LABORATORY QUALITY CONTROL MANUAL

2nd Edition, 1972

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Analytical Quality Control Program
Ada Facility
P. O. Box 1198
Ada, Oklahoma 74820

FOREWORD

Those who generate water quality data have a serious responsibility to those who will use it. Such data often become the basis for various action programs in water pollution control. Among these are: (1) the construction and operation of wastewater treatment works costing millions of dollars; (2) the early detection of trends in water quality degradation that, if allowed to go unchecked, could result in the loss of beneficial water uses; and (3) court actions that could result in the levying of heavy fines and other penalties and even industrial shutdowns.

The significance of water quality data precludes any thought of careless laboratory operation; however, even the best staffed, equipped, and maintained laboratories need some measure of product quality. Conscientious personnel and well equipped laboratories are not enough.

The Environmental Protection Agency (EPA) is concerned about laboratory quality and has initiated a program of improved effort in that direction. This manual deals with two areas of that program; statistical analytical quality control and record keeping. Product quality control is an old technique of the manufacturing industries. The statistics underlying product quality control are a proven technique but their application to routine laboratory production is new. This

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
SURVEILLANCE AND ANALYSIS DIVISION
REGION VI
ANALYTICAL QUALITY CONTROL PROGRAM

The Environmental Protection Agency (EPA) gathers water quality data to determine compliance with water quality standards, to provide information for planning of water resources development, to determine the effectiveness of pollution abatement procedures, and to assist in research activities. In a large measure, the success of the pollution control program rests upon the reliability of the information provided by the data collection activities.

To insure the reliability of physical, chemical, and biological data, EPA's Division of Research has established the Analytical Quality Control (AQC) Laboratory at 1014 Broadway, Cincinnati, Ohio. The AQC program conducted by this Laboratory is designed to assure the validity and, where necessary, the legal defensibility of all water quality information collected by EPA.

The AQC Laboratory is responsible for:

Conducting analytical methods research, providing leadership in the selection of laboratory procedures, conducting a reference sample program for methods verification and laboratory performance, and advising laboratories in the development of internal quality control. In addition, the

Laboratory develops and evaluates automatic water quality monitoring instrumentation and assists EPA's ten Regions in the procurement and installation of this type of equipment.

METHODS RESEARCH

Although analytical methods are available for most of the routine measurements used in water pollution control, there is a continuing need for improvement in sensitivity, precision, accuracy, and speed. Development is required to take advantage of modern instrumentation in the water laboratory. In microbiology, the use of new bacterial indicators of pollution, including pathogens, creates a need for rapid identification and counting procedures. Biological collection methods need to be standardized to permit efficient interchange of data. The AQC Laboratory devotes its research efforts to the improvement of the routine "tools of the trade."

METHODS SELECTION

Assisted by Advisory Committees, the AQC Laboratory provides a program for selecting the best procedures in water and waste analysis from among those that are available. Through the publishing of EPA methods manuals, updated regularly, the program insures the application of uniform analytical methods in all laboratories of EPA. The validity of the chosen procedures and the evaluation of analytical performance are verified by reference sample studies involving participation by regional, basin, and project laboratory staff

personnel. The EPA methods manual is available to any organization upon request.

INTRALABORATORY QUALITY CONTROL

To maintain a high level of performance in daily activities, every analytical laboratory must provide a system of checks on the accuracy of reported results. While this is a basic responsibility of the analyst and his supervisor, the AQC Laboratory provides guidance in the development of model programs which can be incorporated into the laboratory routine.

AQC REGIONAL COORDINATORS

The Administration-wide quality control program is carried out through EPA Regional AQC Coordinators. The Coordinator, appointed by the Regional Administrator, implements the program in his regional laboratory and maintains relations with state and interstate pollution control agencies within the region to encourage their use of EPA methods and active participation in the analytical quality control effort. In addition, the Coordinator brings to the attention of the AQC Laboratory the special needs of his region in analytical methodology.

U. S. GEOLOGICAL SURVEY

Because water quality surveillance is a joint program between EPA, the U. S. Geological Survey (USGS) and the states, the AQC

Laboratory works closely with the USGS in securing uniform methods in both agencies. Through regular interchange of procedural outlines and joint participation in reference sample studies, the two agencies seek to promote complete cooperation in water quality data acquisition.

PROFESSIONAL LIAISON

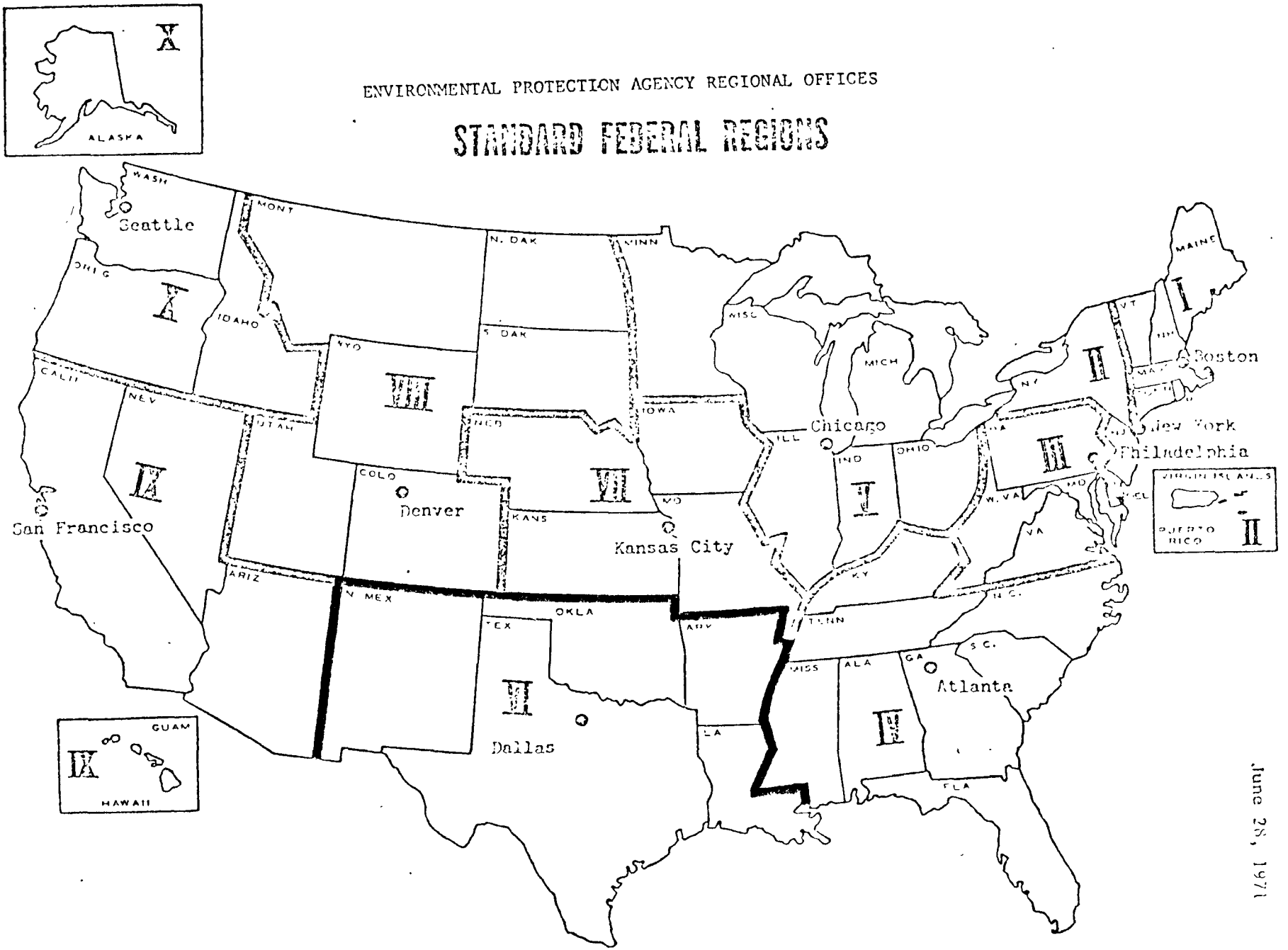
The Laboratory staff, along with other EPA scientists, actively participates in the preparation of *Standard Methods for the Examination of Water and Wastewater* (American Public Health Association) and in subcommittee and task group activities of Committee D-19 of the American Society for Testing and Materials. A senior member of the AQC Laboratory staff is General Referee for Water, Subcommittee D, of the Association of Official Analytical Chemists.

For further information write your Regional Coordinator or

Director
Analytical Quality Control Laboratory
Water Quality Office
Environmental Protection Agency
1014 Broadway
Cincinnati, Ohio 45202

ENVIRONMENTAL PROTECTION AGENCY REGIONAL OFFICES

STANDARD FEDERAL REGIONS



June 28, 1971

Regional Analytical Quality Control Coordinators

Francis T. Brezenski, AQC Coordinator
Environmental Protection Agency
Hudson-Delaware Basins Office
Edison, New Jersey 08817

Harold G. Brown, AQC Coordinator
Environmental Protection Agency
911 Walnut Street, Room 702
Kansas City, Missouri 64106

Charles Jones, Jr., AQC Coordinator
Environmental Protection Agency
1140 River Road
Charlottesville, Virginia 22901

Bobby G. Benefield, AQC Coordinator
Environmental Protection Agency
Ada Facility, P. O. Box 1198
Ada, Oklahoma 74820

James H. Finger, AQC Coordinator
Environmental Protection Agency
Southeast Water Laboratory
College Station Road
Athens, Georgia 30601

Daniel F. Krawczyk, AQC Coordinator
Environmental Protection Agency
Pacific Northwest Water Laboratory
200 South 35th Street
Corvallis, Oregon 97330

LeRoy E. Scarce, AQC Coordinator
Environmental Protection Agency
1819 West Pershing Road
Chicago, Illinois 60605

Donald B. Mausshardt, AQC Coordinator
Environmental Protection Agency
Phelan Building, 760 Market Street
San Francisco, California 94102

Robert L. Booth, AQC Coordinator
Environmental Protection Agency
Analytical Quality Control Laboratory
1014 Broadway
Cincinnati, Ohio 45202

John Tilstra, AQC Coordinator
Environmental Protection Agency
Lincoln Tower Building, Suite 900
1860 Lincoln Street
Denver, Colorado 80203

INTRODUCTION

The precision and accuracy of analytical data produced in the laboratory can be detected by using quality control charts. These control charts serve as "fingerprints" of a laboratory's operations. In addition, the use of these charts enables a supervisor to validate the data produced from a specific laboratory group for the analysis of a specific parameter. These charts indicate when the laboratory is operating normally or abnormally, thus pointing out when data generated should be accepted, questioned, or rejected. In the same manner they indicate when the laboratory is operating at optimum efficiency.

CONSTRUCTION OF CONTROL CHARTS

Two control charts are required to "fingerprint" the laboratory operations for a given analytical procedure. These are referred to as precision and accuracy control charts. Precision control charts are constructed from duplicate sample analyses, whereas accuracy control charts are constructed from spiked or standard sample analyses data. A set of these control charts represents, and is restricted to, a specific laboratory, group of analysts, analytical method, range of concentration, and period of time. To construct the precision and accuracy control charts it is recommended that at least 20 sets of duplicate and 20 sets of spiked sample data from an in-control process be used for the initial construction. The selection of in-control

data can be made on a judgment basis.

It is necessary that the initial sets of data be obtained under the following conditions:

1. Normal laboratory operations
2. Constant analyst or group of analysts
3. Consistent method
4. Narrow range of concentration of the parameter analyzed.

Since the precision and accuracy of the analyses of many parameters are proportional to the concentration of the parameter to be measured, it may be necessary to use several control charts in many different ranges of concentrations for a given parameter.

The control charts are derived from three basic calculations:

1. Standard deviation (S_d) of the differences between duplicates or, in the case of spiked or standard samples, between the known quantity and the quantity obtained.
2. The upper control limit (UL)
3. The lower control limit (LL)

Prior to these calculations, two decisions must be made:

1. The α and β levels
2. The allowable variability levels

By definition, α is the probability of judging the process to be out of control, when in fact, it is in control. It is recommended that α be chosen to lie between the boundaries of .05 and .15, that is, the laboratory personnel are willing to stop the laboratory process somewhere between 5 and 15% of the time, judging it to be out of control, when in fact, it is in control. If the cost of examining a process to determine the reason or reasons for being out of control is considerable, then it may be desirable to choose a low α. Likewise, if the cost is negligible, it may be desirable to choose a larger α value, and thus stop the process more frequently.

On the other hand, β is defined as the probability of judging the process to be in control when it is not. Again, it is recommended that β be chosen to lie between the values of .05 and .15; thus, the laboratory personnel are willing to accept out of control data somewhere between 5 and 15% of the time. The economic considerations used for choosing α are also applicable to the choice of β.

It is also essential to set maximum and minimum allowable variability levels. It is necessary to specify a value for the minimum and maximum amount of variation that will be allowable in the system. These minimum and maximum amounts are referred to as σ_o^2 and σ_1^2 respectively. Where

$$\sigma_o^2 = (\sigma - \Delta \times \sigma)^2 \text{ and}$$

$$\sigma_1^2 = (\sigma + \Delta \times \sigma)^2.$$

The values used for Delta (Δ) should be based on a knowledge of the variation in the procedure under consideration. However, if such knowledge is not available Δ may be arbitrarily set equal to .20.

Mathematical Equations

$$S_d^2 = \frac{\sum_{i=1}^{n} di^2 - \frac{\left(\sum_{i}^{n} di\right)^2}{N}}{N - 1} = \text{Variance of the differences}$$

$$S_d = \sqrt{S_d^2} = \text{Standard deviation of the differences} \qquad (1)$$

$$S_o^2 = (.8S_d)^2 = .64\ S_d^2 \text{ estimates } \sigma_o^2$$

$$S_1^2 = (1.2S_d)^2 = 1.44\ S_d^2 \text{ estimates } \sigma_1^2$$

$$UL(M) = \frac{2 \log_e\left[\frac{1 - \beta}{\alpha}\right]}{\frac{1}{S_o^2} - \frac{1}{S_1^2}} + M \frac{\log_e\left[\frac{S_1^2}{S_o^2}\right]}{\frac{1}{S_o^2} - \frac{1}{S_1^2}} \qquad (2)$$

$$LL(M) = \frac{2 \log_e\left[\frac{\beta}{1 - \alpha}\right]}{\frac{1}{S_o^2} - \frac{1}{S_1^2}} + M \frac{\log_e\left[\frac{S_1^2}{S_o^2}\right]}{\frac{1}{S_o^2} - \frac{1}{S_1^2}} \qquad (3)$$

Where: UL(M) = upper limit at M sets of samples

LL(M) = lower limit at M sets of samples

di = the difference between the i^{th} set of duplicates or spiked samples

N = the total number of sets of duplicates or spiked samples used to construct the control charts

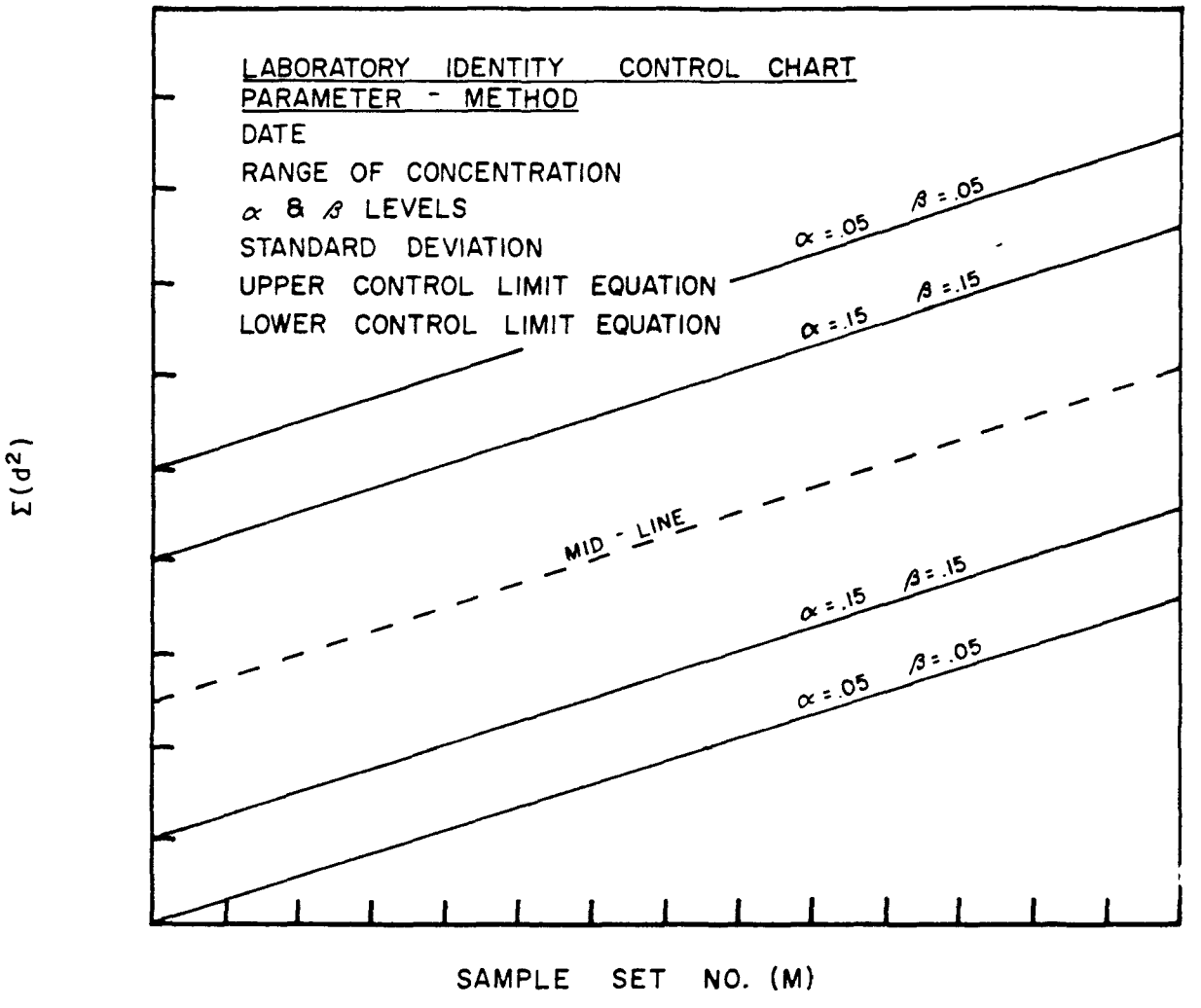
S_o^2 = minimum amount of variation allowed in the system

S_1^2 = maximum amount of variation allowed in the system

α = percent (decimal fraction) of time you are willing to judge the procedure out of control when it is in control

β = percent (decimal fraction) of time you are willing to judge the procedure in control when it is out of control

M = number of sets of duplicates or spiked samples used in calculating the value to be plotted on the chart



EFFECT OF α & β LEVELS ON STANDARD CONTROL CHART

CONTROL CHART

CALCULATIONS

EXAMPLE I

Accuracy Control Chart

Laboratory: Laboratory A

Parameter Analyzed: Total phosphate phosphorus

Method: Colorimetric with persulfate digestion

Date: November 12, 1968

Data:

Results of Analyses of Standards

(mg/l Total PO_4-P)

Actual	Obtained	Difference (di)	di^2
.34	.33	+.01	.0001
.49	.49	.00	.0000
.49	.49	.00	.0000
.68	.65	+.03	.0009
.67	.65	+.02	.0004
.66	.70	-.04	.0016
.83	.80	+.03	.0009
.34	.34	.00	.0000
.50	.47	+.03	.0009
.40	.40	.00	.0000
.50	.53	-.03	.0009
.66	.60	+.06	.0036
.50	.56	-.06	.0036
.52	.59	-.07	.0049
.98	.75	+.23	.0529
.49	.63	-.14	.0196
1.6	1.7	-.10	.0100
1.3	1.2	+.10	.0100

Actual	Obtained	Difference (di)	di^2
3.3	3.3	.00	.0000
4.9	4.6	+.30	.0900
2.3	2.3	.00	.0000
1.3	1.3	.00	.0000
2.3	2.4	-.10	.0100

$$\Sigma di = .27$$

$$\Sigma di^2 = .21$$

$$(\Sigma di)^2 = .07$$

Calculations

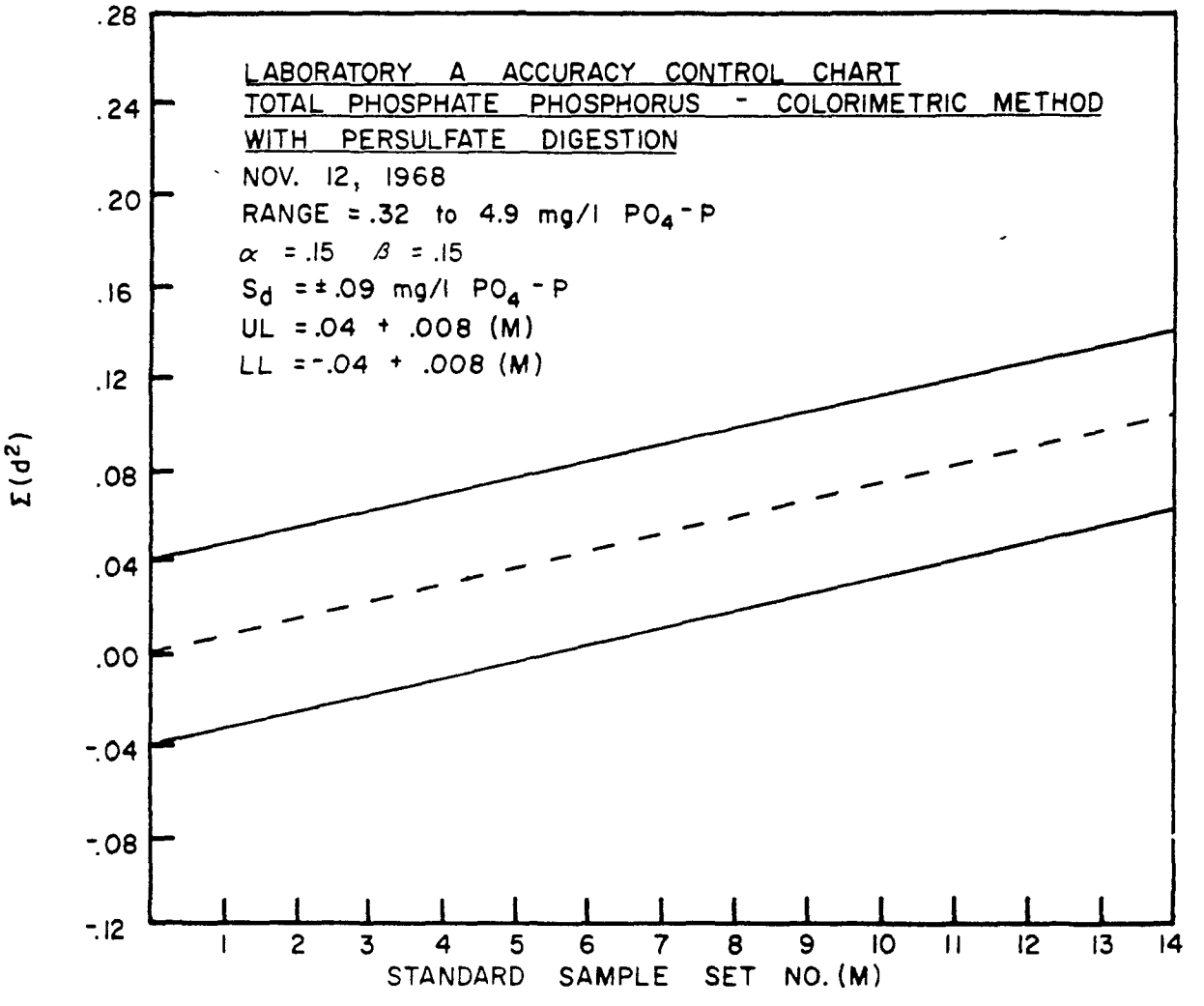
$$S_d^2 = \frac{\Sigma di^2 - \frac{(\Sigma di)^2}{N}}{N - 1} = \frac{.21 - \frac{.07}{23}}{22} = .009$$

$$S_d = \sqrt{S_d^2} = \sqrt{.009} = \pm .09 \qquad (1)$$

$$S_o^2 = (.8S_d)^2 = .64\, S_d^2 = .64(.009) = .006$$

$$S_1^2 = (1.2S_d)^2 = 1.44\, S_d^2 = 1.44\ (.009) = .013$$

$$UL(M) = \frac{2 \log_e \left[\frac{1 - \beta}{\alpha}\right]}{\frac{1}{S_o^2} - \frac{1}{S_1^2}} + M \frac{\log_e \left[\frac{S_1^2}{S_o^2}\right]}{\frac{1}{S_o^2} - \frac{1}{S_1^2}}$$



EXAMPLE 1 - ACCURACY CONTROL CHART

EXAMPLE II

Precision Control Chart

Laboratory: Laboratory AC

Parameter Analyzed: Hexane extractables

Method: Semiwet extraction method

Date: January 5, 1969

Data:

Results of Analyses of Duplicate Samples

(mg/l Hexane Extractables)

Duplicate No. 1	Duplicate No. 2	Difference (di)	di^2
.40	.50	+.10	.0100
.80	.83	+.03	.0009
.63	.60	-.03	.0009
.93	.83	-.10	.0100
1.46	1.16	-.30	.0900
1.20	1.10	-.10	.0100
1.80	1.56	-.24	.0576
2.16	2.20	+.04	.0016
.40	.36	-.04	.0016
.20	.28	+.08	.0064
.40	.30	-.10	.0100
.46	.40	-.06	.0036
.40	.60	+.20	.0400
1.76	1.80	+.04	.0016
.83	.86	+.03	.0009
1.16	1.02	-.14	.0196
.56	.63	+.07	.0049
1.26	1.33	+.07	.0049

Duplicate No. 1	Duplicate No. 2	Difference (di)	di^2
.48	.36	-.12	.0144
.59	.59	.00	.00
.59	.60	+.01	.0001
1.17	1.26	+.09	.0081

$$\Sigma di = -.470$$

$$\Sigma di^2 = .297$$

$$(\Sigma di)^2 = .221$$

Calculations

$$S_d^2 = \frac{\Sigma di^2 - \frac{(\Sigma di)^2}{N}}{N-1} = \frac{.297 - \frac{.221}{22}}{21} = .0137$$

$$S_d = \sqrt{S_d^2} = \sqrt{.0137} = .117 \qquad (1)$$

$$S_o^2 = (.8S_d)^2 = .64\, S_d^2 = .64(.0137) = .00877$$

$$S_1^2 = (1.25_d)^2 = 1.44\, S_d^2 = 1.44(.0137) = .01973$$

$$UL(M) = \frac{2 \log_e \left[\frac{1-\beta}{\alpha}\right]}{\frac{1}{S_o^2} - \frac{1}{S_1^2}} + M \frac{\log_e \left[\frac{S_1^2}{S_o^2}\right]}{\frac{1}{S_o^2} - \frac{1}{S_1^2}}$$

$$= \frac{3.5}{\frac{1}{.0088} - \frac{1}{.0197}} + M \frac{\log_e\left[\frac{.0197}{.0088}\right]}{\frac{1}{.0088} - \frac{1}{.0197}}$$

$$= \frac{3.47}{63.35} + M \frac{.811}{63.35}$$

$$= .054 + .0128(M) \qquad (2)$$

$$LL(M) = \frac{2 \log_e\left[\frac{\beta}{1-\alpha}\right]}{\frac{1}{S_0^2} - \frac{1}{S_1^2}} + M \frac{\log_e\left[\frac{S_1^2}{S_0^2}\right]}{\frac{1}{S_0^2} - \frac{1}{S_1^2}}$$

$$= \frac{-3.47}{63.35} + M \frac{.811}{63.35}$$

$$= -.054 + .0128(M) \qquad (3)$$

Upper limits on the Y-axis:

at M = 0

UL (0) = .05 + 0(.013) = .05;

at M = 14

UL (14) = .05 + 14(.013) = .23

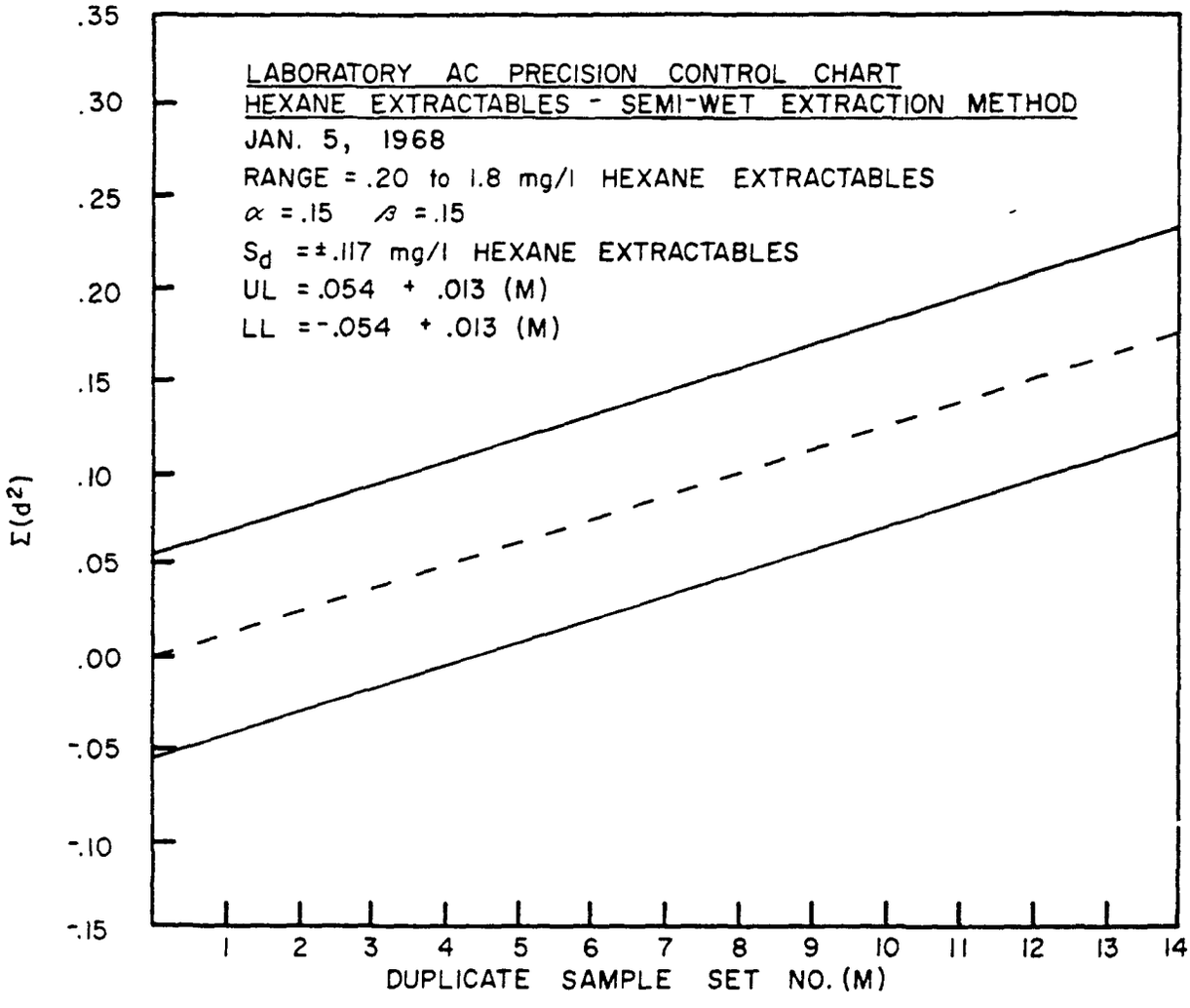
Lower limits on the Y-axis:

at M = 0

LL (0) = -.05 + 0(.013) = -.05;

at M = 14

LL (14) = -.05 + 14(.013) = .13



EXAMPLE 2 - PRECISION CONTROL CHART

USE OF CONTROL CHARTS

Once the control charts are constructed, and prior to their use, consideration must be given to the number of duplicate analyses to be conducted during a series of samples; likewise, the same decision must be made on spiked or standard samples.

In considering the number of duplicate and spiked sample analyses to be conducted in a series of samples, it is necessary to weigh the consequences when the data go out of control. The consequences of this situation are reanalyzing a series of samples or discarding the questionable data obtained. The samples to be reanalyzed are those lying between the last in-control point and the present out-of-control point. A realistic frequency for running duplicate and spiked samples would be every fifth sample; however, economic consideration and experience may require more or less frequent duplicate and spiked sample analyses.

Once the frequency of duplicate and spiked samples has been determined, it is then necessary to prepare spiked or standard samples in concentrations relative to the concentration of the control charts, which should be similar to those of the environmental samples. These spiked or standard samples must be intermittently dispersed among the series of samples to be analyzed and without the analyst's knowledge of concentration. Similarly, duplicate samples must be intermittently dispersed throughout the series of samples to be analyzed, and ideally, without the analyst's knowledge; however, this is sometimes very difficult

to accomplish.

The results of the duplicate and spiked sample analyses should be calculated immediately upon analyzing the samples to allow for early detection of problems that may exist in the laboratory. An example of these calculations follows:

Duplicate Sample No. M	Results No. 1	No. 2	Difference (di)	di^2	$\Sigma(di^2)$
1	5.4	5.2	.2	.04	.04
2	4.8	4.7	.1	.01	.05
3	6.1	5.8	.3	.09	.14

Upon plotting the summation or $\Sigma(di^2)$, one of three possibilities can occur:

1. Out of control on the upper limit
2. In control within the upper and lower limit lines
3. Out of control on the lower limit

Out of Control on Upper Limit

When data goes out of control on the upper limit the following steps should be taken:

1. Stop work immediately
2. Determine problems
    a. Precision control chart
        (1) The analyst

(2) Nature of the sample

(3) Glassware contamination

b. Accuracy control chart

(1) The analyst

(2) Glassware contamination

(3) Contaminated reagents

(4) Instrument problems

(5) Sample interference with the spiked material

3. Rerun samples represented by that sample set number, including additional duplicate and spiked samples.

4. Begin plotting at sample No. 1 on chart.

In Control

When data continuously fall in between the upper and lower control limits, the analyses should be continued until an out-of-control trend is detected.

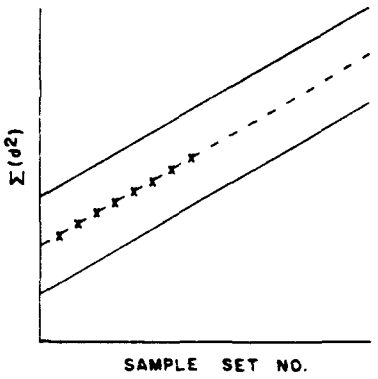
Out of Control on Lower Limit

When data fall out of control on the lower limit, the following steps should be taken:

1. Continue analyses unless trend changes
2. Construct new control charts on recent data
3. Check analyst's reporting of data.

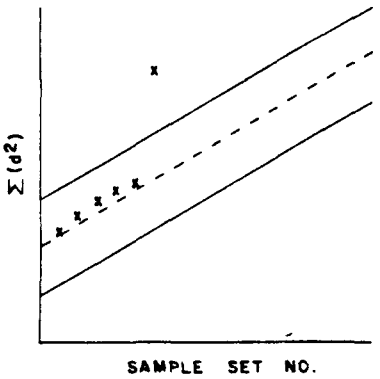
ILLUSTRATIONS OF

CONTROL CHARTS



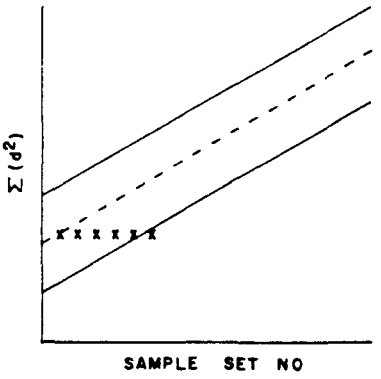
ANALYSIS IN CONTROL

NO PROBLEMS:
CONTINUE ANALYSIS



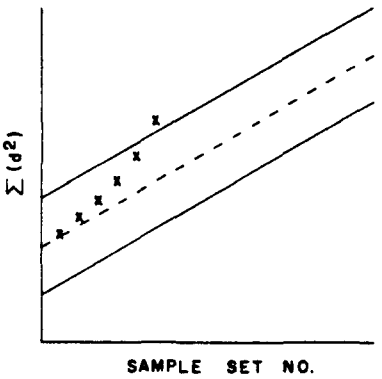
ANALYSIS OUT OF CONTROL
UPPER LIMIT

PROCEDURES:
1. STOP ANALYSIS
2 LOCATE PROBLEM
3 CORRECT PROBLEM
4. RERUN SAMPLES
5. START CHART AT SAMPLE SET NO. 1.



ANALYSIS OUT OF CONTROL
LOWER LIMIT

INCREASED EFFICIENCY OR
FALSE REPORTING
PROCEDURES.
1 CONTINUE ANALYSIS
2 CONSTRUCT NEW CHART
WITH RECENT DATA
3. OBSERVE ANALYST



ANALYSIS OUT OF CONTROL
UPPER LIMIT

CONTINUOUS ERROR TREND
PROCEDURES:
SAME AS ABOVE BUT STOP
ANALYSIS WHEN TREND IS
DETECTED

LABORATORY QUALITY CONTROL CHARTS

b. Analyze spiked or standard samples intermittently dispersed among day's samples without analyst's knowledge of concentration.

c. Calculate $\Sigma(di^2)$ of results as soon as possible

d. Plot $\Sigma(di^2)$ -

(1) Out of control on upper limit -

(a) Stop work

(b) Determine problems

(c) Rerun samples represented by that number

(d) Begin plotting at sample No. 1

(2) In control - continue analyses

(3) Out of control on lower limit -

(a) Continue analyses unless trend changes

(b) Construct new chart on recent data

(c) Check analyst reporting data

e. Compare standard deviation

(1) Other laboratories

(2) Literature

OUTLINE OF PROCEDURES

FOR

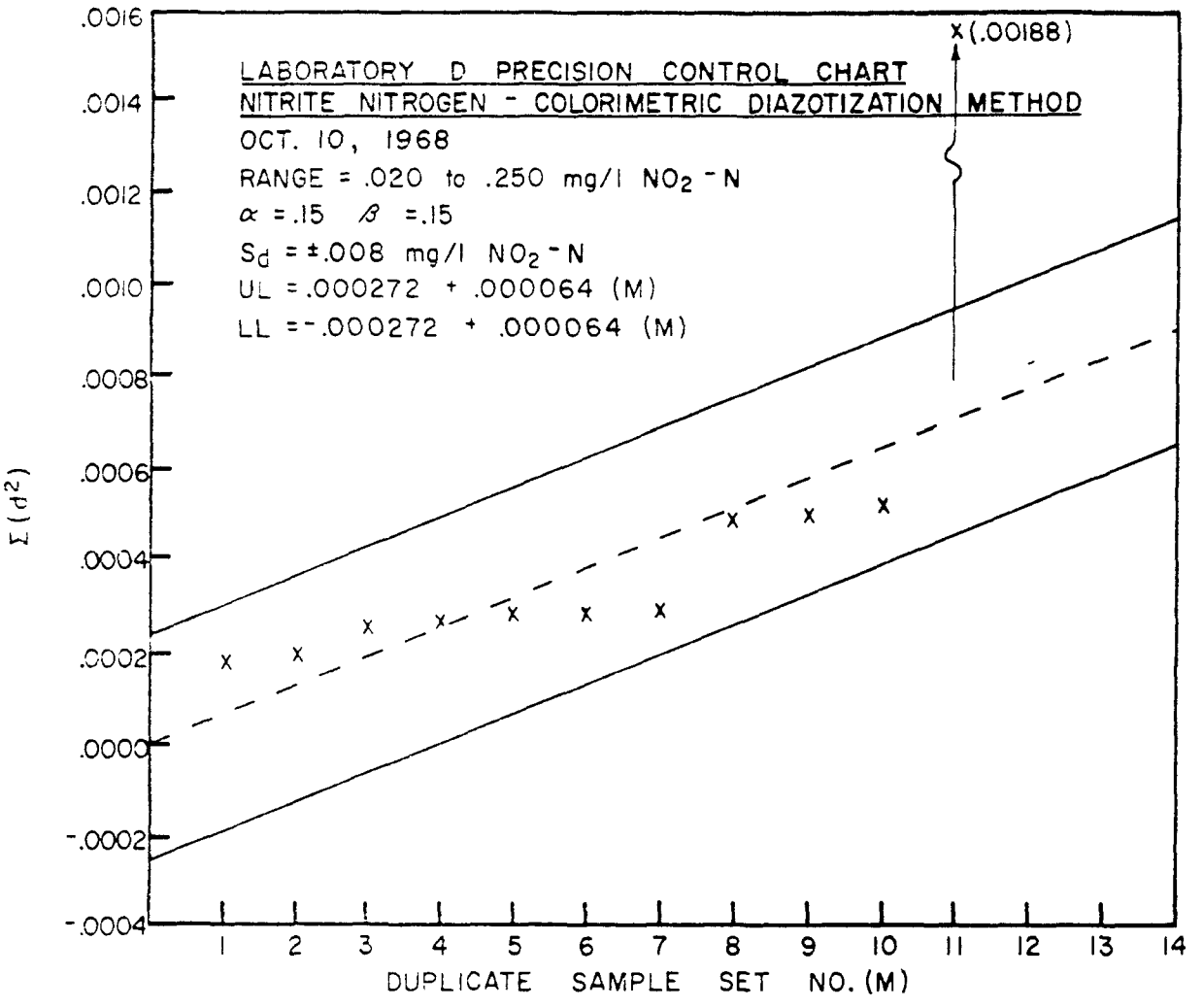
CONSTRUCTING AND USING CONTROL CHARTS IN THE LABORATORY

1. Obtain initial sets of duplicate and spiked or standard sample data for a given parameter under the following conditions -
   a. Normal laboratory operations
   b. Constant analyst or group of analysts
   c. Consistent method
   d. Parameter present in a narrow range of concentration
2. Calculate the following -
   a. Standard deviation
   b. Upper control limits
   c. Lower control limits
3. Construct control charts for precision and accuracy. These charts represent and are restricted to the specific -
   a. Laboratory
   b. Parameter
   c. Range of concentration
   d. Analytical method
   e. Time
4. Use of control charts -
   a. Analyze duplicate samples intermittently throughout day's samples

The primary reasons for data falling out of control on the lower limit are increased efficiency or false data reporting.

Standard Deviation

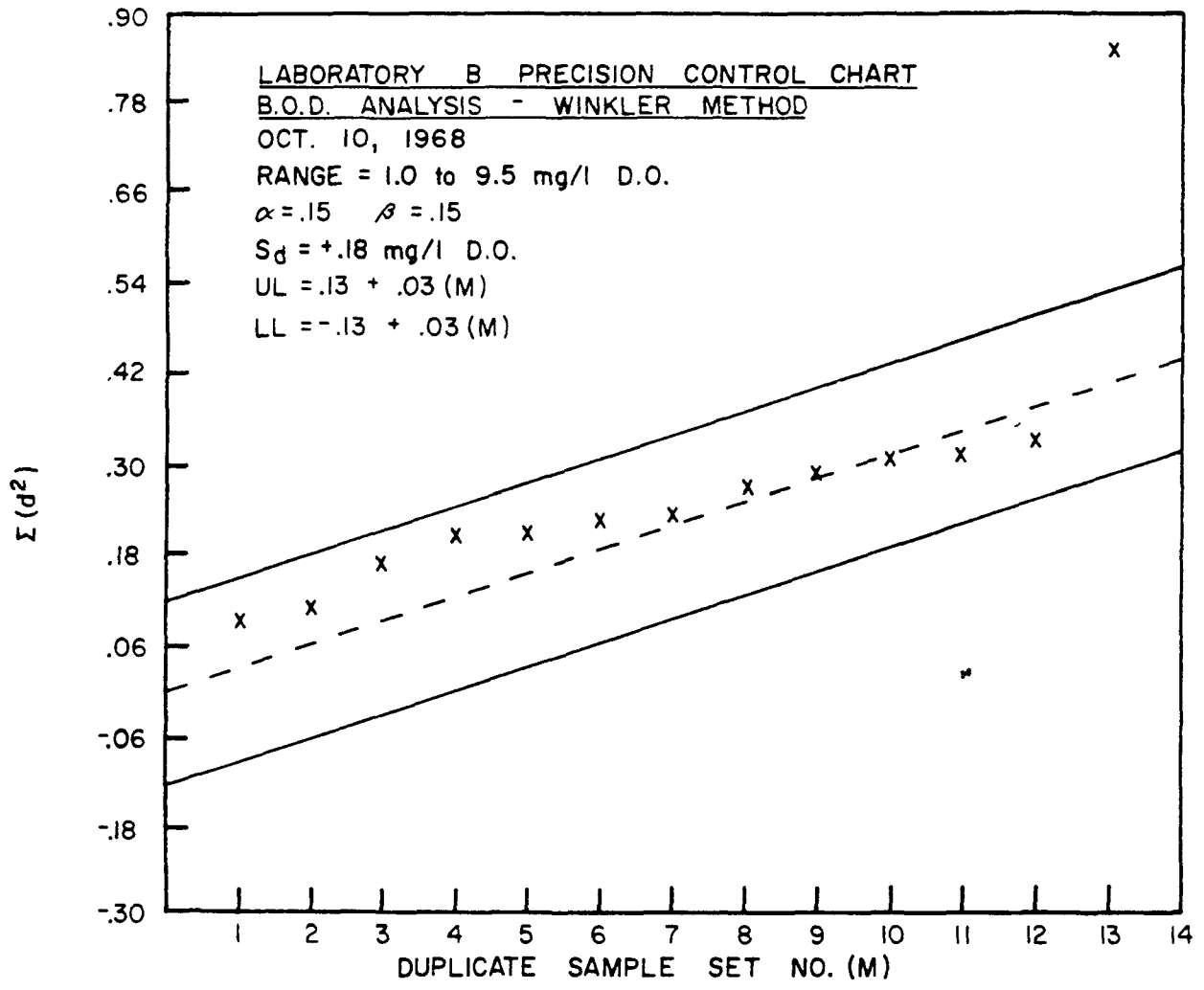
The purpose of calculating the standard deviation is to allow for inter-laboratory comparisons of precision and accuracy as well as similar comparisons with the literature. In this respect the standard deviation can be used as a guide to determine if the laboratory is operating "in the ball park" on precision and accuracy for a given parameter. It should be emphasized that the comparisons of standard deviations should only be used as a guide since the standard deviation of a specific laboratory is characteristic of that laboratory's operations and no other.



CORRECTIVE PROCEDURES:

1. STOP ANALYSIS AT SAMPLE SET 11
2. LOCATE CAUSE OR ASSUME CHANCE CAUSES
3. CORRECT PROBLEM
4. RERUN SAMPLES BETWEEN SAMPLE SETS 10 AND 11
5. BEGIN PLOTTING $\Sigma(d^2)$ AT SAMPLE SET 1

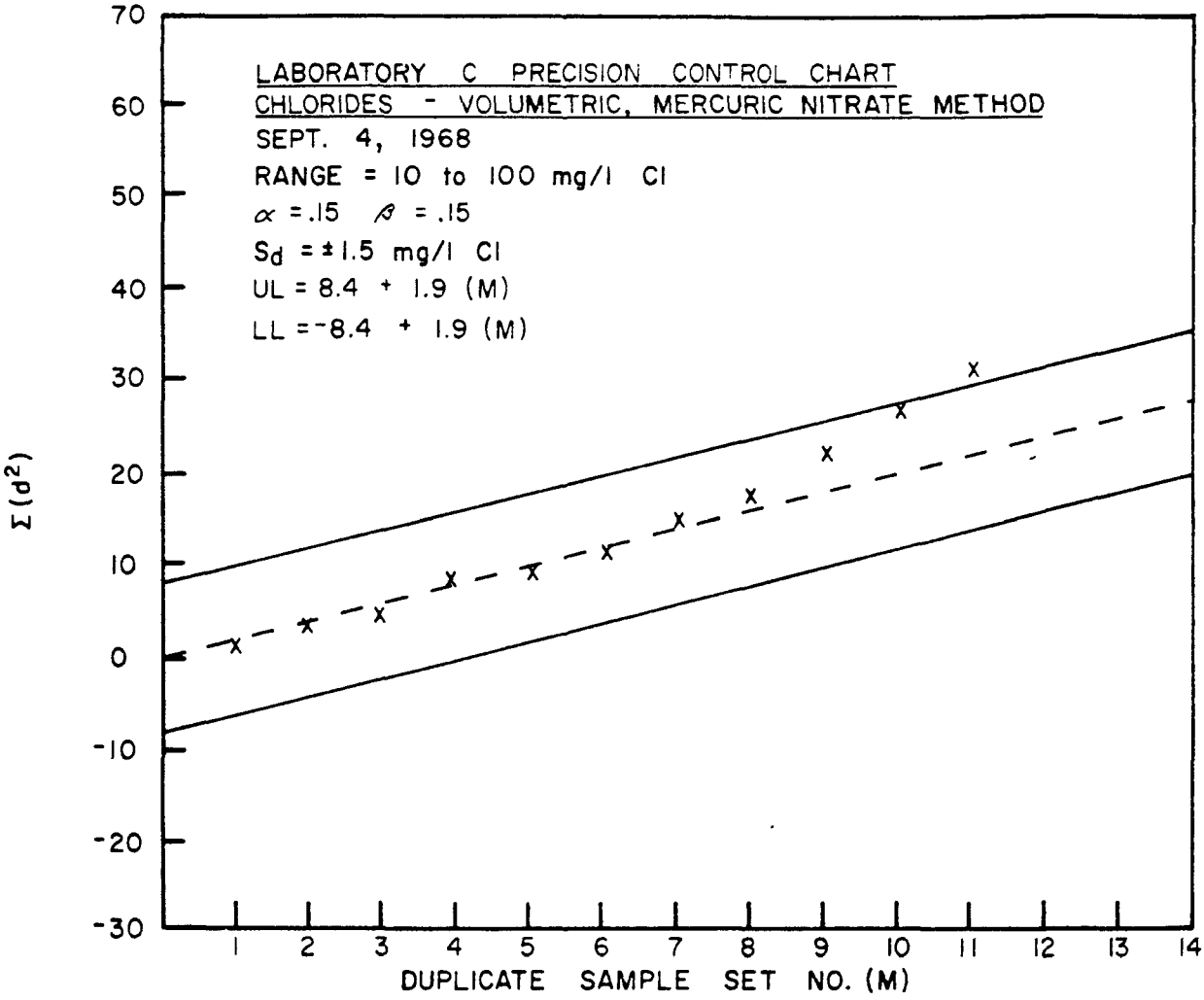
OUT OF CONTROL ON UPPER LIMIT



CORRECTIVE PROCEDURES:

1. STOP ANALYSIS AT SAMPLE SET 13
2. LOCATE CAUSE OR ASSUME CHANCE CAUSES
3. CORRECT PROBLEM IF POSSIBLE
4. SAMPLES CANNOT BE RERUN ON B.O.D. - REJECT ALL DATA BETWEEN SAMPLE SETS 12 & 13
5. IF DUPLICATES ARE RUN ON ALL SAMPLES - REJECT SAMPLE SET 13
6. BEGIN PLOTTING $\Sigma(d^2)$ AT SAMPLE SET 1

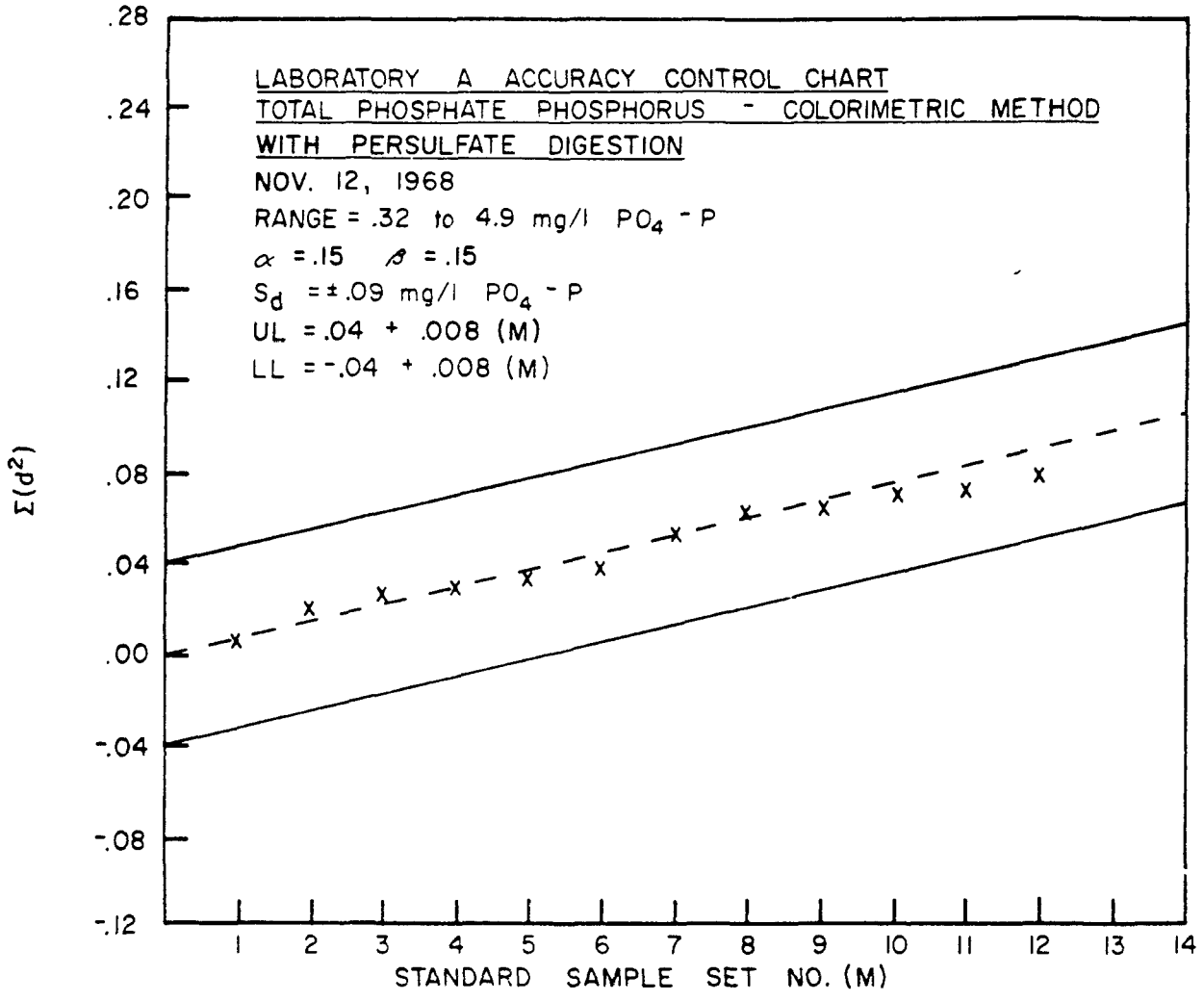
OUT OF CONTROL ON UPPER LIMIT



CORRECTIVE PROCEDURES :

1. ANALYSIS COULD HAVE BEEN STOPPED AT SAMPLE SET 9 OR 10
2. ANALYSIS DEFINITLY STOPPED AT SAMPLE SET 11
3. LOCATE CAUSE
4. CORRECT PROBLEM
5. IF ANALYSIS STOPPED AT SAMPLE SET 9 - RERUN SAMPLES BETWEEN SAMPLE SETS 8 & 9
6. IF ANALYSIS STOPPED AT SAMPLE SET 10 - RERUN SAMPLES BETWEEN SAMPLE SETS 9 & 10
7. IF ANALYSIS STOPPED AT SAMPLE SET 11 - RERUN SAMPLES BETWEEN SAMPLE SETS 10 & 11
8. IN ANY CASE BEGIN PLOTTING $\Sigma(d^2)$ AT SAMPLE SET 1

OUT OF CONTROL ON UPPER LIMIT
(CONTINUOUS ERROR TREND)

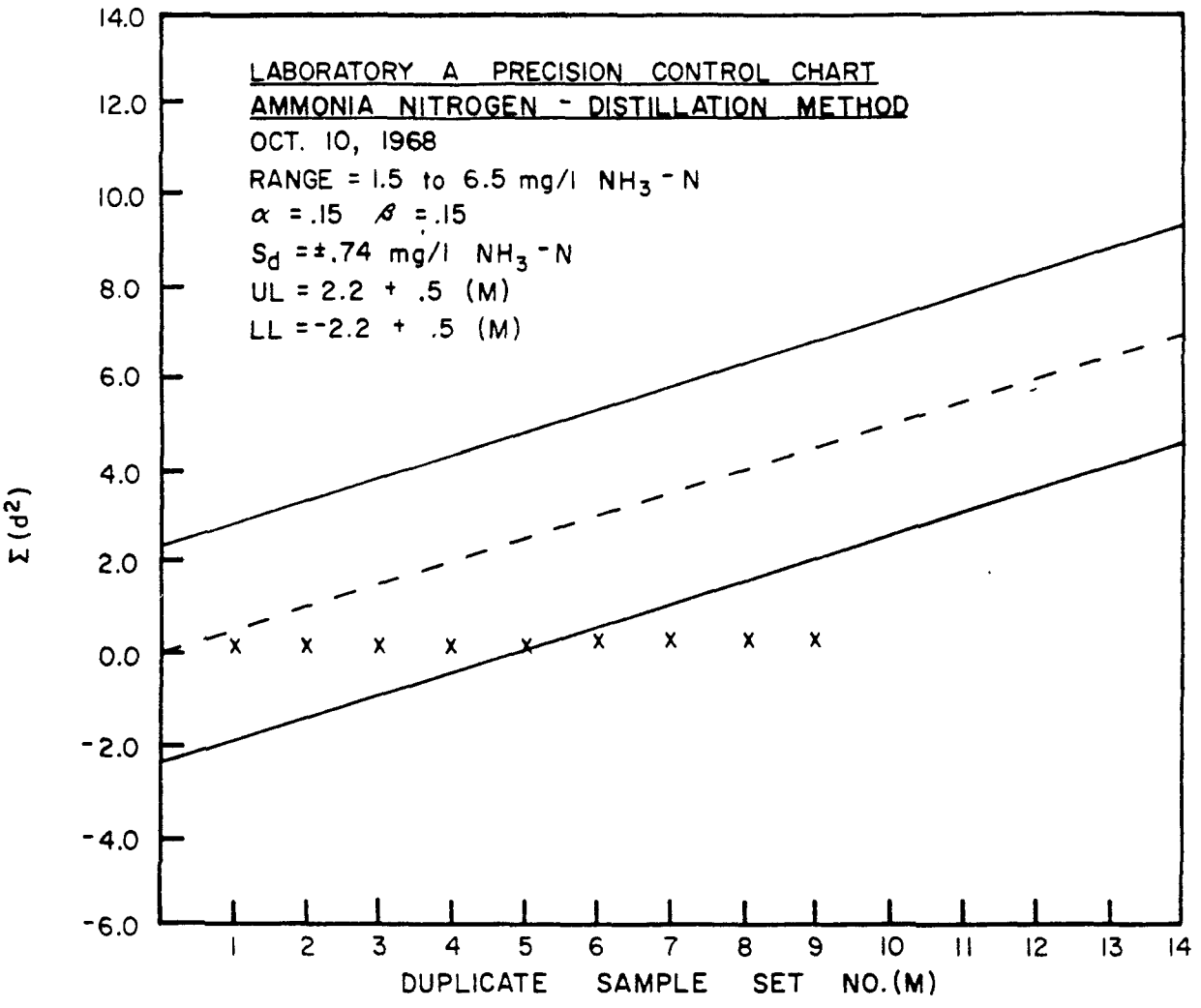


CORRECTIVE PROCEDURES:

1. NO PROBLEMS

2. CONTINUE ANALYSIS

IN CONTROL

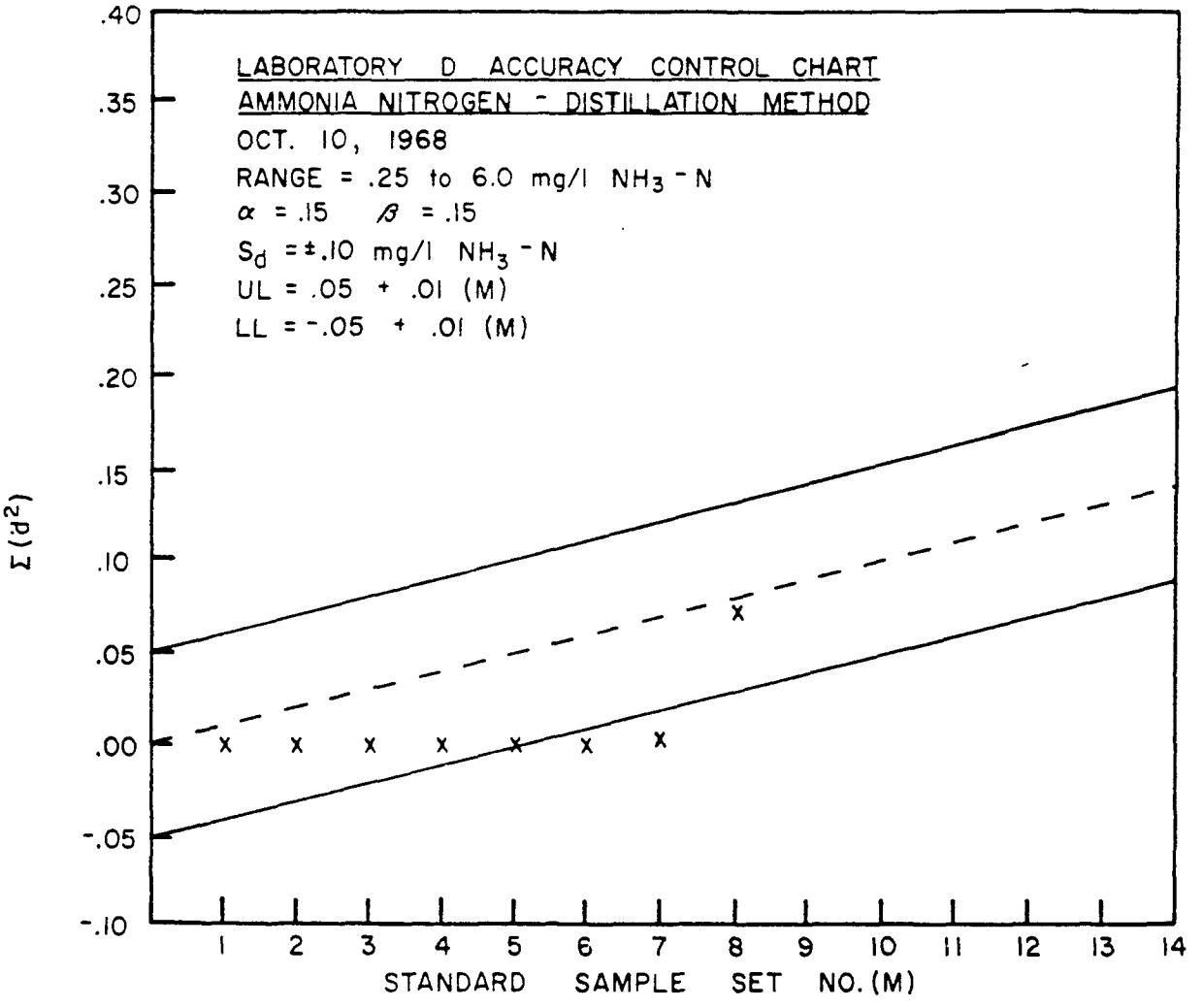


CORRECTIVE PROCEDURES:

1. CONTINUE ANALYSIS BEYOND SAMPLE SET 6 THROUGH SERIES OF SAMPLES UNLESS TREND CHANGES
2. ASSUME INCREASED EFFICIENCY
3. CONSTRUCT NEW CHART ON RECENT DATA
4. BEGIN PLOTTING $\Sigma(d^2)$ AT SAMPLE SET 1
5. OBSERVE ANALYST FOR FALSE REPORTING

OUT OF CONTROL ON LOWER LIMIT

(CONTINUOUS TREND)

