A study of the Drotschmann activity test as applied to chemically prepared manganese dioxide
by James R Thurston

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering
Montana State University

Abstract:
Because of the long time required for determining the battery activity of manganese dioxide by standard drain test methods, the Drotschmann Activity Test was investigated as a method of predicting the efficiency of manganese dioxide samples intended for use in dry cells This thesis presents the original procedure as used by the Signal Corps; revisions made in the original procedure, and results obtained with the revised procedure as applied to the manganese dioxide produced by chemical syntheses at Montana State College* A. study of the original Signal Corps procedure has revealed that the following details caused variation in activity numbers obtained for the same manganese dioxide sample, 1) Shaking rate 2) Reaction time 3) Particle size The results obtained with the revised procedure show that the activity number does not show any correlation with the following (a) high or low drain tests, (b) phase structure, (c) manganese content, (d) available oxygen content, (e) apparent density, (f) pH, (g) water content, (h) manganese oxide content, (i) water of hydration content, and (j) bobbin weights.

At present there is no apparent correlation of activity number with any of the characteristics of battery active manganese dioxide; therefore, it is concluded that the Drotschmann Activity Test as outlined by the Signal Corps is of little use in quality control for the production of manganese dioxide.

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ABSTRACT

Because of the long time required for determining the battery activity of manganese dioxide by standard drain test methods, the Drotschmann Activity Test was investigated as a method of predicting the efficiency of manganese dioxide samples intended for use in dry cells.

This thesis presents the original procedure as used by the Signal Corps; revisions made in the original procedure, and results obtained with the revised procedure as applied to the manganese dioxide produced by chemical syntheses at Montana State College.

A study of the original Signal Corps procedure has revealed that the following details caused variation in activity numbers obtained for the same manganese dioxide sample.

1) Shaking rate
2) Reaction time
3) Particle size

The results obtained with the revised procedure show that the activity number does not show any correlation with the following (a) high or low drain tests, (b) phase structure, (c) manganese content, (d) available oxygen content, (e) apparent density, (f) pH, (g) water content, (h) manganese oxide content, (i) water of hydration content, and (j) bobbin weights.

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INTRODUCTION

The present method of determining the battery activity of manganese dioxide is to make type A dry cells with the manganese dioxide and then to run drain tests on the cells. The time required for fabrication, aging, and testing of the dry cells takes about 10 to 12 days. This time lag is the main disadvantage of this method as a commercial quality control test.

In the commercial production of manganese dioxide it would be desirable to have a chemical test which would give a predictable relationship with drain tests. With this in mind many efforts have been made at the correlation of various chemical and physical factors with battery activity, but these correlations have failed to produce an adequate control test. The chemical and physical factors which have been investigated are (a) manganese content, (b) available oxygen content, (c) phase structure, (d) density, (e) bobbin weights of the cells tested, and (f) impurities (3). It has not been possible to show a direct correlation between battery activity of manganese dioxide and these chemical and physical characteristics, but the following specifications for these characteristics have been established by the U. S. Signal Corps Technical Requirements SCl-3175, 28 July 1955, entitled Manganese Dioxide, Military Battery Grade:

Specifications

Absorbed Moisture as % H_2O	3% max.
Available Oxygen as % MnO_2	85% min.

Total Manganese as % Mn	58% min.
Total Insolubles	3% max.
pH	4.0 - 7.0
Iron as % Fe	0.25% max.
Lead as % Pb	0.25% max.
Total Heavy Metals (Other then Fe and Pb)	0.05% max.
Total Alkali Metals	0.5% max.
Total Alkaline Earth Metals	0.5% max.
Apparent Density as gm/in^3	18 min.
Sieve Size in %: Thru 20 mesh	100
Thru 60 mesh	98.0
Phase Type	Gamma, Rho, Gamma-Rho

Since none of the above chemical or physical factors can be used as a direct measure of the battery activity of manganese dioxide, it was thought that the Drotschmann Activity Test should be evaluated. The procedure used by the Signal Corps which was obtained from an article by Von C. Drotschmann (1), entitled "Determination of the Depolarization Index of Pyrolusite for the Battery Industry," was sent to Dr. Berg upon request. This thesis gives the procedure, revisions, and results obtained with this method of testing the potential of battery-active manganese dioxide.

