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A chemometric evaluation of battery performance under overcharge conditions

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Abstract

The results of overcharge tests performed on seventy automotive batteries from several manufacturers were analyzed by means of a principal component analysis. