MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0360991 3

[redacted]

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

AEC RESEARCH AND DEVELOPMENT REPORT

ORNL-1931
Chemistry-General

4A

STATISTICAL EVALUATION OF METHODS FOR THE ANALYSIS OF DIBASIC ALUMINUM NITRATE (DIBAN)

J. G. Surak
P. F. Thomason

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this document, send in name with document and the library will arrange a loan.

OAK RIDGE NATIONAL LABORATORY
OPERATED BY
UNION CARBIDE NUCLEAR COMPANY
A Division of Union Carbide and Carbon Corporation
UCC
POST OFFICE BOX P · OAK RIDGE, TENNESSEE

[redacted]

[redacted]

[redacted]

[redacted]

ORNL-1931

This document consists of 44 pages.
Copy 4 of 244 copies. Series A

Contract No. W-7405-eng-26

ANALYTICAL CHEMISTRY DIVISION

M. T. Kelley, Director
C. D. Susano, Associate Director

STATISTICAL EVALUATION OF METHODS FOR THE ANALYSIS OF DIBASIC ALUMINUM NITRATE (DIBAN)

J. G. Surak and P. F. Thomason

DECLASSIFIED
CLASSIFICATION CHANGED TO:
BY AUTHORITY OF: TID-1148
BY: O. Menison 8/5/57

Edited by

H. P. Raaen

Date Issued:
SEP 1 1955

OAK RIDGE NATIONAL LABORATORY
Operated by
UNION CARBIDE NUCLEAR COMPANY
A Division of Union Carbide and Carbon Corporation
Post Office Box P
Oak Ridge, Tennessee

[redacted]

[redacted]

[redacted]

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0360991 3

[redacted]

ORNL-1931
Chemistry-General

INTERNAL DISTRIBUTION

[redacted]. C. E. Center
[redacted] Biology Library
[redacted] Health Physics Library
4-5[redacted]entral Research Library
6.[redacted]eactor Experimental
[redacted]gineering Library
7-11. [redacted]oratory Records Department
12. L[redacted]ratory Records, ORNL R.C.
13. C.[redacted] Larson
14. L.[redacted]Emlet (K-25)
15. J. P[redacted]urray (Y-12)
16. A. M.[redacted]inberg
17. E. H.[redacted]lor
18. E. D. S[redacted]ley
19. F. C. Vo[redacted]rLage
20. M. T. Kel[redacted]
21. C. P. Keim[redacted]
22. J. H. Frye,[redacted]
23. W. H. Jordan
24. J. A. Swartout[redacted]
25. F. L. Culler
26. S. C. Lind
27. A. H. Snell
28. A. Hollaender
29. G. H. Clewett
30. K. Z. Morgan
31. T. A. Lincoln
32. A. S. Householder
33. R. S. Livingston
34. D. S. Billington
35. C. E. Winters
36. D. W. Cardwell
37. E. M. King
38. D. D. Cowen
39. J. A. Lane
40. M. J. Skinner
41. G. E. Boyd
42. C. L. Burros
43. J. H. Cooper
44. L. T. Corbin
45. J. H. Edgerton
46. C. Feldman
47. D. J. Fisher
48. U. Koskela
49. W. R. Laing
50. C. E. Lamb
51. D. E. LaValle
52. G. W. Leddicotte
53. S. A. Reynolds
54. P. F. Thomason
55. T. E. Willmarth
56. G. R. Wilson
57. E. I. Wyatt
58. L. J. Brady
59. H. P. House
60. J. R. Lund
61. E. C. Lynn
62. O. Menis
63. A. S. Meyer, Jr.
64. A. F. Roemer, Jr.
65. C. D. Susano
66. C. K. Talbott
67. W. F. Vaughan
68. J. C. White
69. J. P. Young
70. H. P. Raaen
71. H. E. Goeller
72. A. T. Gresky
73. R. P. Wischow
74. C. W. Schersten
75. W. E. Unger
76. R. L. McCutchen
77. R. W. Dodson (consultant)
78. H. Eyring (consultant)
79. J. W. Kennedy (consultant)
80. G. T. Seaborg (consultant)
81. R. H. Muller (consultant)
82. N. H. Furman (consultant)
83. J. G. Surak
84-85. ORNL Document Reference Library, Y-12 Branch

EXTERNAL DISTRI[redacted]ON

[redacted]entative, Wood-Ridge
[redacted]nc.
88-[redacted]Laboratory
[redacted]

[redacted]

94. Armed Forces Special Weapons Project (Sandia)
95. Army Chemical Center
96. Arthur D. Little, Inc.
97-[illegible]. Atomic Energy Commission, Washington
1[illegible] Battelle Memorial Institute
103-10[illegible] Bettis Plant (WAPD)
105-106. Brookhaven National Laboratory
107-108. Union Carbide Nuclear Company (C-31 Plant)
109-111. Union Carbide Nuclear Company (K-25 Plant)
112. Chicago Patent Group
113. Chief of Naval Research
114. Columbia University (Hassialis)
115. Division of Raw Materials, Washington
116. Dow Chemical Company (Rocky Flats)
117. Dow Chemical Company, Pittsubrgh
118-120. duPont Company, Augusta
121. duPont Company, Wilmington
122-124. General Electric Company (ANPD)
125-130. General Electric Company, Richland
131-132. Goodyear Atomic Corporation
133. Hanford Operations Office
134. Iowa State College
135-138. Knolls Atomic Power Laboratory
139-140. Los Alamos Scientific Laboratory
141. Mallinckrodt Chemical Works
142. Materials Laboratory (WADC)
143. Mound Laboratory
144. National Advisory Committee for Aeronautics, Cleveland
145. National Bureau of Standards
146. National Lead Company, Inc., Winchester
147. National Lead Company of Ohio
148. Naval Medical Research Institute
149. Naval Research Laboratory
150. New Brunswick Area Office
151. New York Operations Office
152-153. North American Aviation, Inc.
154. Nuclear Metals, Inc.
155. Patent Branch, Washington
156-159. Phillips Petroleum Company (NRTS)
160. Pratt & Whitney Aircraft Division (Fox Project)
161. Public Health Service
162. Rohm and Haas Company
163. Sandia Corporation
164. Sylvania Electric Products, Inc.
165. Tennessee Valley Authority (Walker)
166. USAF Project Rand
167. U. S. Naval Postgraduate School
168. U. S. Naval Radiological Defense Laboratory
169. UCLA Medical Research Laboratory