METHODS AND PROCEDURES

The Drotschmann Activity Number is the numerical measurement of the reaction rate of manganese dioxide with hydrazine sulfate under controlled conditions. The magnitude of the activity number is directly proportional to the amount of hydrazine sulfate decomposed by the manganese dioxide sample in a given length of time. The procedure used for the determination of activity number is outlined by the Signal Corps as follows (4):

Exactly 0.3000 gr. of manganese dioxide is weighed into a 300 ml Erlenmeyer flask containing 25 ml of 0.2N ammonium hydroxide. Twenty five ml of an aqueous solution of hydrazine sulfate (8 gr/l) are added and the flask shaken for one minute at fifteen-minute intervals. After two hours, the ore is filtered out and the cake washed twice with cold distilled water. To the clear filtrate, 20 ml of 1:4 sulfuric acid to water are added. The solution is then heated to at least 65°C and titrated with 0.1N potassium permanganate. Because the end point is obscure (rose to bright violet), the solution is deliberately over-titrated by about 0.5 ml of the permanganate. Exactly 2.00 ml of 0.1N ferrous ammonium sulfate is then introduced and the solution titrated to an exact end point with the 0.1N potassium permanganate

A blank is run through all steps of the procedure with each set of determinations, omitting only the manganese dioxide sample.

Activity Number = $KMnO_4$ equivalent of blank minus $KMnO_4$ equivalent of sample.

$KMnO_4$ equivalent of blank = ml 0.1N $KMnO_4$ minus 0.1N $KMnO_4$ equivalent of 2 ml ferrous ammonium sulfate solution.

$KMnO_4$ equivalent of sample = ml 0.1N $KMnO_4$ minus 0.1N $KMnO_4$ equivalent of 2 ml ferrous ammonium sulfate solution.

The chemical reaction for this test is believed to be as follows:

$$MnO_2 + 2N_2H_4 \cdot H_2SO_4 \xrightarrow{NH_4OH} MnO + N_2 + 3H_2O + 2(NH_4)_2SO_4$$

The proofs of this reaction are (a) experimental determination that two moles of hydrazine sulfate are decomposed per mole of manganese dioxide decomposed, and (b) determination of the gas liberated from the reaction.

The procedure as outlined by the Signal Corps gave considerable variation in the values of activity number obtained for the same sample. This variation was believed to be caused by inconsistency in duplication of the conditions of the reaction.

The main sources of variation were believed to be (a) shaking rate, (b) reaction time, (c) particle size, (d) washing, and (e) temperature.

In the original procedure, the rate of shaking the sample is entirely dependent upon the analyst. Therefore the effect of this variable upon the values of activity number could easily account for some of the variation in the results obtained. In order to eliminate this human variation in shaking rate, a mechanical shaker, Figure I, was constructed to give constant shaking rates. The purpose of this shaker was to give continual contacting of the hydrazine sulfate solution with the manganese dioxide sample. The values of activity number obtained with different rates of constant shaking and reaction time are presented in Table I. A shaking rate of 70 oscillations per minute and a reaction time of one hour were chosen as standard operating procedure.

Although the standardization of shaking rate and reaction time reduced the spread in duplication values for the same sample, the desired precision was still not obtained. This spread was believed to be caused by the variation in the particle sizes of the 0.300 gram samples of the manganese dioxide being tested. The results of an investigation of particle sizes showed the -160 + 200 mesh particle size to be satisfactory as standard operating procedure.

The washing of the samples after being filtered was thought to be of importance in the duplication of values, but the variation caused by washing technique was minimized by using separate sintered glass suction funnels and the same amount of wash water for each sample. The volume of distilled water used for washing was approximately 250 milliliters or five times the volume of original solution and was used to give five consecutive washings of approximately 50 milliliters each.

The temperature at which the tests were run was room temperature or approximately 25 degrees centigrade.

DISCUSSION OF RESULTS

An investigation of the original Signal Corps procedure showed that variations caused by shaking rate, reaction time, and particle size were important in duplicating activity numbers for the same manganese dioxide sample.

The values of activity number obtained with different rate of shaking and reaction time are given in Table I. These values indicated that as the rate of shaking increased the activity number also increased. This increase in activity number was caused by the increased agitation of the hydrazine sulfate solution with the manganese dioxide sample. The amount of manganese dioxide sample settled at the shaking rate of 50 oscillations per minute was observed to be greater than the amount settled at the shaking rate of 70 oscillations per minute. A greater portion of the manganese dioxide sample was suspended in the hydrazine sulfate solution at the shaking rate of 70 oscillations per minute. It was also observed that as the shaking rate was increased above 70 oscillations per minute the solution tended to splash on to the sides of the flask. This splashing was believed to be serious, because the hydrazine sulfate solution which remained on the sides of the flask did not come in contact with the manganese dioxide sample.

The results from Table I and Figure 2 show that as reaction time increased the activity number increased; however, this was logical, as most reactions tend to approach completion as reaction time is increased. As can be seen from Figure 2, decomposition rate decreased as the reaction progressed, and the magnitude of the activity numbers of the various samples tended to remain in the same order. Therefore it was concluded that a reaction time of one hour was justifiable and was used as a matter of convenience to the analyst.

