design offers high stability, improved readability, and high absorbance measuring capabilities when compared with standard laboratory spectrophotometers. However, since only a single sample thermostated cell holder was available for use and 10 to 15 minutes were required for thermal equilibrium to be reached, the measurement time for three readings per sample was long.

A thermostated automatic multiple sample changer and a digital readout would help reduce the time required for readings and also improve readability. Even though the instrument and method look promising, no conclusions can be drawn until a long-term statistical evaluation of the technique is made. Other studies that should be evaluated are the use of a higher density glass reference filter, different primary standards such as National Bureau of Standards (NBS) plutonium metal, and a detailed interference study of various cations and anions. Another interesting project

would be the evaluation of a photon counting technique for high absorbance measurements.

EXPERIMENTAL

Equipment

Cary Model 16 Spectrophotometer with high-intensity light source (tungsten-halogen) and thermostatted sample cell holder.

Spectrophotometric absorption cells, Beckman 1-cm, glass-stoppered silica.

Flasks, 25-ml volumetric, calibrated by two individuals and the results averaged. The average percent deviation for 20 flasks at the 95% confidence level was $\pm 0.07\%$.

Balance, 5-place Mettler.

Glass filters,^[3] Corning blue filters CS 1-64, cut and polished at various thicknesses and fixed in brass holders as shown in Figure 1. Two sets of these filters were available for use and their absorbances versus air on the Cary 16 are shown in Table I.

REAGENTS

NH₂OH·HCl: A 50.0-g/liter hydroxylamine-hydrochloride solution in 2M HCl was used to reduce the plutonium and bring the flask to mark.

Plutonium Nitrate Standard: A plutonium nitrate solution that had been purified by anion exchange was used in this study. The solution was 6.9M in HNO₃ and had a plutonium concentration of 144.88 g/liter based on four chemical assay analyses. The specific gravity of the solution was measured to be 1.4322 ± 0.0020 . An emission spectrographic

TABLE I
CORNING GLASS FILTERS

	<u>CTL*</u> <u>A/Air</u>	<u>Thickness</u> <u>Inches</u>	<u>TSS**</u> <u>A/Air</u>
1.	1.3979	0.210	1.5820
2.	1.4969	0.220	1.7398
3.	1.5639	0.230	1.8145
4.	1.5705	0.240	1.9001
5.	1.5740	0.250	1.9818
6.	1.5719	0.260	2.068
7.	1.6146	0.270	2.138
8.	1.8119	0.280	2.217
9.		0.290	2.306
10.		0.300	2.384
11.		0.310	2.460

* Chemical Technology Laboratory.

** Technical Services Section.

analysis showed that all impurities in the material were less than 50 ppm.

DISCUSSION

Differential spectrophotometry was first described in 1934 by Kortum and Halban^[12] as the measurement of relative transmittance of a solution of unknown concentration versus a standard solution. Hiskey and coworkers^[9,10,11] later published a series of papers in which the theoretical and practical principles of precision colorimetry and differential spectrophotometry were described. A recent review by Svehla^[13] describes both principles and practical applications.

The technique of differential spectrophotometry results in an effective increase in the absorbance scale. Two sources of error will be found in the measurement of

absorbance. One is contributed by instrument design and analytical technique and the other is inherent within the spectrophotometric method. Figure 2^[8] illustrates the inherent relative error as a function of absorbance for a normal spectrophotometric measurement. It is interesting to note that the relative error becomes very large as the absorbance approaches zero and when it becomes greater than one. When a differential spectrophotometric technique is applied where the reference absorbance is not zero but some standard with a higher absorbance, the inherent relative error is changed significantly as shown in Figure 3.^[8] In this example the relative error decreases with increasing reference absorbance (A_1). Also the error no longer approaches infinity as the absorbance becomes greater than one. However, the maximum absorbance of the reference standard is limited since if the absorbance is too high, insufficient light will result in inaccurate measurements from the phototube. In addition, if the concentration of the material being measured becomes too large, then deviations from Beer's law may become apparent as incomplete complexes are formed. The determination of the optimum reference concentration or absorbance is described later.

Samples for the differential spectrophotometric determination of plutonium were prepared by weighing out different aliquots of a plutonium nitrate standard into preweighed, calibrated, volumetric flasks. The volume of plutonium transferred was calculated from the weight of plutonium nitrate transferred and the predetermined specific gravity of the material. The plutonium(IV) nitrate was reduced by adding 15 to 20 ml of $\text{NH}_2\text{OH}\cdot\text{HCl}$, swirling to mix, and heating for 30 minutes in a water bath at 70 °C. The flasks containing plutonium(III) were allowed to reach a temperature equilibrium by sitting overnight. The next day the flasks

were brought to mark with $\text{NH}_2\text{OH}\cdot\text{HCl}$ and thoroughly stirred using a magnetic stirrer. The samples were transferred to bottles that had been rinsed with deionized water, and thoroughly dried. The bottles were sealed with plastic-lined caps and wrapped with Parafilm[®] (American Can Company). Aliquots were taken from these bottles as needed and the bottles resealed after each use. Aliquots were transferred to 1-cm spectrophotometer cells which had been rinsed with $\text{NH}_2\text{OH}\cdot\text{HCl}$, deionized H_2O , and ethanol. After the cells were filled and stoppered, the surface of the cell was cleaned with a Kim-Wipe[®] (Kimberly-Clark) dampened with ethanol before the absorption measurement was made.

The Cary 16 was allowed to warm up for at least four hours after it had been completely shut down. When only the source had been turned off, the source was turned on and allowed to stabilize for one-half hour. Each day measurements were made, the differential absorption of three glass filters [5, 7, and 8, Chemical Technology Laboratory (CTL)] against a fourth filter (6, CTL) was measured in order to determine if a significant change in the operating conditions of the instrument had occurred and to provide statistical data on the differential absorption measurement in which the chemical material or sample filling variables were minimized. The sample cell holder was temperature-controlled to 25 ± 1 °C. The instrument was balanced before each plutonium measurement using two almost identical glass filters. Each time the sample compartment was opened and closed the cell holder was allowed to come to thermal equilibrium, as noted on the strip chart recorder. The optimum wavelength (≈ 560 nanometers) was chosen for each plutonium sample by determining the wavelength of maximum absorbance for each sample before taking the final reading.

RESULTS

SELECTION OF INSTRUMENT OPERATING PARAMETERS

Hiskey and Young^[9] have described the effect of slit width on the absolute and relative absorption measurements. However, because of the complexity of evaluating the slits by their method, it was decided to follow the recommendations of the manufacturer. Hiskey, Rabinowitz, and Young^[10] described the conditions used for several spectrophotometers--the most notable being the Beckman DU (Beckman Instruments). However none of the instruments studied were dual-beam; and therefore the information could not easily be extrapolated to the Cary 16. The Cary 16 is equipped with a sensitivity meter which is capable of indicating the phototube response to incident light. At a high sensitivity both the signal and phototube noises are increased. According to the Cary 16 Instruction Manual^[8] Section 5.4.(3), the slits should be opened until a sensitivity of 3 is obtained. This setting should provide adequate resolution with very low noise behavior of the null meter. This setting was used for all measurements described in this paper. However it may be worthwhile to carry out the comparison of the spectral bandwidth with the natural bandwidth also described in this section to see if it is possible to obtain even better signal-to-noise characteristics by giving up some resolution. The high-intensity tungsten halogen lamp was utilized for all measurements in this document. This light source provides a 20 to 30% improvement in resolution over the standard tungsten halogen lamp and improves the analyses of samples with high optical densities.

