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SUBJECT: Multifactor Ratio Analysis (Factor Analysis) of Corrosion Data Using Logarithmic Transformations

TO: E. G. Bohlmann

FROM: E. L. Compere

SUMMARY

A simplified analysis method for the examination of complex corrosion data is presented in terms of data from slurry corrosion toroid experiments. This method facilitates the assignment of average effects to specific imposed experimental variables in a test series. It is based on statistical analysis of variance procedures but emphasizes the use of averages and presents results relative to a chosen reference experimental condition. The use of the logarithm of attack rate results in the expression of the effects of variables as ratios or multiplicative terms.

DISCLAIMER

Multifactor Ratio Analysis of Corrosion Data Using Logarithmic Transformations

Drawing valid quantitative conclusions from a complex experimental series of dynamic slurry corrosion tests has been facilitated recently by the use of a simplified analysis procedure which will be referred to as multifactor ratio analysis. The procedure will be discussed below in terms of an example taken from slurry corrosion experiments in toroids, but extension to many other experiment sets will be more or less obvious.

In the example[1] below, a four-toroid test series is reported in which oxygen and hydrogen atmospheres were used in the presence and absence of 0.03 *m* MoO_3 additive. Corrosion data on four pin specimens and the toroid proper were obtained in each test. Data from the series are shown in Table 1.

Table 1. Toroid Tests with ThO_2 Slurries Containing Molybdenum Trioxide

Thoria Preparation: LO-33 to 36 (1600°C-calcined, classified, 1.7 μ)
Concentration: 1600 g of Th per kg of H_2O
Temperature: 280°C
Time: 300 hr
Velocity: 26 fps

Test Results:

Concentration of MoO_3 (*m*)	Metal Attack Rates (mpy) (corrected for slug flow) Toroid	347 SS	Ti-75A	SA-212-B	Zr-3A	pH, Slurry Postrun	Avg. Part. Size, μ Postrun
Oxygen:							
None	1.3	10.0	5.3	12.6	0.7	4.7	1.4
0.03	2.0	6.5	1.1	125.0	2.0	7.8	1.2
Hydrogen:							
None	2.0	78.0	8.2	7.8	1.6	7.7	2.1
0.03	3.6	40.0	15.5	14.5	4.9	8.4	1.7

It was desirable to evaluate the effects of the different independent variables, to determine whether there was any interdependence between them, and to prepare a statement of meaningful results.

Anticipating the results of the analysis, such a statement might be made as follows:

> "Four aqueous slurry corrosion tests, each including evaluation of attack of four pins of different metals and the toroid proper, were carried out using batch LO-33-36 thoria (1600°C, classified, 1.7-μ average diameter) circulated at 26 fps for 300 hr at 280°C with a concentration of 1500 g of Th per kg of H_2O. Atmospheres (O_2 and H_2) and MoO_3 additive concentration (none or 0.03 *m*) were varied. Multi-factor ratio analysis of the data yielded a reference or normalized rate for type 347 stainless steel, with oxygen atmosphere and no additive, of 11 mpy. This characterizes the aggressiveness of the slurry (which appeared to be ordinary in its behavior) as well as the susceptibility of the metal to attack. Various test materials under the above reference conditions exhibited average corrosion susceptibility ratios relative to type 347 stainless steel as indicated by the following multiplicative terms:

347 SS	SA-212-B	Ti-75A	Zr-3A	347 SS Toroid
1.0	1.8	0.3	0.07	0.1

> "Difference between the type 347 toroid piping and type 347 pin specimen is attributed to flow phenomena.

> "For certain materials the results in hydrogen relative to those in oxygen atmosphere were significantly different as indicated by starred values in the following multiplicative terms:

347 SS	SA-212-B	Ti-75A	Zr-3A	Toroid
7*	5*	0.3*	2	1.6

> "For certain materials the results with 0.03 *m* MoO_3 additive relative to those with no additive were significantly different as indicated by starred values in the following multiplicative terms:

347 SS	SA-212-B	Ti-75A	Zr-3A	Toroid Proper
0.6	0.6	4*	3	1.6

> "No significant effect of atmosphere on the effect of additive was noted."

The discussion which follows will be devoted to consideration of the principles and procedures involved in extracting such information from data, such as those of Table 1. First a description of the method will be given, followed by application to the data given in Table 1.

The multifactor ratio analysis method to be described is based on adaptations of statistical analysis of variance procedures. Its major features include an emphasis on the level of the data expressed as averages rather than on the spread or range of variation expressed as sums of squares. A further feature is the expression of comparable results as ratios or multiplicative terms. The purpose of the analysis is to evaluate separately the general effects of different classes and levels of variables by comparing averages.