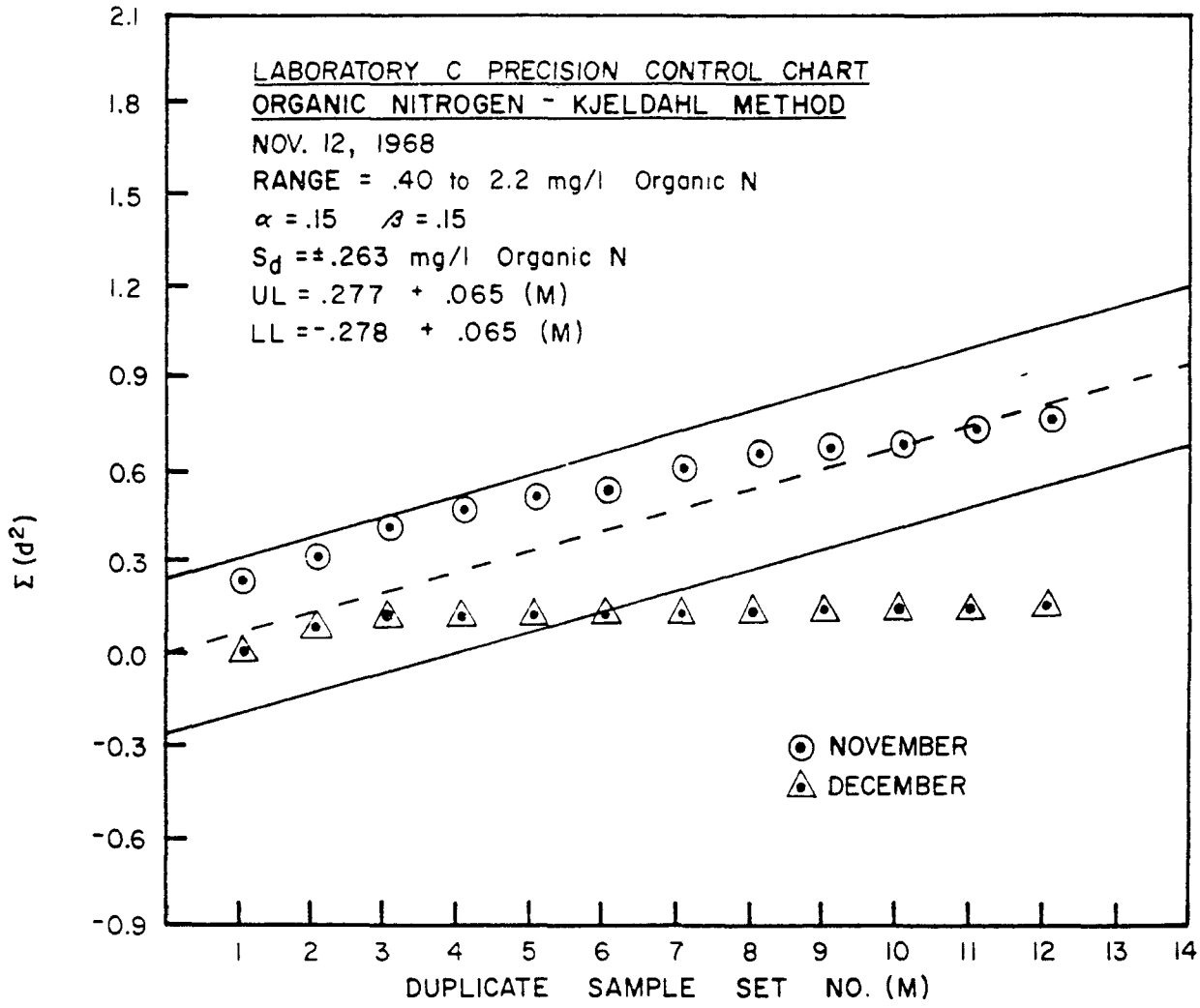


CORRECTIVE PROCEDURES:

1. STOP CHARTING AT SAMPLE SET 8
2. BEGIN NEW CHART BY PLOTTING $\Sigma(d^2)$ OF SAMPLE SET 8 AT SAMPLE SET 1
3. OBSERVE OPERATIONS FOR POSSIBLE PROBLEMS
4. CONTINUE ANALYSIS WITH CAUTION

OUT OF CONTROL ON LOWER LIMIT

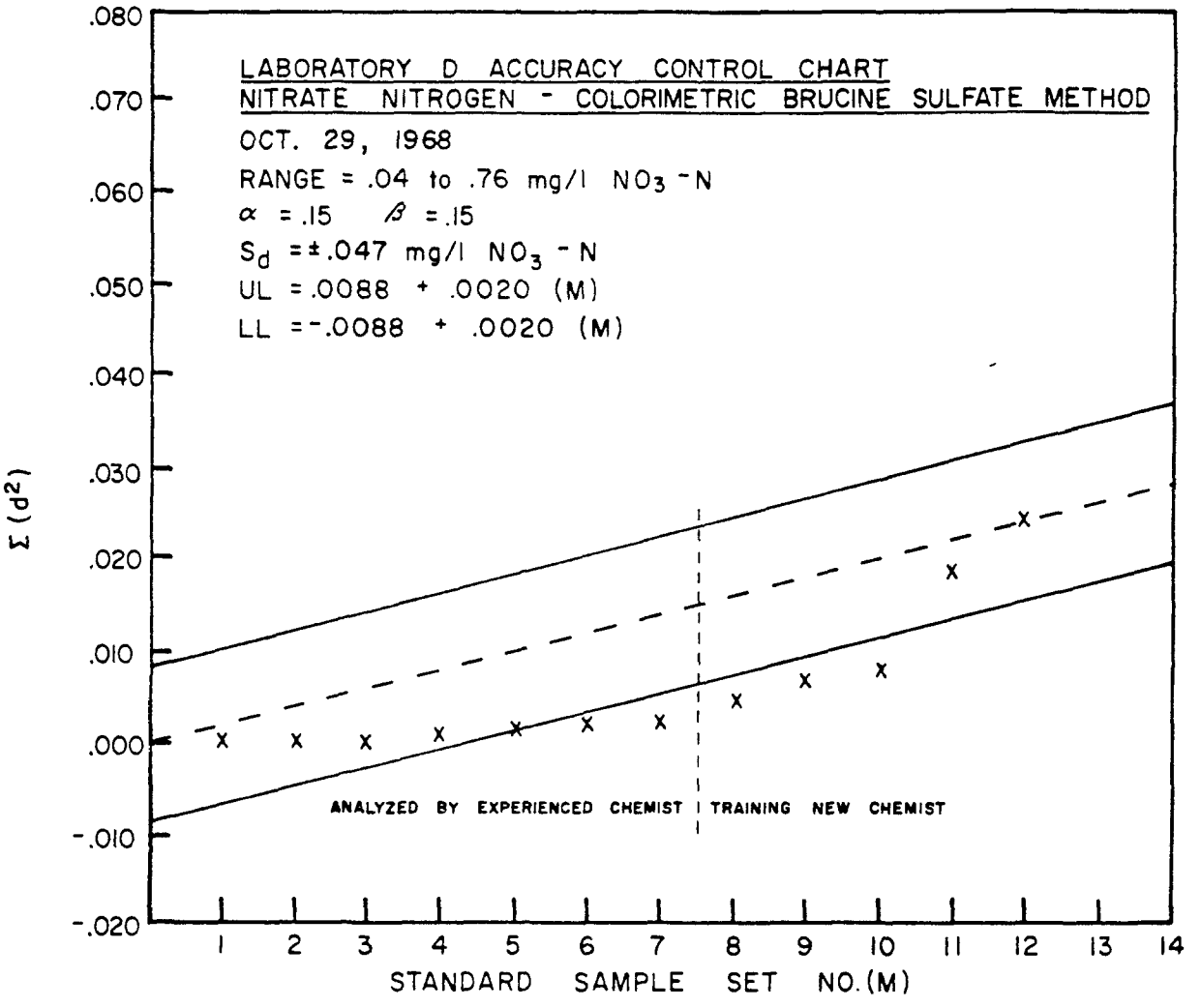
(CHANGE OF TREND)



CORRECTIVE PROCEDURES:

1. NOVEMBER DATA IN CONTROL
2. DECEMBER DATA PLOTTED ON SAME CHART
3. CONTINUE ANALYSIS BEYOND SAMPLE SET 6 THROUGH DECEMBER SAMPLES
4. CONSTRUCT NEW CHART ON RECENT DATA
5. PLOT $\Sigma(d^2)$ ON NEW CHART FOR JANUARY SAMPLES

OUT OF CONTROL ON LOWER LIMIT
(INCREASED EFFICIENCY)



CORRECTIVE PROCEDURES:

1. SAMPLES 1 THROUGH 7 ANALYZED BY EXPERIENCED CHEMIST
2. TRAINING OF INEXPERIENCED CHEMIST BEGAN AT SAMPLE SET 8
3. TRAINING CONTINUED THROUGH SAMPLE SET 11
4. INEXPERIENCED CHEMIST TOOK COMPLETE CONTROL ON SAMPLE SET 12

EFFECT OF TRAINING ON CONTROL CHARTS

OPERATING

CONTROL CHARTS

DATA CARD AND MASTER LOG SYSTEM

An analytical laboratory must have an orderly and efficient system of handling data. This insures the legal defensibility and validity of the data produced in the laboratory. The FWPCA has successfully used such a system over the past several years. Referred to as the data card and master log system, it is composed of two parts:

1. The data cards for recording all raw data and computations made by the analyst
2. The master log for recording a summary of validated data.

The data cards have a consecutive serial number for each parameter being analyzed. All cards are issued by the laboratory supervisor and are accountable. The entire operation of arriving at a value through the various methods of analyses and mathematical calculations is recorded directly on the data cards, step-by-step. The analyst is not to recopy raw data from any other source onto the cards. To insure permanency of these raw data, permanent ink should be used on the data cards. Completed data cards are to be returned to the laboratory supervisor for data validation.

The master log is a bound book with pages arranged in original and tear-out copy order. Page sets are numbered consecutively. The laboratory supervisor records the validated data in the master log

book. Upon completion of a page in the data book, the tear-out copy page is removed and used as a working data sheet by the project director.

Upon completion of a project the numbered data cards and master log book are stored together for safe keeping and future referral.

ILLUSTRATIONS

of

DATA CARDS

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SAMPLE SOURCE (1) DETERMINATION (4)

METHOD (5)

ANALYST (2) REFERENCE (6)

DATA VALIDATED BY: (3)

DATE ANAL.	SAMPLE NUMBER	ALIQUOT	O.D. or %TRANS.		Mg./ALIQUOT		FACTOR	Mg/l	µg/l
(7)	(8)	(9)	(10)		(11)	(12)	(13)	(14)	(15)

KRC-27 RECORD OF COLORIMETRIC DATA

Key to Annotated Items:

Place in this space

(1) The name of the project or the precise location where sample was collected

(2) The signature of the person analyzing the sample

(3) The signature of person validating data

(4) The parameter being analyzed

(5) The name of the analytical method being used to analyze the sample

(6) The name of the publication that lists the method being used in the analysis of the sample, such as *Standard Methods*, 12th edition, 1965

(7) The date the analysis was performed

(8) The number assigned to the individual sample

(9) The number ml. used in the analysis

(10) The optical density or the % transmittance of the sample on a spectrophotometer

(11) The value of the reading from item (10) taken from a standard curve

(12) Blank space to be used at the analyst's discretion

(13) A number arrived at by dividing the number of ml. of sample used in the analysis, into the total number of ml. of liquid required for the analysis, "the dilution factor"

(14) The value obtained by multiplying item (11) times item (13)

(15) The final value in micrograms/liter if desired

SAMPLE SOURCE Big Chemical Co. Outfall

DETERMINATION NO_3-N 00000

METHOD Modified Brucine

ANALYST Jim Bean

REFERENCE EPA Official Method

DATA VALIDATED BY: Charles Hartman

DATE	SAMPLE NUMBER	ALIQUOT	O.D. or %TRANS.		Mg./ALIQUOT		FACTOR	Mg/l	ug/l
3-16-65	S-1	16ml	.266		2.31		1	2.3	
"	S-2	1ml	.215		2.40		10	24.0	
"	S-3	5ml	.166		1.30		2	2.6	

KRC-27 RECORD OF COLORIMETRIC DATA

SAMPLE SOURCE

(1)

ANALYST (2)

DATA VALIDATED BY: (3)

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DATE	SAMPLE NUMBER								
(4)	(5)	(6)							

RECORD OF MISC. SAMPLE DATA

KRC-25
October, 1968

Key to Annotated Items Above:

Place in this space

(1) The name of the project or the particular location where sample was collected

(2) The signature of the person analyzing the sample

(3) The signature of the person validating data

(4) The date the sample was analyzed

(5) The number assigned to the individual sample

(6) The parameter being analyzed

SAMPLE SOURCE
SALT CREEK PROJECT

ANALYST Ann Bond

DATA VALIDATED BY: [illegible]

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DATE	SAMPLE NUMBER	pH	SPECIFIC CONDUCTANCE						
5-10-68	S-1	7.2	7400						
"	S-2	7.3	7,000						
"	S-3	4.5	10,000						

RECORD OF MISC. SAMPLE DATA

KRC-25
October, 1968

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Sample Source (1) Determination (4)

Method (5)

Analyst (2) Reference (6)

Calculation (3) Data Validated By: (7)

Date	Sample Number	Aliquot	Flask Number	Titer	Blank Correction	Corrected Titer	Factor	Mg./L	
(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	

DETERMINATION OF VOLUMETRIC TITRATION

KRC-29
Sept. 1967

Key to Annotated Items Above:

Place in this space

(1) The name of the project or the particular location where sample was collected

(2) The signature of the person analyzing the sample

(3) A brief formula of the method used to obtain the final mg/l in item 16

(4) The parameter being analyzed

(5) The name of the analytical method used to analyze the sample

(6) The name of the publication that lists the analytical method being used

(7) The name of the person validating the data

(8) The date the sample was analyzed

(9) The number assigned to the individual sample

(10) The number of ml. used in the analysis

(11) The number of the flask or etc. used to titrate the sample

(12) The number of ml. of titrant used in titrating the sample

(13) The number of ml. used to obtain an end point of a blank

(14) The value obtained by subtracting item (13) from item (12)

(15) A number obtained by dividing the number of ml. of sample used in the analysis into the total number of ml. of liquid used in the analysis, "the dilution factor"

(16) The value obtained by multiplying item (14) by item (15)

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Sample Source JONES CREEK AT HWY 92

Determination CHLORIDE

Method MERCURIC NITRATE

Analyst Jos. Smith

Reference EPA OFFICAL METHOD

Calculation $Cl^- = (TITER - BLANK) \times 5$

Data Validated By:

Date	Sample Number	Aliquot	Flask Number	Titer	Blank Correction	Corrected Titer	Factor	Mg./L
66 10-10	S-1	100 ml.	1	5.10	.10	5.00	5	25
	S-2	50 ml.	8	9.15	.10	9.05	10	91
	S-3	.5 ml	13	6.10	.10	6.00	1000	6000

DETERMINATION OF VOLUMETRIC TITRATION

KRC-29
Sept. 1967

KRC--26
June 1967

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SOLIDS DETERMINATION

Sample Source (1) Date (3)

Analyst (4)

Data Validated By: (2)

SAMPLE	(5)			
VOLUME ml	(6)			
DISH NUMBER	(7)			
GROSS WEIGHT gm	(8)			
ASHED WEIGHT gm	(9)			
TARE WEIGHT gm	(10)			
RESIDUE gm	(11)			
VOLATILE RESIDUE gm	(12)			
FACTOR	(13)			
TOTAL S. SOLID Mg/l	(14)			
T. SUSPENDED VOLATILE SOLIDS Mg/l	(15)			
TOTAL SOLID Mg/l	(16)			
T. VOLATILE SOLIDS Mg/l	(17)			
TOTAL D. SOLID Mg/l	(18)			

Key to Annotated Items on the Solids Card:

Place in this space

(1) The name of the project or the particular location where sample was collected

(2) The name of the person validating the data

(3) The date the sample was analyzed

(4) The signature of person analyzing the sample

(5) The number assigned to the individual sample

(6) The number of ml. used in the analysis

(7) The number of the container used for the analysis

(8) The weight of the container plus the residue remaining after drying treatment

(9) The weight of the container plus the residue remaining after the 600°C heat treatment

(10) The original dry weight of the container

(11) The value obtained by subtracting item (10) from item (8)

(12) The value obtained by subtracting item (9) from item (8)

(13) The value obtained by the formula $\frac{1000}{\text{Item (6)}} \times 1000$

(14) The value obtained by multiplying item (13) times item (11) if total suspended solids are analyzed

(15) The value obtained by multiplying item (13) times item (12) if total suspended volatile solids are analyzed

(16) The value obtained by multiplying item (13) times item (11) if total solids are analyzed

(17) The value obtained by multiplying item (13) times item (12) if total volatile solids are analyzed

(18) The value obtained by subtracting item (14) from item (16)

KRC-26
June 1967

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SOLIDS DETERMINATION

Sample Source BLUE RIVER PROJECT Date 3-6-59
Analyst Sam Jones
Data Validated By: [illegible]

SAMPLE	S-1	S-2	S-3	
VOLUME ml	10	25	100	
DISH NUMBER	8	17	3	
GROSS WEIGHT gm	23.4010	23.9210	22.1783	
ASHED WEIGHT gm	23.3[illegible]10	23.9210	22.1000	
TARE WEIGHT gm	23.3000	23.5110	22.1000	
RESIDUE gm	.1010	.4100	.0783	
VOLATILE RESIDUE gm	.1000	.0000	.0783	
FACTOR	100,000	40,000	10,000	
TOTAL S. SOLID Mg/l				
T. SUSPENDED VOLATILE SOLIDS Mg/l				
TOTAL SOLID Mg/l	10,100	16,400	783	
T. VOLATILE SOLIDS Mg/l	10,000	0	783	
TOTAL D. SOLID Mg/l				

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Rev.
KRC-28
Mar. 1968 **BIOCHEMICAL OXYGEN DEMAND AT 20°C**

SAMPLE SOURCE (1) DATE (3)
ANALYST (4)
DATA VALIDATED BY: (2)

SAMPLE	(5)					
% CONCENTRATION	(6)					
DAYS INCUBATED	(7)					
TIME	(8)					
BOTTLE #	(9)					
DISSOLVED OXYGEN INITIAL	(10)					
BOTTLE #	(11)					
DISSOLVED OXYGEN FINAL	(12)					
	(13)					
ACTUAL DEPLETION	(14)					
BLANK CORRECTION	(15)					
CORRECTED DEPLETION	(16)					
DILUTION FACTOR	(17)					
B.O.D. mg/l	(18)					
B.O.D. mg/l	(19)					

Key to Annotated Items on Biochemical Oxygen Demand Card:

Place in this space

(1) The name of the project or the particular location the sample was collected

(2) The name of the person validating the data

(3) The date the BOD was set up

(4) The signature of the person analyzing the sample

(5) The number assigned to the individual sample

(6) The % dilution of the sample

(7) The number of days the sample incubated

(8) The time the BOD was set up

(9) The bottle number of the initial DO

(10) The value of the initial DO in mg/l

(11) The bottle numbers of the two samples to be incubated

(12) The final DO value of the two incubated bottles

(13) The average of the values in item (12)

(14) The value obtained by subtracting the value of item (13) from item (10)

(15) The seed correction value. Used only when the sample was seeded

(16) The value obtained by subtracting item (15) from item (14)

(17) The value obtained by dividing the % sample used into 100%

(18) The value obtained by multiplying item (17) by item (18)

(19) The BOD value to be reported

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KRC-28

July 12, 1968 BIOCHEMICAL OXYGEN DEMAND AT 20°C

Sample Source JUMPER CREEK PROJECT Date 5-10-68

Analyst Joe Doe

Date Validated By:

SAMPLE	S-1	S-1	S-1	S-2	S-2	S-2
% CONCENTRATION	100	50	25	50	25	10
DAYS INCUBATED	5	5	5	5	5	5
TIME	2:00 PM →					
BOTTLE NUMBER	341	346	348	410	315	118
DISSOLVED OXYGEN INITIAL	8.15	8.10	8.20	7.95	7.90	8.70
BOTTLE NUMBER	320 / 311	301 / 302	111 / 62	13 / 195	25 / 1	300 / 358
DISSOLVED OXYGEN FINAL	1.53 / 1.01	4.55 / 4.65	6.45 / 6.45	.50 / .61	2.54 / 2.61	6.45 / 6.55
	1.02	4.60	6.45	—	2.60	6.50
ACTUAL DEPLETION	7.13	3.50	1.75	—	5.30	2.20
BLANK CORRECTION	—	—	—	—	—	—
CORRECTED DEPLETION	7.13	3.50	1.75		5.30	2.20
DILUTION FACTOR	1	2	4		4	10
B.O.D. Mg/L	7.13	7.00	7.00		21.2	22.0
B.O.D. Mg/L	7				21	

Card #1

SAMPLE SOURCE (1) DETERMINATION Metals

ANALYST (2) METHOD (4)

Data Validated by: (3) Concentrations expressed in µg/l or mg/l (5)

Date Anal.	Samp. No.	Fact.	As	Be	Ca	Co	K	Li	Mg	NA	Se	Tl	V	Sb
(6)	(7)	(8)	(9)											

Card #2

SAMPLE SOURCE (1) DETERMINATION Metals

ANALYST (2) METHOD (4)

Data Validated by: (3) Concentrations expressed in µg/l or mg/l (5)

Date Anal.	Samp. No.	Fact.	Zn	Cd	B	Fe	Mo	Sn	Mn	Cu	Ag	Ni	Al	Pb	Cr	Ba	Sr
(6)	(7)	(8)	(9)														

RECORD OF METALS ANALYSES

Card # 2 can be used alone or as a continuation for Card # 1

Key to Annotated Items on Record of Metals Analyses:

Place in this space

(1) The name of the project or the precise location where sample was collected

(2) The signature/s of the person/s analyzing the sample/s

(3) The signature of the person validating data

(4) The method used to analyze the sample/s

(5) Indicate the unit in which concentrations are expressed

(6) Date of analyses

(7) The sample number or code

(8) The sample dilution or concentration record

(9) The element analyzed

Card #1

SAMPLE SOURCE STATE RIVER — DETERMINATION Metals
ANALYST Jim Smith — METHOD Atomic Absorption
Data Validated by: Mike Riley — Concentrations expressed in (µg/l) or mg/l

Date Anal.	Samp. No.	Fact.	As	Be	Ca	Co	K	Li	Mg	NA	Se	Tl	V	Sb
5-3-71	AKC-2	1		.13	1.45				4.23	6.93				

Card #2

SAMPLE SOURCE STATE RIVER — DETERMINATION Metals
ANALYST Jim Smith — METHOD Atomic Absorption
Data Validated by: Mike Riley — Concentrations expressed in (µg/l) or mg/l

Date Anal.	Samp. No.	Fact.	Zn	Cd	B	Fe	Mo	Sn	Mn	Cu	Ag	Ni	Al	Pb	Cr	Ba	Sr
5-3-71	AKC-2	1								1.60					3.16		

RECORD OF METALS ANALYSES

Card # 2 can be used alone or as a continuation for Card # 1

LABORATORY SCHEDULE AND DATA RECORD

The "Laboratory Schedule and Data Record" as illustrated in Figure 1 consists of an original and three copies of NCR paper. It serves a twofold purpose:

(1) It lists the parameters that the laboratory is requested to analyze.