170-171. University of California Radiation Laboratory, Berkeley
172-17[redacted]niversity of California Radiation Laboratory, Livermore
17[redacted]ersity of Rochester
175. Vi[redacted]-Carolina Chemical Corporation
176. Vitro [redacted]eering Division
177. Vitro Lab[redacted]ies
178. Western Reser[redacted]rsity (Friedell)
179-243. Technical Informat[redacted]rvice, Oak Ridge
244. Division of Research and Medicine, AEC, ORO

[redacted]

TABLE OF CONTENTS

Page

0. Abstract 1

1. Foreword 2

2. Summary 3

3. Determination of Aluminum 5

3.1 Introduction 5
3.2 Qualitative Spectrographic Method 5
3.3 Gravimetric Methods 6

3.3.1 Hydrolysis of Diban 48-1 with Ammonium Hydroxide 6
3.3.2 Direct-Ignition Method 8
3.3.3 Statistical Evaluation of Gravimetric Methods . . 9

3.4 Potassium Fluoride--Acid Titration Volumetric Method . . 12

3.4.1 Effect of Digestion of Diban 13-RD-66 with Nitric Acid 12
3.4.2 Effect of Sodium Potassium Tartrate as Catalyst . 14

3.5 Oxine Spectrophotometric Method 17

4. Determination of Basicity 21

5. Determination of Nitrate 23

6. Determination of Total Nitrogen 25

7. Determination of Ammonia 26

8. Causes of Error in Determinations of Total Nitrogen and Ammoniacal Nitrogen 27

9. Conclusions and Recommendations 29

10. Acknowledgement 34

11. Appendices 35

11.1 Detailed Calculations for the Statistical Evaluation of Data Presented in Table 2-B 35
11.2 Detailed Calculations for the Statistical Evaluation of Methods Compared in Table 2-C 36

12. Bibliography . . . [redacted] 37

[redacted]

[redacted]

LIST OF TABLES

Table Number	Table Title	Page
1	Qualitative Spectrographic Specifications for Diban	5
2	Aluminum in Diban 48-1: Comparison of Gravimetric Methods by Statistical Evaluation of the Data	7
3	Aluminum in Diban 13-RD-66 and in Diban 48-1 by the Direct-Ignition Method: Determination of the Standard Error of the Average	11
4	Aluminum in Diban 13-RD-66 by Potassium Fluoride--Acid Titration: Effect of Digestion with Conc. HNO_3 upon Diban	13
5	Aluminum in Diban 48-1 by Potassium Fluoride--Acid Titration: Effect of Catalyst on the Precision of the Method	15
6	Spectrophotometric Determination of Aluminum with Oxine; Typical Calibration Data	18
7	Aluminum in Diban 13-RD-66 by the Oxine Spectrophotometric Method	20
8	Basicity (Hydroxyl Value) of Diban 48-1 Determined by the Potassium Oxalate--Acid Titration Method	22
9	Nitrate, Ammonia, and Total Nitrogen in Diban 48-1	24
10	Proposed Specifications for Diban	32
11	Acceptable Limits of Concentrations of Contaminants	33

[redacted]

[redacted]

LIST OF FIGURES

Figure Number	Title	Page
1	Typical Calibration Curve for the Spectrophotometric Determination of Aluminum with Oxine	19

[redacted]

[redacted]

0. Abstract

The indicated methods for determining the following constituents of Diban, which is an aqueous solution of dibasic aluminum nitrate, $Al(OH)_2NO_3$, were evaluated statistically:

1. aluminum by gravimetric, volumetric, and spectrophotometric procedures,
2. basicity (hydroxyl value) by formation of an aluminum complex and titration of the free acid with standard alkali solution,
3. total nitrogen by the Kjeldahl method,
4. ammonia by the Kjeldahl method, and
5. nitrates by means of a cation-exchange resin and titration of the liberated acid with standard alkali solution.

Recommendations are made regarding the preferred methods of determining the constituents in dibasic aluminum nitrate and regarding means of minimizing errors in these analyses.

[redacted]

[redacted]

1. Foreword

Dibasic aluminum nitrate, $Al(OH)_2NO_3$, is a noncrystalline compound in which the nitrate ions do not satisfy the sum of all the charges of the aluminum ions. Its solutions (Diban) have been called "acid deficient", even though they have pH values of approximately 2 to 3. When in the Thorex process, Diban is added to a solution of thorium nitrate, the thorium nitrate can be extracted into tributyl phosphate (TBP) and thus be highly decontaminated from fission products.

Because Diban is to be purchased from various chemical supply houses, the following were considered necessary: (1) a statistical evaluation of methods for determining the constituents of Diban, (2) a study of possible causes of errors in the methods of analysis, and (3) recommendations regarding methods preferred and ways of eliminating errors in the methods. The statistical evaluation and terminology are in accord with those recommended by McCutchen.[3]

Two samples of Diban, supplied by two different chemical houses, were used in this study. In this report, these samples are identified as Diban 48-1 and Diban 13-RD-66.

[redacted]

[redacted]

2. Summary

The gravimetric determination of aluminum by the hydrolytic precipitation of its hydroxide gives satisfactory results for pure salts of the element. Since the amounts of trace impurities in Diban are of the order of 1 wt %, the relatively simple method of gravimetric determination of aluminum by direct ignition can be used. The precision of the method, expressed as relative standard deviation, is 1 % for a 0.50-ml sample ($[Al] \cong 100$ mg/ml).

The volumetric method for the determination of aluminum by complexing with potassium fluoride depends upon the reaction of aluminum hydroxide, formed by the neutralization of an aluminum salt, with potassium fluoride to form the neutral salt $AlF_3 \cdot 3KF$ and to liberate three moles of potassium hydroxide per mole of aluminum present. However, the $[Al(OH)_2]^+$ complex is stable, and prior digestion with nitric acid is required to convert it to Al^{3+} and to make it possible to precipitate the aluminum as $Al(OH)_3$ by the neutralization reaction.

The basicity (hydroxyl value) of Diban is determined by complexing the aluminum in it with potassium oxalate. The formation of the stable, soluble complex between aluminum and oxalate releases the coordinated hydroxyl groups from the coordination sphere of aluminum. These released hydroxyl groups are neutralized by HCl, added in excess, the excess being back-titrated with sodium hydroxide solution. The precision of the method, expressed as relative standard deviation, is 1 % for a 100-µl sample of Diban.

[redacted]

[redacted]

The probable causes of errors in nitrate determinations (total nitrogen and ammoniacal nitrogen) are discussed, and recommendations for minimizing these errors are made. A relative standard deviation of about 2 % and a relative standard error of ± 3 to 4 % for a probability level of 95 % can be obtained.

Conclusions and recommendations based on the statistical evaluation of the data obtained are presented in Section 9.