In order to determine the effect of particle size on activity number, the particle sizes of + 80, -80 + 120, -120 + 160, -160 + 200, -200 + 300, -300 were tested. The samples which were tested, Table II, showed no consistent correlation between particle size and activity number; however, a few samples showed the activity number to increase as the particle size decreased. Also, as can be seen from Table III, the variation between activity numbers for the -160 + 200 particle size was less than the variation for the composite mixture for the same manganese dioxide sample. The -160 + 200 particle size was chosen because it gave the best particle characteristics in the hydrazine sulfate solution. The -160 + 200 particle size tended to remain in suspension with no large particles settling to the bottom of the flask. A smaller particle size was not used because of the formation of colloidal conditions.

The results of the revisions of the original Signal Corps procedure are best shown by the comparison of values obtained by both original and revised procedures for the same manganese dioxide sample. These values, Table IV, showed the variation obtained in duplicate samples to be less for the revised procedure than for the original procedure.

Using the revised procedure, several samples of manganese dioxide were tested in order to show correlation, if any, between activity number and the following (a) high and low drain tests, (b) phase structure, (c) manganese content, (d) available oxygen content, (e) apparent density, (f) pH, (g) water content, (h) manganese oxide content, (i) water of hydration content, and (j) bobbin weights. Although slight modifications were made in reation conditions for the various samples, the general reaction for producing the samples was as follows:

$$MnSO_4 + Cl_2 + 4NaOH \longrightarrow MnO_2 + 2NaCl + Na_2SO_4 + H_2O$$

The samples which were made by this reaction are reported as M-S-Cl with a number following to indicate the reaction number.
The sample "Weco" was obtained from a commercial producer of

manganese dioxide, and the sample S-AP-1 was produced by the oxidation of manganese sulfate by ammonium persulfate under controlled conditions (2). These samples were produced as part of the research in the chemical syntheses of manganese dioxide at Montana State College. The analytical data for the samples were obtained by following Signal Corps procedures (5).

The activity numbers of various samples are presented with drain test data in Table V. Figures 3 and 4 show the same information graphically. The activity numbers for the samples M-S-Cl 87, 88, 89, and 90 were 1.710, 1.950, 1.840 and 1,840 respectively. The high drain tests were 7.1, 8.4, 7.3 and 8.6 hours, and the low drain tests were 136, 111, 112, and 120 hours. As can be seen from the figures or the above data there was no correlation between activity number and either high or low drain tests. Therefore, it is believed that at the present time the use of the Drotschmann Activity Test as an estimate of drain potential of manganese dioxide is not feasible.

Although there was shown to be no correlation between activity number and drain tests, it was thought that the rate at which the manganese dioxide was reduced by the hydrazine sulfate might be related to the phase structure of the manganese dioxide sample being tested. The activity numbers and phase structure data of various samples are presented in Table V. The phase structures of the samples were determined by the Eagle-Picher Company through the use of x-ray diffraction patterns. The activity numbers for the samples M-S-Cl 36, 55a, 85, and 87 were 1.812, 1.819, 1.715 and 1.710 respectively. The phase structures were gamma and epsilon, rho and gamma, epsilon, and rho. As can be seen from Table V or the above data there was no correlation between activity number and phase structure.

Because there was no correlation shown between activity number and either high or low drain tests or phase structure, the relationship of activity number with manganese content, available oxygen content, apparent density, pH, water content, manganese oxide content, water of hydration content, and bobbin weights was studied. The activity number and analytical data of various samples are presented in Table V. As can be seen from Table V, there was no correlation between activity number and the analytical properties of the manganese dioxide samples.

At present there is no apparent correlation of activity number with any of the characteristics of battery active manganese dioxide. It is therefore concluded that the Drotschmann Activity Test as outlined by the Signal Corps is of little use in quality control for the production of manganese dioxide.

SUMMARY

1. The revisions made in the original Signal Corps procedure in order to reduce the variation between activity numbers for the same manganese dioxide sample are as follows:

a) A constant shaking rate of 70 oscillations per minute by a mechanical shaker.

b) A reaction time of one hour.

c) A definite particle size of the sieve range -160 + 200.

2. The activity number does not show any correlation with either high or low drain tests.

3. The activity number does not show any correlation with phase structure.

4. The activity number does not show any correlation with manganese content, available oxygen content, apparent density, pH, water content, manganese oxide content, water of hydration content, and bobbin weights.

5. At present there is no appraent correlation of activity number with any of the characteristics of battery active manganese dioxide; therefore, it is concluded that the Drotschmann Activity Test as outlined by the Signal Corps is of little use in quality control for the production of manganese dioxide.

