Basic Applications of the Analysis of Variance and Covariance in Electrochemical Science and Engineering

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I. INTRODUCTION

An electrochemical scientist specializing in corrosion studies wishes to decide whether tensile and compressive stress measured at various temperatures in samples of corroding metals differ significantly, and if the influence of temperature is statistically important. An electrochemical engineer specializing in process performance/quality control wishes to decide if specific energy requirements of an electrolytic product, varying from plant to plant, are significantly different. The analysis of variance, ANOVA, a *body of statistics*[1] answers such questions. It is devoted to the study of the variability of factors influencing experimental observations, involving simple (one- and two-factor), and complex (multiple-factor) experiments and designs.

If the relative importance of a priori hidden factors is to be determined, the analysis of covariance, ANCOVA, is included in the overall statistical exercise. The scientist may worry about the pretreatment (if any) of the metal samples prior to corrosion, and the engineer may suspect a possible surface quality effect of the anodes used in the cells. The introduction of such concomitant[2] variables or covariates[2,3] renders, when necessary, a more sophisticated picture at the expense of modest additional numerical work.

The purpose of this chapter is to illustrate the application of ANOVA and ANCOVA via selected problems of interest to the electrochemical scientist and engineer. ANOVA categories discussed include one-way classification, latin squares, 2- and 3-way classification involving completely randomized experiments (CRE), randomized block experiments (RBE) and hierarchical arrangements. ANCOVA techniques are limited to one or two concomitant variables, and the effect of their neglect in the overall analysis.

An unfortunate impediment to the application of statistical analysis to experimental data published in the electrochemical literature is the paucity of sufficiently detailed numerical observation sets, including replicate measurements. It is, therefore, inevitable that numerical data in the Tables have to be considered as if they had been obtained in accordance with ANOVA principles. For the sake of illustration of the statistical techniques, it is immaterial whether this imposition is strictly justified, inasmuch as the ultimate objective of tests: the attainment of appropriate decisions, is not compromised.

There is an impressive amount of textbooks (and Internet-based material) devoted to the subject matter in general, and it would be impossible as well as impractical to supply a full list in this chapter. In addition to the comprehensive References [1-3], the text by Snedecor and Cochran[4] is an outstanding source on account of its clarity and organization. Readers interested in pursuing the subject matter at an advanced level will find ample material in the literature to satisfy their needs.

The objective here is not to turn electrochemical scientists and engineers into statisticians, but to promote the appreciation of certain statistical principles and techniques useful to electrochemical process analysis and design.

II. BASIC PRINCIPLES AND NOTIONS

The fundamental role of statistics is to draw inferences about population parameters from parameters of a single sample, or several samples. In fixed-effect experiments the population (or treatment) parameters are considered to be constant and the observations to belong to normal populations with unknown means, and constant variance. The errors associated with the observations are assumed to belong independently to a normal population of mean zero and variance σ^2. A fundamental tenet of ANOVA is the null hypothesis that the population/treatment means are equal, i.e.,

$$H_0 : \mu_1 = \mu_2 = ... = \mu_r \tag{1}$$

if r populations provide the samples. A perhaps more thoughtful way to state Eq. (1) would be that there exists no statistically distinguishable difference between the population means. The alternative (or counter) hypothesis:

$$H_a\text{: at least two means are different} \tag{2}$$

negates H_0. All the tests seen in the sequel have to do with Eqs. (1) and (2), at various levels of complexity.

On what basis can it be decided that H_0 can be rejected in a statistically meaningful manner? Phrasing it otherwise, how much error is committed if H_0 is rejected in favour of H_a, although the latter is false? In ANOVA the magnitude of this (so-called) Type I error depends on the numerical value f of the F-statistic; the Type I error is the probability that in a given test, a numerical value of F would be equal to or exceed f. In classical statistics the 5% Type I error is called *significant*, and the 1% Type I error is called *highly significant*. The less categorical modern statistician would not put the 5% and 1% Type I error on a high pedestal, but would prefer to think in terms of the *P-value*, which is the Type I error committed when the null hypothesis is rejected in face of the observation-based F-statistic. This is a more flexible point of view, where the influence of *outside* (i.e., not necessarily statistical factors) is also taken into account.

Critical values of the F-statistic are determined by the size of the Type I error and the two degrees of freedom, as shown in the partial F-table (Table 1). Extensive tabulations are widely available in statistical textbooks and handbooks.

At very small values of ν_2, the second degree of freedom, the F-test is weak in the sense that the rejection of a null hypothesis will be virtually impossible. As the degrees of freedom increase, rejection of H_0 becomes increasingly possible, regardless of the size of the admitted Type I error α. When the degrees of freedom are fixed, the critical F-values increase with a decrease in the Type I error. If, e.g., a computed F-statistic related to $\nu_1 = 3$ and $\nu_2 = 10$

is f = 5.32, the Type I error is between 1% and 5%; linear interpolation between the critical values yields $\alpha \approx 0.027$, i.e., rejection of H_0 carries an about 2.7% Type I error.

What about the error committed in failing to reject H_0 when it is false? This is the Type II error β (the symbol α is also used for denoting the Type I error). The *power of test*, $(1 - \beta)$, is difficult to compute for the F-distribution, but facilitated by charts e.g., Table 6, pp. 188–193 in Ref. [1].

The computation of the F-statistic can conveniently be followed in ANOVA and ANCOVA tables. An F statistic is obtained as the ratio of two mean squares; the mean squares are themselves obtained from sums of squares divided by their degree of freedom. The degrees of freedom depend on the size of the observation sets, the number of treatments and the type of statistical experiment. ANOVA tables are also a standard component of software packages for computers.

When only two treatments are compared, the F-test can be replaced by a test based on Student's T-statistic, on account of the $f_\alpha(1, \nu_2) = t_{\alpha/2}(\nu_2)$ equivalence.

If H_0 is rejected, a statistical Pandora's box is opened in the sense that various *derivative* null hypotheses can be set up to test if differences in certain means are significant with respect to differences in some other means. A linear combination of treatment means is called a *contrast*, if the sum of the coefficients related to the treatment means is zero. Contrasts are at the heart of multiple comparison methods,[5] but their detailed discussion is outside the scope of this chapter, beyond Section VIII.4.

Notation in the sequel follows closely Guenther's[1] (which agrees to a large extent with a large number of statistics textbooks). Specifically, a random variable or distribution is denoted by a capital letter, and its numerical value by a lower case letter.

III. ANOVA: ONE-WAY CLASSIFICATION

One-way classification (or single-factor) ANOVA deals with differences between means of observations *of a kind* pertaining to treatments. Current efficiencies measured repeatedly at various current densities (e.g., at a certain type of electrode) constitute a proper electrochemical example, where each current density is a treatment, but no other factor is assumed to influence current efficiency.

Table 1
Selected Critical Values of the F-Statistic at Three Magnitudes of the Critical Region

ν_2 \ ν_1	$\alpha = 0.05$ (or 5%)			$\alpha = 0.01$ (or 1%)			$\alpha = 0.001$ (or 0.1%)		
	1	2	3	1	2	3	1	2	3
1	161.4	199.5	215.7	4052	4999.5	5403	4×10^5	5×10^5	5.4×10^5
2	18.51	19.00	19.16	98.50	99.00	99.17	998.5	999.0	999.2
5	6.61	5.79	5.41	16.26	13.27	12.06	47.18	37.12	33.20
10	4.96	4.10	3.71	10.04	7.56	6.55	21.04	14.91	12.55
20	4.35	3.49	3.10	8.10	5.85	4.94	14.82	9.95	8.10

1. Completely Randomized Experiment (CRE)

In a statistical experiment subjects (or units) may be assigned randomly to any one of the r treatments. The null hypothesis

$$H_0 : \mu_1 = \mu_2 = ... = \mu_r \tag{3}$$

is tested against H_a: at least two treatment means are unequal. In terms of the observation set

$$x_{ij} = \mu + \beta_j + e_{ij}; \quad i = 1,2,..., n_j; \quad j = 1,2,..., r \tag{4}$$

the null hypothesis rewritten as

$$H_0 : \beta_j = 0; \quad j = 1,2,..., r \tag{5}$$

with

$$n_1\beta_1 + n_2\beta_2 + ... + n_r\beta_r = 0 \tag{6}$$

is more conducive to ANOVA manipulations. The errors e_{ij} are postulated to belong to the normal distribution N(0;σ^2). As indicated in Section II, this is a fixed-effect formulation, where $\{\beta_j\}_r$ is a set of constant, albeit unknown, measures of deviation from an average of the r population means.