[redacted]

[redacted]

3. Determination of Aluminum

3.1 Introduction

Aluminum is generally determined by gravimetric methods, but other metals present may also be precipitated, which would make it necessary to calculate the amount of aluminum by difference. The few known methods for the volumetric determination of aluminum usually have very limited applications. The purpose of this investigation was to evaluate statistically various methods for the determination of aluminum and to indicate their applicability to the analysis of Diban.

3.2 Qualitative Spectrographic Method

The results of spectrographic analyses of both samples of Diban (48-1 and 13-RD-66) for trace amounts of impurities met the qualitative spectrographic analytical specifications listed in Table 1.

Table 1

Qualitative Spectrographic Specifications for Diban[a]

Intensity	Element[b]
VS	Al
S	None
M	None
W	None
VW	None
T	Fe, Si (ppm)
FT	Ca, Cr, Mg
VFT	B

(a) Proposed by the Chemical Technology Division.
(b) Sought but not found were: Ag, As, Au, Ba, Cu, Hg, Mn, Mo, Na, Ni, Pb, Sn, Ta, Ti, V, and Zn.

[redacted]

[redacted]

3.3 Gravimetric Methods

The usual gravimetric method for the determination of aluminum depends upon the hydrolysis of a soluble salt of aluminum by neutralization of the free and combined acids with ammonia. In the direct determination of aluminum by this procedure, cations of the following metals must be excluded because they will co-precipitate with the aluminum under similar conditions: Fe, Cr, Nb, Be, In, Ga, Ge, Zr, rare earths, Ta, Ti, Si, V, and B. The precipitation of $Al(OH)_3$ is complete between pH 7.0 and 7.5. At pH greater than 10, the hydroxide is appreciably soluble.

3.3.1 Hydrolysis of Diban 48-1 with Ammonium Hydroxide

The equipment, reagents, procedure, and precautions used in the hydrolysis of Diban 48-1 with ammonium hydroxide were those specified by Scott.[1] Samples of Diban 48-1 of 500-µl size were used. The pipet was rinsed three times with 1 N HNO_3 after the Diban was delivered. The results of these analyses are given in Table 2. The aluminum content of Diban 48-1 by this gravimetric method was found to be 102.04 mg/ml ± 1 %. For a 500-µl sample of Diban 48-1, the precision of the method, expressed as relative standard deviation, is 1 %. The detailed calculations of the statistical evaluation of the data are given in Apx. 11.1; these calculations are typical of the other similar statistical evaluations reported herein.

[redacted]

[redacted]

Table 2

Aluminum in Diban 48-1:
Comparison of Gravimetric Methods by Statistical Evaluation of the Data

A. Data

Aluminum, mg/ml		
Hydrolytic Method[a]	Direct-Ignition Method	
	Without conc. HNO_3	With conc. HNO_3
101.27	103.28	103.92
102.12	104.20	102.43
100.42	102.75	102.65
102.96	103.70	103.39
103.49	103.81	103.49
103.43	104.34	104.18
101.59	101.88	103.49

B. Statistical Evaluation of Data

N	7	14
D.F.	6	13
$\bar{X}$	102.04 mg/ml	103.39 mg/ml
S^2	1.088	0.603
S_R	1.02 %	0.75 %
S.E.$_R$[a]	1 %	0.5 %
C.I.[b]	102.0 mg/ml ± 1 %	103.4 mg/ml ± 0.5 %

C. Statistical Evaluation of the Methods

1. Analysis of Variance ("F" test)

$$F_e = \frac{1.088}{0.603} = 1.80$$

F_t = 2.92 (95 % Probability Level)
F_t = 4.62 (99 % Probability Level)

($D.F._1$ = 6 and $D.F._2$ = 13)

2. Homogeneity of Averages[c] (Student's "t" test)

t_e = 3.18

t_t = 2.09 (95 % Probability Level)
t_t = 2.86 (99 % Probability Level)

(D.F. = 19)

(a) 95 % probability level.
(b) C.I. = confidence interval.
(c) See Apx. II for calculations involved in testing the homogeneity of averages.

[redacted]

[redacted]

[redacted]

3.3.2 Direct-Ignition Method

In the direct-ignition method, the Diban 48-1 is oxidized to Al_2O_3 by ignition to constant weight in a muffle furnace at a temperature of 1000° C. Volumes of 0.50 ml of Diban 48-1 were measured by means of a microburet into tared crucibles that had been ignited previously to constant weight. The measured samples were carefully evaporated to dryness on a hot plate or by means of an infrared lamp in order to prevent any losses by spattering. The dehydrated Diban 48-1 samples were then ignited to constant weight in the muffle furnace at 1000° C. Concentrated nitric acid was added to some of the samples before the drying and ignition. The results are given in Tables 2-A.

The results of the statistical evaluation of the data are given in Table 2-B. No significant difference in the precision of the results was observed whether or not the Diban samples were treated with nitric acid. The aluminum concentration of Diban 48-1, determined by the direct-ignition gravimetric method, was found to be 103.39 mg/ml ± 1 % at the 95-% probability level. For a 0.50-ml sample, measured from a microburet, the precision of the method, expressed as relative standard deviation, was ~ 1 %. The average of the results obtained by the direct-ignition method was about 1 % higher than the average of the results obtained by the gravimetric method involving the hydrolysis of an aluminum salt with ammonium hydroxide.

[redacted]

[redacted]

[redacted]

3.3.3 Statistical Evaluation of Gravimetric Methods

Since the qualitative spectrographic analysis of Diban 48-1 showed that the only metal present in large quantity is aluminum and that the other metals present are found in trace quantities only, it was decided to determine statistically whether there is any significant difference between the precision of the two gravimetric methods for the determination of aluminum in Diban. The detailed calculations for the statistical evaluation are given in Apx. 11.2 and summarized in Table 2-C.

The variance ratio or "F" test is used to compare two sets of data to determine whether the difference between the precisions of the two sets of data is significant (see Table 2-C1). For the data obtained by the two gravimetric methods, comparison of the experimental and theoretical "F" values shows that the experimental "F" value is less than the theoretical "F" value at both the 95- and 99-% probability levels, thus indicating that there is no significant difference between the precisions of the two sets of data; therefore, they can be considered to be essentially the same.

For this reason, Student's "t" test was applied to determine whether the difference between the averages of these two sets of data is significant. The results are given in Table 2-C2. Since the experimental "t" value, "t_e", is greater than the theoretical "t" value, "t_t", at both the 95- and 99-% probability levels, the difference between the two averages is significant and is not due to chance variation.