LITERATURE CITED

(1) Drotschman, V.C., Chemiker Zeitung, Vol. 56, Pg. 234-6 (1932).

(2) Nickelson, R. L., M. S. Thesis, Montana State College (1952).

(3) Sadagopachari, R., M. S. Thesis, Montana State College (1953).

(4) Signal Corps Engineering Laboratories, Letter to Montana State College, 26 July 1955.

(5) U. S. Army Signal Corps, Technical Requirements, Manganese Dioxide, Military Battery Grade, SCl-3175, 28 July 1955, Fort Monmouth, New Jersey.

APPENDIX

TABLE I

ACTIVITY NUMBER, SHAKER RATE, AND REACTION TIME DATA

Sample		Shaker Speed (Oscillations per minute)	Time (Hours)	Activity Number (Averages of Duplicates)
M-S-Cl 21	Composite	50	1	1.221
21	"	50	2	1.401
21	"	70	1	1.638
21	"	70	2	2.115
M-S-Cl 26	"	50	1	1.077
26	"	50	2	1.215
26	"	70	1	1.420
26	"	70	2	1.870
M-S-Cl 87	-160/200	70	0.25	1.112
89	"	70	0.25	1.228
90	"	70	0.25	1.267
88	"	70	0.25	1.327
92	"	70	0.25	1.349
M-S-Cl 81	"	70	1	1.745
89	"	70	1	1.835
90	"	70	1	1.840
88	"	70	1	1.950
92	"	70	1	1.952
M-S-Cl 87	"	70	2	2.215
89	"	70	2	2.267
90	"	70	2	2.289
88	"	70	2	2.295
92	"	70	2	2.305

TABLE II

ACTIVITY NUMBER AND PARTICLE SIZE DATE AT A REACTION TIME OF ONE HOUR AND SHAKER RATE OF 70 OSCILLATIONS PER MINUTE

Sample	Particle Size (mesh range)	Activity Number (average of duplicates)
M-S-Cl 61	+80	1.418
	-80 +120	1.469
	-120 +160	1.455
	-160 +200	1.450
	-200 +300	1.457
	-300	1.475
M-S-Cl 61a	+80	1.061
	-80 +120	1.128
	-120 +160	1.134
	-160 +200	1.090
	-200 +300	1.112
	-300	1.284
M-S-Cl 64	+80	1.531
	-80 +120	1.645
	-120 +160	1.790
	-160 +200	1.915
	-200 +360	1.940
	-300	1.995
M-S-Cl 70a	+80	1.808
	-80 +120	1.845
	-120 +160	1.787
	-160 +200	1.77
	-200 +300	1.790
Weco	-120 +160	1.530
	-160 +200	1.560
	-200 +300	1.735
	-300	1.820

TABLE III

ACTIVITY NUMBERS FOR THE COMPOSITE AND -160 + 200 PARTICLE SIZE AT A REACTION TIME OF ONE HOUR AND SHAKER RATE OF 70 OSCILLATIONS PER MINUTE

Sample	Composite Mixture		-160 + 200 Sieve Range	
M-S-Cl 90	1.791		1.819	
	1.847	Δ = .099	1.830	Δ = .021
	1.870		1.840	
	1.890		1.840	
M-S-Cl 92	1.903		1.929	
	1.941	Δ = .141	1.939	Δ = .053
	2.012		1.972	
	2.044		1.982	

TABLE IV

ACTIVITY NUMBERS OBTAINED BY BOTH THE ORIGINAL AND REVISED PROCEDURES

Sample	Activity Number (original procedure)	Activity Number (revised procedure)
M-S-Cl 90	1.572	1.819
	1.589	1.830
	1.611	1.840
	1.633	1.840