Data are arranged so that the factor under consideration is the only difference between groups of independent variables. When this is true, it is called a balanced set.

Various statistical experimental designs, including factorials, may be used. The example used in Tables 1 and 2 in which the effects of atmosphere and the presence of molybdenum trioxide additive on the attack of several metals are examined is a balanced 2 x 2 x 5 set.

Logarithmic Transformation of Data. An important postulate is involved in the choice of mathematical function in which to carry out the computations. It has been suggested[2] that in corrosion studies environmental variables most frequently are found to affect the response of different metals in the same proportion rather than to the same absolute extent. Whether this approach is valid in a particular case must be determined from its utility in providing an appropriate summary of the data, but it appears to be suitable for the majority of cases encountered.

With a proportionate relationship, the effect of different variables would be expressed as ratios or multiplicative terms rather than additive terms. An estimate of corrosion rate under a particular set of conditions thus would be obtained from the analysis as the multiplicative product of all the appropriate relative terms times a reference rate expressed in terms of some standard condition.

The averages and relative terms may be most easily obtained by transforming the observed corrosion rates into logarithms,[2] and obtaining the desired averages from these. The relative terms are all additive, being values of differences of logarithmic averages and are converted into multiplicative terms by taking antilogarithms.

The use of a reference rate has two desirable characteristics. It permits an easy visualization of the results of the present series. Also, more ready comparison may be made when desired with the results of analysis of other series possibly involving other variables.

In the example the normalized attack rate for type 347 stainless steel without additive under oxygen atmosphere (and under the conditions of temperature, concentration, velocity, thoria properties, and other variables common to the set of experimental results under consideration) is used as the reference rate.

Alternate Expression of Effects. The effect of a change in one variable averaged over all the other conditions is referred to as a first-order effect. Secondary effects, or interdependences (statistical interactions), may be stated as such. However, it is frequently relevant to group them with the first-order effects to produce a new statement of primary effects for particular materials and conditions. Thus in our illustration it worked out that the effects of atmosphere and of additive varied so much from metal to metal that it seemed best to state the comparisons in this way. Both ways are developed on the worksheet in Tables 2 and 3, respectively. These tables are in the appendix.

Partially Balanced Sets. Valid comparisons may be made readily only between sets of dependent variables arranged so that groups of similar items under consideration are equivalent except for differences in the independent variable whose effect is being sought. The data of Tables 1 and 2 were a completely balanced set; because regardless of the type of variable under consideration--metal, atmosphere, or additive--it was possible to use all of the data in obtaining averages of groups which differed only in the independent variable under consideration.

Where only partially balanced sets of data are available (as was the case in experiments with sodium aluminate reported elsewhere[3]), the available balanced sets are evaluated first; and then factors involved in tests not in the balanced sets are compared with estimates from the balanced set to evaluate the new factors in the additional test.

In those cases where certain data are duplicated (e.g., repeated experiment, duplicate metal specimens in a test, etc.), an average of the duplicated data should be used in evaluating effects; but residuals of each datum should be calculated and included in the calculation of confidence intervals.

Method Not Omniscient. As a warning against the careless use of the multifactor ratio analysis method, it should be noted that it only serves to provide a numerical statement of certain row and column attributes in an array of data. As always, the association of the results with particular conditions imposed on the test is the inference of the investigator.

Worksheet Procedures. Data from the experimental series[1] concerning the effects of atmosphere and molybdenum trioxide addition reported in Table 1 are tabulated in Part I of Table 2 in the form of logarithmic transformations of corrosion rates arranged in a 4 x 5 array. Evaluation by the alternate procedure is given in Table 3. Table 2 will be considered first.

First-Order Effects. In the application of the method, it was recognized that there are a number of equivalent ways of stating what is algebraically the same, and various procedures have been found useful from time to time. Only one generally useful procedure will be described. This procedure involved obtaining a grand average and expressing row and column averages as variations from the grand average. These were combined as groups representing different variables where required. The difference terms were then expressed relative to the reference condition. Multiplicative terms representing relative effects of the different variables were determined by reversing the logarithmic transformation.

The reference rate was evaluated by summing the grand average and the variation of each reference group average from it. As shown in Part I, D, of Table 2, it represented a rate for the reference material and condition under the assumption that only the general effects were to be taken into account. In the alternate evaluation (Table 3) described below, the assumptions and resultant reference rate were somewhat different.