[redacted]

[redacted]

Impurities in Diban, determined by spectrographic analysis, are of the order of 1 wt %. Some of these trace impurities can be removed by the reprecipitations required by Scott's method.[1] However, the direct-ignition gravimetric method for the determination of aluminum in Diban is recommended in preference to Scott's hydrolytic method and to the various volumetric methods because of its comparative simplicity, rapidity, and precision. A correction factor can be applied to take into account the trace impurities in Diban.

A comparison of the aluminum content of Diban 13-RD-66 and of Diban 48-1 as determined by the direct-ignition gravimetric method was made. The 0.50-ml sample was measured by means of a microburet. The aluminum concentrations were 117.2 and 103.4 mg/ml $\pm$ 1 %, respectively. The results for the gravimetric determination of aluminum in Diban 13-RD-66 and 48-1 by the direct-ignition method are given in Table 3.

[redacted]

[redacted]

Table 3

Aluminum in Diban 13-RD-66 and in Diban 48-1

by the Direct-Ignition Method:

Determination of the Standard Error of the Average

A. Data

Aluminum, mg/ml	
Diban 13-RD-66	Diban 48-1
118.20	103.28
116.08	104.20
118.31	102.75
116.51	103.70
117.88	103.81
115.98	104.34
	101.88

B. Statistical Evaluation of the Data

N	6	7
D.F.	5	6
$\bar{X}$	117.2 mg/ml	103.4 mg/ml
S^2	1.181	0.905
S_R	0.9 %	0.9 %
$S.E._R$ [a]	± 1 %	± 1 %
C.I.	117.2 mg/ml ± 1 %	103.4 mg/ml ± 1 %

(a) 95 % probability level.

[redacted]

[redacted]

3.4 Potassium Fluoride--Acid Titration Volumetric Method

The potassium fluoride--acid titration method for the volumetric determination of aluminum depends upon the reaction of aluminum hydroxide with potassium fluoride to form the neutral salt $AlF_3 \cdot 3KF$; the aluminum hydroxide is formed by the neutralization to the phenolphthalein end point of an aluminum salt with barium hydroxide. Three moles of potassium hydroxide are liberated per mole of aluminum present. The potassium hydroxide that is formed is neutralized with an excess of standard acid, and the excess acid is back-titrated with a standard base.

3.4.1 Effect of Digestion of Diban 13-RD-66 with Nitric Acid

In the determination of aluminum in Diban 13-RD-66, the potassium fluoride--acid titration method written by Walker[9] was followed without modification. Because the pH of the Diban 13-RD-66 was 2.5, no nitric acid was added; this procedure was in accord with Note a of the method.[9] A 200-µl sample was taken. The pipet was rinsed three times with 1 N nitric acid after the Diban was delivered. The data are listed in Table 4-A. The average of the results of the determination of aluminum in Diban 13-RD-66 by this method was approximately 55 % low as compared with the average of the results obtained by the direct-ignition gravimetric method (see Table 3-B). It became apparent that the results were low because $[Al(OH)_2]^+$ is a very stable complex and because the potassium fluoride--acid titration method is intended for the determination of ionic aluminum in aqueous solution.

[redacted]

[redacted]

In view of their experience, the Laboratory and Semi-Works Control Unit suggested that the Diban be digested with concentrated nitric acid in order to convert the complexed aluminum to Al^{3+}. A 200-µl aliquot of Diban was heated to boiling in 5 ml of conc. HNO_3 until the volume of the solution was reduced to approximately 1 ml, the solution was then cooled and analyzed by the potassium fluoride--acid titration method. The results are also listed in Table 4-A.

Table 4

Aluminum in Diban 13-RD-66 by Potassium Fluoride--Acid Titration: Effect of Digestion with Conc. HNO_3 upon Diban

A. Data

	Aluminum, mg/ml	
	Diban not Digested	Diban Digested With conc. HNO_3
	59.1	94.5
	50.1	95.5
	48.1	94.9
	46.9	95.1
	54.8	97.1

B. Statistical Evaluation of Data

N	5	5
D.F.	4	4
$\bar{X}$	51.8 mg/ml	95.4 mg/ml
S	5 mg/ml	1.01 mg/ml
S_R	10 %	1 %

[redacted]

[redacted]

The average of the results obtained when Diban 13-RD-66 was digested with concentrated HNO_3 was in closer agreement with the average of the results obtained by the direct-ignition determination (see Table 3-B) than when no acid digestion was used. Nevertheless, it was approximately 15 % low. The relatively wide range of the results obtained by nitric acid digestion indicated that the optimum conditions required for the conversion of $[Al(OH)_2]^+$ to Al^{3+} need to be established if results of the potassium fluoride--acid titration volumetric method for ionic aluminum in aqueous solution are to be reliable.

3.4.2 Effect of Sodium Potassium Tartrate as Catalyst

The method of Snyder,[7] who used sodium potassium tartrate to catalyze the reaction between aluminum hydroxide and potassium fluoride, was considered. Since it had been established that digestion of Diban with concentrated HNO_3 for several minutes was essential for the conversion of the $[Al(OH)_2]^+$ complex to Al^{3+} for volumetric determination, all samples of Diban 48-1 were given this initial treatment. Samples of 200-µl volume were used, and analyses were made with and without the catalyst. The results are listed in Table 5-A.

[redacted]

[redacted]

Table 5

Aluminum in Diban 48-1 by Potassium Fluoride--Acid Titration:

Effect of Catalyst on the Precision of the Method

A. Data

Aluminum, mg/ml	
Without Catalyst	With Catalyst[a]
93.6	90.4
92.7	87.7
92.7	90.4
91.8	89.0
93.2	89.5
92.7	88.6
91.4	89.9

B. Statistical Evaluation of the Data

N	7	7
D.F.	6	6
$\bar{X}$	92.6 mg/ml	89.3 mg/ml
S^2	0.5882	1.0006
S_R	0.8 %	1 %
S.E.$_R$[b]	1 %	1 %
C.I.	92.6 mg/ml ± 1%	89.3 mg/ml ± 1%

C. Statistical Evaluation of the Procedures

1. Analysis of Variance ("F" test)

$F_e = 1.70$ $F_t = 4.28$ (95 % Probability Level)

$F_t = 8.47$ (99 % Probability Level)

($D.F._1 = 6$, $D.F._2 = 6$)

2. Homogeneity of Averages (Student's "t" test)

$t_e = 6.30$ $t_t = 2.18$ (95 % Probability Level)

$t_t = 3.06$ (99 % Probability Level)

(D.F. = 12)

(a) Sodium potassium tartrate
(b) 95-% probability level

[redacted]

[redacted]

A statistical evaluation was made to determine whether there was any significant difference between the precisions of the two sets of data and between the means of the results. The analysis of variance, "F" test, and the Student's "t" test were applied. The statistical evaluations are summarized in Table 5-B and -C.