M. J. Kupfer, Atlantic Richfield Hanford Company, who initiated the first studies on the Cary 16, indicated that

the inability to exactly reset the slit-width each time it was changed caused an error in the absorbance measurement. He recommended that the slit be taped into place so that it could not be moved. We chose to regulate the slit by the sensitivity meter, resetting the slits each day so that the sensitivity meter read 3. A study was made to determine the effect of fixing the slits on the reproducibility. A visual inspection of the precision from 60 pieces of data collected over a period of two months indicated that no significant and consistent differences in the precision existed between the two techniques. Therefore the slits were not fixed in this study. A more thorough statistical analysis of the data at a later date confirmed that in reading filter number 5, CTL, and filter number 7, CTL, no significant differences in variances existed for free and fixed slits. With standard number 8, CTL, a significantly lower reading variance was observed with fixed slits compared with free slits. The details of this statistical analysis are given in Appendix 4.

The Cary 16 has the capability of reading the absorbance on a high-precision readout tape or by recorder. Mr. Kupfer suggested using the recorder since it offered additional scale expansion capabilities. However the recorder interface requires careful calibration for proper use. Loss of this calibration could result in the loss of data for a long-term comparison study. The recorder also requires a longer time to make the reading. Since the time for analysis was already fairly long, it was decided to use the more convenient tape readout for our studies. A test between the recorder and tape readouts was done at the same time as the fixed slit studies. Again visual inspection indicated no significant advantages of the recorder over the tape readout. The three filters (5, 7, and 8, CTL) had differential absorbances of approximately 0.002 A, 0.048 A, and 0.228 A when read against

the CTL number 6 filter as a reference. A statistical evaluation of these data indicated that with standard numbers 5 and 7 no significant differences were observed for the reading variance between chart and tape readings. The details of the statistical analyses are shown in Appendix 4.

Table II is a summary of the precisions for the three filters (5, 7, and 8) with and without fixed slits and by tape and recorder readout.

TABLE II
COMPARISON OF PRECISIONS FOR GLASS FILTER ABSORBANCE
READINGS FOR TAPED AND UNTAPED SLITS AND FOR RECORDER
AND NULL TAPE READOUTS

Filter No.	Standard Deviation of Absorbance Readings at 95% Confidence Level			
	Recorder		Null Tape	
	Taped Slit	Free Slit	Taped Slit	Free Slit
5	± 0.00069	± 0.00059	± 0.00062	± 0.00027
7	± 0.00088	± 0.00109	± 0.00105	± 0.00101
8	± 0.00032	± 0.00142	± 0.00015	± 0.00120
<u>Combined Taped and Free Deviations</u>				
5	± 0.00072		± 0.00084	
7	± 0.00091		± 0.00097	
8	± 0.00093		± 0.00084	

SELECTION OF OPTIMUM REFERENCE STANDARD

Before a plutonium calibration could be obtained it was necessary to determine the concentration of plutonium for the reference cell that would give the maximum precision. Hiskey and Young^[9] described an experimental method for determining this concentration by comparing a series of standards against standard reference solutions of increasing concentration. Brunner^[4] used standard glass filters in lieu of standards for his studies, using a single-beam

spectrophotometer for his work. This was not possible on the Cary 16 since there were not enough duplicate filters for dual-beam operation. Fifteen standards from 2.03 to 38.57 g/liter Pu were prepared as described. The lowest concentration was used in two spectrophotometer cells to balance the instrument and then used as a reference to measure the higher concentrations. The slope of this line, commonly referred to as the absorptivity coefficient, was then determined by least squares analysis. This procedure was continued until a series of curves were obtained and the instrument capabilities exceeded. A plot of these curves is shown in Figure 4. When a plot is made of the reference concentration versus the slope times the reference concentration, a curve is obtained with a maximum as shown in Figure 5. This reference concentration at which the curve reaches a maximum is the one which will produce the maximum precision.

This maximum occurs on the Cary 16 when 18.157 g/liter plutonium is in the reference cell, as shown in Table III.

TABLE III
RESULTS FROM CURVES TO DETERMINE
THE OPTIMUM REFERENCE PLUTONIUM CONCENTRATION

<u>Pu Concentration</u> <u>g/liter</u>	<u>Slope</u> <u>a'</u>	<u>Reference</u> <u>a' x Concentration</u>
2.01378	0.16161	0.32545
6.05200	0.15543	0.94066
10.09176	0.15555	1.56977
13.75200	0.15354	2.11148
14.02613	0.15601	2.18822
14.93595	0.15312	2.28699
15.79528	0.14930	2.35824
17.27789	0.14398	2.48767
17.84891	0.14012	2.50117
18.15736	0.14529	2.63808
18.73897	0.13489	2.52789
22.15253	0.09667	2.14148

This concentration of Pu would correspond to a glass filter with an absorbance of 3.0 A. This would require duplicate filters that were 0.38-inch thick to test the instrument on the optimum reference concentration. Since duplicate filters with this high an absorbance were not available, it was decided to use the highest absorbing available pair. It is also possible that filters of this thickness cannot be obtained from the manufacturer. Unfortunately the highest matched pair had absorbances of only 1.81 A, which corresponds to approximately 10.9 g/liter plutonium. The curve obtained for the optimum reference concentration may be used to determine the calibration range. It should be noted in Figure 4 that as the reference concentration becomes higher, the linearity of the system appears to decrease. Therefore smaller calibration ranges can probably be expected when a higher reference concentration is used. Based on these data, calibration of the instrument was initiated.

CALIBRATION OF CARY 16

The basic procedure described earlier was used to prepare the plutonium and measure the absorbance. A great deal of effort was taken to make the measurement as accurate and reproducible as possible. Details for the calibration are more fully described in Appendices 1 and 2. For the first calibration a series of nine standards were prepared between 11.2 and 15.8 g/liter Pu. The absorbances of the standards were then measured against the Chemical Technology Laboratory's number 8 glass filter as the reference standard. The absorbance for each standard was measured once each day for three days. The data were then analyzed statistically by D. F. Shepard for precision within a given day and between days. A second set of calibration points that fell over the same concentration range as before but were interspersed

between the original points were prepared and their absorbances measured identically to the earlier calibration. The data for this calibration were analyzed for precision within a given day and between days; then compared with the first curve to determine if any statistical differences existed. The test results are included in this document as Appendix 3.