2. Randomized Block Experiment (RBE)

In a statistical experiment, subjects (or units) may also be assigned randomly to treatments after having been first placed into groups with certain *homogeneous* characteristics. The purpose of RBE is either to remove a nuisance or a believed-to-be unimportant variable, or to identify a variable to which the subjects might be particularly sensitive. Defining

$$\alpha_i \equiv \mu_{i.} - \mu \tag{7}$$

and

$$\beta_j \equiv \mu_{.j} - \mu \tag{8}$$

where $\mu_{.j}$ are the treatment means and $\mu_{i.}$ are the block means, the null hypothesis to test is

$$H_0 : \beta_j = 0; \quad j = 1,2,...,r \tag{9}$$

with alternative hypothesis H_a : at least one β_j is nonzero.

(*i*) *Example 1: A Historical Perspective of Caustic Soda Production*

Table 2 summarizes calculations based on information by Hine,[6] transformed by normalizing the production figures with respect to production in country A observed in 1970. The eight countries cited by Hine are denoted by letters in this Section.

The CRE approach disregards the countries as separate entities, and utilizes only the column totals for ANOVA. The symbol N denotes the total number of observations. The sums of squares are computed as

$$SS_T = \sum_{i=1}^{n_j} \sum_{j=1}^{r} x_{ij}^2 - \frac{T_{..}^2}{N} = 26.2747 \tag{10}$$

$$SS_A = \sum_{j=1}^{r} \frac{T_{.j}^2}{n_j} - \frac{T_{..}^2}{N} = 0.2737 \tag{11}$$

and

$$SS_W = SS_T - SS_A = 26.0010 \tag{12}$$

The degrees of freedom are $(N - 1)$ for SS_T; $(r - 1)$ for SS_A, and $(N - r)$ for SS_W, respectively.

The RBE approach considers the eight countries as blocks. The missing entry for country H in 1970 is estimated[7] to be

$$x_{ij} = \frac{rT'_{.j} + nT'_{i.} - T'_{..}}{(r-1)(n-1)} = 0.241 \tag{13}$$

where the primes denote the totals with one entry missing. Accordingly,

Table 2
Production of Caustic Soda in Coded Units and Countries in Certain Years

Country	1970	1975	1979	$T_{i.}$	$x_{mi.}$
A	1.00	1.12	1.12	3.24	1.080
B	0.35	0.31	0.42	1.08	0.360
C	0.42	0.42	0.54	1.38	0.460
D	0.39	0.39	0.42	1.20	0.400
E	0.69	0.92	1.15	2.76	0.920
F	0.65	0.96	1.31	2.92	0.973
G	3.54	3.23	4.27	11.04	3.680
H	–	0.38	0.46	0.84	0.420
$T_{.j}$	7.04	7.73	9.69	$T_{..} = 24.46$; $x_{m..} = 1.063$	
$x_{m.j}$	1.0057	0.9663	1.2113	$r = 3$; $n_1 = 7$; $n_2 = n_3 = 8$	

$$\sum_{i=1}^{n_j} \sum_{j=1}^{r} x_{ij}^2 = 52.2874$$

ANOVA/CRE

Source	SS	DF	MS	F	P-value
Among columns	0.2737	2	0.1368	0.105	> 0.25
Within columns	26.001	20	1.3		
Total	26.275	22			

$f_{2,20}$ ($\alpha = 0.25$) = 1.49

ANOVA/RBE

Treatments	0.3891	2	0.1945	2.09	0.18
Blocks	25.234	7	3.6048	38.80	< 0.001
Error	1.3003	14	0.0929		
Total	26.923	23			

$f_{2,14}(\alpha = 0.1) = 2.73$; $f_{2,14}(\alpha = 0.25) = 1.53$; $f_{7,14}(\alpha = 0.001) = 7.08$

$$SS_T = \sum_{i,j} x_{ij}^2 - \frac{T_{..}^2}{rn} = 26.9233 \tag{14}$$

$$SS_{Tr} = \sum_{j=1}^{r} \frac{T_{.j}^2}{n} - \frac{T_{..}^2}{rn} = 0.41025 \tag{15}$$

$$SS_{Tr}^{'} = SS_{Tr} - \frac{[T_{i.}^{'} - (r-1)x_{ij}]^2}{r(r-1)} = 0.3891 \tag{16}$$

$$SS_B = \sum_{i=1}^{n} \frac{T_{i.}^2}{r} - \frac{T_{..}^2}{rn} = 25.234 \tag{17}$$

and

$$SS_E = SS_T - SS_B - SS_{Tr}^{'} = 1.3003 \tag{18}$$

The degrees of freedom are $(nr - 1)$ for SS_T, $(r - 1)$ for treatments, $(n - 1)$ for blocks, and $(n - 1)(r - 1)$ for error, respectively. The RBE-based analysis yields the more realistic result that the block effect is extremely significant, while the treatment effect is not significant. The difference between the eight countries is much more important than the years of observation.

(*ii*) *Example 2: Metallic Corrosion*

The partial molal volume of hydrogen gas in Armco iron metal corroded under tensile and compressive stress at various temperatures has been reported[8] as 2.60, 2.69, 2.62, 2.52 cm^3 (tensile stress) and 2.73, 2.74, 2.60, 2.61 cm^3 (compressive stress) at temperatures 27, 40, 50, 60 ^{0}C, respectively. If the volumes are considered to be four random readings per test, i.e., temperature as a factor is ignored, a CRE- based calculation scheme similar to the one shown in Table 2, yields $f = 1.89$ with a Type I error of about 23%. It would be, therefore, rather hazardous to reject the null hypothesis of no difference between the mean partial volumes due to tensile and compression stress.

An RBE-based analysis, with temperature as the second factor, yields a similar result. In this configuration,

$$SS_T = \sum_{i=1}^{n_j} \sum_{j=1}^{r} x_{ij}^2 - \frac{T_{..}^2}{N} = 0.03949 \tag{19}$$

$$SS_{Tr} = \sum_{j=1}^{r} \frac{T_{.j}^2}{n_j} - \frac{T_{..}^2}{N} = 0.007825 \tag{20}$$

$$SS_B = \sum_{i=1}^{n_j} \frac{T_{i.}^2}{r} - \frac{T_{..}^2}{N} = 0.025 \tag{21}$$

and

$$SS_E = SS_T - SS_R - SS_B = 0.006663 \tag{22}$$

The F-statistics can, in effect, be obtained without necessarily constructing an ANOVA table, viz.

for treatments: $$f_{Tr} = \frac{SS_{Tr}}{SS_E} . \frac{(n-1)(r-1)}{r-1} = 3.52 \tag{23}$$

for blocks: $$f_{BL} = \frac{SS_B}{SS_E} . \frac{(n-1)(r-1)}{n-1} = 3.75 \tag{24}$$

Since $f_{1,3}$ = 5.54 (α = 0.10), $f_{1,3}$ = 2.02 (α = 0.25), $f_{3,3}$ = 5.39 (α = 0.10), and $f_{3,3}$ = 2.36 (α = 0.25), neither effect is significant with P-values roughly equal to 0.2, for the mean values of the molal volume of H_2. The result is not surprising in view of the extremely large Type I error that would be committed if the null hypothesis of zero slope in a linear regression on volume versus temperature (independently and combined) were rejected.

IV. ANOVA: TWO-WAY CLASSIFICATION

In two-way (or two-factor) classification the subjects to be measured under each treatment may be grouped according to properties which are expected to influence observations due to each treatment, or the two factors may be treated as sources of equally random observations. This is the process analyst's choice, especially if experiments are to be a priori designed. Accordingly, the evaluation process follows either the CRE or the RBE path.

1. Null and Alternative Hypotheses

The general model can be written as

$$x_{ijk} = \mu + \alpha_i + \beta_j + (\alpha\beta)_{ij} + e_{ijk}; \quad i = 1,2,...,a; j = 1,2,...,b; k = 1,2,...,n \tag{25}$$

where the e_{ijk} errors belong independently to normal population N(0; σ^2), and

$$\sum_i \alpha_i = \sum_j \beta_j = \sum_{i,j} (\alpha\beta)_{ij} = 0 \tag{26}$$

The three null hypotheses can be stated as $\alpha_i = 0$; $\beta_j = 0$; $(\alpha\beta)_{ij} = 0$ for all pertinent indices. The alternative hypotheses state that not all α_i, not all β_j, and not all $(\alpha\beta)_{ij}$ are zero. The presence of the $(\alpha\beta)_{ij}$ terms assumes interaction between the two factors; if the hypothesis that the sum of these terms is zero, cannot be rejected, the two factor effects (or factor/treatment and block effects) are simply additive.

2. Illustration of Two-Way Classification: Specific Energy Requirement for an Electrolytic Process

Selecting three anode types to be tested in electrolyzers at four plant locations, an electrochemical engineer intends to determine the relative importance of these two factors on the specific energy requirement (SER) for a certain electrolytic product. In each case three replicate measurements have been made as shown in Table 3. For the sake of comparison via identical experimental data, it is assumed that the measurements were obtained either by a CRE-based, or an RBE-based experimental protocol.

In the CRE-based approach, the pertinent sums of squares are

$$SS_T = \sum_{i=1}^{a}\sum_{j=1}^{b}\sum_{k=1}^{n} x_{ijk}^2 - \frac{T_{...}^2}{abn} = 250.06 \tag{27}$$

$$SS_{Tr} = \frac{\sum_{i=1}^{a}\sum_{j=1}^{b} T_{ij.}^2}{n} - \frac{T_{...}^2}{abn} = 185.72 \tag{28}$$

$$SS_E = SS_T - SS_{Tr} = 64.33 \tag{29}$$

$$SS_A = \frac{\sum_{j=1}^{b} T_{i..}^2}{bn} - \frac{T_{...}^2}{abn} = 117.06 \tag{30}$$

$$SS_B = \frac{\sum_{j=1}^{b} T_{.j.}^2}{an} - \frac{T_{...}^2}{abn} = 49.06 \tag{31}$$

$$SS_{AB} = SS_{Tr} - SS_A - SS_B = 19.61 \tag{32}$$

Table 3
Analysis of SER Observations (kWh/metric ton) via Two-Factor Experiment

Plant location (A levels)	Anode type (B levels) 1	2	3	$T_{i..}$
1	7.5	10.0	11.0	
	9.5	12.0	8.5	80.5
	6.0	9.0	7.0	
2	8.5	12.0	13.0	
	5.0	9.0	9.5	85.0
	6.5	11.0	10.5	
3	4.5	6.0	5.0	
	6.0	7.5	2.5	43.5
	3.0	5.0	4.0	
4	7.0	10.5	9.5	
	4.0	8.0	7.5	65.0
	5.5	7.0	6.0	
$T_{.j.}$	73.0	107.0	94.0	$T_{...}$ = 274.0

ANOVA/CRE

Source	SS	DF	MS	F	P-value
Treatment A	117.06	3	39.02	14.56	< 0.001
Treatment B	49.06	2	24.53	9.15	< 0.0013
Treatment AB (interaction)	19.61	6	3.27	1.22	> 0.25
Error	64.33	24	2.68		
Total	250.06	35			

$f_{2,24}(\alpha = 0.001) = 9.34$; $f_{2,24}(\alpha = 0.005) = 6.66$; $f_{3,24}(\alpha = 0.001) = 7.55$; $f_{6,24}(\alpha = 0.25) = 1.41$

ANOVA/RBE

Source	SS	DF	MS	F	P-value
Treatment A	117.06	3	39.02	23.42	< 0.001
Treatment B	49.06	2	24.53	14.72	< 0.001
Treatment AB	19.61	6	3.27	1.96	0.123
Block	24.68	2	12.34	7.41	0.004
Error	39.65	22	1.67		
Total	250.06	35			

$f_{2,22}(\alpha = 0.005) = 6.81$; $f_{2,22}(\alpha = 0.001) = 9.61$; $f_{3,22}(\alpha = 0.001) = 7.71$; $f_{6,22}(\alpha = 0.1) = 2.06$; $f_{6,22}(\alpha = 0.25) = 1.42$

The degrees of freedom are (abn – 1) for SS_T, (a –1) for SS_A, (b – 1) for SS_B, (a – 1)(b – 1) for SS_{AB}, and (ab[n – 1]) for SS_E, respectively. The P-values indicate that

1. the effect of plant location on SER is extremely important,
2. the effect of anode type used is extremely important, and
3. interaction between plant location and anode type is negligible, i.e., the *behaviour* of each anode type is independent of plant location.

In the RBE-based approach, the sum of squares due to blocking is

$$SS_{BL} = \frac{\sum_{i=1}^{a} T_{..k}^2}{ab} - \frac{T_{...}^2}{abn} = 24.68 \tag{33}$$

and the error sum of squares is accordingly modified to

$$SS_E = SS_T - SS_{BL} - SS_{Tr} = 39.65 \tag{34}$$

The rest of the sums of squares remain unchanged. The degrees of freedom are (abn – 1) for SS_T , (a – 1) for SS_A , (b – 1) for SS_B , (a – 1)(b – 1) for SS_{AB}, and (n – 1)(ab – 1) for SS_E, respectively. Consequently, plant location and anode type are extremely significant , the replication effect is at least highly significant, but interaction between plant location and anode type is insignificant. The CRE and RBE lead to essentially identical statistical conclusions.

V. ANOVA: THREE-WAY CLASSIFICATIONS

The mathematical framework required for the analysis of three treatment categories and their possible interactions is cumbersome, and since it has been described at length in the textbook literature, only a numerical summary of analysis pertaining to a specific illustration is discussed in this Section.

In an electrolytic process the concentration of an undesirable byproduct content in the exit stream from a flow electrolyzer is considered to depend on electrolyzer type, temperature and current density. Table 4 shows measured values of byproduct

Table 4
Analysis of Byproduct Content Levels (ppm) via Completely Randomized Three-Factor Experiment

Current density (Level C)	Single tank electrolyzer (Level A) Temperature (Level B)			Electrolyzer/mixer cascade (Level A) Temperature (Level B)			Totals
	1	2	3	1	2	3	
1	140	160	182	150	160	191	983
2	139	145	172	98	115	148	817
3	94	108	141	71	80	119	613
Totals		1281			1132		2413

ANOVA

Source	SS	DF	MS	F	P-value
Treatment A	1233.4	$a - 1 = 1$	1233.4	67.06	0.0017
Treatment B	6066.8	$b - 1 = 2$	3033.4	164.86	< 0.001
Treatment C	11448.5	$c - 1 = 2$	5724.3	311.23	< 0.001
Treatment AB	41.43	$(a - 1)(b - 1) = 2$	20.72	1.13	> 0.25
Treatment AC	1219.1	$(a - 1)(c - 1) = 2$	609.5	33.14	0.0042
Treatment BC	52.2	$(b - 1)(c - 1) = 4$	13.1	0.71	> 0.25
Treatment ABC (error)	73.6	$(a - 1)(b - 1)(c - 1) = 4$	18.4		
Total	20075.0	$abcn - 1 = 17$			

$f_{1,4}(\alpha = 0.005) = 31.33$; $f_{1,4}(\alpha = 0.001) = 74.14$; $f_{2,4}(\alpha = 0.001) = 61.25$; $f_{2,4}(\alpha = 0.005) = 26.28$; $f_{2,4}(\alpha = 0.25) = 2.00$

concentration by randomization among treatments A, B and C. Treatment A has two levels, representing a simple tank flow electrolyzer, and an electrolyzer-mixer cascade with recycle to the electrolyzer. Treatment B consists of three temperature levels, and Treatment C carries three current density levels. In view of the lack of replicate observations, the mean square of the ABC treatment interaction serves for the computation of the F-statistics.[9] The electrolyzer/temperature and temperature/current density effects are additive, but all other treatments are strongly significant. They indicate the acute sensitiveness of the undesired byproduct concentration to all operating factors considered in the analysis; this may be good news for the process analyst in providing a wide choice for controlling its presence in the effluent.

VI. ANOVA: LATIN SQUARES (LS)

The LS technique aims to reduce the number of observations required to extract the desired information from data, and it can be a good choice for removing (unwanted) sources of variation. In this respect, it can be regarded as an alternative to randomized blocks.