TABLE V

ACTIVITY NUMBER, DRAIN TESTS, PHASE STRUCTURE, AND ANALYTICAL DATA

Sample	Activity Number	High Drain Hrs.	Low Drain Hrs.	Phase Structure	% Mn	% O_2 as MnO_2	Density gm/in^3	pH	% H_2O	% MnO	% H_2O of Hyd.	Bobbin weights
M-S-C1 6a-160/200	1.090	4.7	140	Rho, some R	59.2	92.5	13.0	5.7	2.5	0.8	6.7	10.3
" 41 "	1.300	3.6	136	Gamma, some Rho	59.7	90.6	14.4	7.3	0.8	3.1	6.3	11.25
" 61 "	1.450	4.7	102		58.5	90.6	10.8	6.5	13.4	1.5	7.9	8.95
" 46a "	1.490	3.9	152	Gamma, some Rho	57.8	94.6	12.8	6.7	0.7	0.0	5.1	9.75
Weco* "	1.560	6.5	140	Gamma	---	---	---	---	---	---	---	---
M-S-C1 10 "	1.621	6.0	122	Beta	63.1	92.4	12.2	7.0	2.3	6.1	1.5	9.85
" 40 "	1.695	5.2	116	Beta, some Gamme, Rho, Sigma	57.4	86.8	10.6	7.2	1.7	3.2	10.0	9.75
" 63 "	1.706	2.9	91	Rho, Some R	60.0	93.6	10.4	5.8	2.0	1.0	5.4	9.8
" 87 "	1.710	7.1	136	Rho	60.8	89.8	13.8	5.8	3.0	5.1	5.1	9.3
" 85 "	1.715	6.5	115	Epsilon	59.1	82.22	12.0	7.0	4.8	9.1	8.7	8.9
" 64 "	1.720	5.3	117		59.7	94.0	10.0	5.5	1.0	0.3	5.7	9.7
" 69 "	1.730	4.75	124		58.3	90.9	9.7	5.8	3.2	1.1	8.0	9.0
" 79 "	1.733	4.7	114		58.2	84.6	10.7	7.7	5.8	6.2	9.2	8.8
" 67 "	1.745	4.2	106		58.1	90.6	9.3	5.7	3.3	1.1	8.3	9.5
" 84 "	1.762	5.6	115		57.8	85.03	11.6	6.7	2.7	5.2	9.8	8.8
" 68 "	1.770	4.3	106		58.1	90.1	9.4	5.5	4.2	1.6	8.3	9.5
" 36 "	1.812	1.6	143		61.1	86.0	10.9	6.2	0.3	8.6	5.4	9.3
" 55a "	1.819	1.5	149.5	Gamma and Epsilon	62.0	89.1	10.0	5.9	1.5	7.2	3.7	9.0
S-AP 1 "	1.830	---	----	Alpha	---	---	---	---	---	---	---	---
M-S-C1 89 "	1.840	7.3	112	Rho and Gamma	58.0	82.2	12.3	6.1	3.4	7.7	10.1	9.0
" 90 "	1.840	8.6	120		59.1	86.7	11.8	5.9	2.6	5.4	8.9	8.9
" 66 "	1.845	4.8	108		59.9	91.7	10.2	5.3	2.9	2.5	5.8	9.7
" 86 "	1.871	8.2	131		59.3	86.4	12.4	6.1	2.7	6.0	7.6	9.1
" 80 "	1.930	1.5	99	S, Some Sigma	58.0	81.4	8.3	7.2	3.7	8.4	10.2	8.3
" 92 "	1.939	8.25	137		57.0	81.4	12.7	6.2	3.5	7.2	11.4	9.1
" 88 "	1.950	8.4	111	S	57.8	83.0	10.7	5.7	3.5	6.8	10.2	8.9

