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A rapid test to determine the state of an electrochemical process

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The application of a rapid method based on Shafer's theory of evidence and Narasimhan's computation procedure is illustrated in the testing of changes in the steady state of electrochemical processes. Specific examples comparing numerical results to those of conventional multivariate statistics demonstrate the attractiveness of the approach.

1. Introduction

Several years ago a new approach to probability [1], called the mathematical theory of evidence (MTE) was presented. Its major tenet, the degree of belief a proposition can be accorded on the basis of evidence, and the combination of degrees of belief based on distinct bodies of evidence permits the computation of belief functions assigned to events. The strength of belief in an event is expressed as a fraction of unity, upon appropriate manipulations. An interesting philosophical aspect of the theory lies in its divergence from classical Bayesian probability theory, although the latter may be regarded as a special case of evidence theory. Although not yet known widely, recent specific applications to fault diagnosis [2] and to the detection of changes in steady states [3] portray the potential usefulness of this method in applied sciences and engineering as an inviting alternative to conventional methods of multivariate statistical analysis. The purpose of this paper is to show its applicability to the evaluation of electrochemical system performance: the numerical results of analysis are compared to those of the multivariate statistical approach [4, 5].

2. Summary of Narasimhan's technique [3] of the MTE approach

The objective is to detect changes in a steady state using N experimental measurements of independent state variables obtained in two successive time periods. Three belief functions are assigned respectively to three propositions, namely that the process has not changed its steady state (S); the process has changed its state from the first to the second observation period (C); it is not possible to state with certainty that there has been a change in the state of the process from the first to the second observation period (uncertainty proposition U). Then, the combined belief in the three propositions is expressed by Demster's rule [1, 3]:

$$\phi(S) = \prod_{i=1}^{p} [f_i(S) + f_i(U)] \qquad (1)$$

$$\phi(C) = \prod_{i=1}^{p} [f_i(C) + f_i(U)] \qquad (2)$$

$$\phi(U) = \prod_{i=1}^{p} f_i(U) \qquad (3)$$

The belief functions are computed according to the magnitude of the t^2 statistic of each process variable i:

$$t_i^2 = N\frac{(\overline{y}_i - \overline{x}_i)^2}{s_{y_i}^2 + s_{x_i}^2}, \quad i = 1, \ldots, p \qquad (4)$$

where $\overline{x}_i$ is the mean of the measurements (of variable i) in the first observation period, $\overline{y}_i$ is the mean of such measurements in the subsequent observation period and $s_{y_i}^2$, $s_{x_i}^2$ are the sample variances associated with x_i and y_i, $i = 1, \ldots, N$, respectively. The t_i^2 are random variables obeying Hotelling's T^2 distribution [4, 6]; as discussed briefly in the Appendix, in the two-sample problem of interest here, the T^2 distribution coincides with the F distribution with degrees of freedom p and $2N - 2$. The computation scheme for the belief functions shown in Table 1 indicates clearly that if t_i^2 is less than the critical value of F at a level of confidence α, the belief assigned to a change in the steady state indicated by the ith process variable is nil, whereas a t_i^2 value larger than the critical F assigns zero belief to a lack of change in the steady state. In consequence, the degree of uncertainty is pegged to the extent of belief in the existence or non-existence of the tested steady state. Equations 1–3 indicate that the composite belief is a product of individual beliefs, which is analogous to the elementary theorem of the probability of simultaneously occurring events: the overall probability is the product of individual and independent single-event probabilities.

3. Computational aspects

The evaluation of $f_i(S)$ in Step 2a and $f_i(C)$ in Step 2b may require numerical values of the F variate at values of α not listed in commonly available tabulations. A close approximation is obtained by various polynomials and asymptotic forms [7]; if N is sufficiently small, the (α, F) relationship is calculable, e.g. by the

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Table 1. The scheme of computation for belief functions based on the MTE theory[1] *(α = level of confidence)*

Step 1: Compute t_i via Equation 4; $i = 1, \ldots, p$	
Step 2a: if $t_i^2 \leqslant F_{1,2N-2}(\alpha)$ then:	Step 2b: if $t_i^2 > F_{1,2N-2}(\alpha)$ then:
$f_i(S) = Pr\,[F \geqslant t_i^2]$	$f_i(S) = 0$
$f_i(C) = 0$	$f_i(C) = \dfrac{2\alpha - 1 + (1-\alpha)Pr[F \leqslant t_i^2]}{\alpha}$
$f_i(U) = 1 - f_i(S)$	$f_i(U) = 1 - f_i(C)$