Assume that the performance of an electrolyzer is determined by the size of the corroded fraction of an electrode surface upon a reference duration of electrolysis. Postulating three levels of operating conditions, three levels of current density, and three electrode types A, B and C, the LS-based experimental protocol, illustrated in Table 5, requires only nine observations instead of running twenty seven experiments to deal with every possible set of conditions. This is achieved via specific assignment schemes of the electrode types. The null hypotheses can be written as

$$H_0\colon \mu_{..1} = \mu_{..2} = \mu_{..3} = \mu \tag{35}$$

$$H_0^{'}: \mu_{1..} = \mu_{2..} = \mu_{3..} = \mu \tag{36}$$

$$H_0^{''}: \mu_{.1.} = \mu_{.2.} = \mu_{.3.} = \mu \tag{37}$$

The pertinent sums of squares are computed as

$$SS_T = \sum_{i,j,k} x_{ijk}^2 - \frac{T_{...}^2}{r^2} = 934.00 \tag{38}$$

$$SS_R = \frac{\sum_{i=1}^{r} T_{i..}^2}{r} - \frac{T_{...}^2}{r^2} = 484.67 \tag{39}$$

$$SS_C = \frac{\sum_{j=1}^{r} T_{.j.}^2}{r} - \frac{T_{...}^2}{r^2} = 206.00 \tag{40}$$

Table 5
Latin Square Experiment Applied to the Electrode Corrosion Problem

Current density	Electrolyzer 1	Electrolyzer 2	Electrolyzer 3	$T_{i..}$
1	A: $x_{111} = 41$	B: $x_{122} = 39$	C: $x_{133} = 55$	135
2	B: $x_{212} = 66$	C: $x_{223} = 55$	A: $x_{231} = 63$	184
3	C: $x_{313} = 59$	A: $x_{321} = 39$	B: $x_{332} = 42$	140
$T_{.j.}$	166	133	160	$T_{...} = 459$

Randomly assigned order to electrode types: A → 1; B → 2; C →3

$$\sum_{ijk} x_{ijk}^2 = 24343; \quad \frac{T_{...}^2}{N} = 23409; \quad T_{..1} = 143; \quad T_{..2} = 147; \quad T_{..3} = 169$$

ANOVA

Source	SS	DF	MS	F	P-value
Rows	484.67	2	242.34	4.30	0.217
Columns	206	2	103	1.83	> 0.25
Treatments	130.67	2	65.33	1.16	> 0.25
Error	112.66	2	56.33		
112.66					
2					
56.33					
Total	934	8			

$f_{2,2}$ (α = 0.25) = 3.00; $f_{2,2}$ (α = 0.10) = 9.00

$$SS_{Tr} = \frac{\sum_{k=1}^{r} T_{..k}^2}{r} - \frac{T_{...}^2}{r^2} = 130.67 \quad (41)$$

$$SS_E = SS_T - SS_R - SS_C - SS_{Tr} = 112.66 \quad (42)$$

The degrees of freedom are $(r^2 - 1)$ for SS_T, $(r - 1)$ for SS_R, SS_C , SS_{Tr}, and $(r - 1)(r - 2)$ for SS_E, respectively. The ANOVA table shows that neither null hypothesis can be rejected without committing a serious Type I error.

The array in Table 5 is one of many possible random assignments. For instance, the arrangement 2:1:3 for rows, 3:1:2 for columns and A→2; B→3; C→ 1 would finally produce the array

	Electrolyzer 1	Electrolyzer 2	Electrolyzer 3
Current density 1	x_{112}	x_{123}	x_{131}
Current density 2	x_{213}	x_{221}	x_{231}
Current density 3	x_{311}	x_{322}	x_{333}

and the test would require conditions different from those in Table 5. Consequently, ANOVA may well lead to different conclusions. In any event, Table 5 would suggest to a process analyst that variability of electrode corrosion is most likely due to other (possibly undetected) physical reasons. This kind of result is one important benefit of statistical analysis.

VII. APPLICATIONS OF THE ANALYSIS OF COVARIANCE (ANCOVA)

The analysis of covariance accomplishes the same task of eliminating variables of no interest as do randomized blocks and Latin squares, but in a conceptually different manner. It employs concomitant variables, also known as cofactors, to *sharpen* the testing of null hypotheses. The desired outcome is the reduction of the mean square error with respect to treatment, block, etc. mean squares, i.e., the attainment of sufficiently large F-statistics for the rejection of H_0 at the expense of a (very) small Type I error.

A case in point is a statistical interpretation of the results of the design calculation for a single-pass high conversion electrochemical reactor presented by Rode et al.[10] For the sake of discussion, model-computed velocity, pressure drop, and average current density data in Table 4[10] are considered *as if they had been measured* in both non-segmented and segmented cell. The two cells are defined as the treatments, and velocity and pressure drop as concomitant-variable/cofactor candidates.

1. ANCOVA with Velocity as Single Concomitant Variable

The array in Table 6 provides quantities required for ANCOVA in conjunction with CRE (Pattern A) and RBE (Pattern B).

(*i*) *Pattern A(CRE)*

The postulates (1) y_{ij} belong independently to normal population $N(\mu_{ij},\sigma^2)$, $i = 1,2,\ldots,n_j$; $j = 1,2,\ldots,r$; (2) $\mu_{ij} = \mu + \beta_j + \gamma(x_{ij} - x_{m..})$; (3) $n_1\beta_1 + n_2\beta_2 + \ldots + n_r\beta_r = 0$ lead to hypotheses

$$H_0 : \beta_j = 0; \quad j = 1,\ldots,r \tag{43}$$

$$H_a : \text{not all } \beta_j \text{ are zero} \tag{44}$$

Table 6
Data Array for ANCOVA with Velocity as a Single Concomitant Variable (Section VI.1)
$r = 2$; $n_j = n = 6$; $N = 12$

	Treatment			
	$j = 1$ (non-segmented cell)		$j = 2$ (segmented cell)	
	x_{i1} (cm/s)	y_{i1} (kA/m^2)	x_{i2} (cm/s)	y_{i2} (kA/m^2)
	16.1	8.206	17.8	9.091
	6.04	6.154	7.68	7.828
	2.68	4.103	4.20	6.413
	1.01	2.051	2.31	4.699
	0.447	1.026	1.55	3.565
	0.212	0.513	1.15	2.790
$T_{x.j}$	26.489		34.69	
$T_{y.j}$		22.053		34.386
34.386	4.4148		5.782	
$x_{m.j}$		3.6755		5.7310
$y_{m.j}$				

$T_{ix.}$ ($i = 1,\ldots,6$): 33.90; 13.720; 6.880; 3.320; 1.997; 1.362
$x_{mi.}$ ($i = 1,\ldots,6$): 16.95; 6.86; 3.44; 1.66; 0.999;0.681
$T_{iy.}$ ($i = 1,\ldots,6$): 17.300;13.980; 10.516; 6.750; 4.591; 3.303
$y_{mi.}$($i = 1,\ldots,6$): 8.650; 6.990; 5.258; 3.375; 2.296; 1.652
$\sum_{i=1}^{6}\sum_{j=1}^{2} x_{ij}^2 = 706.6624$; $\sum_{i=1}^{6}\sum_{j=1}^{2} y_{ij}^2 = 355.1916$; $\sum_{i=1}^{6}\sum_{j=1}^{2} x_{ij} y_{ij} = 451.3841$

and

$$H_0^*: \gamma = 0 \tag{45}$$

$$H_a^*: \gamma \neq 0 \tag{46}$$

Equation (43) states that all modified (*corrected*) treatments effects, due to the concomitant variable, are equal, and Eq. (45) states that the concomitant variable is not required. From Table 6, the sums of squares are computed as

$$SS_{xT} = \sum_{i=1}^{n_j}\sum_{j=1}^{r} x_{ij}^2 - \frac{T_{x..}^2}{N} = 394.76 \tag{47}$$

$$SS_{xTr} = \sum_{j=1}^{r} \frac{T_{x.j}^2}{n_j} - \frac{T_{x..}^2}{N} = 5.60 \tag{48}$$

$$SS_{xE} = SS_{xT} - SS_{xTr} = 389.15 \tag{49}$$

$$SS_{yT} = \sum_{i=1}^{n_j}\sum_{j=1}^{r} y_{ij}^2 - \frac{T_{y..}^2}{N} = 89.74 \tag{50}$$

$$SS_{yTr} = \sum_{j=1}^{r} \frac{T_{y.j}}{n_j} - \frac{T_{y...}^2}{N} = 12.66 \tag{51}$$

$$SS_{yE} = SS_{yT} - SS_{yTr} = 77.07 \tag{52}$$

For ANCOVA three sums of products are also needed:

$$SP_T = \sum_{i=1}^{n_j}\sum_{j=1}^{r} x_{ij}y_{ij} - \frac{T_{x..}T_{y..}}{N} = 163.64 \tag{53}$$

$$SP_{Tr} = \sum_{j=1}^{r} \frac{T_{x.j}T_{y.j}}{n_j} - \frac{T_{x..}T_{y..}}{N} = 8.43 \tag{54}$$

$$SP_E = SP_T - SP_{Tr} = 155.21 \tag{55}$$

In order to calculate pertinent F-statistics, three modified sums of squares are obtained as

$$SS'_{yT} = SS_{yT} - \frac{(SP_T)^2}{SS_{xT}} = 21.91 \tag{56}$$

$$SS'_{yE} = SS_{yE} - \frac{(SP_E)^2}{SS_{xE}} = 15.16 \tag{57}$$

$$SS'_{yTr} = SS'_{yT} - SS'_{yE} = 6.75 \tag{58}$$

Bypassing the ANOVA table, the F-statistic related to Eqs. (43) and (44) are computed as

$$f_{r-1,N-r-1} = \frac{SS'_{yTr}}{SS'_{yEr}} \cdot \frac{N-r-1}{r-1} = 4.05 \tag{59}$$

Since $f_{1,9} = 5.12$ ($\alpha = 0.05$) and $f_{1,9} = 3.36$ ($\alpha = 0.10$), H_0 in Eq.(43) may be rejected (with a Type I error of about 8%), indicating that the modified/corrected treatments are not significantly different.