(2) It serves as a permanent record for the data, listing all pertinent information about each sample/s.

The "Schedule" is completed by the person/s requesting analytical services, and is delivered to the laboratory with the samples. After the laboratory personnel validate the data on the data cards, the data are transferred to the "Schedule" and forwarded to the chief of the laboratory for a final review. Upon his approval the original is filed in the "Master Data Log". The first copy is forwarded to the person who requested the analytical services; the second copy is forwarded to STORET (if applicable); the third copy is retained by the person requesting the data when he delivered the samples to the laboratory.

LABORATORY SCHEDULE AND DATA RECORD

ENVIRONMENTAL PROTECTION AGENCY
TECHNICAL SUPPORT BRANCH
ROBERT S. KERR RESEARCH CENTER

PROJECT NAME (1) SAMPLES COLLECTED BY (3)

SAMPLES RECEIVED AT LABORATORY BY (2) DATA REVIEWED BY (4) DATE (5)

CODE NUMBER	(6)										
STATION DESCRIPTION	(7)										
COLLECTION DATE	(8)										
TIME	(9)										
LAB ARRIVAL DATE	(10)										
LATITUDE (11)	° ' "	° ' "	° ' "	° ' "	° ' "	° ' "	° ' "	° ' "	° ' "	° ' "	° ' "
LONGITUDE	° ' "	° ' "	° ' "	° ' "	° ' "	° ' "	° ' "	° ' "	° ' "	° ' "	° ' "
(12)	(13) (14)										

ALL RESULTS IN mg/l UNLESS OTHERWISE INDICATED — COLOR & pH IN UNITS — TURBIDITY IN ... — SPECIFIC CONDUCTANCE IN µmhos/cm

Key to Annotated Items:

Place in this space

(1) The name of the project or the precise location where the sample was collected

(2) Signature of the person who received the sample/s in the laboratory

(3) The signature/s of the person/s who collected the sample/s

(4) The signature of the person making the final review of the data

(5) The date of the final data review

(6) The code or number assigned to the sample/s

(7) A precise description of where the sample was collected

(8) The date the sample was collected

(9) The time the sample was collected

(10) The date the sample arrived in the laboratory

(11) The latitude and longitude of the sampling point (if desired)

(12) The name of the parameter to be analyzed

(13) A check mark if it is desired that this sample be analyzed for this parameter

(14) The value of the analysis for this parameter

LABORATORY SCHEDULE AND DATA RECORD

ENVIRONMENTAL PROTECTION AGENCY
TECHNICAL SUPPORT BRANCH
ROBERT S KERR RESEARCH CENTER

PROJECT NAME Big River SAMPLES COLLECTED BY Jim Smith, Joe Jones

SAMPLES RECEIVED AT LABORATORY BY Kel Dahl DATA REVIEWED BY Jhon Joe DATE 10-03-71

CODE NUMBER	BR 1	BR 2	BR 3	BR 4	BR4-A	BR 5	BR 6
STATION DESCRIPTION	River Mile 14. Hy Brdg on 76	River Mile 17. 1/2 mi below dam	River mile 18. 1/4 mi below Good Creek	River mile 25. Oil Refinery Eff #1	River Mile 25.1, oil refinery Effluent #2	River Mile 30. Hy Brdg on 31	River Mile 35
COLLECTION DATE	10-01-71	10-01-71	10-01-71	10-01-71	10-01-71	10-01-71	10-01-71
TIME	0900	0930	0945	1015	1020	1050	1120
LAB ARRIVAL DATE	10-01-71	10-01-71	10-01-71	10-01-71	10-01-71	10-01-71	10-01-71
LATITUDE	° ' "	° ' "	° ' "	° ' "	° ' "	° ' "	° ' "
LONGITUDE	° ' "	° ' "	° ' "	° ' "	° ' "	° ' "	° ' "
TOC	✓ 10.3	✓ 9.6	✓ 10.4	✓ 34.6	✓ 36.3	✓ 11.9	✓ 11.6
COD	✓ 61	✓ 62	✓ 59	✓ 112	✓ 110	✓ 71	✓ 70
Org-N	✓ .63	✓ .54	✓ .51	✓ 5.1	✓ 2.3	✓ .57	✓ .69
NH_3-N	✓ .31	✓ .35	✓ .32	✓ 5.3	✓ 5.9	✓ .53	✓ .49
NO_3-N	✓ 10	✓ .11	✓ .11	✓ .38	✓ .26	✓ .13	✓ .11

ALL RESULTS IN mg/l UNLESS OTHERWISE INDICATED — COLOR & pH IN UNITS — TURBIDITY IN JTU — SPECIFIC CONDUCTANCE IN μmhos/cm

ADDENDA SHEET

TO THE PUBLICATION:

"AN ANALYTICAL QUALITY CONTROL PROGRAM FOR EFFICIENT LABORATORY MANAGEMENT"

The following paper, "An Analytical Quality Control Program for Efficient Laboratory Management," was written for presentation at the 20th Annual Oklahoma Industrial Waste and Pollution Control Conference, Oklahoma State University, Stillwater, Oklahoma, March 31-April 1, 1969. It should be noted that several name and title changes have occurred since the paper was published in 1969:

Federal Water Pollution Control Administration, U. S. Department of the Interior is now the U. S. Environmental Protection Agency;

Mr. R. E. Crowe is now attached to the Research and Development Program, U. S. Environmental Protection Agency, Washington, D.C.

Dr. R. Harkins is now Mathematical Statistician, Ada Facility, Surveillance and Analysis Division, U. S. Environmental Protection Agency, Ada, Oklahoma;

Mr. J. Kingery is now Mathematical Statistician, Ada Facility, Surveillance and Analysis Division, U. S. Environmental Protection Agency, Ada, Oklahoma, and

Mr. B. G. Benefield is now Chemist, Ada Facility, Surveillance and Analysis Division, U. S. Environmental Protection Agency, Ada, Oklahoma.

AN ANALYTICAL QUALITY CONTROL PROGRAM FOR EFFICIENT LABORATORY MANAGEMENT*

by

R. E. Crowe, R. Harkins, J. Kingery, and B. G. Benefield**

Introduction

Quality control procedures in general have been used since man began his thinking process. Galileo, in his experiments to determine the surface tensions of liquids, gave detailed instructions for obtaining a consistent set of results (1). The artisan guilds of the Middle Ages prescribed extended apprenticeships before a person was considered a master craftsman. This training maintained a level of competence within the guild (2). Dr. A. Shewhart of Bell Telephone Laboratories developed the basic theory of control charts in the 1920s (3). This was the beginning of industrial use and acceptance of these and other statistical techniques to measure the quality of products of a manufacturing process. The development of these techniques in industry led to their limited use in the analytical laboratory (4).

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* A paper scheduled for presentation at the 20th Annual Oklahoma Industrial Waste and Pollution Control Conference, Oklahoma State University, Stillwater, March 31-April 1, 1969.

** Respectively, Chief, Chemistry and Biology Section, Technical Assistance, Technical Services Program; Acting Chief, Pollution Surveillance, Technical Services Program; Mathematical Statistician, Pollution Surveillance, Technical Services Program; and Chemist, Chemistry and Biology Section, Technical Assistance, Technical Services Program, all of the Robert S. Kerr Water Research Center, Federal Water Pollution Control Administration, U. S. Department of the Interior, Ada, Oklahoma.

Although laboratory operations are not considered to be manufacturing processes, it can be recognized that the analytical data produced by any laboratory are, in actuality, the products of that process. As with industry, a quality control program should be employed in the laboratory to insure the quality of its products, which in turn, characterize the normal laboratory operations, and detect abnormal operations when they occur. This paper presents one such program for consideration as a tool in characterizing a laboratory's operations and maintaining quality control in the laboratory.

Laboratory "Fingerprint"

Anyone who has worked in, supervised, or managed the operations of an analytical laboratory is well aware of the basic tools for determining quality of data produced. These tools are duplicate sample analyses and spiked or standard sample analyses. These have been used to indicate the precision and accuracy of the process producing the data.

Those who have used these tools recognize the difficulty involved in making a decision as to the validity of the data produced based on duplicate and spiked or standard sample analyses. The common practice has been to visually observe the data and arbitrarily judge their acceptability with no concrete basis for the decision. Obviously, it would be advantageous to have a so-called "fingerprint" of the precision and accuracy for the normal operations of a specific laboratory group for the analysis of a specific parameter.

"Fingerprints" of this nature can tell us many things about the laboratory's operations. For example, they could tell us when problems exist with the analysts, reagents, glassware, instruments, etc. They could indicate whether the laboratory is operating normally or abnormally, thus pointing out when data generated should be accepted, questioned, or rejected. In addition, they could tell us when the laboratory is operating at optimum efficiency. As with industry, the laboratory sometimes generates products which are not acceptable. In these cases, samples must be analyzed again to produce acceptable results. These "fingerprints" could help us determine which samples or sets of samples should be reanalyzed.

The laboratory "fingerprints" we refer to are in the form of control charts. The construction and use of such charts are discussed below.

Construction of Control Charts

As we have indicated, two control charts are required to "fingerprint" the laboratory operations for a given analytical procedure. These are referred to as precision and accuracy control charts. Precision control charts are constructed from duplicate sample analyses data; accuracy control charts are constructed from spiked or standard sample analyses data. A set of the two represents, and is restricted to, a specific laboratory, group of analysts, analytical method, range of concentration and period of time. To construct the precision and accuracy control charts, it is necessary to obtain several sets of duplicate and spiked

or standard sample data. The greater the number of sets of initial data obtained, the better the "fingerprint" of the laboratory operations. Economics must be considered, however, in obtaining the initial sets of data. It is recommended that at least 20 sets of duplicate and 20 sets of spiked sample data from an in-control process be used to initially construct the control charts. The selection of in-control data can be a judgment decision or, if desired, extreme values can be systematically eliminated by the Dixon and Massey method (5) of processing data for extreme values.

The initial sets of data must be obtained under the following conditions:

1. Normal laboratory operations
2. Constant analyst or group of analysts
3. Consistent method
4. Narrow range of concentration of the parameter analyzed.

The reasons for the first three conditions are obvious; number 4 needs more explanation.

The precision and accuracy of the analyses for many parameters are proportional to the concentration of the parameter to be measured. This may require the use of several control charts in varying ranges of concentrations for a given parameter. Only experience will dictate this. It is important to note here that there is complete control over the range of concentration of spiked samples or standard samples, but little

or no control over the range of concentration of the duplicate samples.

It is important also to point out the basic differences between a spiked and a standard sample. These terms have been used synonymously at times in the discussion of accuracy data; however, the two differ greatly. A spiked sample can be defined as an environmental sample to which has been added or "spiked" a known quantity of that parameter already present in the sample in significant concentrations. The environmental sample obviously must be analyzed before as well as after the "spiking" of the sample. Spiked samples should be used in situations where knowledge is insufficient as to the interferences of the method or of the environment from which the sample was obtained. This situation might also necessitate a complete and independent study of the interferences.

A standard sample can be defined as one prepared by adding a known concentration of a given parameter to distilled water. The sample should then be analyzed identically to the environmental samples. A standard sample can be used in situations where the interferences of the method with the environment are sufficiently known. In other words, a standard sample can be used where interferences of the method are not questioned, and the assumption made that interferences are absent. A standard sample has the inherent disadvantage of unusual appearance, so that the analyst is aware of its introduction into a series of environmental samples. This could create bias in the results.

The control charts are derived from three basic calculations. No attempt is made here to develop the mathematics upon which the control charts are based. However, references are given so that those who wish to delve more deeply into the subject may do so (6).

These basic calculations are:

1. Standard deviation of the differences between duplicates, or in the case of spiked or standard samples, between the known quantity and the quantity obtained.
2. The upper control limit
3. The lower control limit.

Prior to these calculations, two decisions must be made:

1. The α and β levels
2. The allowable variability levels

By definition, α is the probability of judging the process to be out-of-control, when in fact, it is in-control. It is recommended that α be chosen to lie within the boundaries of .05 and .15; that is, the laboratory personnel are willing to stop the laboratory process somewhere between 5 and 15 percent of the time, judging it to be out-of-control, when in fact, it is in-control. If the cost of examining a process to determine the reason or reasons for being out-of-control is considerable, then it may be desirable to choose a low α. Likewise, if the cost is negligible, it may be desirable to choose a larger α value and thus stop the process more frequently.

On the other hand, β is defined as the probability of judging the process to be in-control when it is not. Again, it is recommended that β be chosen to lie between the values of .05 and .15; thus, the laboratory personnel are willing to accept out-of-control data somewhere between 5 and 15 percent of the time. The economic considerations used in choosing α also apply in choosing β. The effects of varying α and β are demonstrated in Figure 1.

It is also essential to set maximum and minimum allowable variability levels. It is necessary to specify a value for the minimum and maximum amount of variation that will be allowable in the system. These minimum and maximum amounts are referred to as σ_o^2 and σ_1^2 respectively. The values used should be based on a knowledge of the variation in the procedure under consideration. However, if no such knowledge is available, the values may be arbitrarily set at $\sigma_o^2 = (\sigma - .20\sigma)^2$ and $\sigma_1^2 = (\sigma + .20\sigma)^2$.

$$S_d^2 = \frac{\sum_{i=1}^{n} di^2 - \frac{\left(\sum_{i}^{n} di\right)^2}{N}}{N - 1} = \text{Variance of the differences}$$

$$S_d = \sqrt{S_d^2} = \text{Standard deviation of the differences} \qquad (1)$$

$$S_o^2 = (.8S_d)^2 \text{ estimates } \sigma_o^2$$

$$S_1^2 = (1.2S_d)^2 \text{ estimates } \sigma_1^2$$

$$UL(M) = \frac{2 \log_e\left[\frac{1-\beta}{\alpha}\right]}{\frac{1}{S_o^2} - \frac{1}{S_1^2}} + M \frac{\log_e\left[\frac{S_1^2}{S_o^2}\right]}{\frac{1}{S_o^2} - \frac{1}{S_1^2}} \qquad (2)$$

$$LL(M) = \frac{2 \log_e\left[\frac{\beta}{1-\alpha}\right]}{\frac{1}{S_o^2} - \frac{1}{S_1^2}} + M \frac{\log_e\left[\frac{S_1^2}{S_o^2}\right]}{\frac{1}{S_o^2} - \frac{1}{S_1^2}} \qquad (3)$$

Where: UL(M) = Upper limit at M sets of duplicate or spiked samples.

LL(M) = Lower limit at M sets of duplicate or spiked samples.

di = The difference between the i^{th} set of duplicates or spiked samples.

n = The total number of sets of duplicates or spiked samples used to construct the control charts.

S_o^2 = Minimum amount of variation allowed in the system.

S_1^2 = Maximum amount of variation allowed in the system.

α = Percent of time you are willing to judge the procedure out-of-control when it is in-control.

β = Percent of time you are willing to judge the procedure in-control when it is out-of-control.

M = Number of sets of duplicates or spiked samples used in calculating the value to be plotted on the chart.

For clarification purposes, an example of using the above equations in making the calculations is given below. The example involves the measurement of total phosphate phosphorus by the colorimetric, with persulfate digestion, method. Twenty-three sets of standards at concentrations

varying from .32 to 4.9 mg/l of total phosphate phosphorus were used in the calculations. It was assumed that there was no appreciable proportional error in this range of concentration. Also, by visual observation we did not reject any data as being out of control.

Results of Analyses of Standards

(mg/l Total PO_4-P)

Actual	Obtained	Difference (di)	di^2
.34	.33	+.01	.0001
.49	.49	.00	.0000
.49	.49	.00	.0000
.68	.65	+.03	.0009
.67	.65	+.02	.0004
.66	.70	-.04	.0016
.83	.80	+.03	.0009
.34	.34	.00	.0000
.50	.47	+.03	.0009
.40	.40	.00	.0000
.50	.53	-.03	.0009
.66	60	+.06	.0036
.50	.56	-.06	.0036
.52	.59	-.07	.0049
.98	.75	+.23	.0529
.49	.63	-.14	.0196
1.6	1.7	-.10	.0100
1.3	1.2	+.10	.0100
3.3	3.3	.00	.0000
4.9	4.6	+.30	.0900
2.3	2.3	.00	.0000
1.3	1.3	.00	.0000
2.3	2.4	-.10	.0100

$$\Sigma di = .27$$

$$\Sigma di^2 = .21$$

$$(\Sigma di)^2 = .07$$

$$S_d^2 = \frac{\Sigma di^2 - \frac{(\Sigma di)^2}{N}}{N-1} = \frac{.21 - \frac{.07}{23}}{22} = .009$$

$$S_d = \sqrt{S_d^2} = \sqrt{.009} = \pm .09 \qquad (1)$$

$$S_o^2 = (.8S_d)^2 = .64S_d^2 = .64(.009) = .006$$

$$S_1^2 = (1.2S_d)^2 = 1.44S_d^2 = 1.44(.009) = .013$$

$$UL(M) = \frac{2 \log_e \left[\frac{1-\beta}{\alpha}\right]}{\frac{1}{S_o^2} - \frac{1}{S_1^2}} + M \frac{\log_e \left[\frac{S_1^2}{S_o^2}\right]}{\frac{1}{S_o^2} - \frac{1}{S_1^2}}$$

$$= \frac{3.5}{\frac{1}{.006} - \frac{1}{.013}} + M \frac{\log_e \left[\frac{.013}{.006}\right]}{\frac{1}{.006} - \frac{1}{.013}}$$

$$= \frac{3.5}{90} + M \frac{.69}{90}$$

$$= .039 + .0077(M) \qquad (2)$$

$$LL(M) = \frac{2 \log_e \left[\frac{\beta}{1-\alpha}\right]}{\frac{1}{S_o^2} - \frac{1}{S_1^2}} + M \frac{\log_e \left[\frac{S_1^2}{S_o^2}\right]}{\frac{1}{S_o^2} - \frac{1}{S_1^2}}$$

$$= \frac{-3.5}{90} + M \frac{.69}{90}$$

$$= -.039 + .0077(M) \qquad (3)$$

We are now prepared to construct an accuracy control chart. The upper limits on the Y-axis can be calculated using equation (2):

at M = 0

UL (0) = .04 + 0(.008) = .04;

at M = 14

UL (14) = .04 + 14(.008) = .15

These two points can now be plotted to form the upper limit line as shown in Figure 2.

The lower limits on the Y-axis can be calculated using equation (3):

at M = 0

LL (0) = -.04 + 0(.008) = -.04;

at M = 14

LL (14) = -.04 + 14(.008) = .07

These two points can now be plotted to form the lower limit line as shown in Figure 2.

It should be noted that the Y-intercept for the lower control line is the negative of that for the upper control line. This is because α and β are equal. If they are not equal, this condition will not exist.

Figure 2 now represents an accuracy control chart for total phosphate phosphorus which is characteristic of the laboratory operations restricted to the conditions specified on the chart. Only an accuracy control chart has been demonstrated here. The same procedures should be followed to produce a precision control chart.

Use of Control Charts

Now that the control charts have been constructed, we are prepared to plot the values obtained from duplicate and spiked sample results from a series of sample analyses. At this point a decision must be made as to the number of duplicate analyses to be conducted during a series of samples; the same decision must be made on spiked or standard samples. This decision is primarily one of economics.

In considering the number of duplicate and spiked sample analyses to be conducted in a series of samples, it is necessary to weigh the consequences when the data goes out-of-control. The consequences involve reanalyzing a series of samples, or discarding the questionable data obtained. The samples to be reanalyzed should be those lying between the last in-control point and the present out-of-control point. For example, if you have a 100 sample series to be analyzed, and a duplicate and spiked sample are analyzed only once in the series (in the area of the 50th sample) the consequences, if this one sample is out-of-control, are that the first 50 samples must be reanalyzed or discarded.

If all 100 samples were analyzed prior to calculating and plotting the out-of-control samples, then all 100 would need to be reanalyzed or discarded. If duplicate and spiked samples are analyzed more frequently and more realistically, such as at every fifth sample, then it is apparent that, if one sample goes out-of-control, it is necessary to reanalyze only the nine in between the two in-control points, or only five if the laboratory operations are halted at the out-of-control point. In addition, the more frequently the duplicate and spiked samples that are analyzed, the greater the chances of detecting abnormal operations as they occur. Also to be considered are the economics involved in the method used and the stability of the sample. A good example lies in the biochemical oxygen demand (BOD) analysis. It is obvious that this method requires five days, and the sample could not be reanalyzed after that time lapse. For these reasons we conduct duplicate analyses on each BOD analysis and report only those that are in-control.

Once the frequency of duplicate and spiked samples has been determined, it is necessary to prepare spiked or standard samples in concentrations relative to those of the control charts which should be similar to concentrations of the environmental samples. These spiked or standard samples must be intermittently dispersed among the samples of the series to be analyzed and without the analyst's knowledge of concentration. Similarly, duplicate samples must be intermittently dispersed throughout

the series of samples to be analyzed, and ideally without the analyst's knowledge; however, this is sometimes very difficult to accomplish.