[1] Following Narasimhan *et al.* [3] with some changes in notation.

expression

$$1 - \alpha = (1 - x)^{1/2}\left[1 + \frac{x}{2} + \frac{3}{8}x^2 + \frac{3.5.7.\ldots(v-3)}{2.4.6.\ldots(v-2)}x^{(v-2)/2}\right] \quad (5)$$

where $x \equiv v/(v + F)$ and $v = 2N - 2$. On the other hand, if $v \geqslant 6$ (corresponding to $N \geqslant 4$) a t_i^2 value above 14 ($F_{1,6} = 13.75$ at $\alpha = 0.01$) assigns at a highly significant level a strong belief that the steady state in process variable i has changed. Similarly, a t_i^2 value less than 1.71×10^{-4} ($F_{6,1} = 5859$ at $\alpha = 0.01$) assigns at a highly significant level a strong belief that there is no change in the steady state of process variable i. (In neither case is a detailed computation via Table 1 necessary.)

4. Comparison with multivariate statistical analysis

As discussed by Narasimhan *et al.* [5], the procedure via conventional multivariate statistics consists of two tests. In the first one the null hypothesis $\mathbf{S}_1 = \mathbf{S}_2$ is tested, where $\mathbf{S}_1$ and $\mathbf{S}_2$ are the sample estimates of the true measurement error covariance matrices $\mathbf{\Sigma}_1$ and $\mathbf{\Sigma}_2$ for the first and second observation periods, respectively. In the second part the null hypothesis $\overline{\mathbf{x}_1} = \overline{\mathbf{x}_2}$ is tested, where $\overline{\mathbf{x}_1}$ and $\overline{\mathbf{x}_2}$ are the means of the observations in the first and second observation periods, respectively. The exact procedure, described in detail in the Appendix of [5], requires time-consuming vector–matrix manipulations, and an *a priori* trial-and-error probability computation involving the χ^2 distribution, for the testing of the first null hypothesis. The test statistic in the analysis of the second null hypothesis is distributed as Hotelling's T^2 variable [4] via the relationship

$$T_\alpha^2 = p\,\frac{2N-2}{2N-1-p}\,F_\alpha(v_1, v_2) \quad (6)$$

where $v_1 \equiv p$ and $v_2 \equiv 2N - 1 - p$ are the degrees of freedom of the F distribution. If the computed T^2 is larger than T_α^2 given by Equation 6 at a specified level of significance α, the $\overline{\mathbf{x}_1} = \overline{\mathbf{x}_2}$ hypothesis is rejected and a change in the steady state is indicated. In studying the power of this composite test procedure Narasimhan *et al.* [5] have shown that the probability or rejecting the $\overline{\mathbf{x}_1} = \overline{\mathbf{x}_2}$ null hypothesis when one or more process variables have changed their states can be as low as 0.2 under certain conditions unless p and N are sufficiently high. They have also shown [3] that the MTE method has a virtually identical power structure: it follows that failure to reject the $\overline{\mathbf{x}_1} = \overline{\mathbf{x}_2}$ null hypothesis (multivariate statistical approach) or a large value of $F(S)$ obtained by the MTE method may not be conclusive if p and N are small.

5. Application to electrochemical processes: numerical illustrations

5.1. *Example 1: continuous-flow electrolysis*

In a continuous-flow electrolytic process three process variables, the cathodic current density ($i = 1$), the concentration of a certain impurity in the anolyte ($i = 2$) and the anode dissolution rate ($i = 3$), are considered to represent fully the state of the process, to be mutually independent and are measured five times over a certain time period. Table 2 contains sets of measurements taken in two adjacent time periods (of equal length). Has the process changed its steady state from one time period to the other?

The t^2 variates are computed via Equation 4:

$$t_1^2 = 5(6.46 - 4.86)^2/(0.3528 + 0.04285) = 32.86$$

$$t_2^2 = 5(2.92 - 3.28)^2/(0.1467 + 0.06708) = 3.031$$

$$t_3^2 = 5(0.118 - 0.082)^2/(3.686 \times 10^{-4} + 1.7 \times 10^{-4}) = 12.03$$

Table 2. Process variable measurements in two adjacent observation periods (Example 1)