In the first set of calibration points no significant difference was noticed in the slopes for the three curves. However a difference in the intercepts was detected which amounted to 0.01 g/liter Pu. The cause of this shift has not been determined. The second set of data showed no differences in slope or intercept. For the first curve the higher point, 15.86759 g/liter standard, appeared to be outside the linear region of the calibration. The high and low points, 15.56702 and 10.87224 g/liter of the second series of standards, appeared to fall outside the linear range of the calibration. The standard deviation for an absorbance reading was ± 0.000389 A. When the two calibrations were compared, no significant difference was detectable at the 95% confidence level. Therefore the curves were combined, eliminating any outside points, and evaluated statistically. The observed standard deviation of the average reading about the line was ± 0.000424 A or 0.0028 g/liter Pu or between 0.025 and 0.019% for a plutonium range of 11 to 15 g/liter. The poor linearity at the higher concentrations was possibly due to incomplete reduction of the Pu(IV). It was also felt that the slow auto-oxidation of Pu(III) to Pu(IV) may have been responsible for the shift in intercept in the first series of standards. A valence determination of one of these standards indicated that no Pu(IV) was present; however the stability of the standards was questioned because fairly large volumes of the plutonium nitrate

standard with 6.9M HNO₃ were required for some of the dilutions. The effect of large amounts of HNO₃ was unknown. In future work a standard with a higher concentration of plutonium nitrate which is lower in nitric acid should be used to avoid this possible interference. Winkle's paper indicates that a slight interference may exist for HNO₃, but the article does not clearly state the levels of HNO₃ tested or the effect of time on the result.

DAILY CONTROL OF INSTRUMENT

In order to follow the performance of the instrument on a day-to-day basis without possible variations due to the chemical procedure, the differential absorbance of three glass filters relative to a fourth filter was measured each day the instrument was used. A single absorbance measurement per filter was taken and recorded. Data were collected on 27 days over a period from October 19, 1971, to March 17, 1972. The absorbances of the numbers 5, 7, and 8 Chemical Technology Laboratory filters were read against the CTL number 6 filter. The standard deviation for these readings are shown in Table IV.

TABLE IV
PRECISION OF ABSORBANCES BETWEEN GLASS FILTERS

Filter #5	$\bar{x} = 0.00230 \pm 0.00045$
Filter #7	$\bar{x} = 0.04503 \pm 0.00095$
Filter #8	$\bar{x} = 0.23501 \pm 0.00093$

These standard deviations are considerably higher than those recorded for the two sets of calibration data (± 0.000389 A) over two weeks. If we assume these errors are representative of the errors that could be expected for the analysis over a long period of time, then Pu errors would be $\pm 0.05\%$. Unfortunately this is only an extrapolation of what might be

expected; and for valid information the plutonium method would need to be evaluated over an extended time.

DIRECTION OF FUTURE WORK

The work that has been performed to date should provide the basis for a highly precise plutonium assay method. Not only has this work pointed out the advantages of the Cary 16, it has also pointed out some disadvantages and some possible modifications which would be helpful. This study has also provided information for some interesting new experiments which would be valuable to plutonium assay and differential spectrophotometric problems. Following is a list of some of the modifications to the procedure and instrument that may merit further consideration in new studies.

- Higher absorbance glass reference standard. The effect of operating the Cary 16 with the optimum reference filter should be studied. This would require obtaining two matched filters with absorbances of approximately 3.0.
- Different plutonium primary standards with higher Pu concentration and lower HNO_3 should be analyzed and the results compared with normal titrimetric Pu assay results.
- The use of National Bureau of Standards plutonium metal as a primary standard should be explored so that the method would not be dependent on normal chemical assay procedures for standardization of plutonium.
- An interference study should be made for cations and anions and the effect of these materials on the stability of the plutonium(III) color.

- The study of the optimum slit width should be extended comparing the natural band width and spectral width and then selected based on optimum precision and spectrum purity from interferences.
- The Cary 16 should be modified to include an automatic constant temperature sample chamber and a digital readout of absorbances to at least the fourth decimal place. These accessories would enable a larger throughput of samples and allow a constant readability error over the entire absorbance range.
- The advantages of the ultimate precision method described by Svehla^[13] should be investigated for possible applications to the Cary 16 and plutonium assay.

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REFERENCES

1. G. Phillips, "Precise Determination of Plutonium by Differential Spectrophotometry," *Analyst*, Vol. 83, pp. 75-79, February 1958.

2. G.W.C. Milner, D. Crossley, I. G. Jones, and G. Phillips, "The Rapid Dissolution of Plutonium Dioxide by a Sodium Peroxide Sinter, Followed by Determination of the Plutonium Content by Differential Spectrophotometry," *Analyst*, Vol. 90, pp. 732-735, December 1965.
3. L. W. Winkle, *A Differential Spectrophotometric Determination of Plutonium(III) Using Colored Glass Filters*, ISO-SA-16, Isochem Inc., Richland, Washington, May 1966.
4. R. D. Brunner, *Plutonium Measurement by Differential Spectrophotometry*, ARH-289, Atlantic Richfield Hanford Company, Richland, Washington, January 1968.
5. PG Report 290W, *Analytical Method for the Determination of Plutonium in Plutonium Metal (Differential Spectrophotometry)*, Windscale, 1968.
6. Cary Report AR 16-1, "High Precision Spectrophotometric Measurements with the Cary 16," August 1969.
7. Cary Applications Report AR 14-2, "Optimum Spectrophotometer Parameters," March 1967.
8. Cary Model 16 Spectrophotometer Operating Manual.
9. C. F. Hiskey and I. G. Young, "Principles of Precision Colorimetry, Absorption Law Deviations in Relative Transmittance," *Analytical Chemistry*, Vol. 23, No. 9, pp. 1196-1201, September 1951.
10. C. F. Hiskey, J. Rabinowitz, and I. G. Young, "Principles of Precision Colorimetry, Measuring Maximum Precision Attainable with Commercial Instruments," *Analytical Chemistry*, Vol. 22, No. 12, pp. 1464-1470, December 1950.
11. C. F. Hiskey, "Principles of Precision Colorimetry," *Analytical Chemistry*, Vol. 21, No. 12, pp. 1440-1446, December 1949.

12. H. von Halban, *Physic Chemistry A112:321* (1924).
13. G. Svehla, "Differential Spectrophotometry," *Talanta*, Vol. 13, pp. 641-666, 1966.

FIGURE 1
FILTER ASSEMBLY

FIGURE 2

RELATIVE ERROR AS A FUNCTION OF TRANSMITTANCE

FIGURE 3

ERROR OF MEASUREMENT

FIGURE 4
ABSORBANCE CURVES FOR INCREASING PLUTONIUM REFERENCE CONCENTRATIONS

FIGURE 5
DETERMINATION OF OPTIMUM REFERENCE PLUTONIUM CONCENTRATION

APPENDICES

APPENDIX 1

DETAILED SAMPLE PREPARATION PROCEDURES

Procedure	Comments
1. Pre-weigh a dry calibrated 25-ml volumetric flask with stopper. Record this weight.	Clean flasks are stored in a dessicator before weighing. Weigh on a five-place balance.
2. Pipet the desired aliquot of plutonium into the pre-weighed flask and insert ground glass stopper.	Avoid touching ground glass with Pu solution. Carefully survey flask for outside contamination. The specific gravity of the plutonium should be the average of at least three values with a known precision.
3. Weigh the 25-ml volumetric flask with Pu and stopper and record the weight.	Do not weigh a contaminated flask outside the hood. Always carefully survey before removing a flask from the hood.
4. Add hydroxylamine hydrochloride until the flask contains about 15 to 20 ml total volume.	Brown Pu(IV) nitrate should change to the deep blue of Pu(III).
5. Place the flask in a water bath at 70 °C for at least 30 min.	Longer times may be used without problems in the method. This step removes any remaining traces of Pu(IV) and improves the kinetics of the reaction when HNO ₃ is present.
6. Remove the flask and allow it to reach thermal equilibrium by sitting overnight.	Shorter times may result in an incorrect volume measurement due to temperature variations in calibrating the flask or insufficient time for the flask to reach the same structural equilibrium as when it was calibrated.