It cannot be overemphasized that the results of the duplicate and spiked samples must be calculated immediately upon analyzing the samples. This will allow the $\Sigma(d^2)$ to be plotted as soon as possible on the control charts so that any existing problems can be corrected and samples promptly reanalyzed. A brief and simplified example of these calculations is:

Duplicate Sample No. M	Results No. 1	No. 2	Difference (d)	d^2	$\Sigma(d^2)$
1	5.4	5.2	.2	.04	.04
2	4.8	4.7	.1	.01	.05
3	6.1	5.8	.3	.09	.14

Following each calculation, the summation or $\Sigma(d^2)$ is plotted on a chart similar to Figure 2, plotting Σd^2 against the sample number. Upon plotting $\Sigma(d^2)$ one of three possibilities will occur:

1. Out-of-control on the upper limit
2. In-control within the upper and lower limit lines
3. Out-of-control on the lower limit

Each of these possibilities will now be discussed in detail.

There are generally two types of out-of-control on the upper limit conditions. One type is illustrated in Figure 3. This occurs when the laboratory is operating quite normally and suddenly a point goes

out-of-control, usually extremely far from the upper control line. The other type of condition is one in which you have a continuous error trend; in other words, you are approaching an out-of-control condition at a consistent rate, usually forming a trend line in the direction of and at an angle to, the upper control limit line as illustrated in Figure 4. The latter condition (Figure 4) is advantageous over the former since problems can usually be detected early in the continuous error trend condition and corrected before out-of-control actually occurs. The former (Figure 3) case yields no such warning; the operations go out-of-control with no prior indication of a problem. When the operations go out-of-control at the upper limit, obviously the laboratory operations are to be stopped as soon as possible so that the problems can be located and corrected before proceeding with the analysis. Also, keep in mind that it is possible to go out-of-control for no other reason than chance causes. Then the samples in question are to be reanalyzed with duplicate and spiked samples. The first duplicate and spiked sample data are to be plotted, beginning with Sample No. 1 on the control chart. The primary reason for starting at position No. 1 on the control chart is that, since we are plotting the summation of the differences squared, the out-of-control point dominates the next point, thus continuing out-of-control even though it could actually be in-control.

What problems are associated with laboratory operations being

out-of-control? The answer depends upon whether it is a precision control or an accuracy control chart. The causes for out-of-control on the precision chart are usually one or more of the following:

1. The analyst
2. Nature of the sample
3. Glassware contamination

Obviously, we are not concerned over reagents or instrumentation in precision, since analyzing a duplicate sample would duplicate any reagent or instrument error. The analyst is probably the primary source of precision errors; however, the nature of the sample is not to be overlooked. By the nature of the sample we mean the homogeneity of the sample in relation to its amenability to being separated into two equal parts to allow a true duplicate analysis. In the case of samples that contain oils or clumps of insoluble material, it is practically impossible to obtain a duplicate sample. Glassware contamination is probably the least frequent contributor to imprecision; however, it does occur. One flask can be contaminated, where another is not.

Six problems are associated, singly or in combination, with an out-of-control condition on an accuracy control chart. They are:

1. The analyst
2. Glassware contamination
3. Contaminated reagents
4. Instrumentation

5. Sample interference with the spiked material

6. Contaminated laboratory atmosphere

All weigh fairly evenly as possible causes of inaccuracy.

The second possibility is where the laboratory is operating in-control within the upper and lower limit lines. This possibility is illustrated in Figure 5. Under these conditions there is no cause for concern over the quality of the data, and samples should be continually analyzed until either a trend develops or a result goes out-of-control at the upper limit.

The remaining possibility is out-of-control on the lower limit as illustrated in Figure 6. This situation is indicative of greater precision and accuracy being attained by a laboratory. This probably would show up in the first plotting on the first control chart, because the more experience the laboratory gains in analyzing a specific parameter by a specific method, the more precise and accurate that laboratory becomes until optimum operation is achieved. When this situation occurs, it is not necessary to stop the analyses; instead, analyzing should continue on the particular sample series involved (unless the trend changes signigicantly). It is then necessary to construct a new control chart using the latest duplicate and spiked sample data. The new control chart will then represent the current operating characteristics of the laboratory at that time. In the situation of a new laboratory analyzing a new parameter using an unfamiliar method, several charts may be constructed before optimum

operating conditions are attained.

Another reason for an out-of-control on the lower limit occurrence would be the analyst's reporting of false data. This is particularly true with duplicate sample analyses where the analyst is aware of the duplicate sample. This would not be the case with spiked sample analyses since the analyst would not have knowledge of the concentration of the parameter in the standard or spiked sample. If the analyst is suspected of reporting false duplicate data, it would be necessary to mask the duplicate samples so that the analyst is not aware of their presence.

It should also be pointed out that analyzing a duplicate or spiked sample many times with special attention will produce more precise and accurate data than under normal operations. This, in turn, would produce an out-of-control on the lower limit condition.

Again, there will be cases where data are out-of-control for no apparent reason. Many such cases can be attributed to chance causes which will occur occasionally.

Standard Deviation

Mentioned previously were the three basic calculations required to "fingerprint" a laboratory's operations. We have discussed the upper and lower control limits. Now let us briefly discuss the third calculation, that of the standard deviation. The purpose of calculating the standard deviation is to allow inter-laboratory comparisons of precision

and accuracy. It also allows similar comparisons with the literature. In this respect, it can be used as a guide to determine if the laboratory is operating "in the ball park" on precision and accuracy for a given parameter. It should be emphasized that the comparisons of standard deviations should be used only as a guide since the standard deviation of a specific laboratory is characteristic of that laboratory's operations and no other.

Summary

Some type of analytical quality control program is necessary for efficient laboratory management and to validate analytical data. Since analytical data are the products of the analytical laboratory, we must know which products to reject and which are to be accepted as valid. The quality of the laboratory products will vary as long as humans are involved in the analyses; therefore, it is important to know when the variations go beyond those occurring under normal laboratory operations so that the end product quality is known.

This paper discusses the construction and use of laboratory "fingerprints", in the form of control charts, to identify and characterize the operations of a laboratory. These "fingerprints" or control charts are limited to the laboratory from which the data are produced. They are also restricted to the conditions under which the samples are analyzed. They were constructed intentionally with the use of basic mathematical equations, thus encouraging their use.

The uses of control charts are detailed. Three possible occurrences when plotting analytical data on the control charts are described, these being:

1. Out-of-control on the upper limit
2. In-control
3. Out-of-control on the lower limit

The charts are interpreted and recommendations made as to what to do when the laboratory operations deviate from normal.

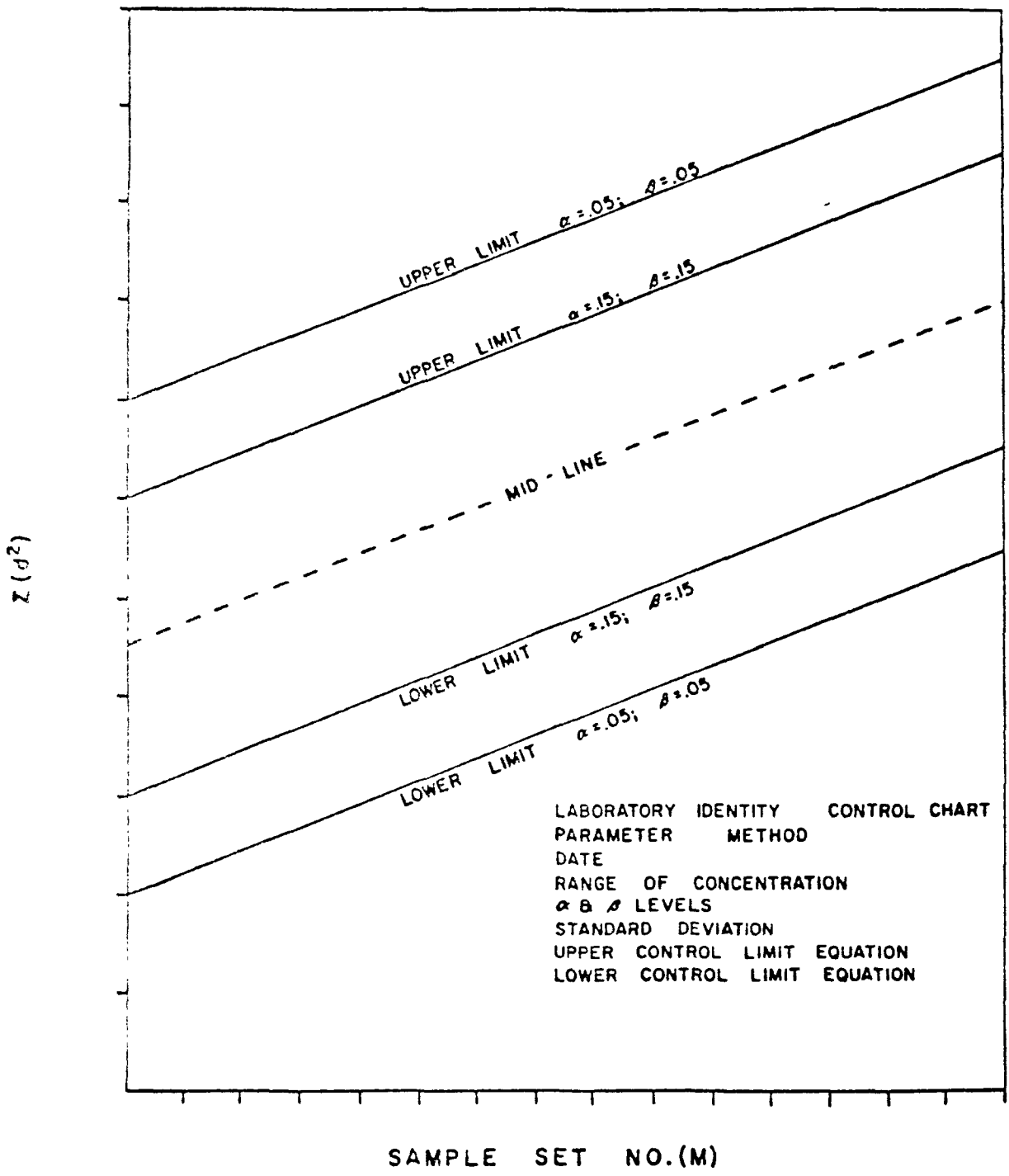
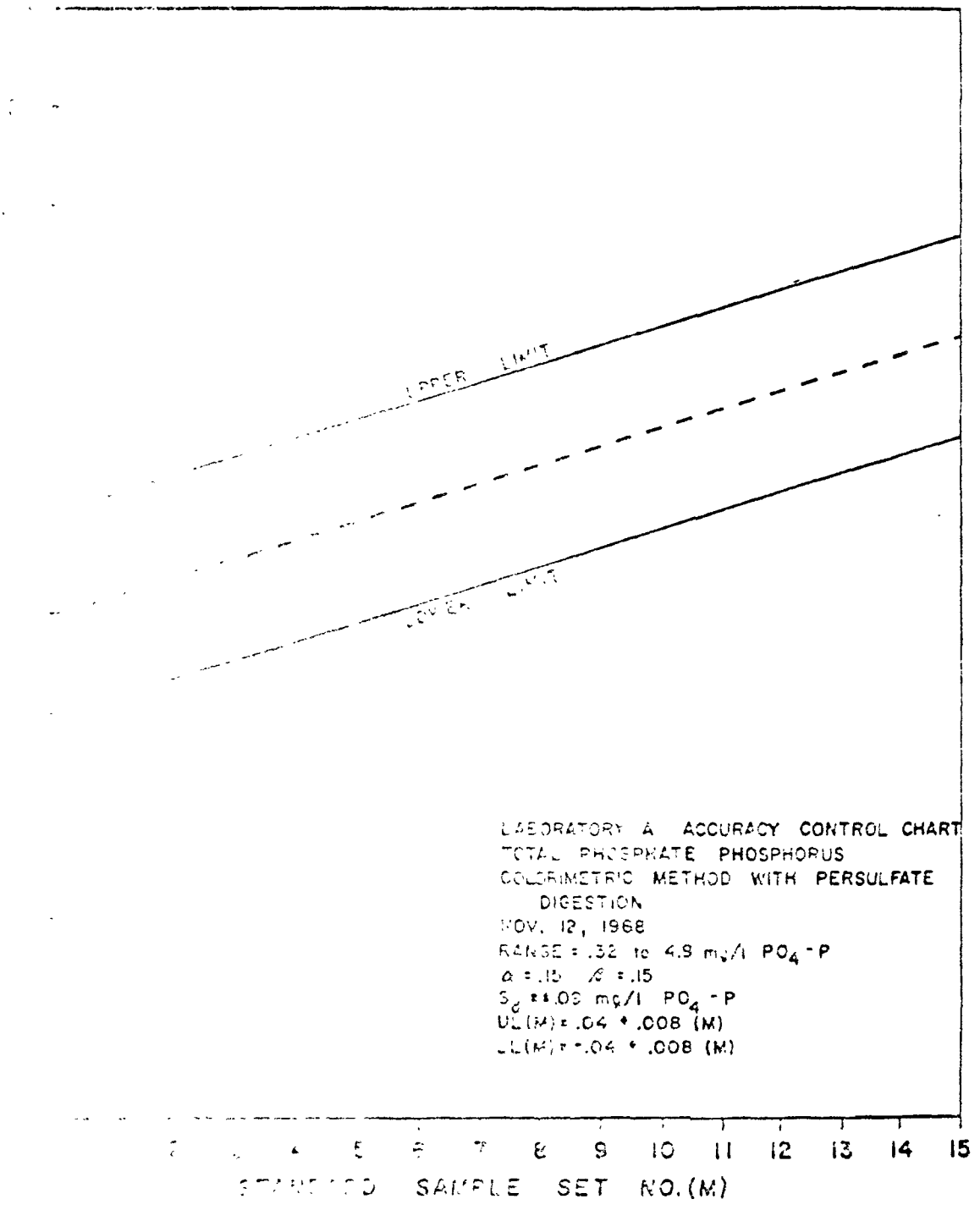


FIGURE 1 - EFFECT OF VARYING α & β


UPPER LIMIT
LOWER LIMIT
LABORATORY A ACCURACY CONTROL CHART
TOTAL PHOSPHATE PHOSPHORUS
COLORIMETRIC METHOD WITH PERSULFATE DIGESTION
NOV. 12, 1968
RANGE = .32 to 4.9 mg/l PO_4-P
α = .15 β = .15
S_o = ±.03 mg/l PO_4-P
UL(M) = .04 + .008 (M)
LL(M) = -.04 + .008 (M)
5 6 7 8 9 10 11 12 13 14 15
STANDARD SAMPLE SET NO.(M)

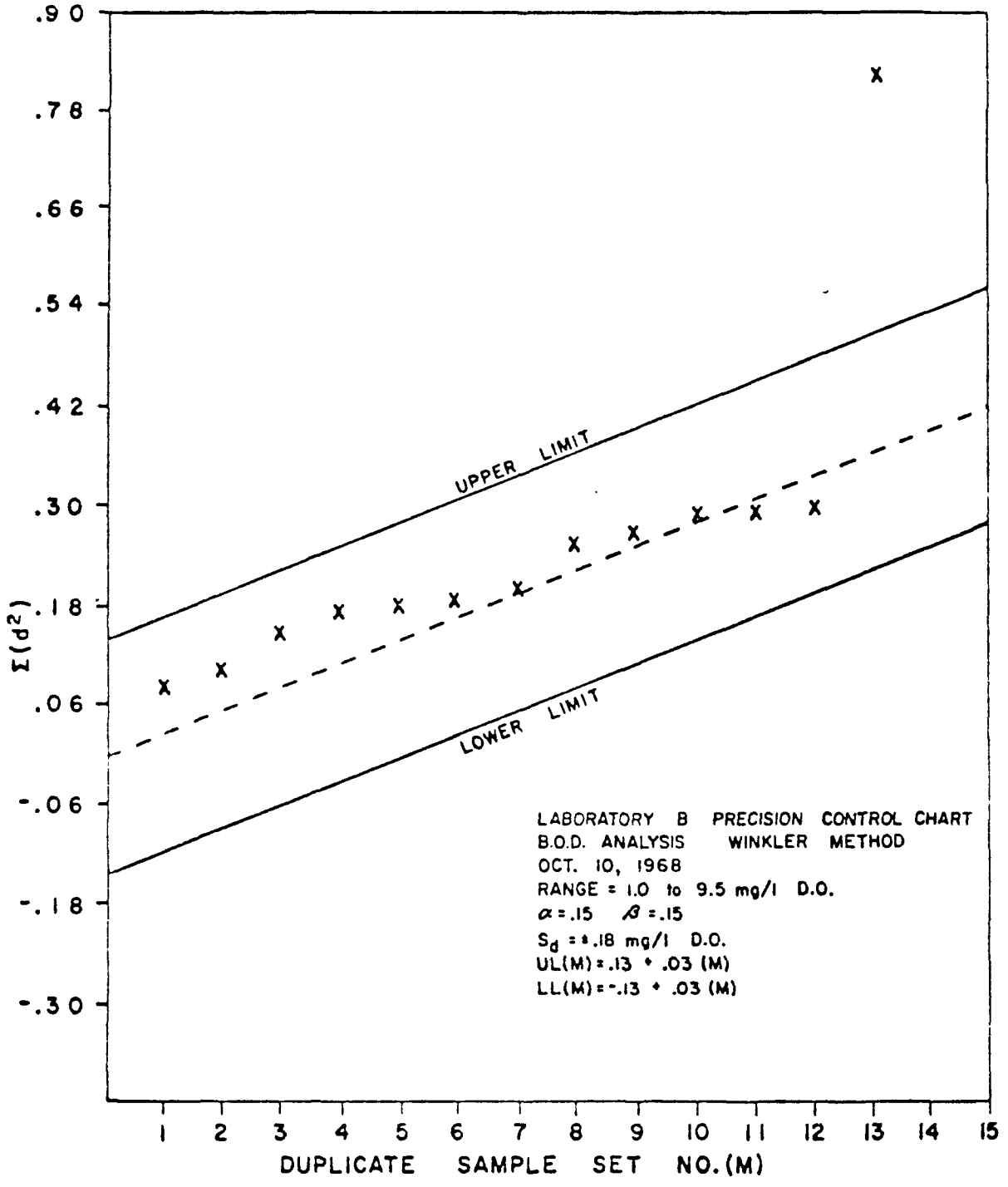


FIGURE 3 - OUT-OF-CONROL ON UPPER LIMIT

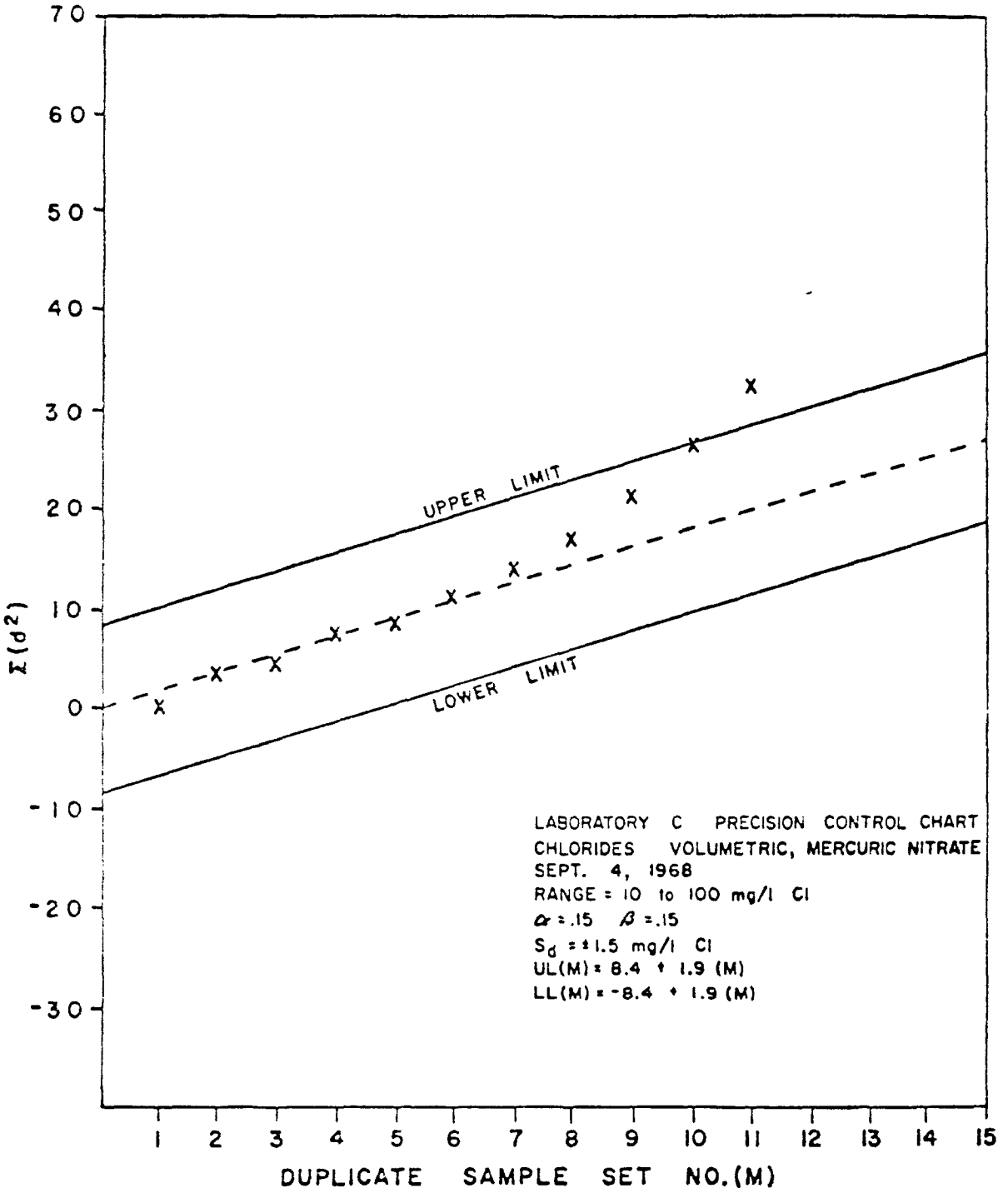


FIGURE 4 - OUT-OF-CONTROL ON UPPER LIMIT
(CONTINUOUS ERROR TREND)