To test H_0 in Eq. (45), the corresponding F-statistic, computed as

$$f_{1,N-r-1} = \frac{(SP_E)^2}{(SS_{xE})(SS'_{yE})} \cdot \frac{N-r-1}{r-1} = 36.75 \tag{60}$$

strongly favours H_a^*, i.e., velocity most definitely qualifies as a concomitant variable.

(ii)* *Pattern B(RBE)

In this configuration there are six block elements for each treatment and (1) $\mu_{ij} = \mu + \alpha_i + \beta_j + \gamma(x_{ij} - x_{m..})$; (2) $\alpha_1 + \alpha_2 + \ldots + \alpha_n = 0$; $\beta_1 + \beta_2 + \ldots + \beta_r = 0$ are postulated. In other words,

$$H_0 : \beta_j = 0;\ j = 1,\ldots,r \tag{61}$$

and

$$H_a : \text{not all } \beta_j \text{ are zero} \tag{62}$$

The sums of squares for the blocks are determined as

$$SS_{xB} = \sum_{j=1}^{r} \frac{T_{ix.}^2}{r} - \frac{T_{x..}^2}{N} = 388.92 \tag{63}$$

$$SS_{yB} = \sum_{j=1}^{r} \frac{T_{iy.}^2}{r} - \frac{T_{y..}^2}{N} = 75.99 \tag{64}$$

Consequently, the error squares are found to be

$$SS_{xE} = SS_{xT} - SS_{xB} - SS_{xTr} = 0.234 \tag{65}$$

$$SS_{yE} = SS_{yT} - SS_{yB} - SS_{yTr} = 1.083 \tag{66}$$

The product sums arising from the RBE approach are

$$SP_B = \sum_{i=1}^{n} \frac{T_{ix.}T_{iy.}}{r} - \frac{T_{x..}T_{y..}}{N} = 155.61 \tag{67}$$

$$SP_E = SP_T - SP_B - SP_{Tr} = -0.396 \tag{68}$$

For the calculation of the F-statistics, further sums of squares are needed, namely:

$$SS'_{yE} = SS_{yE} - \frac{(SP_E)^2}{SS_{xE}} = 0.413 \tag{69}$$

$$SS'_{y(Tr+E)} = SS_{yTr} + SS_{yE} - \frac{(SP_{Tr} + SP_E)^2}{SS_{xTr} + SS_{xE}} = 2.706 \tag{70}$$

$$SS'_{yTr} = SS'_{y(Tr+E)} - SS'_{yE} = 2.293 \tag{71}$$

Testing the validity of H_0 in Eq. (61), the F-statistic

$$f_{r-1,[(n-1)(r-1)-1]} = \frac{SS'_{yTr}}{SS'_{yE}} . \frac{[(n-1)(r-1)-1]}{r-1} = 22.22 \tag{72}$$

rejects H_0 at a highly significant level in favour of H_a in Eq. (62), in as much as $f_{1,4}(\alpha = 0.01) = 21.20$. The Type I error of this rejection is about 0.95% ($f_{1,4} = 31.33$ at $\alpha = 0.005$), and it can be stated that the modified/corrected treatment effects are highly significantly different.

The validity of H_0^* in Eq. (45) is determined by

$$f_{1,[(n-1)(r-1)-1]} = \frac{(SP_E)^2}{(SS_{xE})(SS'_{yE})} . \frac{[(n-1)(r-1)-1]}{r-1} = 6.55 \tag{73}$$

and it follows that rejection of H_0^* in favour of H_a^* in Eq. (46) carries a Type I error of about 6% [$f_{1,4} = 4.54$ and 7.71, at $\alpha = 0.1$, and 0.05, respectively). The necessity of retaining the concomitant variable may well be an admissible conclusion, since 6% is reasonably close to the significant level. If H_0^* is not rejected from a traditional viewpoint, ANOVA is recommended[11] for testing H_0. In that instance, both treatment effects and block effects are more than highly significant with F-statistics 58.41 (treatments) and 70.03 (blocks), inasmuch as the critical F-values are $f_{1,5}$ = 47.18 and $f_{2,5}$ = 37.12 (α = 0.001). The final result is (not surprisingly) the same. A similar procedure would apply if the pressure drop alone were considered to be the sole concomitant variable.

2. ANCOVA with Velocity and Pressure Drop Acting as Two Concomitant Variables

With two covariates, analysis requires a complex calculation procedure[12-14] in order to test the null hypothesis of no differences between the adjusted treatment means. Extension to several covariates is relatively straightforward[15] as an elegant application of matrix algebra. Table 7.65[16] provides a useful summary of the origin of corrected sums of squares, their degrees of freedom and associated computing formulae.

The principal result of ANCOVA applied to the high-conversion chemical reactor summarized in Table 7 is that rejection of the null hypothesis carries a Type I error of approximately 7.8%. Recalling the a priori postulate that x, y and z are measurements in randomly arranged experiments (instead of model-based numbers), a process analyst may conclude on the basis of a comprehensive understanding of the electrochemical process, that even an almost 8% Type I error may be judged to be sufficiently small to accept H_a. If so, the segmented and the non-segmented reactors are believed to behave differently. A process analyst strictly obeying conventional statistics, on the other hand, would conclude that the two reactors are not significantly different.

3. Two Covariate-Based ANCOVA of Product Yields in a Batch and in a Flow Electrolyzer

Table 8 contains hypothetical product yield data obtained via randomly arranged measurements in a batch electrolyzer, and in a flow electrolyzer with a fixed flow rate. The concentration of a contaminant ionic species and current density at the working electrode are considered to be the concomitant variables/cofactors. The ANOVA table signals no significant difference between the

Table 7
Data Array for ANCOVA with Velocity and Pressure Drop as Concomitant Variables (Section VI.2)

Treatment					
$j = 1$ (non-segmented cell)			$j = 2$ (segmented cell)		
x_{i1} (cm/s)	z_{i1} (kPa)	y_{i1} (kA/m^2)	x_{i2} (cm/s)	z_{i2} (kPa)	y_{i2} (kA/m^2)
16.1	29.0	8.206	17.8	32.0	9.091
6.04	10.9	6.154	7.68	14.0	7.828
2.68	4.83	4.103	4.20	7.6	6.413
1.01	1.81	2.051	2.31	4.1	4.699
0.447	0.805	1.026	1.55	2.8	3.565
0.212	0.381	0.513	1.15	2.1	2.790
Total: 26.489	47.726	22.053	34.69	62.6	34.386
Mean: 4.4148	7.954	3.6755	5.7820	10.4330	5.7310

ANOVA

{degrees of freedom: $(rn - 3)$ for SS_T; $(r - 1)$ for SS_{Tr}; $[r(n - 1) - 2]$ for SS_E}

Source	SS	DF	MS	F	P-value
Treatments	7.7456	1	7.7456	4.29	0.078
Error	14.4560	8	1.8070		
Total	22.2016	9			

$f_{1,8}$ (α =0.10) = 3.46; $f_{1,8}$ (α = 0.05) = 5.32

Table 8
Data Array for ANCOVA with Containment Impurity and Current Density as Concomitant Variables (Section IV.3)

Treatment					
$j = 1$ (batch electrolyzer)			$j = 2$ (flow electrolyzer with fixed flowrate)		
x_{i1} (mass%)	z_{i1} (kA/m^2)	y_{i1} (%)	x_{i2} (mass%)	z_{i2} (kA/m^2)	y_{i2} (%)
1.5	1.1	90	1.9	3.0	87
2.0	2.8	82	2.1	4.0	84
2.5	3.5	85	2.2	1.5	87
2.8	3.0	87	2.4	5.0	83
3.5	0.9	90	2.6	6.0	82
Total: 12.30	11.3	434	11.2	19.5	423
Mean: 2.46	2.26	86.8	2.24	3.90	84.6

ANOVA

Source	SS	DF	MS	F	P-value
Treatments	9.7513	1	9.7513	1.61	~ 0.25
Error	36.2753	6	6.0459		
Total	46.0266	7			

$f_{1,6}$ (α = 0.25) = 1.62

two kinds of electrolyzer, inasmuch as the opposite conclusion can be reached only at an inadmissibly high 25% error. If the cofactors are suppressed, a conventional ANOVA test yields a similar result with $f = 1.42$. Since $f_{1,18} = 1.54$ ($\alpha = 0.25$), rejecting H_0 would be highly unadvisable.