*Sample obtained from commercial producer

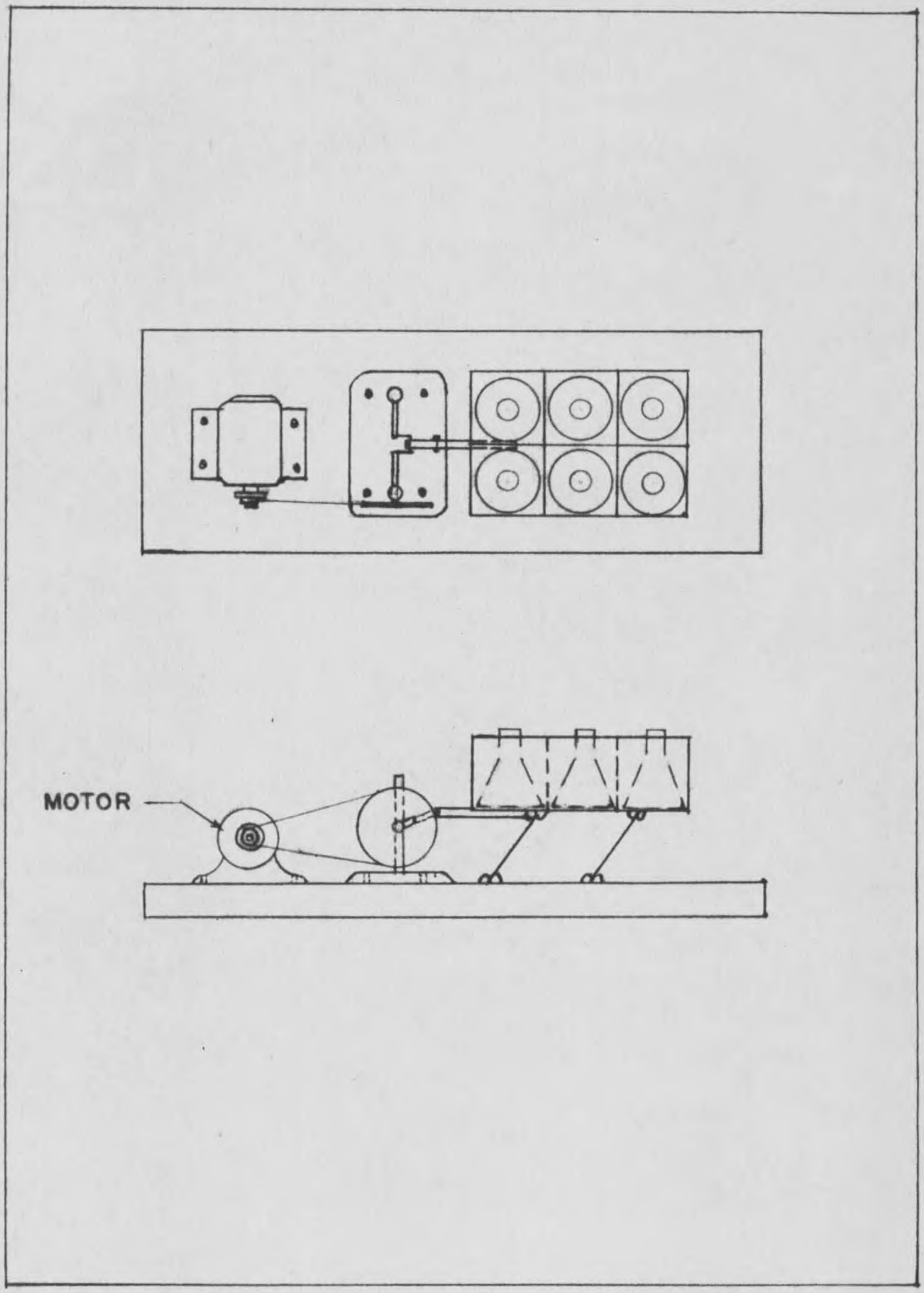

Figure 1. Mechanical Shaker

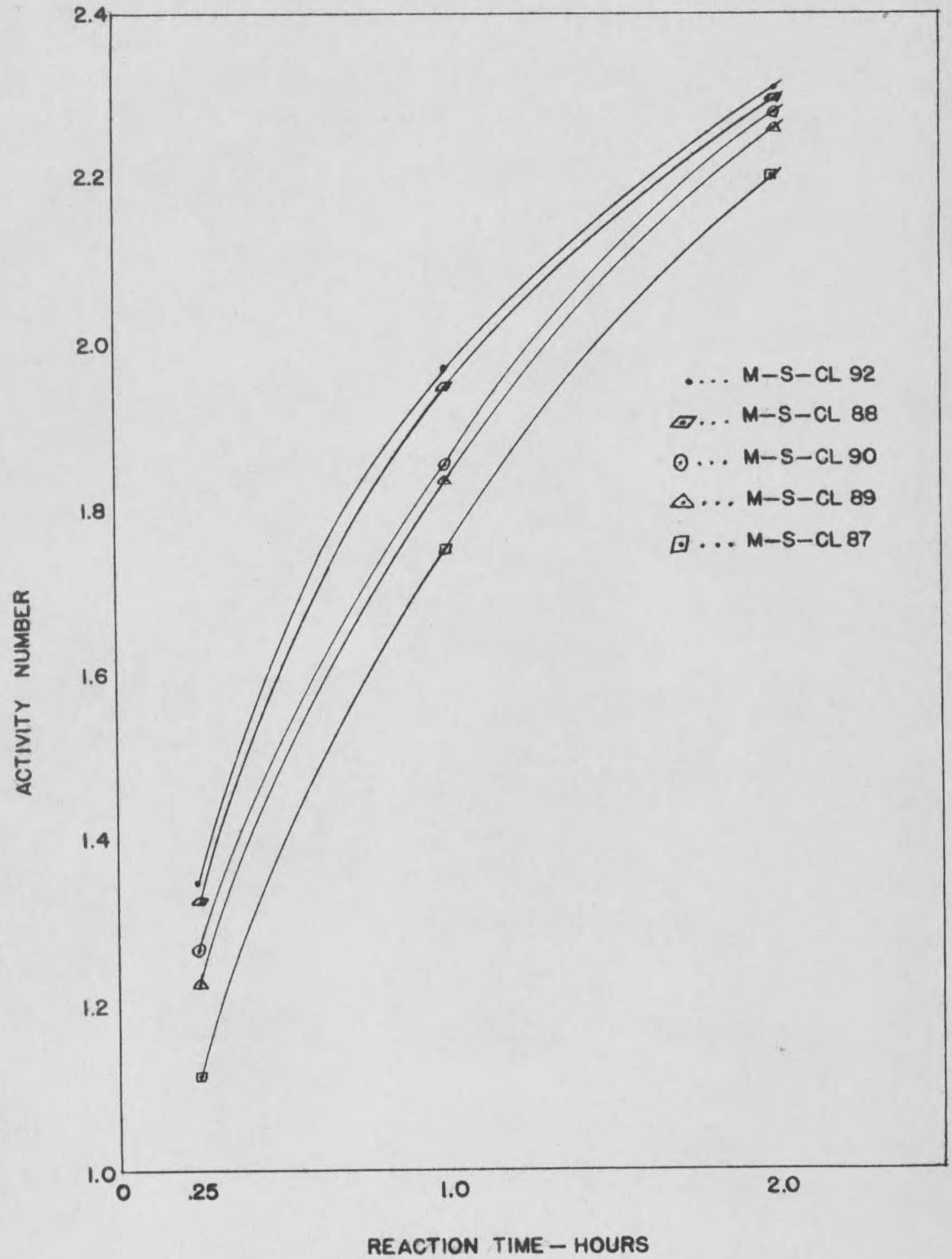