Residuals and Confidence Intervals. Residual values from the general effects were computed by taking the difference between observed values and values calculated from the estimates of general effects, or equivalently calculated from grand average and row and column variations. From these, estimates of confidence intervals for individual data items were computed using tables of Student's "t" for the appropriate degrees of freedom and confidence levels, values were computed for 50% (entirely trivial) and 95% (definitely significant) intervals, and corresponding multiplicative terms for individual data items. The value for any group may be estimated from the logarithmic confidence interval for individual data items by dividing it by the square root of the number of items in the group.

Interdependences. Subgroup averages of the residuals were obtained, representing secondary effects or interdependences, and residuals taken from these as shown in Parts III and IV. A considerable interdependence of certain factors was found.

Examination of the metal x atmosphere and metal x additive effect (Table 2, Part III) indicated that there was a great deal of variation between metals as to the effects of atmosphere and additive; so much so as to overshadow seriously the general effects shown in Table 2, Part I. Consequently, it appeared desirable to combine the general and secondary effects into a new statement of effects, specific for individual metals. This is shown as the alternate evaluation, Table 3. Such a procedure is not usually necessary, but follows the principle that the major relationships shown by the data should be epitomized by the summary of the results of the analysis.

Alternate Evaluation. As a result of this procedure it was necessary to compute a new reference rate, adjusted from the grand average by metal effects (Part I, A), metal x atmosphere, and metal x additive effects. Within its range of uncertainty it agrees with the previous value. However, the effects of atmosphere and additive appear to be much more clearly indicated for each metal by this method.

The effect of additive on atmosphere effect for individual metals is a third-order effect and uses the remaining degrees of freedom. According to this pattern of evaluation, it cannot be separated from random error. If it were desired to assume zero error, and thus obtain an estimate of the effect, it could be evaluated for each metal as:

$$1/2 \left[(\text{none}, O_2) + (0.03\,m, H_2) - (\text{none}, H_2) - (0.03\,m, O_2) \right] .$$

Examination of the residuals shown in Table 2, Part IV, and the over-all additive x atmosphere effect shown in Table 2, Part III, C, indicate that this effect is considerably smaller than the metal x atmosphere and metal x additive effects, and that it would not be unreasonable to regard it as random error. Levels of the individual variation are also in agreement with estimates of usual random error in this type of experiment. Because the residuals are only trivially changed after the alternate evaluation of Table 3, it has not appeared necessary to re-evaluate the residuals or the confidence intervals. It is recognized that the confidence interval would be changed (slightly) because of 5 active degrees of freedom rather than 4.

Resume. The multifactor ratio analysis method is based on the comparison of averages obtained from balanced sets of data. The independent variables of each part to be compared from the sets are the same except for that variable from the effect of which is being sought. Results are presented relative to an arbitrarily chosen reference condition. The use of logarithms of attack rate results in the expression of effects as multiplicative factors. Interactions, or the effect of one variable on another, may be developed. The evaluation of residuals permits the estimation of confidence intervals which may be used to determine which of the effects obtained above are statistically significant. The procedure may be extended to the examination of unbalanced sets.

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1. L. Rice, S. A. Reed, and E. L. Compere, HRP Quar. Prog. Rep. for Periods Ending April 30 and July 31, 1958, ORNL-2561, pp 184, 186.

2. H. C. Bowen, C. Groot, and J. L. Jaech, "Variable Interaction: A Statistical Solution," Corrosion, 15, 83t-84t (Feb. 1959).

3. L. Rice, S. A. Reed, and E. L. Compere, HRP Quar. Prog. Rep. for Periods Ending April 30 and July 31, 1958, ORNL-2561, pp 184-5.

APPENDIX

Table 2. Ratio Analysis Work Sheet

I. General Effect of Major Variables: Original data from Table 1 here stated as log transformation of rate, 10 log mpy.[a]

MoO_3	Atm.	347	Ti-75A	SA-212-B	Zr-3A	Toroid	Avg.	Variation from Grand Average
None	O_2	10.0	7.2	10.9	- 1.5	1.1	5.5	- 2.3
0.03 *m*	O_2	8.1	0.2	20.8	3.0	3.0	7.1	- 0.7
None	H_2	18.9	9.1	8.9	1.8	3.0	8.3	+ 0.5
0.03 *m*	H_2	16.0	11.8	11.5	6.8	5.1	10.2	+ 2.4
Column Avg.		13.2	7.1	13.0	2.5	3.1	7.8	Grand Avg.
Variation from Grand Avg.		+ 5.4	- 0.7	+ 5.2	- 5.3	- 4.7		