4. Covariance Analysis for a Two-Factor, Single Cofactor CRE

The performance of a cathodic process is analyzed in the following manner. As shown in Table 9, two levels of electrolyte composition (A_1 and A_2) and three different cathodes (levels B_1, B_2, B_3) are employed to determine the fraction of current wasted on hydrogen evolution at various settings of the cathode current density. The latter is taken to be the single concomitant variable.

The underlying postulate states that the y_{ijk} measurements (%-wasted current) belong to a normal population with mean μ_{ijk} and variance σ^2, and that in the expression

$$\mu_{ijk} = \mu + \alpha_i + \beta_j + (\alpha\beta)_{ij} + \gamma(x_{ijk} - x_{m..}) \tag{74}$$

the parameters obey the condition

$$\sum_{i=1}^{a} \alpha_i = \sum_{j=1}^{b} \beta_j = \sum_{i=1}^{a} (\alpha\beta)_{ij} = \sum_{j=1}^{b} (\alpha\beta)_{ij} = 0 \tag{75}$$

The null hypothesis set may be written as

$$H_0^{'} : \alpha_i = 0; i = 1,2,...,a; H_a^{'} : \text{not all } \alpha_i \text{ are zero} \tag{76}$$

$$H_0^{''} : \beta_j = 0; j = 1,2,...,b; H_a^{''} : \text{not all } \beta_j \text{ are zero} \tag{77}$$

$$H_0^{'''} : (\alpha\beta)_{ij} = 0; i = 1,2,...,a; j = 1,2,...,b; H_a^{'''} : \text{ not all } (\alpha\beta)_{ij} \text{ are zero} \tag{78}$$

and, in addition,

$$H_0^{*} : \gamma = 0; H_a^{'''} : \gamma \neq 0 \tag{79}$$

Table 9
Data Array for ANCOVA in Section IV.4 with Current Density as Single Concomitant Variable (Two-Factor CRE)

Level B_1 Cathode 1		Level B_2 Cathode 2		Level B_3 Cathode 3	
x (A/dm^2)	y (%)	x (A/dm^2)	y (%)	x (A/dm^2)	y (%)
		Level A_1			
4.0	9.5	3.0	8.5	5.0	9.0
3.5	8.0	4.0	10.0	4.0	8.5
4.0	9.5	4.5	8.5	4.0	9.0
5.0	10.5	4.0	9.0	3.0	8.0
4.5	10.0	4.0	9.0	4.0	8.5
		Level A_2			
5.0	10.0	5.0	10.0	4.5	9.5
3.0	9.5	3.0	9.0	3.0	8.5
3.5	9.5	4.0	9.5	2.5	7.5
4.5	11.0	4.5	9.0	5.0	10.5
3.0	8.8	4.0	9.5	3.5	8.5

Totals	X	Y
$T_{1..}$	60.5	135.5
$x_{m1..}$	58.0	140.3
$T_{.1.}$	40.0	96.3
$T_{.2.}$	40.0	92.0
$T_{.3.}$	38.5	87.5
$T_{...}$	118.5	275.8
Overall mean	3.950	9.193

Q	$\sum_{i=1}^{a}\sum_{j=1}^{b}\sum_{k=1}^{n} Q_{ijk}$
x^2	483.25
y^2	2554.44
xy	1100.65

$a = 2$; $b = 3$; $n = 5$; $N = 30$

Table 10
ANCOVA Array for the Data Shown in Table 9

Source[a]	SS_x	SP	SS_y	SS'_y	DF	MS'_y	F	P-value
A	0.208	– 0.4	0.745	1.452	1	1.452	5.56	0.028
B	0.150	0.665	3.873	2.928	2	1.464	5.61	~ 0.01
AB	0.517	0.115	0.0487	0.167	2	0.0834	0.31	> 0.25
Error	14.3	10.86	14.252	6.005	23	0.2611		
Total	15.18	11.24	18.919					

$f_{1,23}(\alpha = 0.025) = 5.75$; $f_{1,23}(\alpha = 0.05) = 4.28$; $f_{2,23}(\alpha = 0.01) = 5.66$

[a]Degrees of freedom: $(a - 1)$ for Treatment A; $(b - 1)$ for Treatment B; $(a - 1)(b - 1)$ for Treatment AB; $[ab(n - 1) - 1]$ for Error; $(abn - 2)$ for Total.

The involved computation scheme, presented in sufficient detail by e.g., Guenther,[17] yields the numerical values assembled in Table 10. The electrolyte composition effects are significant, but not highly significant, and rejection of $H_0^{'}$ carries an about 3% Type I error. The cathode type effects are essentially highly significant, since rejection of $H_0^{''}$ carries at most a 1% Type I error. The combined effects of the two treatments are additive, since $H_0^{'''}$ cannot be rejected. Finally, H_0^{*} is rejected at an extremely high level of confidence, because the computed F-statistic

$$f = \frac{(SP_E)^2}{(SS_{xE})(MS'_{yE})} = \frac{(10.86)^2}{(14.3)(0.2611)} = 31.59 \qquad (80)$$

is considerably larger than the critical value $f_{1,23}$ = 14.19 (α = 0.001). Consequently, the current density is rightly considered to be the concomitant variable.

VIII. MISCELLANEOUS TOPICS

1. Estimation of the Type II Error in ANOVA

In general, a Type II error is committed when a false hypothesis is not rejected. More specifically, the experimenter or process analyst not rejecting H_0 when H_a is true risks this error. The usual symbol for Type II error is β, and the power of the test is $(1 - \beta)$. Since the latter is the probability of rejecting the false null hypothesis when the alternative hypothesis is true, it follows that if $H_a = H_0$, the power is the same as α, i.e., the Type I error.

The computation of power is straightforward if α and β can readily be computed on the basis of normal, binomial, Poisson, etc. cumulative probability distributions. For instance, an analyst may be given the statement that one half of a particular type of low-temperature non-aqueous cells will retain its design potential at a 2.1 Ah capacity under a set load and temperature during discharge. The analyst might then decide that if out of 100 randomly chosen cells 57 (or more) cells are still operational after the passage of 2.1 Ah, the null hypothesis $H_0 : p = 0.5$ will be rejected in favour of H_a : $p > 0.5$. Using the normal distribution as a close approximation to the rigorous binomial, the Type I error is about 8.1%. If the true fraction (unknown to the process analyst) of the surviving cells were, however, 0.6, then the Type II error and power would be about 27% and 73%, respectively. If the true fraction were 0.7, β = 0.0024 (i.e., 0.24%) and $(1 - \beta)$ would be about 98.8%. However, if the true fraction were 0.55, the Type II error would be a rather large 66%, but of very small importance, since the two postulated means are very close. Such calculations, because of their relative simplicity, are routine subject matter in elementary textbooks on statistics.

The computation of power in ANOVA is considerably more complicated, involving numerical integration arising from the theory of the non-central F-distribution. To avoid this encumbrance, the Pearson-Hartley graphs[18-20] established for α = 0.05 and α = 0.01 can be employed. The power is given in terms of the second degree of freedom (ν_2) and a non-centrality parameter ψ as a function of the first degree of freedom (ν_1) of the F-distribution.

The results of a one-way classification test, shown in Table 11, are employed for illustration. Electrolysis is assumed to have been carried out at three different current densities in eight identical cells assigned to each current density, with current efficiency measured in each cell. The P-value is about 0.08 and it follows that the null hypothesis of insignificant current density effects cannot be conventionally rejected. In other words, the cell-to-cell variations are too large to assign variability to current density, at least by a one-way classification. The question of Type II error arises when at least one of the current efficiency sets pertaining to a particular current density differs from the rest, but this is unknown to the process analyst. Since the ψ parameter depends on the true variance σ^2, it is convenient to set this deviation in terms of σ-multiples. The analyst may postulate e.g., a $\beta_1 = \beta_3 = \beta$; $\beta_2 = \beta + k\sigma$ deviation scheme, where k is an arbitrary constant. In a one-way classification test the non-centrality parameter can be written for treatment sets of equal size as[21]

$$\psi = \frac{1}{\sigma}\left(\frac{n}{r}\sum_{j=1}^{r}\beta_j^2\right)^{1/2} \tag{81}$$

hence, in the case under discussion,

$$\psi = \frac{1}{3}\sqrt{2nk} \tag{82}$$

Table 11
Analysis of Type II Error in One-Way Classification Employing Three Current Density Levels as Treatment in Eight Cells Each

Source	SS	DF	MS	F	P-value
Among treatments	169.00	2	84.50	2.91	0.08
Within Treatments	610.00	21	29.05		
Total	779.00	23			
	$f_{22,21}$ ($\alpha = 0.05$) = 3.47; $f_{2,21}$ ($\alpha = 0.1$) = 2.58				

	k	ψ	$(1-\beta)$	
			$\alpha = 0.05$	$\alpha = 0.01$
$n = 8$; $r = 3$	1.0	4/3	~ 0.45	~ 0.20
	1.5	2	~ 0.81	~ 0.58
	2.0	8/3	~ 0.98	~ 0.90

is the final form of the parameter. Table 11 demonstrates the sensitiveness of power to ψ, at a fixed degree of freedom. For a one-sigma deviation of the mean ($k = 1$) the power of the test is expectably low.