A comparison of the experimental "F" value with the theoretical "F" value shows that the experimental value is much lower than the theoretical value for both the 95- and 99-% probability levels; this indicates no significant difference between the precisions of the two sets of data--they can be considered to be essentially the same.

Student's "t" test was applied to determine whether the difference between the averages of the results obtained by the two procedures was significant. Because the experimental "t" value is much greater than the theoretical "t" value at both the 95- and 99-% probability levels, the difference between the two averages is considered to be significant and is not due to chance variations. The result obtained in the absence of sodium potassium tartrate was slightly better.

The use of sodium potassium tartrate, as specified by the method of Snyder,[7] has no particular advantage because it neither decreased significantly the reaction time nor improved the results (see Table 5). In fact, a serious error was possible if the sodium potassium tartrate was added to a strongly acidic solution of the aluminum. The tartrate formed the highly insoluble potassium acid tartrate, which precipitated immediately. The precipitate, which is

[redacted]

acidic in nature, redissolves slowly and results in a poor end point with phenolphthalein. The precision of the data of the procedures, expressed as relative standard deviation, was approximately 1 % in both cases. The average of the results obtained for Diban 48-1 by the volumetric methods (both with and without catalyst) was approximately 10 % lower than the results obtained by the direct-ignition method (see Table 3-B). This discrepancy may be due to (a) incomplete conversion of $\left[Al(OH)_2\right]^+$ to Al^{3+} in the nitric acid digestion step, (b) an uncertain end point in the back-titration since titrant is added until a faint-pink color is reached and remains for 30 seconds[9], or to (c) the addition of an excess of barium hydroxide when the Diban is neutralized, which would give low aluminum results. These sources of error must be eliminated if the results of the potassium fluoride--acid titration volumetric method for the determination of aluminum in Diban are to be reliable.

3.5 Oxine Spectrophotometric Method

A direct spectrophotometric determination of microgram amounts of aluminum is based on the formation of the internal salt of aluminum hydroxyquinolate, extraction of this complex into chloroform and measurement of the transmittancy of the yellow extract. The aluminum--oxine complex is slightly soluble in water and can be extracted quantitatively into chloroform from an acetate-buffered (pH 4.5 to 6.5) aqueous solution. The complex absorbs strongly at a wavelength of 395 mμ and follows Beer's law in the concentration range of 0 to 6 μg of aluminum per ml of chloroform.

[redacted]

[redacted]

The oxine spectrophotometric method for aluminum, written by Miller,[4] was followed without modification in the analysis of Diban 13-RD-66. A calibration curve (Fig. 1) was obtained by measuring the transmittancy for a series of solutions that contained various known amounts of aluminum from 10 to 50 µg. The calibration data are given in Table 6.

Table 6

Spectrophotometric Determination of Aluminum With Oxine[6]; Typical Calibration Data

	Transmittancy, %			
	Tests			
Aluminum, µg	1	2	3	Average
10	55.1	56.4	60.0	57.2
20	32.0	31.1	35.0	32.7
30	19.6	18.6	20.2	19.5
40	—	11.4	11.6	11.5

A 100-ml volume of Diban 13-RD-66 in a volumetric flask was diluted to 500 ml with 1 N nitric acid. For the aluminum determination, aliquots were taken of such size that each contained approximately 15 to 30 µg of aluminum. The procedure was the same as that used in the preparation of the calibration curve.[4] The aluminum in the extract was determined from the transmittancy and calibration curve. The total

[redacted]

[redacted]

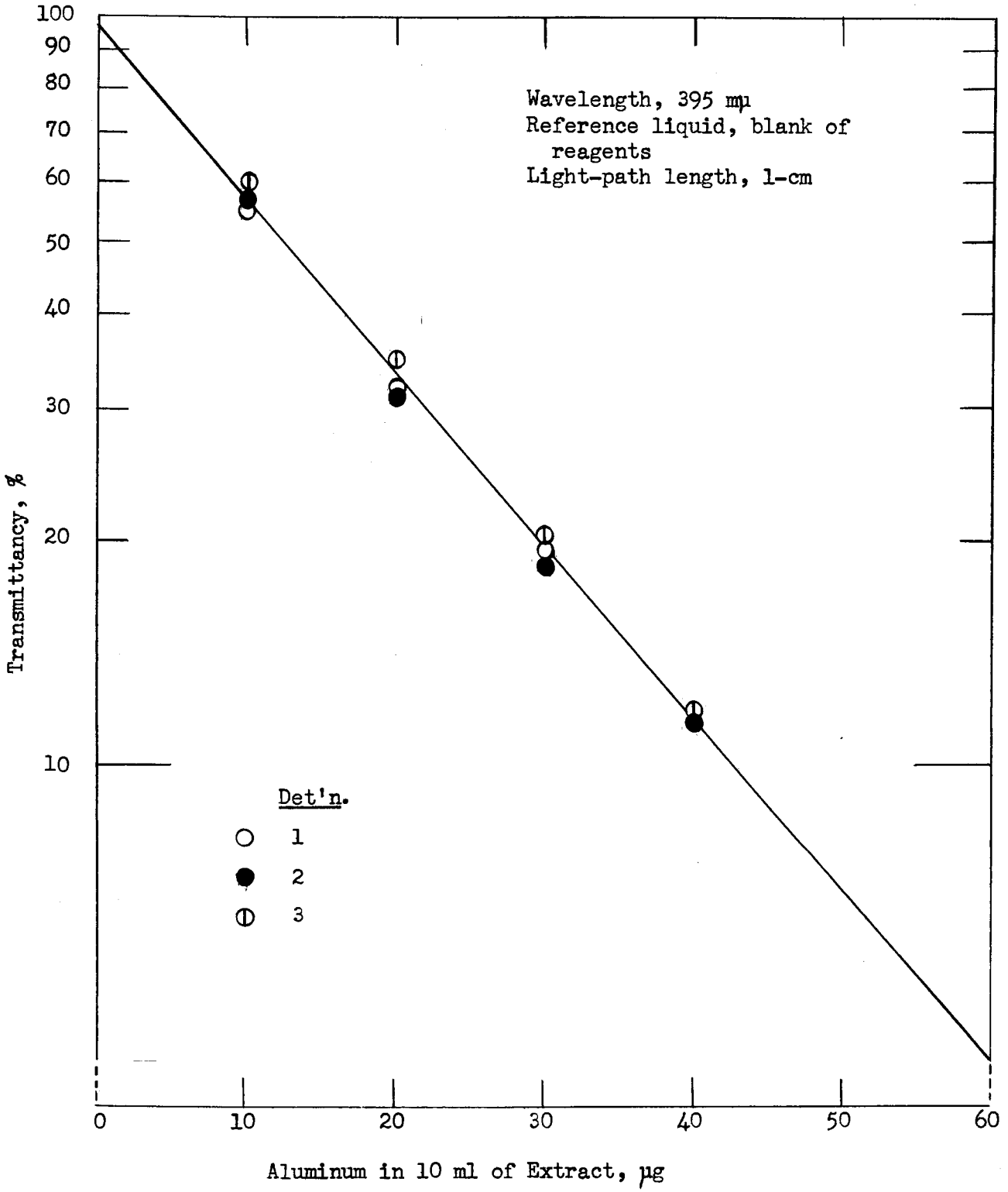

Fig. 1 Typical Calibration Curve for the Spectrophotometric Determination of Aluminum With Oxine

[redacted]

[redacted]

aluminum content of the sample was then computed. The results are presented in Table 7.