A. Relative Effect of Metals (average for all additives and atmospheres):

	347	Ti-75A	SA-212-B	Zr-3A	Toroid
Variation from Reference	0*	- 6.1	- 0.2	-10.7	-10.1
Relative Effect of Metal as Ratio (antilog)	1.0*	0.25	1.0	0.09	0.09

B. Relative Effect of Atmosphere (average for all metals and additives):

Variable	Average Group Variation from Grand Average	Group Variation from Reference	Relative Effect of Variables, Factor (antilog)
O_2	- 1.5	0*	1.0*
H_2	+ 1.5	+ 3.0	2.0

C. Relative Effect of Additives (average for all metals and atmospheres):

None	- 0.9	0*	1.0*
0.03 *m* MoO_3	+ 0.9	+ 1.8	1.5

D. Reference Rate for 347 Stainless Steel, O_2; No Additive: (normalized for general effects averaged across all metals)

$$7.8 + 5.4 - 1.5 - 0.9 = 10.8 = 10 \log 12$$

Reference Rate = 12 mpy

Table 2. Ratio Analysis Work Sheet (cont'd.)

II. Residuals (observed - calculated)[b] Before Consideration of Secondary Effects

e.g., for first item, 10.0 - (7.8 - 2.3 + 5.4) = - 0.9

MoO_3	Atm.	347	Ti-75A	SA-212-B	Zr-3A	Toroid
None	O_2	- 0.9	+ 2.4	+ 0.2	- 1.7	+ 0.3
0.03 *m*	O_2	- 4.4	- 6.2	+ 8.5	+ 1.2	+ 0.6
None	H_2	+ 5.2	+ 1.5	- 4.6	- 1.2	- 0.6
0.03 *m*	H_2	+ 0.4	+ 2.3	- 3.9	+ 1.9	- 0.4

Degrees of freedom: Total: 20 (including mean)
Mean or reference rate: 1 absolute

First-Order Effects	
Metal	4 relative
Atmosphere	1 relative
Additive	1 relative

Secondary Effects	
Atm. x met.	4 relative
Add. x met.	4 relative
Atm. x add.	1 relative
Add. x atm. x met.	4 relative

Estimated confidence intervals (±) of individual values (first-order effects only):
Degrees of freedom: 13 = 20 - 1 - 4 - 1 - 1

$$\Sigma r^2 = 218.12$$

$$S^2 = \Sigma r^2/13^2 = 16.8$$

$$S = 4.1$$

$$CI_{50\%} = (13^{t}50)\ S = \pm\ 2.8$$

$$CI_{95\%} = (13^{t}95)\ S = \pm\ 8.8$$

III. Secondary Effects (interdependences)

A. Effect of metal on atmosphere effect (average for all additives)

	Avg. Effect, All Metals	Add'nl. Effect for Given Metal and Atmos. 347	Ti-75A	SA-212-B	Zr-3A	Toroid
O_2	(-1.5)	- 2.7	- 1.9	+ 4.4	- 0.3	+ 0.5
H_2	(+1.5)	+ 2.8	+ 1.9	- 4.3	+ 0.3	- 0.5

B. Effect of metal on additive effect (average for all atmospheres)

	Average	Add'nl. Effect for Given Metal and Additive				
None	(-0.9)	+ 2.1	+ 2.0	- 2.2	- 1.5	- 0.2
0.03 *m* MoO_3	(+0.9)	- 2.0	- 1.9	+ 2.3	+ 1.6	+ 0.1

Table 2. Ratio Analysis Work Sheet (cont'd.)

C. Effect of additive on atmosphere effect (average for all metals)

	None	0.03 *m*
O_2	+ 0.1	- 0.1
H_2	- 0.1	0.0

IV. Residuals After Secondary Effects

MoO_3	Atm.	347	Ti-75A	SA-212-B	Zr-3A	Toroid
None	O_2	- 0.5	+ 2.1	- 2.1	0.0	- 0.1
0.03 *m*	O_2	+ 0.3	- 2.2	+ 1.9	0.0	+ 0.1
None	H_2	+ 0.4	- 2.3	+ 2.0	- 0.1	+ 0.2
0.03 *m*	H_2	- 0.4	+ 2.3	- 1.9	0.0	0.0

Est. Confidence Interval (±) of Individual Values (including secondary effects)

Degrees of freedom = 20 - 1 - 4 - 1 - 1 - 4 - 4 - 1 = 4

$\Sigma r^2 = 36.19$ $\quad CI_{50} = {}_4t_{50}\ S = 2.2$

$S^2 = \Sigma r^2/4 = 9.05$ $\quad CI_{95} = {}_4t_{95}\ S = 8.3$

$S = 3.0$

Confidence Intervals of Secondary Effect Terms (two items in each averaged for secondary effects III, A and B, or V, A and B)

Trivial (CI 50%): $2.2/\sqrt{2} = 1.6$

Antilog ± 1.6 gives ratio limits <1.4 or >0.7

Definitely Significant: (CI 95%) $8.3/\sqrt{2} = 5.9$

Antilog ± 5.9 gives ratio limits >4 or <0.3

* Reference condition.

a) Weight gain or zero values are arbitrarily assigned a corrosion rate of 0.1 mpy.

b) Trivial numerical inconsistencies may have occurred due to rounding-off error.