Procedure	Comments
	Water baths may be used to speed up the cooling process; however the effect on structural variables are still unknown.
7. The next day carefully bring the flask to mark with $\text{NH}_2\text{OH}\cdot\text{HCl}$, add a glass or Teflon stir bar, stopper, and stir for at least 15 minutes.	The stirring should be vigorous with a visible vortex at the surface of the solution.
8. Transfer the stirred solution to a clean, dry, 40-ml vial. Cap with a polyethylene-lined cap and seal with Parafilm.	Vials should be pre-rinsed three times with deionized H_2O and air-dried. Transfer with transfer pipet to avoid excessive contamination of the flask.
9. Rinse flask with $\text{NH}_2\text{OH}\cdot\text{HCl}$ to clean; then rinse with deionized H_2O . Final cleanup is done with an ultrasonic washer.	Solutions are now ready for spectrophotometric measurements.

Calculation of Volume of Plutonium Standard Added to Flask

A = weight of empty flask + stopper in grams.

B = weight of flask, + Pu solution + stopper in grams.

D = specific gravity of Pu solution in g/ml.

B-A = weight of Pu added in grams.

Volume of Pu = $\frac{B-A}{D}$ ml.

Grams per liter Pu in 25-ml flask = $\frac{\text{standard Pu value g/liter}}{\text{dilution factor}}$

Dilution Factor = $\frac{\text{calibration value for flask}}{\text{volume of Pu}}$

APPENDIX 2DIFFERENTIAL ABSORBANCE MEASUREMENTS
USING THE CARY 16 SPECTROPHOTOMETERStart-Up

1. Turn on the power switch. The instrument should warm up for 4 hr before using.
2. Turn visible lamp source on to NORMAL intensity. Light source should be switched to high-intensity one-half hour before making measurements.

If the instrument is going to be used for an extensive period of time the power should be left on overnight (except on weekends); however the light source should be turned off each night.
3. Turn on the Lauda water bath: See Operating Manual for details on setting temperature.

First the circulatory switch. Turn off each day after using.

Second the compressor switch.
4. Turn on recorder power switch and set recorder interface ACCESSORY to OUT.
5. Set the other controls on the electronics cabinet and monochromator as follows:
 1. Mode--Double Beam (DB).
 2. Beam Interchange--Normal.
 3. UV Lamp--Off.
 4. Gain--is inoperative in double-beam mode.
 5. Wavelength--set to 560 nm.

Zero Operations

6. Open the sample chamber as if hinged on the left.	This removes the high voltage from the phototube, preventing large quantities of light to enter which may cause the tube to become unstable.
7. Place the reference filter in the back holder. Place the matching filter in the front holder and close the sample chamber.	Filters should be cleaned each day with lens' tissue dampened with absolute ethanol. Filters should be marked so that they may be placed in the holder in the same orientation each time.
8. Set the ABSORBANCE RANGE switch on the monochromator to ZERO.	Set the NULL control so that it reads 0 absorbance or 100% T. This is done so that when a sample is read the null meter will always be zeroed by adjusting the absorbance to increasing values.
9. Adjust the slit so that the sensitivity meter reads exactly "3".	The normal slit width was 0.1 mm for this setting. If larger slits become necessary, the light source or light path should be checked.
10. Turn the Cary 16 BALANCE control to bring the null indicator hand to the center line.	The needle fluctuations should be less than 1/8" on either side for normal characteristics. Adjust the control so that the needle spends an equal amount of time on either side.

Recorder Zero Operations

11. Place RANGE switch on 0.1.	This corresponds to 0.01 when the 10 mV span plug is used.
12. Turn ZERO SUPPRESS switch to ZERO on both knobs.	

13. Put PERIOD switch on "5".
14. Turn CHART SPEED on LOW.
15. Adjust recorder BALANCE control to zero chart pen.
16. Turn the PERIOD control to "20".
17. Recheck null meter. If off center, readjust and recheck recorder chart for zero. Note stability of base line reading after a 2-min scan.
18. Rezero null meter and chart after each reading.

Sample Absorbance Measurement

19. Transfer a portion of the reduced sample to a clean, 1-cm spectrophotometer cell and stopper.

The sample cell should be cleaned with $\text{NH}_2\text{OH}\cdot\text{HCl}$ reagent, deionized H_2O , and absolute ethanol. The cell should be dried by using a vacuum to pull air through the cell. A slurp line with a clean slurp tip is adequate. The outside of the cell should be wiped down with a lens' tissue dampened with ethanol and dried with a fresh lens' tissue.

Transfer the solution with a clean transfer pipet being careful not to touch the ground glass joint. Touch pipet to side of cell (not the face) and fill cell slowly to prevent any possible air bubbles from forming. Fill only to the height necessary to cover cell holder window.

Overfilling can result in a contaminated ground glass

- stopper and later cell and instrument contamination.
20. Remove front glass filter and place cell into sample holder. Outside of cell should be carefully surveyed for contamination before placing into instrument. Cell should be marked so that its orientation may be kept the same for all measurements.
21. Turn ABSORBANCE RANGE control to DIRECT. Turn ABSORBANCE RANGE to ADD-1 for absorbances greater than "1".
22. Adjust NULL control so that needle is slightly to the right of the center line. Final adjustment is made after temperature equilibrium is reached.
23. Turn recorder RANGE to "2.0".
24. Turn recorder PERIOD control to "1".
25. Turn ZERO SUPPRESS control to increasing values (0.1, 0.2, etc.) in order to get the pen as close to zero as possible and still stay on the chart. Record the ZERO SUPPRESS settings.
26. Turn the RANGE control in the same manner to raise the pen as close to "1.0" as possible and stay on the chart. Record the RANGE setting.
27. Turn chart drive to low.
28. Use WAVELENGTH knob to obtain exact peak as noted by the maximum position of the recorder pen and null meter needle to the right. The exact location of the peak is determined in this manner for each sample absorbance measurement.