	First period			*Second period*		
	$i = 1$ (A dm^{-2})	$i = 2$ (ppm)	$i = 3$ (g day^{-1})	$i = 1$ (A dm^{-2})	$i = 2$ (ppm)	$i = 3$ (g day^{-1})
	7.0	3.2	0.11	5.1	3.5	0.08
	6.4	3.2	0.14	4.9	3.0	0.07
	6.9	3.1	0.09	4.7	3.2	0.09
	5.5	2.3	0.12	4.6	3.1	0.10
	6.5	2.8	0.13	5.0	3.6	0.07
Mean value	6.46	2.92	0.118	4.86	3.28	0.082
Variance	0.3528	0.1467	3.686×10^{-4}	0.04285	0.06708	1.7×10^{-4}

and compared to the critical values of the random variable F_α with degrees of freedom $v_1 = 1$ and $v_2 = 2(5) - 2 = 8$: $F_{0.05}(1, 8) = 5.82$ and $F_{0.01}(1, 8) = 11.26$ [8]. Following the steps described in Table 1, the belief functions are computed to be:

$$f_1(S) = 0$$

$$f_2(C) = [2\alpha - 1 + (1 - \alpha)(1)]/\alpha = 1 \quad \text{for all } \alpha$$

$$f_2(U) = 0$$

$$f_2(S) = 0.125$$

$$f_2(C) = 0$$

$$f_2(U) = 0.875$$

$$f_3(S) = 0$$

$$f_3(C) = [2(0.05) - 1 + (1 - 0.05)(0.996)]/0.05 = 0.932 \quad (\alpha = 0.05)$$

$$f_3(C) = [2(0.01) - 1 + (1 - 0.01)(0.996)]/0.01 = 0.604 \quad (\alpha = 0.01)$$

$$f_3(U) = 0.068 \quad (\alpha = 0.05)$$

$$f_3(U) = 0.396 \quad (\alpha = 0.01)$$

The combined beliefs are given by Equations 1–3 as:

$$\phi(S) = (0 + 0)(0.125 + 0.875)(0 + 0.068) = 0 \quad (\alpha = 0.05)$$

$$\phi(S) = (0 + 0)(0.125 + 0.875)(0 + 0.396) = 0 \quad (\alpha = 0.01)$$

$$\phi(C) = (1 + 0)(0 + 0.875)(0.932 + 0.068) = 0.875(\alpha = 0.05)$$

$$\phi(C) = (1 + 0)(0 + 0.875)(0.604 + 0.396) = 0.875 \quad (\alpha = 0.01)$$

$$\phi(U) = (0)(0.875)(0.068) = 0 \quad (\alpha = 0.05)$$

$$\phi(U) = (0)(0.875)(0.396) = 0 \quad (\alpha = 0.01)$$

Upon normalization (i.e. dividing each ϕ by $\phi(S) + \phi(C) + \phi(U)$) the final values are $\phi(S) = 0$; $\phi(C) = 1$; $\phi(U) = 0$ at both levels of significance, indicating a very strong belief that the steady state has changed from one observation period to the next one.

Conventional multivariate statistical analysis fails to reject the null hypothesis that the covariance matrices of the two observation periods are identical at both levels of significance, but it rejects the null hypothesis that the two sets of mean observations are equal ($T^2 = 33\,274$). The final result of the two methods is the same but the MTE calculation sequence is much faster.

Table 3. Process variable measurements in two adjacent observation periods (Example 2)

	First period		*Second period*	
	$i = 1$ (%)	$i = 2$ (°C)	$i = 1$ (%)	$i = 2$ (°C)
	53.5	94.1	50.5	93.9
	54.2	94.1	51.2	95.1
	54.7	95.2	55.3	96.2
	53.6	96.1	52.8	94.2
	56.2	95.8	55.4	94.2
	52.8	94.9	52.1	96.1
	51.1	94.3	54.5	94.9
	55.3	95.7	52.1	95.0
	55.9	95.8	55.7	95.2
	54.7	96.2	53.1	92.9
Mean value	54.22	95.22	53.27	94.77
Variance	2.3618	0.6773	3.4468	1.0090

5.2. *Example 2*

A fuel cell is operated at a certain portion of its full power capacity and its operating state is considered to be described by its efficiency ($i = 1$) and temperature ($i = 2$). The observation sets in two consecutive time periods are shown in Table 3.