A major role of power lies in determining the size of observations required for a pre-set value of errors. With the data in Table 11, if the required power is at least 0.90 when the Type I error is 0.05, a quick successive iteration involving $\nu_1 = 2$, $\nu_2 = 3n - 3$, Eq. (82), and the Pearson-Hartley graphs leads to $n = 21$ when $k = 1$. This means that at least 21 identical cells should be operated at each current density, in order to ensure a Type II error not exceeding 10%. Such an arrangement may, of course, not be practical, and the process analyst would have to settle for a lower power in order to keep down the number of experimental cells.

2. Hierarchical Classification

Consider electrodes delivered to a company operating several electrolytic plants using a large number of multiple-electrode cells. The electrodes contain an electro-catalyst whose percentage in the electrodes varies randomly (but within close limits). The process analyst may wish to determine if plant-to-plant variations, and/or cell-to-cell variations within a plant are significant by using the hierarchical classification procedure. In its fixed-effect version, electrode samples are taken randomly from b number of cells in a plant chosen from a number of plants, and n number of electrodes per cell. It is postulated that each population is normal, having the same variance. The observations of catalyst content in an electrode can then be written as

$$x_{ijk} = \mu + \alpha_i + B_{ij} + e_{ijk} \tag{83}$$

where e_{ijk} are normally distributed with zero mean and variance σ^2. Also, $\alpha_1 + \alpha_2 + \ldots + \alpha_a = 0$, and $B_{i1} + B_{i2} + \ldots + B_{ib} = 0$; $i = 1,2,\ldots, a$. The hypotheses may then be expressed as

$$H_0 : \alpha_i = 0; i = 1,2,..., a \tag{84}$$

$$H_a : \text{not all } \alpha_i \text{ are zero} \tag{85}$$

$$H_0^{'} : B_{ij} = 0;\ \ i = 1,2,..., a;\ \ j = 1,2,..., b \tag{86}$$

$$H_a^{'} : \text{not all } B_{ij} \text{ are zero} \tag{87}$$

In this classification, SS_T and SS_A have essentially the same role as in two-factor analysis, and $SS_{B(A)}$ is the sum of squares for variation levels of factor B *within* factor A (i.e., cells within plants). Consequently, SS_E is the same sum of squares for

Table 12
Hierarchical Classification Table for Coded Catalyst Content with a = 3 Electrolytic Plants, b = 4 Cells per Plant, and n = 5 Electrodes Taken Randomly from Each Cell

$T_{11.} = 15.6$;	$T_{21.} = 23.2$;	$T_{31.} = 35.3$;	$T_{12.} = 18.7$;	$T_{22.} = 18.1$;	$T_{32.} = 29.6$;
$T_{13.} = 18.3$;	$T_{23.} = 22.1$;	$T_{33.} = 36.3$;	$T_{14.} = 19.7$;	$T_{24.} = 23.8$;	$T_{34.} = 33.3$
$T_{1..} = 72.3$;	$T_{2..} = 87.2$;	$T_{3..} = 134.5$;	$T_{...} = 294$;	$\sum_{ijk} x_{ijk}^2 = 1586.46$	

ANOVA

Source	SS	DF	MS	F	P-value
Levels of A	105.47	2	52.73	86.30	< 0.001
Levels of B within A	11.04	9	1.23	2.01	0.063
Error	29.35	48	0.611		
Total	145.86	59			

$f_{2,48}(\alpha = 0.001) = 8.06$; $f_{9,48}(\alpha = 0.05) = 2.09$; $f_{9,48}(\alpha = 0.10) = 1.77$

variations within the same B-level within the same A-level (i.e., electrodes from the same cell). Table 12 shows a numerical illustration with a = 3, b = 4, and n = 5. The sums of squares are computed as

$$SS_T = \sum_{i=1}^{a}\sum_{j=1}^{b}\sum_{k=1}^{n} x_{ijk}^2 - \frac{T_{...}^2}{abn} = 145.86 \tag{88}$$

$$SS_A = \frac{\sum_{i=1}^{a} T_{i..}^2}{bn} - \frac{T_{...}^2}{abn} = 105.47 \tag{89}$$

$$SS_{B(A)} \frac{\sum_{i=1}^{a}\sum_{j=1}^{b} T_{ij.}^2}{n} - \frac{\sum_{i=1}^{a} T_{i..}^2}{bn} = 11.04 \tag{90}$$

$$SS_E = SS_T - SS_A - SS_{B(A)} = 29.35 \tag{91}$$

The degrees of freedom are (abn – 1) for SS_T, (a – 1) for SS_A, $a(b – 1)$ for $SS_{B(A)}$, and $ab(n – 1)$ for SS_E, respectively.

The results indicate that the catalyst content of the electrodes varies sharply from plant to plant, but variations between cells within plants are not significant. This finding would suggest the possibility of a faulty distribution scheme to the process analyst.

Hierarchical classification with mixed-model and random-effect model formulations, the estimation of the Type II error,[22] and related analysis of covariance have been discussed elsewhere.[23]

3. ANOVA-Related Random Effects

The basic tenet of fixed-effect based analysis is that the treatments are self-contained populations. If, however, treatments are considered to be samples of a large treatment population, then the β_j parameters are no longer (unknown) constants, but random variables belonging to the normal distribution N(0;σ^2). In fact, the means μ_1, $\mu_2, \ldots, \mu_r$ are themselves random. Under such circumstances the null and alternative hypotheses are:

$$H_0 : \sigma_\beta^2 \le K_0\sigma^2 \tag{92}$$

$$H_a : \sigma_\beta^2 \ge K_0\sigma^2 \tag{93}$$

where K_0 is an arbitrary constant. These hypotheses are more practical than the perhaps more obvious hypotheses of the β-variance being zero or non-zero. Alternatively, the confidence interval of the σ_β^2/σ^2 ratio may be established by the inequality

$$\frac{1}{n}\left(\frac{MS_A}{MS_W}\frac{1}{F_{r-1;N-r;1-0.5\alpha}}-1\right) < \sigma_\beta^2/\sigma^2 < \frac{1}{n}\left(\frac{MS_A}{MS_W}\frac{1}{F_{r-1;N-r;0.5\alpha}}-1\right) \tag{94}$$

may be employed in lieu of Eqs. (92) and (93). It is worth noting that the sample-based estimate of the variance, s_β^2, is given by the expression

$$s_\beta^2 = \frac{MS_A - MS_W}{n} \tag{95}$$

for treatment observations of equal size.

In the case of randomized blocks Eq. (86) is slightly modified; the MS_A/MS_W ratio is replaced by the MS_{Tr}/MS_E ratio, and the second degree of freedom of the F-statistic becomes $\nu_2 = (n-1)(r-1)$.

When treatment observations are of unequal size, the parameter

$$n' = \frac{\left(\sum_{j=1}^{r} n_j\right)^2 - \sum_{j=1}^{r} n_j^2}{(r-1)\sum_{j=1}^{r} n_j} \tag{96}$$

replaces n in Eq. (94).