29. Turn PERIOD switch to "20" and allow chart to continue to run in low.	The sample will require about 10 min to come to a temperature equilibrium as noted on the chart by the absence of any drift.
30. When the chart indicates the absorbance is no longer changing (<1 small chart division for a 2- to 3-min scan) then rezero the null meter and read the absorbance on the NULL tape. Record the chart reading and turn off the drive.	Continued drift could indicate instrument malfunction. Repeat Step 28 after temperature equilibrium is reached.
31. Remove the sample cell, transfer the solution to a waste container for HCl-Pu rework	Clean the cell by rinsing at least twice with $\text{NH}_2\text{OH}\cdot\text{HCl}$ reagent, deionized H_2O, and ethanol. Dry the cell thoroughly before refilling.
32. Continue reading samples by repeating the procedure starting at Step 6.	Three readings per sample should be made for better precision.
33. When finished for the day, remove cells and filters, clean and store in dust-free containers. Turn off recorder, Lauda bath, and visible lamp. Turn ABSORBANCE RANGE, INTERFACE RANGE, and ZERO SUPPRESS (both controls) to zero or lowest value.	

Calculation of Absorbance from Recorder Reading:

$$\left[\frac{\text{Chart Reading}}{\text{Sample}} \times \frac{\text{Sample Range}}{10} - \frac{\text{Baseline Reading}}{\text{at Zero}} \times \frac{\text{Range}}{10} \right] + \text{Zero Suppress} = \text{Absorbance}$$

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APPENDIX 3

DETAILED STATISTICAL ANALYSIS OF CARY 16 CALIBRATION DATA

This Appendix in main is a letter from D. F. Shepard to W. I. Winters describing the results of the statistical analysis of the calibration data for the Cary 16.

The following information describes the contents of the tables attached to Mr. Shepard's letter. It must be remembered that two sets of calibration points were analyzed. The absorbance for each set was measured once a day for three days. A comparison between the three readings and the three least squares curves was then made for each set of data. Finally, a comparison was made between the two sets of calibration points to determine if they were significantly different.

TABLE 1, SET 1

Statistical Analysis of Absorbance of First Set of Calibration Points

Each column: the absorbances obtained for a given standard on that given day.

Fourth column: the average of the three-day absorbance readings.

NOTE: The F Ratio of 47.18343 indicates that there is a significant difference in the three readings. This is noticeable in the low average absorbance for the third day of readings (0.4124).

Standard deviation: for a single reading.

TABLE 1, SET 2

Statistical Analysis of Absorbances for the Second Set of Calibration Points

NOTE: The F Ratio for columns is not significant for the second set of points, indicating no differences in the readings for each day.

TABLE II, SET 1

Individual Readings - Least Squares of Each Day's Readings

Standard Deviation b_1 : standard deviation of the slope.

Standard Deviation b_0 : standard deviation of the intercept.

TABLE III, SET 1

Individual Readings Combined or Least Squares Analyses of Data Using Three Days' Readings.

TABLE IV, SET 1

Comparison of Individual Curves

NOTE: F Ratio for Means about line is 18.92010, indicating a significant change in intercept between the three curves for the first set of data.

NOTE: F Ratio for Between Slopes is small (0.58217), indicating no significant changes in slopes.

The bottom analysis is the same as the top except the high point has been eliminated.

TABLE V

Individual Least Squares Analyses of Second Set of Calibration Points for Each Day

NOTE: Interpretation is same as the for Table II, Set 1.

TABLE VI

Combined Least Squares Analyses of Second Set of Calibration Points

NOTE: Interpretation is same as that for Table III, Set 1.

NOTE: F Ratio indicates no significant differences in the slope or intercepts for the three calibration curves on the second set of data.

TABLE VIII

Combined Least Squares Calibration Data for Both Sets of Calibration Curves

TABLE IX

Comparison of Set 1 Calibration with Set 2 Calibration

NOTE: F Ratio indicates that there are no significant differences between the two curves at the 95 percent confidence level.

Date: May 12, 1972
To: W. I. Winters
From: D. F. Shepard *D. F. Shepard*
Subject: CALIBRATION OF CARY 16

The reading error for absorption observed was ± 0.000389 or ± 0.0026 g/liter in the 11 to 15 g/liter range. The major source of error was the shift observed between the three readings of the first set. The shift amounted to 0.01 g/liter Pu.

A two-way analysis of variance (Table I) showed a highly significant difference between the three readings obtained on the first set of calibration standards. The second set, however, indicated no difference between the three readings. The overall standard deviation for an absorbance reading was ± 0.000389 .

For the first set, the 15.86759 g/liter standard appeared to be outside the linear region of the calibration. For the remaining eight standards three individual calibration equations and an overall equation were derived (Tables II and III). A comparison of the three equations showed, as expected, a highly significant shift or change in intercept. There was no significant difference observed for the three slopes (Table IV).

For the second set, both the 10.87224 and the 15.56702 g/liter standards appeared to be outside the linear region. The individual calibration equations and the overall equation are given in Tables V and VI. The comparison of the three equations (Table VII) showed no significant differences between the three equations.

After elimination of the 15.56702 g/liter standard from the first set as possibly outside the linear range, the overall equation based on the average of the three readings was derived and is given in Table VIII. An examination of the residuals (Table IX) indicated no significant difference between the two calibrations. The observed standard deviation of the average reading about the

W. I. Winters
Page 2
May 12, 1972

line was 0.00424 or 0.0028 g/liter Pu.

The Cary 16 appears to give the best precision of any method for the measurement of Pu in plutonium nitrate solutions at the 11 to 15 g/liter range. The method, however, appears to be subject to shifts in the intercept of the calibration equation.

DFS:e

Att. (9)

cc: MH Campbell (w/att.)

TABLE 3-1
TWO-WAY ANALYSIS OF VARIANCE
One Observation Per Cell

N Column = 3, N Row = 9

Set 1

			<u>Average</u>	
	.0595	.0605	.0583	.0594
	.1519	.1515	.1505	.1513
	.2410	.2403	.2395	.2402
	.3291	.3288	.3278	.3285
	.4138	.4129	.4118	.4128
	.4969	.4961	.4950	.4960
	.5953	.5946	.5932	.5943
	.6750	.6744	.6737	.6743
	.7631	.7622	.7618	.7623
	.4139	.4134	.4124	.4132
Source	Sum of Squares	°F	Mean Square	F Ratio
Row	1.381841620	8	.172730202	.142621104562ex 07
Column	.000011428	2	.000005714	47.18343
RxC	.000001937	16	.000000121	1.00000

Standard Deviation = $\pm .00034801$

Set 2

			<u>Average</u>	
	.0076	.0078	.0077	.0077
	.1996	.1998	.1996	.1996
	.2844	.2849	.2847	.2846
	.3709	.3709	.3707	.3708
	.5486	.5482	.5483	.5483
	.6302	.6318	.6307	.6309
	.7140	.7128	.7130	.7132
	.3936	.3937	.3935	.3936
Source	Sum of Squares	°F	Mean Square	F Ratio
Row	1.144093569	6	.190682261	.998998960495ex 06
Column	.000000162	2	.000000081	.42661
RxC	.000002290	12	.000000190	1.00000

Standard Deviation = $\pm .00043689$

Standard Deviation Reading (combined both sets) = $\pm .00038854$

TABLE 3-II

Set 1

Individual Readings

$y = -1.635371149 + .151318689 x$
 Std. Dev. $y = \pm 0.000351559$ Std. Dev. $b_0 = \pm 0.001244799$ Std. Dev. $b_1 = \pm 0.000093444$