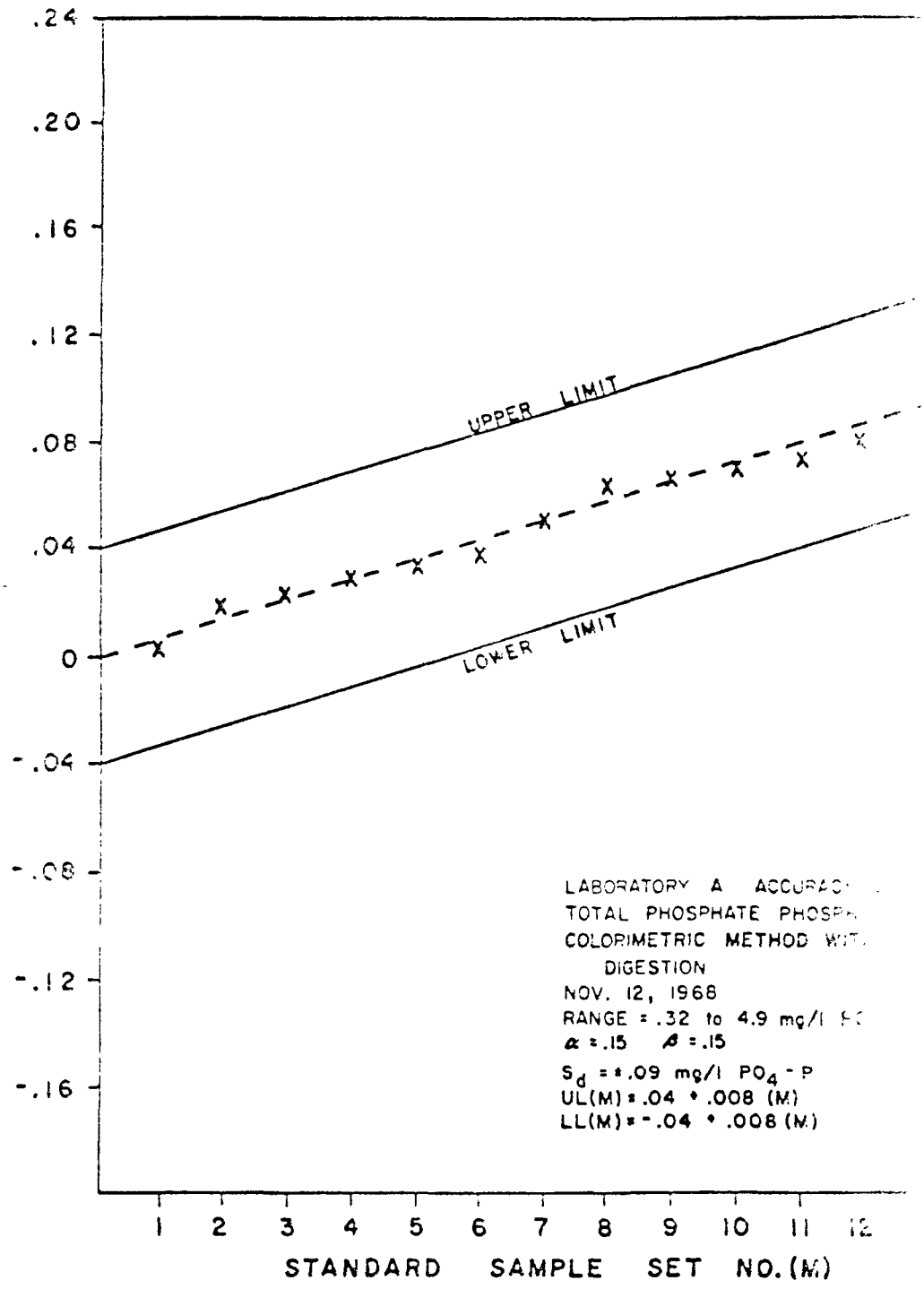


FIGURE 5 - IN-CONTROL WITHIN L

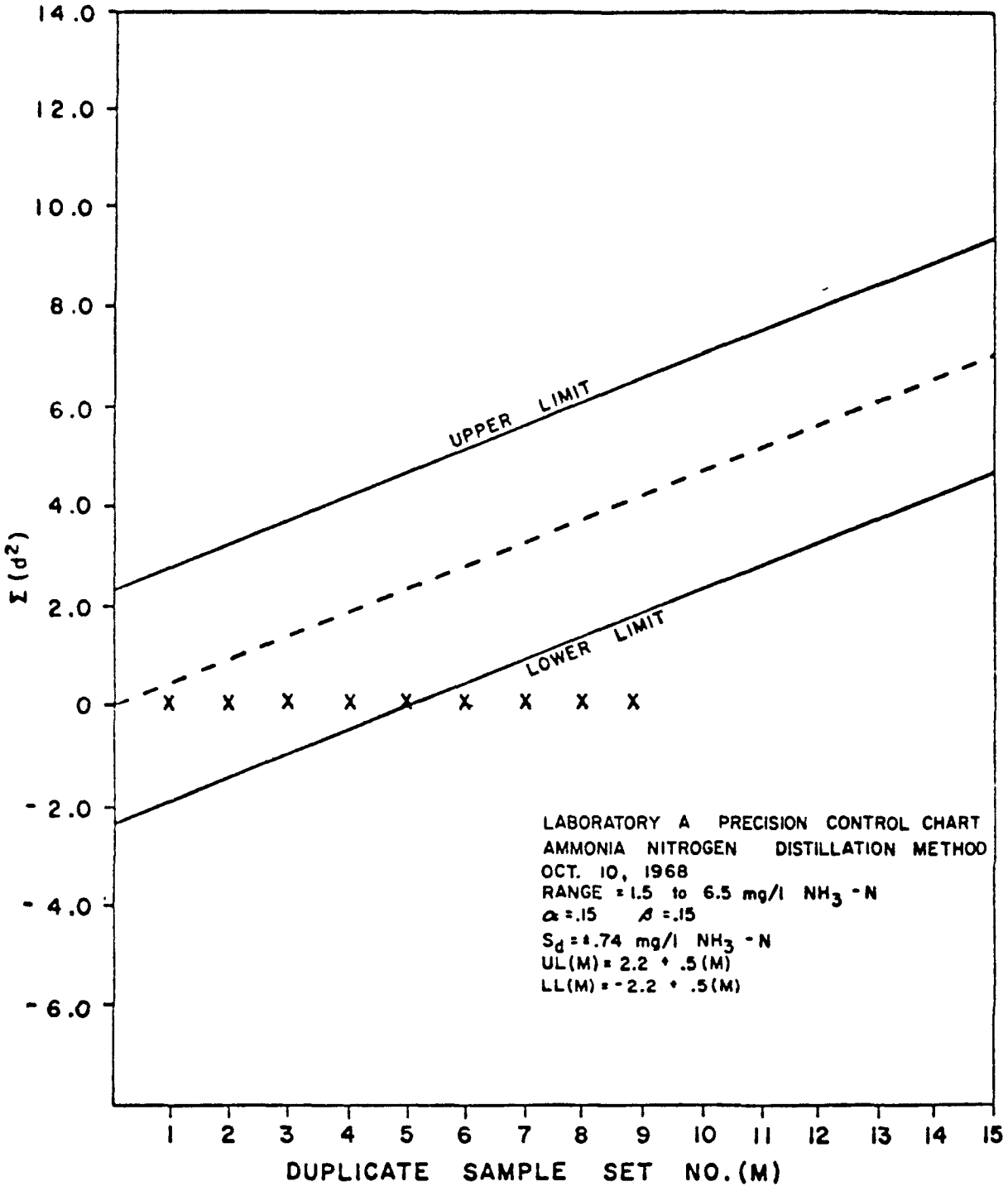


FIGURE 6 - OUT-OF-CONTROL ON LOWER LIMIT

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY'S ANALYTICAL QUALITY CONTROL PROGRAM*

Revised by

Bobby G. Benefield**

INTRODUCTION

The Environmental Protection Agency (EPA) gathers water quality data to determine compliance with water quality standards, to provide information for planning water resources development, to determine the effectiveness of pollution abatement procedures, and to assist in research and technical services activities. The sources of these data are not only the EPA laboratories but other Federal, city, State, and industry laboratories.

In a large measure the success of the pollution control program rests upon the reliability of the information provided by the data collection activities.

To insure the reliability of physical, chemical, and biological data, the EPA's Division of Research has established the Analytical Quality Control (AQC) Laboratory at 1014 Broadway, Cincinnati, Ohio.

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* Originally entitled "The Federal Water Pollution Control Administration's Analytical Quality Control Program" and written in 1969 by Mr. R. E. Crowe, then Chief, Chemistry and Biology Section, Technical Assistance, Technical Services Program, Robert S. Kerr Water Research Center, Federal Water Pollution Control Administration, U. S. Department of the Interior, Ada, Oklahoma. This revision was presented by Mr. Larry J. Streck, Chemist, Chemical and Biological Sciences Program, Office of Technical Programs, Environmental Protection Agency, Robert S. Kerr Water Research Center, Ada, Oklahoma, during Training Course No. 161.2, "Planning and Administrative Concepts of Water Quality Surveys," March 22-26, 1971, at the Robert S. Kerr Water Research Center, Ada, Oklahoma

** Analytical Quality Control Regional Coordinator, Region VI, Environmental Protection Agency, Robert S. Kerr Water Research Center, Ada, Oklahoma.

The program conducted by this laboratory is designed to assure the validity and, where necessary, the legal defensibility of all water quality information collected.

HISTORY

The Federal Water Pollution Control Administration (FWPCA), presently EPA, recognized the need for an analytical quality control program in September 1966. Following this recognition, the first meeting on analytical quality control in the FWPCA was held in Cincinnati, Ohio, in January 1967. This meeting was attended by appropriate representatives from FWPCA's nine (presently ten) regions.

The purpose was to bring together as a working group those FWPCA personnel professionally and technically oriented and most knowledgeable in analytical chemical methods and procedures used to identify, measure, and characterize various types of water pollution. This group was designated as the Committee on Methods Validation and Analytical Quality Control. The Committee includes scientists who actively participate in the preparation of *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association (APHA) and in subcommittee and task group activities on Committee D-19 of the American Society for Testing and Material (ASTM). In addition one of the scientists is General Referee for Water, Subcommittee D of the Association of Official Analytical Chemists.

At the Cincinnati meeting subcommittees were chosen to study the then existing analytical chemical methods for investigating water quality and to recommend the best of these methods for official designation by the FWPCA. These subcommittees were further broken down into specific

parameter groups which, for one reason or another, were related. A Chairman was appointed for each of the subcommittees. The objectives set by these subcommittees to be accomplished by the fall of 1967 were:

1. To select those parameters which would be of use in the examination of water quality.
2. To review the analytical methods available for analyzing these parameters.
3. To formulate a list of the best methods available for immediate use.

Meeting these objectives represented the first major task to be accomplished by the newly organized Analytical Quality Control Section, which at the time was a part of FWPCA's Division of Pollution Surveillance.

In October 1967, the Committee on Methods Validation and Analytical Quality Control held its second meeting -- again in Cincinnati. At this time the initial task of the Analytical Quality Control Program was complete. The product of this first pioneering step was the publication and distribution of the *FWPCA Official Interim Methods for Chemical Analyses of Surface Waters*, September 1968.

In addition to the methods selection and validation activity, the Analytical Quality Control Program was being re-organized as a Laboratory of the FWPCA's Division of Research with the establishment of regional coordinators throughout the United States to coordinate program activities in each FWPCA region. Bringing the program to this point was a major step.

The AQC Laboratory is currently engaged in: (1) the selection and validation of methods for biological and microbiological determinations much the same as was done for chemical determinations (the biological

methods manual will be available soon after January 1972); (2) intra-laboratory quality control programs; (3) interlaboratory quality control programs; and (4) publishing the third edition of the *Methods for Chemical Analysis of Water and Wastes*, 1971.

ORGANIZATION

The Analytical Quality Control Program of the EPA is carried out through an Analytical Quality Control Laboratory assisted by advisory committees on methods selection, regional quality control coordinators, and laboratory quality control officers. The organization and functions of these groups are described below.

Analytical Quality Control Laboratory

The Analytical Quality Control Laboratory is composed of five sections - Chemistry, Biology, Microbiology, Instrument Development, and Methods and Performance Evaluation. The laboratory staff coordinates the AQC Program, carries out methods development, conducts a continuing reference sample service, and statistically evaluates laboratory performance.

Regional Coordinators

To emphasize quality control participation at the regional level, each Regional Director appoints a coordinator whose primary functions are to implement the analytical quality control program in all EPA laboratory activities within his region, and to assist or offer advice to appropriate groups outside the EPA concerning any phase of analytical quality control in the laboratory. Through individual quality control officers he provides leadership within the regional laboratory components, insuring the usefulness of this data for all regional functions.

In addition, the coordinator keeps the Regional Director advised on analytical quality control activities in the laboratory under his jurisdiction and informs the Analytical Quality Control Laboratory of his region's needs in methods development and data validation. The regional AQC coordinators and their respective regions are:

Regional Analytical Quality Control Coordinators

Francis T. Brezenski, AQC Coordinator
Environmental Protection Agency
Hudson-Delaware Basins Office
Edison, New Jersey 08817

Harold G. Brown, AQC Coordinator
Environmental Protection Agency
911 Walnut Street, Room 702
Kansas City, Missouri 64106

Charles Jones, Jr., AQC Coordinator
Environmental Protection Agency
1140 River Road
Charlottesville, Virginia 22901

Bobby G. Benefield, AOC Coordinator
Environmental Protection Agency
Ada Facility, P. O. Box 1198
Ada, Oklahoma 74820

James H. Finger, AQC Coordinator
Environmental Protection Agency
Southeast Water Laboratory
College Station Road
Athens, Georgia 30601

Daniel F. Krawczyk, AQC Coordinator
Environmental Protection Agency
Pacific Northwest Water Laboratory
200 South 35th Street
Corvallis, Oregon 97330

LeRoy E. Scarce, AOC Coordinator
Environmental Protection Agency
1819 West Pershing Road
Chicago, Illinois 60605

Donald B. Mausshardt, AQC Coordinator
Environmental Protection Agency
Phelan Building, 760 Market Street
San Francisco, California 94102

Robert L. Booth, AQC Coordinator
Environmental Protection Agency
Analytical Quality Control Laboratory
1014 Broadway
Cincinnati, Ohio 45202

John Tilstra, AQC Coordinator
Environmental Protection Agency
Lincoln Tower Building, Suite 900
1860 Lincoln Street
Denver, Colorado 80203

Laboratory Quality Control Officers

This officer, usually a senior member of the laboratory staff, is appointed by the Laboratory Director and is responsible, through him, to the Regional Quality Control Coordinator. He is concerned with the analytical quality control of EPA laboratories within the region.

RESPONSIBILITIES

National

The national responsibilities of the EPA's analytical quality control program are primarily those of the Analytical Quality Control Laboratory in Cincinnati, Ohio. These responsibilities are described below.

Methods Research

Although analytical methods are available for most of the routine measurements used in water pollution control, there is a continuing need for improvement in sensitivity, precision, accuracy, and speed. Development is required to take advantage of modern instrumentation in the water laboratory. In microbiology, the use of new bacterial indicators of pollution, including pathogens, creates a need for rapid identification and counting procedures. Biological collection methods need to be standardized to permit efficient interchange of data. The Analytical Quality Control Laboratory devotes its research efforts to the improvement of the routine tools of the trade; therefore, it has nationwide responsibility for the guidance of a program to develop reliable analytical methods for water and wastewater analyses.

Methods Selection

The AOC Laboratory provides the program for the selection of the best available procedures in water and waste analyses. This includes certification of the methods through an adequate testing program. Through the publishing of EPA methods manuals, updated regularly, the program insures the uniform application of analytical methods in all laboratories of the EPA.

Interlaboratory Quality Control

The Analytical Quality Control Laboratory is responsible for maintaining a reference sample program for methods verification and laboratory performance evaluation of all EPA laboratories. This also includes the validation of chosen procedures of existing or new developmental methods of analysis.

Intralaboratory Quality Control

To maintain a high performance level in daily activities, every analytical laboratory must utilize a system of checks on the accuracy and precision of reported results. While this is a part of the responsibility of the analyst and his supervisor, the Analytical Quality Control Laboratory is responsible for guidance in the development of model quality control programs which can be incorporated into the laboratory routine.

Regional

The regional responsibilities are essentially those of the regional coordinator and the laboratory quality control officers of a particular region. The regional coordinator is responsible for implementing the nationwide program in the EPA regional laboratory and maintaining appropriate relations with other federal agencies, with state and interstate pollution control agencies, and with industry to encourage their use of the EPA methods and their participation in the analytical quality control effort. In addition, the regional coordinator is responsible for bringing to the attention of the AQC Laboratory any special needs of his region in analytical methodology and any analytical quality control problems that occur.

The laboratory quality control officer is responsible for carrying out an intralaboratory quality control program within the EPA laboratory in his region, assuring the use of certified methods by the laboratory staffs and securing participation in regular check sample analyses.

EPA OFFICIAL METHODS

Missions assigned to EPA by the Water Quality Act of 1965 and the Clean Water Restoration Act of 1966 created a need for methods capable of developing water quality data to measure the effectiveness of the Nation's water pollution control programs. The methods must be uniform throughout the Agency and based on sound, scientific investigations. Further, they must be available to all other elements of the water pollution control field involved in, or affected by, water quality standards, and must be acceptable as legally defensible in Federal and State enforcement actions to abate water pollution.

The first edition of a methods manual was entitled the *FWPCA Official Interim Methods for Chemical Analyses of Surface Waters* and was a major step in this direction and represented the first product of the EPA's Analytical Quality Control Program.

To acquaint you with the manual and its implications, it seems appropriate to discuss it at this time. As I have said, this manual represents the selections made by a committee of senior EPA laboratory personnel, working under the guidance of the Analytical Quality Control Laboratory. The Committee consulted all the available literature, including *Standard Methods for the Examination of Water and Wastewater*, *ASTM Manual of Industrial Water*, and current technical journals. This manual in first edition was limited in number, and thus was not available to the general public. The second edition, entitled, *FWPCA Methods for Chemical Analyses*

of Water and Wastes was published in July 1969 and was available for all who desired copies. A third edition was published in 1971. It is entitled *Methods for Chemical Analysis of Water and Wastes* and is available upon request.

An analytical quality control manual is also available. It is entitled *Control of Chemical Analyses in Water Pollution Laboratories.* This manual deals exclusively with quality control within the laboratory.

The 1971 methods and the laboratory quality control manual can be obtained by sending a request to your regional coordinator. For those of you who are in this region (Region VI) the address is

Robert S. Kerr Water Research Center
United States Environmental Protection Agency
P. O. Box 1198
Ada, Oklahoma 74820

Attention: Bobby G. Benefield
AQC Regional Coordinator

SUMMARY

In order that industry, state and interstate pollution control agencies, the EPA and other Federal agencies can effectively relate water quality data and feel secure that water quality data produced from all the laboratories concerned are valid, the EPA organized an analytical quality control program. The organization and responsibilities of this program nationally and regionally have been discussed.

The success of this program depends upon the active participation of managers, supervisors, and analysts in not only the EPA, but in all groups concerned with characterizing and maintaining water quality. Therefore, it is essential that the philosophy of quality control be understood and accepted by all levels in any laboratory organization.

INTRODUCTION

In the "Quality Control of Chemical Analysis" section of this manual, it was stated that one of the basic assumptions made in the construction of control charts is that the spiked sample data or duplicate data should be the products from an "in-control" process.

This addenda offers a statistical method by which the validity of this assumption may be evaluated.

ELIMINATION OF OUTLIERS

If obviously large differences exist between matched pairs from spiked or duplicate data and if an assignable cause for this difference is not known, then an unbiased method for rejection of outliers must be used. Two such methods are given below (1).

TEST 1: ESTIMATE OF σ_d AVAILABLE

A statistic which can be used to detect outliers in either direction (too large or too small) is $q = W/S_d$, where W is the range of the differences and S_d is an independent estimate of the population standard deviation of the differences (σ_d).

Percentiles of the sampling distribution of q are given in Table 1.

If a significantly large value is obtained, it should not be used in subsequent calculations. A check should be made in an attempt to find assignable causes for the large value(s).

EXAMPLE I

Precision Control Chart

Laboratory: Laboratory A

Parameter Analyzed: Alkalinity as $CaCO_3$

Method:

Date: [illegible]

Data:

Results of Analyses of Duplicate Samples

(Mg/l Alkalinity as $CaCO_3$)

Set No.	Duplicate No. 1	Duplicate No. 2	Difference
1	96.0	100.0	-4.0
2	222.0	218.0	4.0
3	244.0	242.0	2.0
4	79.0	80.0	-1.0
5	524.0	526.0	-2.0
6	410.0	414.0	-4.0
7	118.0	118.0	0.0
8	70.0	70.0	0.0
9	50.0	50.0	0.0
10	297.0	303.0	-6.0
11	307.0	312.0	-5.0
12	296.0	303.0	-7.0
13	180.0	186.0	-6.0
14	211.0	214.0	-3.0
15	214.0	212.0	2.0
16	215.0	216.0	-1.0
17	139.0	142.0	-3.0
18	122.0	124.0	-2.0
19	127.0	127.0	0.0
20	444.0	464.0	-20.0
21	109.0	109.0	0.0
23	89.0	87.0	2.0

W = Range = d(max) - d(min) = 4.0 - (-20.0) = 24.0

S_d = 3.7867 with 42 degrees of freedom*

$q = W/S_d = 24/3.7869 = 6.3376$

The 95 percentile value for the distribution of $q = W/S_d$ with K = 23 and d.f. = 40 is 5.26 (Table 1). The computed q is greater than the tabulated q, therefore, conclude that the difference resulting from the duplicate set #20 is truly an outlier and should be eliminated from control chart calculations. This procedure may be iterated for all suspected outliers.