Table 13 contains assumed membrane deterioration data observed with four different membranes employed over a three-month period in three different electrolyzers. Fixed-effect based

Table 13
RBE Applied to the Membrane Deterioration Problem in Section VIII.2[a]

Blocks	Treatment				$T_{i.}$	$x_{mi.}$
	Membrane 1	Membrane 2	Membrane 3	Membrane 4		
Electrolyzer1	7.4	9.3	11.1	10.5	38.3	9.58
Electrolyzer2	3.9	8.7	8.1	9.9	30.6	7.65
Electrolyzer3	10.2	9.4	8.5	12.1	40.2	10.05
$T_{.j}$	21.5	27.4	27.7	32.5	Overall sum: 109.1	
$x_{m.j}$	7.17	9.13	9.23	10.83	Overall mean: 9.09	

ANOVA

Source	SS	DF	MS	F	P-value
Treatments	20.2833	2	10.1417	4.01	0.084
Blocks	12.9225	3	4.3075	1.70	0.154
Error	15.1834	6	2.5306		
Total	43.3892	11			

$\nu_1 = 3$; $\nu_2 = 6$

Type I error, α	0.10	0.05	0.01	0.002
$f_{\alpha/2}$	4.76	6.60	12.92	23.70
$f_{1-\alpha/2}$	0.1119	0.0678	0.0223	0.00753

[a]The entries are on a dimensionless scale 1 (best) – 15 (worst)

ANOVA fails to distinguish between electrolyzers (blocks) and membranes (treatments). If, however, the electrolyzers are taken to be a sample of a large number of similar electrolyzers slated for the same process with the same membrane types, the confidence intervals of the σ_β^2/σ^2 variance ratio, shown in Table 14, indicate a large domain of possible β-variance values.

The effect of treatment population size on this confidence interval is illustrated in Table 15. The first ANOVA array is established by considering the first three current density (25, 50, 75 mA/cm^2) treatments of anodes constructed of eight different alloys in a primary alkaline battery whose anode efficiency was studied by Paramasivan et al.[24] The second array refers to the entire experimental set with three additional treatments (100,125,150 mA/cm^2). Since the magnitude of the F-statistics indicates an extremely small Type I error in both cases, the conclusion that both current density and alloy composition exhibit extremely important effects is the same for the subset and the full set. The major difference is in the considerable reduction in the width of the confidence interval for the β-variance, owing to the larger amount of information rendered by the six-treatment set.

Table 14
The Effect of the Type I Error on the Confidence Interval for the Variance Ratio via Equation (94)

α	Lower bound of variance ratio*	Upper bound of variance ratio
0.10	0	11.56
0.05	0	19.27
0.01	0	59.33
0.002	0	176.38

* negative lower limits are replaced by zero

4. Introductory Concepts of Contrasts Analysis

As mentioned briefly in Section II, contrasts analysis is a means of deciding what treatment means are statistically different, if ANOVA rejects the null hypothesis of treatment-mean equality. An especially thorough discussion[25] indicates the variety of techniques available for analysis; in this Section only the method by Scheffé[5,26,27] is illustrated, on account of its generality and the convenience of using F-distribution (instead of special distributions required by other methods, e.g., Duncan's, Tukey's, etc.)

Table 15
ANOVA of Anode Efficiency Data in Table 6[22]

Treatments: current density; blocks: alloy composition

(a) Subset of 3 treatments ($n = 8$; $r = 3$)

Source	SS	DF	MS	F	P-value
Treatments	995.25	2	497.63	101.33	< 0.001
Blocks	418.50	7	59.79	12.17	< 0.001
Error	68.75	14	4.91		
Total	1482.5	23			

$f_{2,14}(\alpha = 0.001) = 11.78$; $f_{7,14}(\alpha = 0.001) = 7.08$

(b) Total set of 6 treatments ($n = 8$; $r = 6$)

Source	SS	DF	MS	F	P-value
Treatments	2732.50	5	546.50	102.74	< 0.001
Blocks	362.33	7	51.76	9.73	< 0.001
Error	186.17	35			
Total	3281.00	47			

$f_{5,35}(\alpha = 0.001) = 5.30$; $f_{7,35}(\alpha = 0.001) = 4.60$

95% confidence interval of $\sigma_\beta^2 / \sigma^2$

Number of treatments	Lower limit	Upper limit
3	2.48	499.4
6	4.20	79.6

Table 16
Contrasts Analysis Related to a One-Way Classification ANOVA of SER Data

Treatments[a]			
Plant 1	Plant 2	Plant 3	Plant 4
4.714	4.757	4.843	5.057
4.671	4.971	4.628	5.271
4.500	4.671	4.671	5.357
T_j : 13.885	14.399	14.142	15.685
$x_{m,j}$: 4.628	4.800	4.714	5.228

$$\sum_{ij} x_{ij}^2 = 282.1935$$

ANOVA

Source	SS	DF	MS	F	P-value
Among treatments	0.6393	3	0.2131	11.60	0.0037
Within treatments	0.1469	8	0.0184		
Total	0.7862	11			

$f_{3,8}(\alpha = 0.005) = 9.60$; $f_{3,8}(\alpha = 0.001) = 15.83$

Differences in observation means

4 – 1: 0.6	4 – 3: 0.514	4 – 2: 0.428
2 - 1: 0.172	2 – 3: 0.086	
3 – 1: 0.086		

[a]The entries are in units of MWh/metric ton of sodium chlorate

The gist of the method is to ascertain if (selected) sample-mean differences are larger or not than the right hand side of Eq. (97).Denoting an arbitrary sample mean difference as Δ_{ij}, if the condition

$$\Delta_{ij} > [(r-1)F_{\alpha,r-1,N-r}(MS_W \sum_{j=1}^{r} \frac{c_j^2}{n_j})]^{1/2} \tag{97}$$

is satisfied, the treatment means in question are different at an α-level of significance. Eq. (97) applies to one-way classification only, each classification having its own set of conditions. Specifically, in the case of randomized blocks, MS_W in Eq. (97) is replaced by MS_E and the second degree of freedom is $\nu_2 = (n-1)(r-1)$.

Table 16 contains observations of SER from four plants producing electrolytic sodium chlorate. The null hypothesis of no plant-to-plant difference in SER is rejected with a Type I error of about 0.4%, hence at least two means are highly significantly different. At $\alpha = 0.01$, the critical F-statistic is $f_{0.01,3,8} = 7.59$, and considering differences between only two means, Eq. (97) yields the condition $\Delta_{ij} > 0.528$, which is satisfied only by $(5.228 - 4.628) = 0.6$, all other differences being smaller than 0.528. It then follows, that the method identifies only the $(\mu_4 - \mu_1)$ difference as highly significant. If $\alpha = 0.05$ is chosen, $f_{0.05,3,8}$ being 4.07, the significance condition $\Delta_{ij} > 0.387$ identifies the mean-differences $(\mu_4 - \mu_1)$, $(\mu_4 - \mu_3)$ and $(\mu_4 - \mu_2)$ as significant. Other contrast-analytic methods do not necessarily lead to the same results; it is to be noted that Scheffé's test is the "most conservative with respect to Type I error and will lead to the smallest number of significant differences."[28]

IX. FINAL REMARKS

The fundamental postulate of ANOVA, that observations belong to normal distributions with a constant (albeit usually unknown) variance cannot be *ab ovo* guaranteed. It is known, however, that the F-test for the equality of means is insensitive to deviations from normality,[29] and in the case of large observations, normality is a good approximation to the real distribution of data.

To query the postulate of constant variance (i.e., to test the homogeneity of the observations), the Bartlett test is commonly used in ANOVA. The test can be carried out either by using tables of Bartlett's probability distribution,[30] or by chi-square distribution tables of a statistic whose sampling distribution is nearly chi-square.[31] The test is particularly recommended for treatments carrying observations of unequal size. For equal-size observations, a quick test[32] consists of comparing the ratio of the largest to the smallest treatment variance to critical values of the F_{max}-statistic in appropriate tables.[33]

The major relevance of material presented in this chapter, best viewed as an *appetite-whetter*, resides in economy. Proper statistical techniques can save considerable time and effort to the experimenter and the process analyst in trying to extract the largest possible amount of information from available data, and to optimize the size of statistically meaningful experiments.

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LIST OF PRINCIPAL SYMBOLS

a, b, r	factor dimension
CRE	completely randomized experiment
DF	degree of freedom
e	error
F	F-statistic; f its numerical value
H_0	null hypothesis
H_a	alternative (or counter) hypothesis
L	contrast
MS_Q	means square related to quantity Q
n	observation size per treatment
N	total observation size
$N(\mu;\sigma^2)$	normal distribution with mean μ and variance σ^2
RBE	randomized block experiment
SER	specific energy requirement
SP_Q	sum of products related to quantity Q
SSQ	sum of squares related to quantity Q
SS'_Q	modified sum of square related to quantity Q
T	sum of observations
x, y	observed quantity

Subscripts

A	among groups (or treatments)
A, B, C	treatment (factor)
AB, BC, ABC	interaction
BL	block
C	column
E	error
R	row
T	total
Tr	treatment
x, y	observations
W	within groups (or treatments)

Greek Symbols

α	deviation variable, and size of Type I error
β	deviation variable, and size of Type II error
μ	treatment mean
σ^2	variance
ν	degree of freedom

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