Run	x	y	Calc. - Obs. y	Sum of Diff.	
1	11.203250	.059500	.000389	.000389	
2	11.810040	.151900	-.000191	.000198	
3	12.399770	.241000	-.000054	.000144	
4	12.979290	.329100	-.000461	-.000317	
5	13.544640	.413800	.000386	.000068	
6	14.089540	.496900	-.000260	-.000191	
7	14.740690	.595300	-.000129	-.000321	
8	15.270370	.675000	.000321	.000000	
n	Sum x	Sum x**2	Sum y	Sum y**2	Sum xy
8	106.037590	1419.650672	2.962500	1.421149	41.408864

$y = -1.632077615 + .151038145 x$
 Std. Dev. $y = \pm 0.00486343$ Std. Dev. $b_0 = \pm 0.001722042$ Std. Dev. $b_1 = \pm 0.000129270$

Run	x	y	Calc. - Obs. y	Sum of Diff.	
1	11.203250	.060500	-.000459	-.000459	
2	11.810040	.151500	.000188	-.000270	
3	12.399770	.240300	.000460	.000190	
4	12.979290	.328800	-.000509	-.000319	
5	13.544640	.412900	.000779	.000460	
6	14.089540	.496100	-.000119	.000340	
7	14.740690	.594600	-.000271	.000069	
8	15.270370	.674400	-.000069	.000000	
n	Sum x	Sum x**2	Sum y	Sum y**2	Sum xy
8	106.037590	1419.650672	2.959100	1.417432	41.359827

$y = -1.635289587 + .151192767 x$
 Std. Dev. $y = \pm 0.00463515$ Std. Dev. $b_0 = \pm 0.001641213$ Std. Dev. $b_1 = \pm 0.000123202$

Run	x	y	Calc. - Obs. y	Sum of Diff.	
1	11.203250	.058300	.000260	.000260	
2	11.810040	.150500	-.000196	.000063	
3	12.399770	.239500	-.000034	.000029	
4	12.979290	.327800	-.000714	-.000685	
5	13.544640	.411800	.000762	.000076	
6	14.089540	.495000	-.000053	.000023	
7	14.740690	.593200	.000196	.000220	
8	15.270370	.673700	-.000220	.000000	
n	Sum x	Sum x**2	Sum y	Sum y**2	Sum xy
8	106.037590	1419.650672	2.949800	1.411224	41.238747
n	Sum x	Sum x**2	Sum y	Sum y**2	Sum xy
24	318.112770	4259.952016	8.871400	4.249805	124.007439

TABLE 3-III

Set 1

Individual Readings Combined

$$y = -1.634246120 + .151183201 x$$

$$\text{Std. Dev. } y = \pm .000820567$$

$$\text{Std. Dev. } b_0 = \pm .001677468$$

$$\text{Std. Dev. } b_1 = \pm .000125924$$

Run	x	y	Calc. - Obs. y	Sum of Diff.
1	11.203250	.059500	-.000002	-.000002
2	11.810040	.15190	-.000666	-.000669
3	12.399770	.241000	-.000609	-.001278
4	12.979290	.329100	-.001095	-.002374
5	13.544640	.413800	-.000324	-.002698
6	14.089540	.496900	-.001044	-.003742
7	14.740690	.595300	-.001001	-.004743
8	15.270370	.675000	-.000622	-.005366
9	11.203250	.060500	-.001002	-.006369
10	11.810040	.151500	-.000266	-.006636
11	12.399770	.240300	.000090	-.006545
12	12.979290	.328800	-.000795	-.007340
13	13.544640	.412900	.000575	-.006764
14	14.089540	.496100	-.000244	-.007009
15	14.740690	.594600	-.000301	-.007310
16	15.270370	.674400	-.000022	-.007333
17	11.203250	.058300	.001197	-.006136
18	11.810040	.150500	.000733	-.005402
19	12.399770	.239500	.000890	-.004511
20	12.979290	.327800	.000204	-.004307
21	13.544640	.411800	.001675	-.002631
22	14.089540	.495000	.000855	-.001775
23	14.740690	.593200	.001098	-.000677
24	15.270370	.673700	.000677	.000000

n	Sum x	Sum x**2	Sum y	Sum y**2	Sum xy
24	318.112770	4258.952016	8.871400	4.249805	124.007439

TABLE 3-IV

Set 1

Comparison of Individual Calibration Curves

Comparison of k Linear ($y = b_0 + b_1x$) Regression Lines (Ref. Brownlee, pp. 329-342)

Line	n	Sum x	Sum x**2	Sum y	Sum y**2	Sum xy
1	9	121.905180	1671.431084	3.725600	2.003470	53.517422
2	9	121.905180	1671.431084	3.721300	1.998381	53.454104
3	9	121.905180	1671.431084	3.711600	1.991563	53.326677
Sum	27	365.715540	5014.293252	11.158500	5.993414	160.298203

k	b0	b1	Std. Dev. y	Std. Dev. b0	Std. Dev. b1
1	-1.631627179	.151021019	.000807707	.002447679	.000179610
2	-1.628706198	.150770096	.000840334	.002546553	.000186865
3	-1.632436113	.150965898	.000673516	.002041026	.000149770
Sum	-1.630923163	.150919005	.000996347	.001743213	.000127916

Analysis of Variance

Source	Sum of Squares	°F	Mean Square	F Ratio
One line	.000000	1	.000000	.00037
Means about line	.000011	1	.000011	18.92010
Between slopes	.000000	2	.000000	.58217
About individual lines	.000012	21	.000000	1.00000
Due over-all line	1.381829	1	1.381829	
About over-all line	.000024	25	.000000	

Comparison of k Linear ($y = b_0 + b_1x$) Regression Lines (Ref. Brownlee, pp. 329-342)

Line	n	Sum x	Sum x**2	Sum y	Sum y**2	Sum xy
1	8	106.037590	1419.650672	2.962500	1.421148	41.408864
2	8	106.037590	1419.650672	2.959100	1.417432	41.359827
3	8	106.936589	1419.560672	2.949800	1.411224	41.238747
Sum	24	318.112770	4258.952016	8.871400	4.249804	124.007438

k	b0	b1	Std. Dev. y	Std. Dev. b0	Std. Dev. b1
1	-1.635370854	.151318667	.00068978	.000244237	.000018334
2	-1.632077231	.151038116	.000478658	.001694831	.000127227
3	-1.635289314	.151192746	.000403882	.001430064	.000107351
Sum	-1.634245800	.151183176	.000790465	.001615930	.000121304

Analysis of Variance

Source	Sum of Squares	°F	Mean Square	F Ratio
One line	-.000000	1	-.000000	-.00172
Means about lines	.000010	1	.000010	81.65769
Between slopes	.000000	2	.000000	2.11136
About individual lines	.000002	18	.000000	1.00000
Due over-all lines	.970551	1	.970551	
About over-all line	.000013	22	.000000	