* S_d obtained from an independent set of duplicates with 43 observed pairs.

TABLE 1.' 95 Percentile of the Distribution of $q = W/S_d$

W is the range of K observations and d.f. is the degrees of freedom in the independent standard deviation S_d.

d.f. \ K	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
1	18.0	27.0	32.8	37.1	40.4	43.1	45.4	47.4	49.1	50.6	52.0	53.2	54.3	55.4	56.3	57.2	58.0	58.8	59.6
2	6.09	8.3	9.8	10.9	11.7	12.4	13.0	13.5	14.0	14.4	14.7	15.1	15.4	15.7	15.9	16.1	16.4	16.6	16.8
3	4.50	5.91	6.82	7.50	8.04	8.48	8.85	9.18	9.46	9.72	9.95	10.2	10.4	10.5	10.7	10.8	11.0	11.1	11.2
4	3.93	5.04	5.76	6.29	6.71	7.05	7.34	7.60	7.83	8.03	8.21	8.37	8.52	8.66	8.79	8.91	9.03	9.13	9.23
5	3.64	4.60	5.22	5.67	6.03	6.33	6.58	6.80	6.99	7.17	7.32	7.47	7.60	7.72	7.83	7.93	8.03	8.12	8.21
6	3.46	4.34	4.90	5.31	5.63	5.89	6.12	6.32	6.49	6.65	6.79	6.92	7.03	7.14	7.24	7.34	7.43	7.51	7.59
7	3.34	4.16	4.68	5.06	5.36	5.61	5.82	6.00	6.16	6.30	6.43	6.55	6.66	6.76	6.85	6.94	7.02	7.09	7.17
8	3.26	4.04	4.53	4.89	5.17	5.40	5.60	5.77	5.92	6.05	6.18	6.29	6.39	6.48	6.57	6.65	6.73	6.80	6.87
9	3.20	3.95	4.42	4.76	5.02	5.24	5.43	5.60	5.74	5.87	5.98	6.09	6.19	6.28	6.36	6.44	6.51	6.58	6.64
10	3.15	3.88	4.33	4.65	4.91	5.12	5.30	5.36	5.60	5.72	5.83	5.93	6.03	6.11	6.20	6.27	6.34	6.40	6.47
11	3.11	3.82	4.26	4.57	4.82	5.03	5.20	5.35	5.49	5.61	5.71	5.81	5.90	5.99	6.06	6.14	6.20	6.26	6.33
12	3.08	3.77	4.20	4.51	4.75	4.95	5.12	5.27	5.40	5.51	5.62	5.71	5.80	5.88	5.95	6.03	6.09	6.15	6.21
13	3.06	3.73	4.15	4.45	4.69	4.88	5.05	5.19	5.32	5.43	5.53	5.63	5.71	5.79	5.86	5.93	6.00	6.05	6.11
14	3.03	3.70	4.11	4.41	4.64	4.83	4.99	5.13	5.25	5.36	5.46	5.55	5.64	5.72	5.79	5.85	5.92	5.97	6.03
15	3.01	3.67	4.08	4.37	4.60	4.78	4.94	5.08	5.20	5.31	5.40	5.49	5.58	5.65	5.72	5.79	5.85	5.90	5.96
16	3.00	3.65	4.05	4.33	4.56	4.74	4.90	5.03	5.15	5.26	5.35	5.44	5.52	5.59	5.66	5.72	5.79	5.84	5.90
17	2.98	3.63	4.02	4.30	4.52	4.71	4.86	4.99	5.11	5.21	5.31	5.39	5.47	5.55	5.61	5.68	5.74	5.79	5.84
18	2.97	3.61	4.00	4.28	4.49	4.67	4.82	4.96	5.07	5.17	5.27	5.35	5.43	5.50	5.57	5.63	5.69	5.74	5.79
19	2.96	3.59	3.98	4.25	4.47	4.65	4.79	4.92	5.04	5.14	5.23	5.32	5.39	5.46	5.53	5.59	5.65	5.70	5.75
20	2.95	3.58	3.96	4.23	4.45	4.62	4.77	4.90	5.01	5.11	5.20	5.28	5.36	5.43	5.49	5.55	5.61	5.66	5.71
24	2.92	3.53	3.90	4.17	4.37	4.54	4.68	4.81	4.92	5.01	5.10	5.18	5.25	5.32	5.38	5.44	5.50	5.54	5.59
30	2.89	3.49	3.84	4.10	4.30	4.46	4.60	4.72	4.83	4.92	5.00	5.08	5.15	5.21	5.27	5.33	5.38	5.43	5.48
40	2.86	3.44	3.79	4.04	4.23	4.39	4.52	4.63	4.74	4.82	4.91	4.98	5.05	5.11	5.16	5.22	5.27	5.31	5.36
60	2.83	3.40	3.74	3.98	4.16	4.31	4.44	4.55	4.65	4.73	4.81	4.88	4.94	5.00	5.06	5.11	5.16	5.20	5.24
120	2.80	3.36	3.69	3.92	4.10	4.24	4.36	4.48	4.56	4.64	4.72	4.78	4.84	4.90	4.95	5.00	5.05	5.09	5.13
∞	2.77	3.31	3.63	3.86	4.03	4.17	4.29	4.39	4.47	4.55	4.62	4.68	4.74	4.80	4.85	4.89	4.93	4.97	5.01

TEST 2: ESTIMATE OF σ_d NOT AVAILABLE

A statistic which can be used to detect outliers when an estimate of the population standard deviation of differences (σ_d) is not known is described below.

The test proceeds as follows:

1. Arrange the data in ascending order.

2. If

$3 \leq n \leq 7$ compute r_{10}

$8 \leq n \leq 10$ compute r_{11}

$11 \leq n \leq 13$ compute r_{21}

$14 \leq n \leq 25$ compute r_{22}

n is the number of differences between matched pairs of spiked or duplicate data. Compute r_{ij} as follows:

r_{ij}	if d_n is suspect	if d_1 is suspect
r_{10}	$(d_n - d_{n-1})/(d_n - d_1)$	$(d_2 - d_1)/(d_n - d_1)$
r_{11}	$(d_n - d_{n-1})/(d_n - d_2)$	$(d_2 - d_1)/(d_{n-1} - d_1)$
r_{21}	$(d_n - d_{n-2})/(d_n - d_2)$	$(d_3 - d_1)/(d_{n-1} - d_1)$
r_{22}	$(d_n - d_{n-2})/(d_n - d_3)$	$(d_3 - d_1)/(d_{n-2} - d_1)$

3. Look up $r_{.98}$ for r_{ij} as defined in Step 2 in Table 2.

4. If $r_{ij} > r_{.98}$, reject the observation, otherwise, do not reject.

EXAMPLE II

Consider the data used in Example I.

The number of duplicates (n) lies between 25 and 14, therefore, we will compute r_{22} as follows:

$$r_{22} = (d_3 - d_1)/(d_{n-2} - d_1) = [(-6) - (-20)] \;/\; [(2) - (-20)]$$
$$= 14/22 = .6363,$$

which is greater than $r_{.98,23} = .422$. Therefore, we reject the suspected outlier.

This procedure may be iterated until all suspected outliers have been checked.

TABLE 3. CRITERIA FOR REJECTION OF OUTLYING OBSERVATIONS

Statistic	Number of Observations(n)	98 Percentile
r_{10}	3	.976
	4	.846
	5	.729
	6	.644
	7	.586
r_{11}	8	.631
	9	.587
	10	.551
r_{21}	11	.638
	12	.605
	13	.578
r_{22}	14	.602
	15	.579
	16	.559
	17	.542
	18	.527
	19	.514
	20	.502
	21	.491
	22	.481
	23	.472
	24	.464
	25	.457

TEST FOR "IN-CONTROL"

Once a useable set of data is at hand, it is necessary to compute the mean difference and the standard deviation of the mean difference. Since the theoretical difference between duplicates of the same material is zero, Student's t distribution can be used to test the hypothesis that the average difference of the population sampled differs significantly from zero. If it does not, then the process is judged to be in control and subsequent computations for constructing the control chart are considered valid.

The data in Table 1, with duplicate set #20 eliminated, will be used for expository purposes. The t test is performed as follows:

$\bar{d}$ - average difference = -1.5652

$S_{\bar{d}} = S_d / \sqrt{K} = 0.95869$

$t = \bar{d} / S_{\bar{d}} = -2.4339$ with 23 degrees of freedom

The 95 percentile value for the t distribution with 22 degrees of freedom (Table 3) is 2.074. The absolute value of the computed t is greater than the tabulated t. Therefore, it is concluded that the mean difference of the sampled population is significantly different from zero.

A word of caution is noteworthy here in confusing the terms "significantly different" and "meaningfully different." It is possible to obtain a significant difference that is not meaningful. An example would be a significant difference of .005 mg/l when the accuracy of the measuring procedure is only, say, ± .05 mg/l. In this case, the data would be judged to be in control, and the control chart constructed from the data would be considered valid.

TABLE 3. Values of Student's t

Probability of a larger value of a t = .05

d.f.	t
1	12.706
2	4.303
3	3.182
4	2.776
5	2.571
6	2.447
7	2.365
8	2.306
9	2.262
10	2.228
11	2.201
12	2.179
13	2.160
14	2.145
15	2.131
16	2.120
17	2.110
18	2.101
19	2.093
20	2.086
21	2.080
22	2.074
23	2.069
24	2.064
25	2.060
26	2.056
27	2.052
28	2.048
29	2.045
30	2.042
40	2.021
60	2.000
120	1.960
∞	1.960
d.f.	0.025

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[1] Dixon, W. J. and Massey, F. T., Jr. "Introduction to Statistical Analysis", McGraw-Hill, Second Edition

COMPUTER APPROACH

TO

QUALITY CONTROL PROCEDURES

INTRODUCTION

The measure of effectiveness of any procedure requiring mathematical manipulation of numbers is most often inversely proportional to the amount of hand calculations required. In an effort to minimize the mathematical involvement of the laboratory scientist when using these quality control procedures, a computer program has been developed and refined in such a way as to give all pertinent information in a well formated, easy to use and store printout.

The utility of this program, of course, depends upon the availability of some form of data processing equipment. For those who have a computer available for their use, the following documentation package is provided on a Fortran IV program written for an 8K IBM 1130 with a Disk Monitor System. This program could be easily modified for any computer system having a Fortran Compiler.

In using spiked or standard samples to check accuracy, a significant t value may result due to a consistent over or under reporting of concentrations. This is bias inherent in the procedure. Efforts should be made to ascertain the cause for this discrepancy and remove it if possible. If it can not be eliminated, past experience on the part of the analyst must suffice in determining if this difference is meaningful.

SIGMA QUALITY CONTROL

A. ABSTRACT

The Sigma Quality Control Chart program has been designed to calculate basic descriptive statistics and the control line equations necessary for constructing cumulative-sum quality control charts.

The input is in the form of duplicate or paired standard and observed values. The following output is provided for each data set.

1. Sample identification
2. Original data
3. Basic Descriptive Statistics
   a. average difference (DBAR)
   b. standard deviation of the average difference (SDBAR)
   c. computed Student's "t" value (T)
   d. ALPHA
   e. BETA
   f. DELTA
   g. variance of the differences
   h. standard deviation of the differences
   i. sum of differences
   j. sum of squares
   k. maximum allowable variance (S(1)SQUARED)
   l. mimimum allowable variance (S(0)SQUARED)
4. Equations for upper limit line and lower limit line evaluated for M = 6 and 10.

B. METHOD OF SOLUTION

The computer solves for values according to the following set of equations:

1. $\bar{d}$ = DBAR = $[\sum_i (X_i - Y_i)]/N$, = $(\sum_i d_i)/N$

   where N = Number of pairs.

2. $S_d^2 = [\sum_i d_i^2 - (\sum_i d_i)^2/N]/(N - 1)$

3. $S_d = \sqrt{S_d^2}$

4. $S_{\bar{d}}$ = SDBAR = $S_d/\sqrt{N}$

5. $S_o^2 = (1 - \Delta)^2 \cdot S_d^2$

6. $S_1^2 = (1 + \Delta)^2 \cdot S_d^2$

7. $$UL(M) = \frac{2 \log_e \left(\frac{1-\beta}{\alpha}\right)}{\frac{1}{S_o^2} - \frac{1}{S_1^2}} + \frac{\log_e \left(\frac{S_1^2}{S_o^2}\right)}{\frac{1}{S_o^2} - \frac{1}{S_1^2}} (M)$$

8. $$LL(M) = \frac{2 \log_e \left(\frac{\beta}{1-\alpha}\right)}{\frac{1}{S_o^2} - \frac{1}{S_1^2}} + \frac{\log_e \left(\frac{S_1^2}{S_o^2}\right)}{\frac{1}{S_o^2} - \frac{1}{S_1^2}}$$

C. FORMATS

1. Control Card

cc	ITEM
1- 3	Number of pairs of data
4- 6	Alpha
7- 9	Beta
10-11	Delta
13-33	Parameter name
35-55	Description of method
57	X if wet lab, blank otherwise
59	X if instrument lab, blank otherwise
61	X if Precision Control Chart, blank otherwise
63	X if Accuracy Control Chart
66-80	Range data covers

2. Data Cards

cc	ITEM
1- 7*	value for first duplicate÷ or standard‡
8-14*	value for second duplicate÷ or observed‡

* Decimal point must be punched.

÷ for duplicate data on Precision Control Charts.

‡ for standard and observed values on Accuracy Control Charts.

3. Last Card

cc	ITEM
1-80	9's

D. OPERATING PROCEDURES

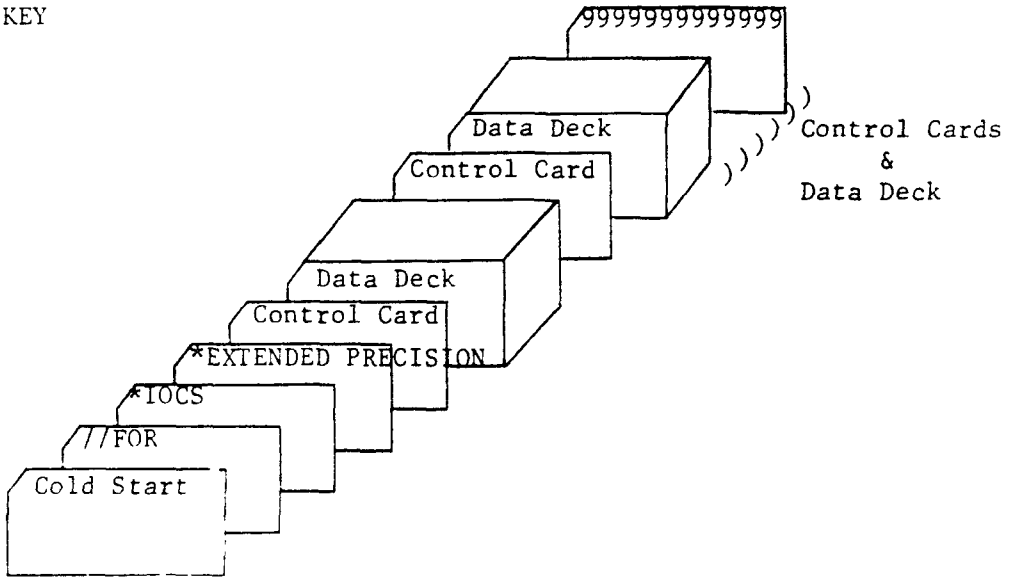
1. Load data into hopper of 1442 and press START.

2. Press IMMEDIATE STOP, RESET, and PROGRAM LOAD on the CPU.

3. Ready printer.

4. When the keyboard select light comes on, type in a six digit date, i.e., 071369.

E. DECK KEY



F. PROGRAM LISTING


```
// JOB     2222

LOG DRIVE   CART SPEC   CART AVAIL  PHY DRIVE
   0000        2222        2222        0000

V2 M04   ACTUAL  8K  CONFIG  8K

// FOR
*IOCS(CARD,TYPEWRITER,KEYBOARD,1132 PRINTER,DISK)
*LIST SOURCE PROGRAM
*EXTENDED PRECISION
      DIMENSION XL(2),XL(2),M(2),PAR(2_),RANGE(15) ,METH(2)
      WRITE(1,51)
51    FORMAT(1X,'TYPE IN SIX DIGIT DATE')
      READ(6,52)IDAY ,MO,IYR
52    FORMAT(3I2)
888    WRITE(3,801)
801   FORMAT(1H1)
C     CONTROL CARD N IS THE NUMBER OF CARDS A IS ALPHA B IS BETA
      READ(2,1)N,A,B,D,PAR,METH  ,WET,INST,PREC,ACC,RANGE
1     FORMAT(I3,2F3.2,F2.2,T13,21A1,1X,21A1,1X,A1,1X,A1,1X,A1,1X,A1,2X,1
     *5A1)
      IF(A-9.99 )444,810,444
444   WRITE(3,50)IDAY,MO,IYR
50    FORMAT(1X,'ROBERT S. KERR WATER RESEARCH CENTER',26X,I2,'-',I2,'-'
     *,I2,///,1X,'SIGMA QUALITY CONTROL CHART INFO.')
      WRITE(3,400)PAR,METH  ,WET,INST,PREC,ACC,RANGE
400   FORMAT(//,' PARAMETER--',21A1,' METHOD--',21A1,//,1X,' WET--',A1,'
     * INST.--',A1,' PREC.--',A1,' ACC.--',A1,'  RANGE   ',15A1 )
      WRITE(3,900)
900   FORMAT(//,9X,'X',12X,'Y',12X,'D')
      SUM=.
      SUMSQ=.
C     COMPUTE THE SUM AND THE SUM OF THE SQUARES
      DO 3 I=1,N
      READ(2,2)  D1,D2
2     FORMAT(2F7.0)
      DI= I-.2
      WRITE(3,600) D1,D2,DI
600   FORMAT(1X,F12.4,1X ,F12.4,1X,F12.4)
      SUM=SUM+DI
3     SUMSQ=SUMSQ+DI**2
C     COMPUTE THE VARIANCE AND STANDARD DEVIATION
      VAR=(SUMSQ-((SUM**2)/N))/(N-1)
      STD=VAR**.5
      NM1=N-1
      XN=N
      DBAR=SUM/XN
      SDBAR=STD/XN**.5
      T=DBAR/SDBAR
      WRITE(3,909)DBAR,SDBAR,T,NM1
909   FORMAT(//,' DBAR',21X,'=',F16.7,/,1X,'SDBAR',30X,'=',F16.7,/,1X,'T'
     *,34X,'=',F16.7,1X,'WITH ',I3,' D.F.')
      S2=(N-1)**2*VAR
      S1=(N-1)**2*VAR
```

```
      F1=((1-B)/A)
      F2=S1/SO
      A1  =(2*ALOG(F1))/((1/SO)-(1/S1))
      DO 11L=1,2
      IF (L-2)12,13,13
12    M(1)=6
      GO TO 14
13    M(2)=10
14    B1=(ALOG(F2)/((1/SO)-(1/S1)))
      B2=B1*M(L)
      UL(L)=A1+B2
      F3=B/(1-A)
      A2  =(2*ALOG(F3))/((1/SO)-(1/S1))
11    XL(L)=A2  +B2
      WRITE(3,4) A,B,D
4     FORMAT(1X,'ALPHA',30X,'=',7X,F4.2,/,1X,'BETA',31X,'=',7X,F4.2,/,1X
     *,'DELTA',30X,'=',7X,F4.2)
      WRITE(3,22)VAR,STD
22    FORMAT(1X'VARIANCE OF THE DIFFERENCES',8X,'=',   F16.7,/,1X,'STAND
     *ARD DEVIATION OF DIFFERENCES',2X,'=',   F16.7)
      WRITE(3,21) SUM,SUMSQ
21    FORMAT(1X,'SUM OF DIFFERENCES',17X,'=',   F16.7 ,/,1X,'SUM OF SQUA
     *RES',21X,'=',   F16.7)
      WRITE(3,6) SO,S1
6     FORMAT(//,' S(0) SQUARED=',F16.7,3X,'S(1) SQUARED=',F16.7)
      WRITE(3,7)
7     FORMAT(//,20X ,'A',20X,'B', 9 X,'M')
      WRITE(3,8)
8      FORMAT(1X,71('-'))
      DO20 K=1,2
      WRITE(3,9)A1,B1,M(K) ,UL (K)
9      FORMAT(1X,'UL(M)=',2X, F15.6,4X,'+',2X,F15.6,'(M)',2X,I2,3X,'=',F
     $15.6)
20     CONTINUE
      DO25K=1,2
      WRITE(3,10) A2  ,B1,M(K),XL(K)
10    FORMAT(1X,'LL(M)=',1X,F16.6,4X,'+',2X,F15.6,'(M)',2X,I2,3X,'=',F15
     *.6)
25     CONTINUE
      WRITE(1,800)
800   FORMAT(1X,'END OF JOB')
      GO TO 888
810    CALL EXIT
      END

FEATURES SUPPORTED
 EXTENDED PRECISION
 IOCS

CORE REQUIREMENTS FOR
 COMMON       0  VARIABLES     304  PROGRAM     976

 END OF COMPILATION
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G. SAMPLE PROBLEM

SAMPLE X X X X 1-1.MG/L

[illegible] PSK[illegible]

[illegible].34	.33
.49	.49
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	.55
[illegible]	[illegible]
.33	[illegible]
.34	.34
[illegible]	.47
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]

[illegible] 999999999999999999999999999999999999999999999999999999999999