Table 7

Aluminum in Diban 13-RD-66 by the Oxine Spectrophotometric Method

A. Data

Aluminum, mg/ml
135
123
128
125
118
128
120

B. Evaluation of the Data

$N = 7$

$\bar{X} = 126$ mg/ml

$S = 6$ mg/ml

$S_R = 5$ %

$S.E._R = \pm 5$ % (95 % probability level)

$C.I. = 126$ mg/ml ± 5 %

The aluminum content of Diban 13-RD-66, determined by the spectrophotometric oxine method,[4] was found to be 126 mg/ml ± 4 % at the 95-% probability level. In the transmittancy range of 40 to 80 %, the precision of the data taken by this method and expressed as relative standard deviation was approximately 5 %. This spectrophotometric method is especially practical for the determination of micro quantities of aluminum and for the analysis of radioactive samples. The Diban purchased from commercial sources will be nonradioactive and will have an aluminum content of approximately 4.0 M; therefore, there is no advantage in using the spectrophotometric oxine method for the aluminum determination.

[redacted]

[redacted]

4. Determination of Basicity

Diban is a solution of a compound in which the nitrate ions do not satisfy the charges of the aluminum ions. Solutions of this type are sometimes called "acid deficient" even though the pH may be low. Although it is possible to calculate the hydroxyl molarity of Diban by taking the difference between the aluminum molarity and the nitrate molarity, assuming that any residual nitrate is associated with the ammonia that is present as an impurity, nevertheless, an analytical procedure for the determination of the hydroxyl value is recommended. An hydroxyl value obtained by calculation is affected by an accumulation of errors in the determinations of the constituents of Diban. Also, the determination of hydroxyl will serve as an additional check on whether the results of the other procedures account for 100 % of the constituents of Diban.

The procedure written by Wilson[11] was followed. To 100 µl of Diban 48-1, a 500-µl volume of standard hydrochloric acid solution, approximately 3 N was added. The aluminum in $Al(OH)_2NO_3$ was complexed with potassium oxalate; this reaction released the coordinated hydroxyl groups from the coordination sphere of the aluminum. The released hydroxyl groups neutralized some of the hydrochloric acid that was added in excess, and the excess acid was then back-titrated with standard sodium hydroxide solution, approximately 0.1 N, to a pH of 7.0. The Beckman automatic titrator was used. Data from these analyses are given in Table 8.

[redacted]

[redacted]

Table

Basicity (Hydroxyl Value) of Diban 48-1 Determined by The Potassium Oxalate--Acid Titration Method(11)

A. Data

Basicity, N	
7.25	7.20
7.30	7.25
7.25	7.30
7.20	7.20
7.20	7.20
7.25	7.30

B. Statistical Evaluation of the Data

$N = 12$

$\bar{X} = 7.24\ \underline{N}$

$S = 0.04\ \underline{N}$

$S_R = 0.5\ \%$

$S.E._R = \pm\ 0.5\ \%$ (95-% probability level)

$C.I. = 7.24\ \underline{N} \pm 0.5\ \%$

The precision of the data taken by this method and expressed as relative standard deviation is 0.5 %. Possible deviations from the true hydroxyl value are discussed in Section 9 of this report.

[redacted]

[redacted]

[redacted]

5. Determination of Nitrate

The nitrates in Diban are those associated with the aluminum as $Al(OH)_2NO_3$ and those associated with the ammonium ion, an impurity which is formed in the process of manufacturing Diban. The nitrates are determined indirectly by passing a volume of Diban through a cation-exchange resin (acid-form), and titrating the total liberated nitric acid to the methyl red indicator end point.

In the analysis of Diban 48-1, the procedure written by Walker[10] was followed. A 0.5-ml sample of Diban 48-1 was pipeted onto the Dowex 50 (12 % cross-linked, 200 to 400 mesh) resin column. The total liberated nitric acid was titrated with standard sodium hydroxide solution, approximately 0.1 N, to a methyl red indicator end point or to pH 5.0 as indicated by the Beckman automatic titrator. See Table 9 for the experimental results.

In the preparation of the hydrogen form of the Dowex-50 cation-exchange resin, it is imperative that the resin be washed free from anions and that the washings be neutral to methyl red indicator. Conditions that reduce column efficiency, such as channeling and entrapment of air, must be prevented. This procedure permits the rapid determination of nitrates in Diban; the precision of the data taken by this method and expressed as relative standard deviation is about 2 %.

[redacted]

[redacted]

Table 9

Nitrate, Ammonia, and Total Nitrogen in Diban 48-1

A. Data

	Nitrogen, N		
	Nitrate (Ion Exchange)(10)	Ammonia (Kjeldahl)(2)	Total (Kjeldahl)(2)
	4.03	0.121	4.20
	3.89	0.121	4.16
	3.95	0.131	4.22
	3.91	0.121	4.00
	4.03	0.131	4.15
	4.04	0.121	4.24
	3.93	0.121	4.26
	4.05	--	4.14

B. Evaluation of the Data

N	8	7	8
$\bar{X}$	3.98 N	0.123 N	4.17 N
S	0.07 N	0.005 N	0.08 N
S_R	2 %	4 %	2 %
$S.E._R$(a)	2 %	5 %	2 %
C.I.	3.98 N ± 2 %	0.123 N ± 5 %	4.17 N ± 2 %

(a) 95-% probability level

[redacted]

[redacted]

6. Determination of Total Nitrogen

Total nitrogen in Diban 48-1 was determined by reducing the inorganic nitrates to ammonia in an alkaline solution by means of Devarda's alloy.(2) The ammonia evolved was distilled into 4 % boric acid solution and titrated with standard acid. The procedure and apparatus used were adapted from the method written by Surak.(8) Devarda's alloy was used to reduce the inorganic nitrates and nitrites present, and the ammonia evolved was steam-distilled into 4 % boric acid solution that contained brom cresol green--methyl red mixed indicator. The pH of the boric acid solution was previously adjusted to 5 by use of a pH meter. Initially, the indicator was pink in color but during the distillation the color changed to green when the distillate became buffered at a pH 8. The distillate was titrated to a pH of 5 with standard hydrochloric acid solution, approximately 0.1 N, by means of a Beckman automatic titrator (see Table 9).