Figure 2. Activity Number vs. Reaction Time

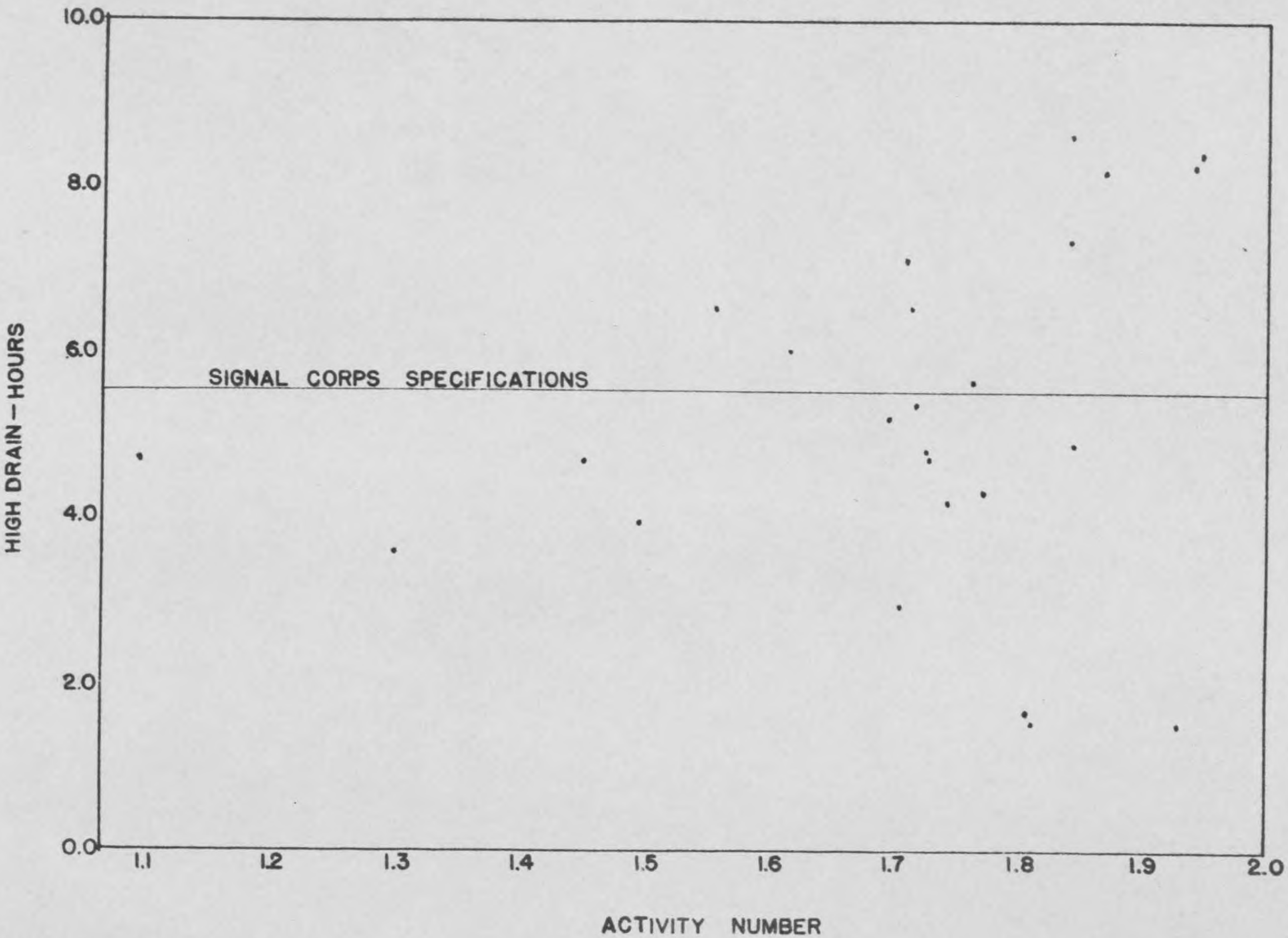

Figure 3. Activity Number vs. High Drain Test Data