The t^2 variates

$$t_1^2 = 10(54.22 - 53.27)^2/(2.3618 + 3.4468) = 1.554$$

$$t_2^2 = 10(95.22 - 94.77)^2/(0.6773 + 1.0090) = 1.201$$

being smaller than the appropriate critical values of $F_{0.05}(1, 18) = 4.414$ and $F_{0.01}(1, 18) = 8.29$ [8], the belief functions are computed at both levels of significance via Step 2a in Table 1. The results of the calculation given in Table 4 may be compared to the conventional multivariate statistical analysis, which fails to reject the null hypothesis of equal covariance matrices at both levels of significance as well as the null hypothesis of equal observation means (the computed $T^2 = 3.117$ is less than the critical value of $T^2 = 7.61$ ($\alpha = 0.05$) and $T^2 = 12.94$ ($\alpha = 0.01$)). The MTE method assigns a reasonable degree of belief to the hypothesis that there has been no change in the state of operation; it also indicates a weak but not negligible belief in the opposite, and an equal degree of uncertainty about the two beliefs. The result of the

Table 4. Summary of the theory of evidence approach to the fuel cell operation in Example 2

	Level of significance						
	$\alpha = 0.05$		$\alpha = 0.01$				
	$i = 1$	$i = 2$	$i = 1$	$i = 2$			*Normalized*
$f_i(S)$	0.282	0.286	0.282	0.286	$\phi(S)$	1	0.477
$f_i(C)$	0	0	0	0	$\phi(C)$	0.548	0.261
$f_i(U)$	0.768	0.714	0.768	0.714	$\phi(U)$	0.548	0.261

conventional multivariate method is not an acceptance of the no-change hypothesis, but simply an incapability to reject it: there is no numerical indication of the weakness of this result, in contrast to the MTE approach which yields a quantitative measure of uncertainty.

5.3. *Example 3*

This is a variation of Example 1, by assuming that the cathodic current density ($i = 1$) alone is sufficient to fully represent the state of the electrolytic process in any observation period. The combined belief functions

$$\phi(S) = f_1(S) + f_1(U) = 0$$
$$\phi(C) = f_1(C) + f_1(U) = 1$$
$$\phi(U) = f_1(U) = 0$$

are identical numerically to those obtained in Example 1; this finding indicates that there was a sufficiently large change in the cathodic current density to induce a change in the state of the process; it does not follow, however, that the anolyte impurity and anode dissolution rate are indifferent process variables. Comparison with conventional multivariate statistical analysis is simple in this 'single-parameter' case, where the critical region for the test statistic [4] in the covariance-matrix test

$$W = \left(\frac{S_1 S_2}{S_1^2 + S_2^2} \right)^4 \tag{7}$$

is given as:

$$W_\alpha > \exp\left[-\tfrac{7}{8} X_\alpha\right] \tag{8}$$

and X_α must satisfy the approximate probability condition

$$Pr\,(\chi_1^2 \leqslant X_\alpha) = 1 - \alpha \tag{9}$$

for the χ^2 distribution, with one degree of freedom. From Table 2, $W = 0.0937$ and since [8] $X = 3.84$ ($\alpha = 0.05$) and $X = 6.63$ ($\alpha = 0.01$), it follows that the null hypothesis of equal covariance matrices is rejected at a highly significant level. The null hypothesis of equal means is similarly rejected at a highly significant level by the Student's t-test comparing the test-statistic value of:

$$t = \frac{6.46 - 4.86}{(0.3528 + 0.04285)^{1/2}}\, 5^{1/2} = 5.69$$

to the critical values of $t = 2.776$ ($\alpha = 0.05$) and $t = 4.604$ ($\alpha = 0.01$) with four degrees of freedom [8]. Both methods indicate strongly a change in the state of the electrolytic process, but the MTE method remains faster even in the single parameter case.

6. Extensions and limitations

The MTE approach is not limited to two consecutive observation periods; for the detection of a change in a slowly varying steady state several observation periods may, in fact, be necessary. In one strategy [5] the period pairs (1; 2), (1; 3), (1; 4), etc. are subjected to the test until a change is found at the kth period; then the pairs (k; $k + 1$), (k; $k + 2$), etc. are tested in the same fashion. Alternatively, the (1; 2), (2; 3), etc. observation pairs can be tested in a similar fashion. Rapidly changing steady states (generated for example by random variations in a plant) would most likely be sensed by tests on only two adjacent observation periods.

The knowledge of the full set of independent process variables which fully characterizes the process is of crucial importance, since if for an arbitrary jth variable $f_j(S) = f_j(U) = 0$, the MTE approach indicates no change in the steady state even if $f_i(S) \neq 0$, $f_i(U) \neq 0$ for all the other $i \neq j$ process variables. If, therefore, the jth variable is not included (e.g. by ignorance) in the set, the results are misleading. The attractiveness of the MTE approach increases with the size of the set because each additional computation of the t^2 statistic, belief functions, and composite beliefs adds a minimal encumbrance, whereas the increase in vector–matrix dimensions due to an increase in p renders the conventional multivariate statistical approach numerically more cumbersome: at large p, a digital computer is necessary for efficient calculation, whereas MTE-based calculations can be carried out on pocket calculators.