If the precautions presented in Section 8 of this report are observed, the precision of the data taken by this method and expressed as relative standard deviation is 2 %.

[redacted]

[redacted]

7. Determination of Ammonia

Free ammonia in Diban 48-1 was determined by distilling a sample of Diban directly with alkali. This procedure is identical with the procedure for the nitrate determination except that the reduction with Devarda's alloy was omitted.

If the suggestions presented in Section 6 are followed, a relative standard deviation of about 4 % can be realized (see Table 9).

[redacted]

[redacted]

8. Causes of Errors in Determinations of Total Nitrogen and Ammoniacal Nitrogen

Errors that may occur in the Kjeldahl method for the determination of nitrogen, together with suggestions for minimizing these errors, are discussed in the following paragraphs.

1. In Devarda's method,[2] a fine mist of alkali is entrained by the liberated hydrogen. A simple Hopkins bulb does not adequately prevent the fine mist from contaminating the distillate. A scrubber designed by the authors[8] reduces the carry-over of spray.

2. A cold-water bath should be used to control the temperature of the reaction between the Devarda's alloy and the alkali. The evolution of hydrogen should be controlled to prevent the carry-over of a fine spray of alkali into the distillate. When the reaction has subsided or when most of the hydrogen has been evolved, steam distillation can be started. The rate of steam distillation should be controlled. Initial steam distillation at too rapid a rate will cause the ammonia to escape through the boric acid solution without being absorbed.

3. Cleanliness is of utmost importance. Detergents and soap films must be removed from receivers that contain the boric acid solution. The assembled Kjeldahl apparatus should be cleaned out by steaming prior to its use in order to wash out any adhering alkaline spray.

4. The volume of distillate that is collected for the blank should be the same as that for the determinations.

[redacted]

[redacted]

5. Although the solution can be titrated manually to the end point of a brom cresol green--methyl red mixed indicator, it is recommended that the Beckman automatic titrator be used and that the titration be made to the pH of the blank (pH 5.0).

6. Since boric acid becomes buffered at a pH of 8, sufficient boric acid must be used to ensure that all the ammonia evolved is absorbed.

7. The pH of the 4 % boric acid solution should be adjusted initially to 5 (pink color of the mixed indicator), and the back titration should be made to this same pH value (refer to notes in Surak's method[8]).

8. If the solid NaOH used for making the 40- to 50-% NaOH solution is not of reagent grade, it is recommended that Devarda's alloy be added to the NaOH solution to reduce any nitrate impurities to ammonia, which can then be removed by boiling the NaOH solution. The pretreated NaOH solution should be filtered through glass wool to remove excess alloy.

9. It is necessary to analyze separate samples of Diban for the determination of free ammonia and for total nitrogen by the Kjeldahl method.

[redacted]

[redacted]

9. Conclusions and Recommendations

On the basis of the data obtained by the various methods used for the analysis of dibasic aluminum nitrate (Diban) and of the statistical evaluation of the data, the following recommendations are submitted:

1. The direct-ignition gravimetric method is recommended for the determination of aluminum in Diban. A correction factor for the trace quantities of metallic impurities may be necessary.

2. In any of the volumetric methods for the determination of aluminum in Diban, it is necessary to convert the aluminum that is complexed as $\left[Al(OH)_2\right]^+$ to Al^{3+} in order for the results of volumetric methods(7) for aluminum to be reliable. It will be necessary to determine the optimum conditions for the complete conversion. It is also recommended that pH rather than a phenolphthalein end point, detected visually, be the criterion for the end point of the titration.

3. In the determination of nitrates and ammoniacal nitrogen in Diban by the modified Devarda method, the suggestions and precautions listed in Section 8 should be observed.

4. Basicity (hydroxyl value) of Diban should be determined directly rather than by difference. It will then serve as an additional check on whether the results of the other procedures account for 100 % of the components of Diban. An hydroxyl value obtained by calculation is affected by an accumulation of errors in the determinations of the various constituents of Diban.

[redacted]

[redacted]

5. Impurities, such as ammonium nitrate and sometimes the nitrite, will be formed during the preparation of Diban. The aluminum amalgam that is used in the preparation of Diban can reduce some of the nitrates and nitrites present to ammonia. Another source of ammonia is the reaction of the aluminum amalgam with any adhering film of oil or grease that may adhere to the aluminum metal. Appreciable amounts of these impurities would give erroneous hydroxyl values in the determination of basicity. Consider ammonium nitrate, which is subject to hydrolysis according to the equation

$$NH_4NO_3 + H_2O \rightleftharpoons NH_4OH + HNO_3.$$

Since the NH_4OH is a weak base and incompletely dissociated, part of the standard acid would be used to repress the hydrolysis of the NH_4NO_3. Consequently, the volume of standard base used in back titration would be smaller than that required if NH_4NO_3 were absent, and therefore the hydroxyl value (basicity) calculated for such a solution would be high. A similar error would occur if nitrites were present in Diban. In both cases, the greater the quantity present, the higher will be the resulting hydroxyl number. It is recommended that any reducing substances that are formed in Diban during its preparation be destroyed and also that the quantity of ammonium and nitrite ions, introduced as impurities during the preparation of Diban, be kept to a minimum.

6. Diban solutions should be clear. A turbidity indicates that the Diban contains a suspension of aluminum hydroxide. The Chemical Development Section of the Chemical Technology Division has demonstrated

[redacted]

that Diban of the composition 4 M Al^{3+}, 6 to 8 N OH^-, and 4 to 6 N NO_3^-, is stable for several months if it is not exposed to air.

Recent modifications of the Thorex process utilize a more dilute solution of Diban. These modifications are based upon using a 0.2 M "acid deficient" aluminum nitrate solution as the scrub solution in place of the 0.75 M solution, as is specified in the original flow sheet. Both specifications are listed in Table 10. In addition, the specifications proposed by the Chemical Development Section of the Chemical Technology Division (see Tables 10 and 11) should be the criteria for purchasing dibasic aluminum nitrate for Thorex process use from chemical supply houses.