Table 3. Alternate Evaluation of Factors:
Primary Effect on Particular Metal of Atmosphere and Additive

A. Atmosphere (sum of average and additional effects, Table 2, III-A)

	347	Ti-75A	SA-212-B	Zr-3A	Toroid
O_2	- 4.1	- 3.3	+ 2.9	- 1.8	- 1.0
H_2	+ 4.3	+ 3.4	- 2.8	+ 1.8	+ 1.0
Variation of H_2 Rel. to O_2	+ 8.4	+ 6.7	- 5.7	+ 3.6	+ 2.0
Rel. Effect of H_2, Ratio (antilog)	7	5	.3	2	1.6

B. Additive (sum of average and additional effects, Table 2, III-B)

	347	Ti-75A	SA-212-B	Zr-3A	Toroid
None	+ 1.2	+ 1.1	- 3.1	- 2.4	- 1.1
0.03 *m* MoO_3	- 1.1	- 1.0	+ 3.2	+ 2.5	+ 1.0
Variation of 0.03 *m* MoO_3 Rel. to None	- 2.3	- 2.1	+ 6.3	+ 4.9	+ 2.1
Rel. Effect of 0.03 *m* MoO_3 Ratio (antilog)	0.6	0.6	4	3	1.6

C. Reference Rate (normalized on stainless steel data only), 347 Stainless Steel, O_2, No Additive

$$7.8 + 5.4 - 4.1 + 1.2 = 10.3 = 10 \log 11$$

Reference rate = 11 mpy

D. Order of Merit of Metals (this readjusts from merit under "average" conditions relative to 347 under "average" conditions, to merit of metal under reference condition relative to 347 under reference condition)

Value from I, A	0	- 6.1	- 0.2	-10.7	-10.1
Correction for 347 from "average" to reference condition					
(III, A) O_2	(- 2.7)	2.7	2.7	2.7	2.7
(III, B) No Additive	(+ 2.1)	- 2.1	- 2.1	- 2.1	- 2.1
Correction for metal from "average" to reference condition					
(III, A) O_2	- 2.7	- 1.9	+ 4.4	- 0.3	+ 0.5
(III, B) No Additive	+ 2.1	2.0	- 2.2	- 1.5	- 0.2
Adjusted order of merit	0	- 5.4	+ 2.6	-11.9	- 9.0

This order of merit compares normalized value for metal, under O_2 and without additive, to the normalized value for 347 SS under O_2 and without additive.

Table 3. Alternate Evaluation of Factors: Primary Effect on Particular Metal of Atmosphere and Additive (cont'd.)

E. Summary

By this method the following statement may be used as a summary: (log units) and multiplicative terms:

Reference Condition (selected): O_2 Atmosphere, No Additive

Rate of 347 SS Normalized, to Reference Condition (10.3) = 11 mpy

Effect	347	Ti-75A	SA-212-B	Zr-3A	Toroid	Average
Metal Rel. to 347 SS (ref. condition)	(0)	(-5.4)	(+2.6)	(-11.9)	(-9.0)	--
	1.0	0.3	1.8	0.07	0.13	-
H_2 Rel. to O_2	(+8.4)	(+6.7)	(-5.7)	(+ 3.6)	(+2.0)	(+3.0)
	7	5	0.3	2.5	1.6	2.0
0.03 *m* MoO_3 Rel. to None	(-2.3)	(-2.1)	(+6.3)	(+ 4.9)	(+2.1)	(+1.8)
	0.6	0.6	4	3	1.6	1.5
Residual or Atm. x Add.	(-0.3)	(+2.4)	(-1.8)	(+ 0.1)	(+0.1)	

F. Degrees of Freedom for "Alternate Evaluation"

Mean, or ref. rate	1 absolute)	5 absolute
Metals effect	4 relative)	
Atmos. x metals effect	5 relative	
Addit. x metals effect	5 relative	
Addit. x atm. x metals effect	5 relative	

$$S = \sqrt{\Sigma r^2/5} = \sqrt{9.11/5} = 1.4$$

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