TABLE 3-V

Individual Calibration Equations for Set 2

Winters #2 Elim 1 and 7

$y = -1.628912057 + .150739576 x$
 Std. Dev. $y = \pm .000546537$
 Std. Dev. $b_0 = \pm .003104668$
 Std. Dev. $b_1 = \pm .000229186$

Run	x	y	Calc. - Obs. y	Sum of Diff.
1	12.132260	.199600	.000299	.000299
2	12.694440	.284400	.000242	.000542
3	13.261470	.370900	-.000783	-.000241
4	14.444810	.548600	-.000107	-.000349
5	14.989170	.630200	.000349	.000000
n	Sum x	Sum x**2	Sum y	Sum y**2
5	67.522150	917.534879	2.033700	.956404
				Sum xy
				28.321174

$y = -1.631666702 + .150971696 x$
 Std. Dev. $y = \pm .000661393$
 Std. Dev. $b_0 = \pm .003757120$
 Std. Dev. $b_1 = \pm .000277350$

Run	x	y	Calc. - Obs. y	Sum of Diff.
1	12.132260	.199800	.000161	.000161
2	12.694440	.284900	-.000065	.000095
3	13.261470	.370900	-.000460	-.000364
4	14.444810	.548200	.000890	.000526
5	14.989170	.631800	-.000526	.000000
n	Sum x	Sum x**2	Sum y	Sum y**2
5	67.522150	917.534879	2.035600	.958349
				Sum xy
				28.348153

$y = -1.629483380 + .150786325 x$
 Std. Dev. $y = \pm .000392915$
 Std. Dev. $b_0 = \pm .002232000$
 Std. Dev. $b_1 = \pm .000164766$

Run	x	y	Calc. - Obs. y	Sum of Diff.
1	12.132260	.199600	.000295	.000295
2	12.694440	.284700	-.000035	.000260
3	13.261470	.370700	-.000535	-.000274
4	14.444810	.548300	.000296	.000021
5	14.989170	.630700	-.000021	.000000
n	Sum x	Sum x**2	Sum y	Sum y**2
5	67.522150	917.534879	2.034000	.956728
				Sum xy
				28.325491
n	Sum x	Sum x**2	Sum y	Sum y**2
15	202.566450	2752.604638	6.103300	2.871481
				Sum xy
				84.994819

TABLE 3-VI
Combined Calibrations Equations for Set 2

Winters #2 Elim 1 and 7

$$y = -1.630020718 + .150832533 x$$

$$\text{Std. Dev. } y = \pm .000500715$$

$$\text{Std. Dev. } b_0 = \pm .001642197$$

$$\text{Std. Dev. } b_1 = \pm .000121226$$

Run	x	y	Calc. - Obs. y	Sum of Diff.	
1	12.1322260	.199600	.000318	.000318	
2	12.6944440	.284400	.000313	.000632	
3	13.261470	.370900	-.000658	-.000026	
4	14.444810	.548600	.000126	.000099	
5	14.989170	.630200	.000633	.000733	
6	12.132260	.199800	.000118	.000852	
7	12.694440	.284900	-.000186	.000665	
8	13.261470	.370900	-.000659	.000006	
9	14.444810	.548200	.000526	.000532	
10	14.989170	.631800	-.000966	-.000433	
11	12.132260	.199600	.000318	-.000114	
12	12.694440	.284700	.000013	-.000100	
13	13.261470	.370700	-.000459	-.000560	
14	14.444810	.548300	.000426	-.000133	
15	14.989170	.630700	.000133	.000000	
n	Sum x	Sum x**2	Sum y	Sum y**2	Sum xy
15	202.566450	2752.604638	6.103300	2.871481	84.994819

$$y = 10.806847181 + 6.629813753 x$$

$$\text{Std. Dev. } y = \pm .003319664$$

$$\text{Std. Dev. } b_0 = \pm .002331378$$

$$\text{Std. Dev. } b_1 = \pm .005328504$$

Run	x	y	Calc. - Obs. y	Sum of Diff.	
1	.199600	12.132260	-.002101	-.002101	
2	.284400	12.694440	-.002073	-.004175	
3	.370900	13.261470	.004375	.000199	
4	.548600	14.444810	-.000846	-.000647	
5	.630200	14.989170	.004214	-.004861	
6	.199800	12.132260	-.000776	-.005637	
7	.284900	12.694440	.001241	-.004396	
8	.370900	13.261470	.004375	-.000021	
9	.548200	14.444810	-.003498	-.003520	
10	.631800	14.989170	.006393	.002872	
11	.199600	12.132260	-.002101	.000770	
12	.284700	12.694440	-.000084	.000686	
13	.370700	13.261470	.003049	.003735	
14	.548300	14.444810	-.002835	.000899	
15	.630700	14.989170	-.000899	-.000000	
n	Sum x	Sum x**2	Sum y	Sum y**2	Sum xy
15	6.103300	2.871481	202.566450	2752.604638	84.994819

TABLE 3-VII
Second Set Comparison of Readings

Comparison of k Linear ($y = b_0 + b_1x$) Regression Lines (Ref. Brownlee, pp. 329-342)

Line	n	Sum x	Sum x**2	Sum y	Sum y**2	Sum xy
1	5	67.522150	917.534879	2.033700	.956404	28.321174
2	5	67.522150	917.534879	2.035600	.958349	28.348153
3	5	67.522150	917.604637	2.034000	.956728	28.325491
Sum	15	202.566450	2752.604637	6.103300	2.871481	84.994818

k	b0	b1	Std. Dev. y	Std. Dev. b0	Std. Dev. b1
1	-1.628910408	.150739454	.000511386	.002904986	.000214445
2	-1.631666432	.150971676	.000581938	.003305766	.000244031
3	-1.629481304	.150786172	.000453112	.002573955	.000190009
Sum	-1.630019382	.150832434	.000480808	.001576906	.000116407

Analysis of Variance

Source	Sum of Squares	°F	Mean Square	F Ratio
One line	-.000000	1	-.000000	-.00135
Means about line	.000000	1	.000000	1.55443
Between slopes	.000000	2	.000000	.32004
About individual lines	.000002	9	.000000	1.00000
Due over-all line	.388126	1	.388126	
About over-all line	.000003	13	.000000	

TABLE 3-VIII

Winters' Cary 16, Sets #1 + #2 Omit Runs 1, 15, and 16

$$y = -1.632649540 + .151047472 x$$

$$\text{Std. Dev. } y = \pm .000504511$$

$$\text{Std. Dev. } b_0 = \pm .001511375$$

$$\text{Std. Dev. } b_1 = \pm .000112719$$

Run	x	y	Calc. - Obs. y	Sum of Diff.	
1	11.203250	.059430	.000143	.000143	
2	11.810040	.151300	-.000072	.000070	
3	12.132260	.199660	.000237	.000307	
4	12.399770	.240260	.000044	.000352	
5	12.694400	.284660	.000147	.000499	
6	12.979290	.328560	-.000720	-.000220	
7	13.261470	.370830	-.000368	-.000588	
8	13.544640	.412830	.000404	-.000184	
9	14.089540	.496000	-.000460	-.000644	
10	14.444810	.548360	.000842	.000197	
11	14.740690	.594360	-.000465	-.000267	
12	14.989170	.630700	.000726	.000458	
13	15.270370	.674360	-.000458	.000000	
n	Sum x	Sum x**2	Sum y	Sum y**2	Sum xy
13	173.55970	2337.184535	4.991310	2.373461	69.663652