[redacted]

Table 10

Proposed Specifications for Diban[a]

	Old (1953)	New (1955)
Al^{3+}	3.74 M[a]	3.5 M maximum 3.2 M minimum
OH^-	7.50 M	2.4 M minimum 2.8 M maximum
N, total by Kjeldahl	5.80 M	8.65 M maximum
NO_3^-, by Ion-Exchange	5.04 M	6.8 M minimum
NH_3 by Distillation	0.55 M	0.25 M maximum
Cations, total normality ($3\ Al^{3+} + NH_3$)	11.77 N	(Omit)
Anions, total normality ($OH^- + NO_3^-$)	12.54 N	(Omit)
OH/Al Ratio	2.01[c]	0.75 (typical)
NH_3/OH Ratio	0.073	(Omit)
Specific Gravity	~ 1.35	~ 1.35

(a) Proposed by Chemical Development Section, Chemical Technology Division.

(b) An aluminum concentration of 4.0 M was preferred.

(c) An OH/Al ratio of 1.95 to 2.00 was preferred.

[redacted]

[redacted]

Table 11

[redacted]

Acceptable Limits of Concentrations of Contaminants[a]

Contaminants	Maximum Parts of Contaminants per Million Parts of Al_2O_3[b]
B	50
Be	2
Li	200
Ca	20
Mg	100
P	5000
Si	2000
Fe, Cr, Ni	5000
Cu	20
Ga	300
Hg	2000
Mn	1500
Ti	60
V	600

(a) The Chemical Technology Division recommends that a maximum tolerance also be applied to the total amount of halides, alkali and alkaline earth metals (Na, K, etc.), and spurious anions (SO_4^{2}, PO_4^{3}, etc.).

(b) Old and new specifications identical.

[redacted]

[redacted]

10. Acknowledgement

The authors wish to thank Mrs. Roberta McCutchen for her assitance in the preparation of the statistical evaluations given in this report.

[redacted]

[redacted]

11. Appendices

11.1 Detailed Calculations for the Statistical Evaluation of Data Presented in Table 2-B

Statistical evaluation of results obtained for the determination of aluminum in Diban 48-1 and the calculations used in the evaluation are given for the following data :

Aluminum in Diban 48-1

Hydrolytic Gravimetric Method of Scott[1]

Aluminum mg/ml (x)	$(x - \bar{X})$	$(x - \bar{X})^2$
101.27	0.77	0.5929
102.12	0.08	0.0064
100.42	1.62	2.6244
102.96	0.92	0.8464
103.49	1.45	2.1025
102.43	0.39	0.1521
101.59	0.45	0.2025
Σx = 714.28		$\Sigma(x-\bar{X})^2$ = 6.5272

Number of determinations (N) = 7

Degrees of Freedom (D.F.) = 6

Variance (S^2) = 6.5272/6 = 1.0879

Standard Deviation (S) = $\sqrt{1.0879}$ = 1.04 mg/ml

Average $(\bar{X})$ = 714.28/7 = 102.04 mg/ml

Relative Standard Deviation $(S_R) = \frac{1.04 \times 100}{102.04} = 1.02\ \%$

Standard Error of the Average (S.E.) = $\pm$ S t/ $\sqrt{N}$ = 1.04 x 0.92 = $\pm$ 0.96 mg/ml

$(S.E._R) = \pm$ St/ $\sqrt{N}$ = 1.02 x 0.92 = $\pm$ 1 %

t/ $\sqrt{N}$ = 0.92 (95% probability level, at 6 degrees of freedom)

Confidence Interval (C.I.) = $\bar{X} \pm S.E._R$ = 102.04 mg/ml $\pm$ 1 %.

[redacted]

[redacted]

11.2 Detailed Calculations for the Statistical Evaluation of Methods Compared in Table 2-C

Calculations for testing the homogeneity of averages for the data given in Table 2-C are as follows:

Homogeneity of Averages (Students "t" Test)

$$t_e = \frac{(\bar{X}_1 - \bar{X}_2)}{\sqrt{N_1 S_1^2 + N_2 S_2^2}} \times \sqrt{\frac{(N_1 N_2)(N_1 + N_2 - 2)}{N_1 + N_2}}$$

$$t_e = \frac{(103.39 - 102.04)}{\sqrt{8.439 - 7.615}} \times \sqrt{\frac{(14)\ (7)\ (14 + 7-2)}{14 + 7}} = 3.18$$

$N_1 S^2_1 = (14)(0.603) = 8.439$

$N_2 S^2_2 = (7)(1.088) = 7.615$

D.F. $= N_1 + N_2 - 2$

D.F. $= (14 + 7) - 2 = 19$

Theoretical Values for "t" at D.F. = 19

t_t = (95 % probability level) = 2.09

t_t = (99 % probability level) = 2.86

[redacted]

[redacted]

12. Bibliography

1. N. H. Furman, Scott's Standard Methods of Chemical Analysis, Vol. I, p. 8, Van Nostrand, New York, 1939.

2. H. A. Lepper, Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists, 6th ed., p. 28, Assoc. Offic. Agr. Chemists, Washington, 1945.

3. R. L. McCutchen, "Statistical Treatment of Data," Method Nos. 1 0060 and 9 0050, ORNL Master Analytical Manual .

4. F. J. Miller, "Aluminum in the Presence of Thorium, Spectrophotometric Oxine (8-Hydroxyquinoline) Method" Method No. 9 0122020, (2-19-54), ORNL Master Analytical Manual, ORNL CF-53-1-235, Vols. I and III. (Classified).

5. H. S. Miller, "A Source of Loss of Ammonia in Kjeldahl Distillations," Ind. Eng. Chem., Anal. Ed., 8, 50 (1936).

6. A. L. Prince, "Report on Nitrogen," J. Assoc. Offic. Agr. Chemists, 8, 410 (1925).

7. L. J. Snyder, "Rapid Volumetric Method for Aluminum," Ind. Eng. Chem., Anal. Ed., 17, 37 (1945).

8. J. G. Surak, "Lithium Nitride in Lithium Metal -- Micro Kjeldahl Distillation Method," Method Nos. 1 220013 and 9 0072001, (7-30-54), ORNL Master Analytical Manual. (Manual No. 1 (record) only).

9. R. L. Walker, "Aluminum, Potassium Fluoride - Acid Titration Method," Method Nos. 1 210270 and 9 00710270, (5-20-54), ORNL Master Analytical Manual.

10. R. L. Walker, "Aluminum in Thorex Process Solutions, Indirect Ion-Exchange Method," Method No. 9 0122021, (9-25-53), ORNL Master Analytical Manual, ORNL CF-53-1-235, Vols. I and III. (Classified).

11. G. R. Wilson, "Free Acid in Thorex Process Solutions," Method No. 9 012205, (2-17-53), ORNL Master Analytical Manual, ORNL CF-53-1-235, Vols. I and III. (Classified).

[redacted]