Ther most important limitations of the MTE method are related to the error structure of observations: the measurements must contain only normally distributed random errors with zero mean vector $\mathbf{O}$ and their true covariance matrix $\mathbf{\Sigma}$ (usually unknown) should be diagonal and a constant from one observation period to the other. Further, the process variables must be independent, inasmuch as the belief functions can be significantly biased otherwise. Finally, the probability of false null hypothesis rejection and the power of the MTE method cannot be calculated directly: extensive simulation studies [3, 5] indicate, however, that the proportion of simulation trials rejected by MTE and the power of conventional multivariate analysis (based on Hotelling's T^2 distribution) are virtually the same under identical simulation conditions.

7. Concluding remarks

An interesting question arising from this analysis is whether the method is capable of indicating the length of transients between successive steady states. Since the constancy of the describing state variables within each observation period is an underlying assumption for the test [3], if this constancy condition is not satisfied, the MTE method will yield a relatively large belief for change, or a relatively large belief for uncertainty, even if $\phi(S)$ is not small. It is a matter of engineering judgement whether a process undergoes a series of transitions between successive steady states, or is in a truly dynamic state: the method will, in any event, indicate a variation in the state and therein lies its strength.

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Appendix

The T^2 statistic is defined as:

$$T^2 = N(\bar{X} - \bar{\mu})^T S^{-1}(\bar{X} - \mu) \qquad \text{(A1)}$$

where $\bar{X}$ is the mean vector of a sample of size N, μ is the population mean vector and **S** is the sample covariance matrix, an unbiased estimate of the true (population) covariance matrix Σ. Let $X_j, j = 1, \ldots, N$ be sample observations from the $N(\mu, \Sigma)$ population. Then, the distribution of the

$$T^2 = N(\bar{X} - \mu_0)^T S^{-1}(\bar{X} - \mu_0) \qquad \text{(A2)}$$

statistic is related to the non-central F distribution with non-centrality parameter $N(\mu - \mu_0)^T \Sigma^{-1}(\mu - \mu_0)$. If, specifically, $\mu = \mu_0$ (i.e. a null hypothesis with a specified value of μ), the F distribution is central and the critical region of the hypothesis test at a level of significance α is

$$T^2 > T_\alpha^2$$

where

$$T_\alpha^2 = \frac{(N-1)p}{N-p} F_\alpha(p; N-p) \qquad \text{(A3)}$$

The t^2 statistic defined by Equation 4 is a random variable distributed as T^2 with corresponding degrees of freedom (of the related F distribution) 1; $2N - 2$ [3, 5]. It follows from Equation A3 that

$$T_\alpha^2 = F_\alpha(1; 2N - 2) \qquad \text{(A4)}$$

in this particular instance; the fact that an F value with one degree of freedom can be considered as a square of Student's t-statistic is well known in single-variate statistics (e.g. [9]).

References

[1] G. Schafer, 'A Mathematical Theory of Evidence', Princeton Univ. Press, Princeton, New Jersey (1976).
[2] M. A. Kramer, *AIChE J.* **33** (1987) 130.
[3] S. Narasimhan, Chen Shan Kao and R. S. H. Mah, *ibid.* **33** (1987) 1930.
[4] T. W. Anderson, 'An Introduction to Multivariate Statistical Analysis', Ch. 5, 2nd edn. (1984); 1st edn. (1958), Wiley, New York.
[5] S. Narasimhan, R. S. H. Mah, A. C. Tamhane, J. W. Woodward and J. C. Hale, *AIChE J.* **32** (1986) 1409.
[6] H. Hotelling, *Ann. Math. Stat.* **2** (1931) 360.
[7] M. Abramowitz and I. A. Stegun (eds), 'Handbook of Mathematical Functions', Section 26.6, Dover Publications Inc., New York (1965).
[8] W. H. Beyer (ed.), 'Handbook of Tables for Probability and Statistics', Section VI 1, The Chemical Rubber Co., Cleveland, Ohio (1966).
[9] J. Mandel, 'The Statistical Analysis of Experimental Data', Section 8.7, Dover Publ. Inc., New York (1964).