TABLE 3-IX
Comparison of Set #1 and Set #2

Winters' Cary 16

Calc. 5/12/72 DFS

One-Way Analysis of Variance Unequal Groups

	x				Ave. y	°F	Var. y	Std. Dev. Ave. y	
1	.000143	-.000072	.000044	-.000720	.000404				
	-.000460	-.000465	-.000458		-.000198	7	.00000014	.000135	
2	.000237	.000147	-.000368	.000842	.000726	.000316	4	.00000023	.000217

Sum = .000000 N = 13 Ave. = .00000000

Source	Sum of Squares	°F	Mean Square	F Ratio
Groups	.000000815	1	.000000815	4.52892
Error	.000001980	11	.000000180	1.00000

Std. Dev. Ave. y = $\pm .00017105$

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APPENDIX 4STATISTICAL ANALYSIS OF CARY 16
ABSORBANCE READINGS ON GLASS STANDARDS

Date: November 30, 1972

To: W. I. Winters

From: D. F. Shepard *D. F. Shepard*

Subject: STATISTICAL ANALYSIS OF CARY 16:
ABSORBANCE READINGS OF GLASS STANDARDS

The data obtained by making five replicate readings on three different glass standards using both fixed and free slit, and chart readings or tape readings were examined using a two-way and one-way analysis of variance. The detailed analyses of variance tables are attached.

With standards #5 and #7 no significant differences were observed for the reading variance between free and fixed slits or between chart and tape readings.

A significantly (@ 0.95 level) lower reading variance was observed for standard #5 as compared with #7 and #8.

With standard #8 a significant (@ 0.999 level) lower reading variance was observed with the fixed slit as compared with the free slit.

With standard #5 the average free slit reading was significantly (@ 0.999 level) lower than for the fixed slit. No significant difference was observed between the chart and tape averages.

With standard #7 the average free slit reading was significantly (@ 0.975 level) lower than for the fixed slit; and the tape average was significantly (@ 0.999 level) higher than the chart.

W. I. Winters
Page 2
November 30, 1972

With standard #8 the average free slit reading was significantly (@ 0.99 level) higher than for the fixed slit; and the tape average was significantly (@ 0.975 level) higher than for the chart.

Three tables are attached for your information.

DFS:e

Att. (3)

TABLE 4-I

Cary 16 Pu Data, W. I. Winters, ARH-N-212, p. 3

11/30/72 DFS

Absorbance x 100

x = 1 Chart, free slit x = 2 Chart, fixed slit
 x = 3 Tape, free slit x = 4 Tape, fixed slit

Glass Standards

ONE-WAY ANALYSIS OF VARIANCE UNEQUAL GROUPS

x						Ave. y	°F	Var. y	Std. Dev. Ave. y
Standard #5									
1	.185	.190	.205	.217	.161	.1916	4	.000451	.009505
2	.202	.215	.255	.251	.253	.2352	4	.000617	.011110
3	.170	.190	.210	.220	.155	.1890	4	.000730	.012083
4	.225	.215	.265	.260	.255	.2440	4	.000505	.010049
						.21495	16	.000576	.010731
Standard #7									
1	4.750	4.747	4.793	4.783	4.692	4.7530	4	.001566	.017700
2	4.783	4.764	4.848	4.788	4.787	4.7940	4	.001005	.014180
3	4.820	4.800	4.860	4.850	4.770	4.8200	4	.001350	.016431
4	4.870	4.830	4.930	4.860	4.850	4.8680	4	.001420	.016852
						4.80875	16	.001335	.016343
Standard #8									
1	22.736	22.731	22.771	22.793	22.857	22.7776	4	.002621	.022898
2	22.731	22.722	22.740	22.753	22.736	22.7364	4	.000131	.005124
3	22.790	22.830	22.800	22.820	22.900	22.8230	4	.001870	.019339
4	22.780	22.780	22.790	22.790	22.780	22.7840	4	.000030	.002449
						22.7815	16	.001163	.015251

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TABLE 4-II

Cary 16 Pu Data, Page 3, ARH-N-212, W. I. Winters 11/30/72 DFS

Standard #5 (Glass)

Absorbance x 100

TWO-WAY ANALYSIS OF VARIANCE (m OBS. PER CELL)

N Col. = 2

N Row = 2

m = 5

Free	Fixed	
.1850	.2020	
.1900	.2150	
.2050	.2550	
.2170	.2510	
.1610	.2530	
.1916	.2352	.21340 Chart
.1700	.2250	
.1900	.2150	
.2100	.2650	
.2200	.2600	
.1550	.2550	
.1890	.2440	.21650 Tape
.1903	.2396	.21495

Source	Sum of Squares	°F	Mean Square	F Ratio	
Row	.000048050	1	.000048050	.08342	
Column	.012152450	1	.012152450	21.09800	Sign. .999
RxC	.000162450	1	.000162450	.28203	
Error	.009216000	16	.000576000	1.00000	

Standard #7 Absorbance x 100

TWO-WAY ANALYSIS OF VARIANCE (m OBS. PER CELL)

N Col. = 2

N Row = 2

m = 5

Free	Fixed	
4.7500	4.7830	
4.7470	4.7640	
4.7930	4.8480	
4.7830	4.7880	
4.6920	4.7870	
4.7530	4.7940	4.7735- Chart
4.8200	4.8700	
4.8000	4.8300	
4.8600	4.9300	
4.8500	4.8600	
4.7700	4.8500	
4.8200	4.8680	4.84400 Tape
4.7865	4.8310	4.80875

Source	Sum of Squares	°F	Mean Square	F Ratio	
Row	.024851250	1	.024851250	18.60819	Sign. .999
Column	.009901250	1	.009901250	7.41388	Sign. .975
RxC	.000061250	1	.000061250	.04586	
Error	.021368000	16	.001335500	1.00000	

TABLE 4-III

Cary 16 Pu Data, Page 3, ARH-N-212, W. I. Winters 11/30/72 DFS

Standard #8 Absorbance x 100

TWO-WAY ANALYSIS OF VARIANCE (m OBS. PER CELL)

N Col. = 2

N Row = 2

m = 5

Free	Fixed	
22.7360	22.7310	
22.7310	22.7220	
22.7710	22.7400	
22.7930	22.7530	
22.8570	22.7360	
22.7776	22.7364	22.75700 Chart
22.7900	22.7800	
22.8300	22.7800	
22.8000	22.7900	
22.8200	22.7900	
22.9000	22.7800	
22.8280	22.7840	22.80600 Tape
22.8028	22.7602	22.78150

Source	Sum of Squares	°F	Mean Square	F Ratio	
Row	.012005000	1	.012005000	10.32000	Sign. 0.99
Column	.009073800	1	.009073800	7.80021	Sign. 0.975
RxC	.000009800	1	.000009800	.00842	
Error	.018612400	16	.001163275	1.00000	

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