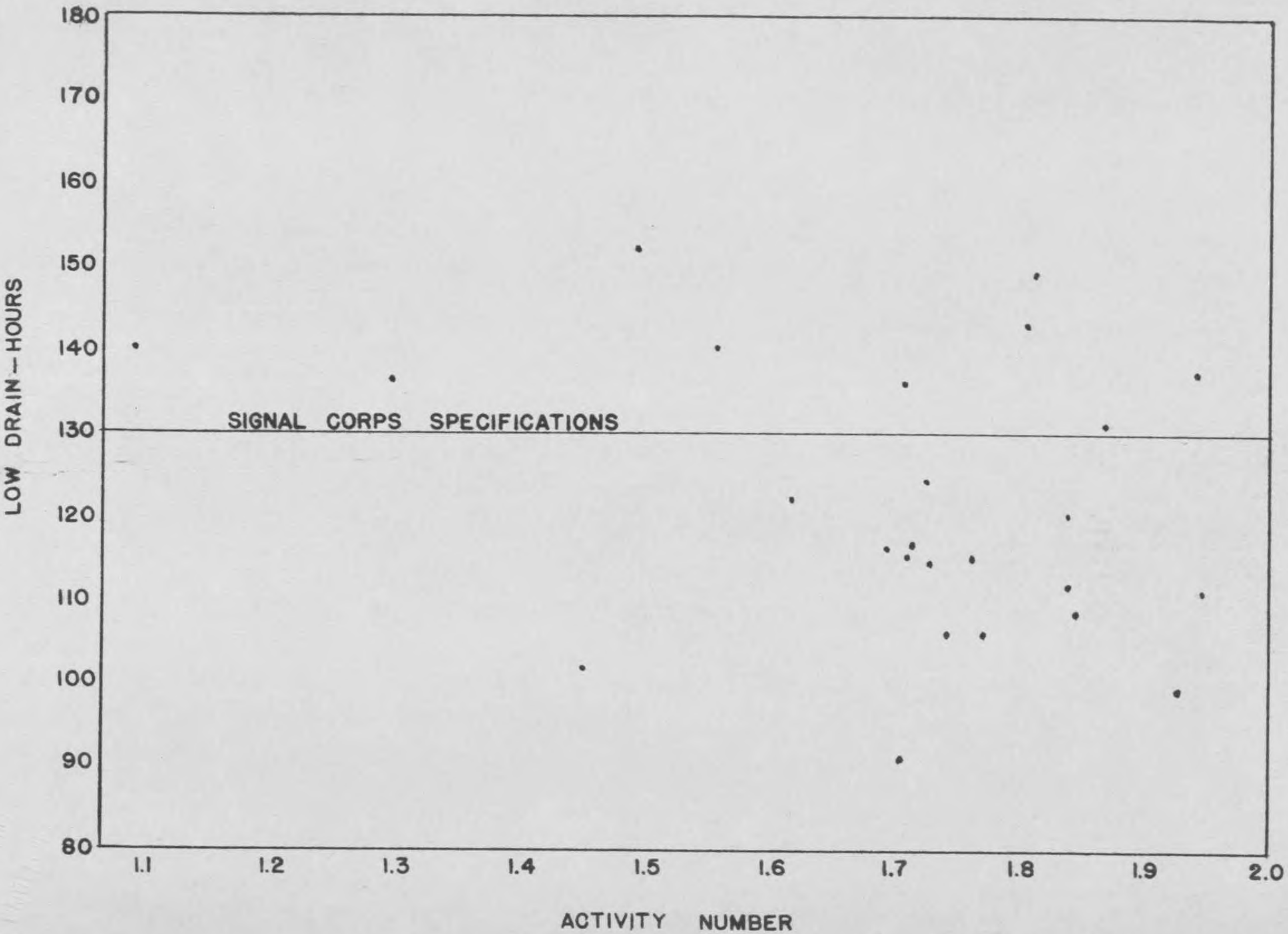

Figure 4. Activity Number vs. Low Drain Test Data

	NAME AND ADDRESS
2-4-62	Alan Buckla...
	1221 So. 3rd St.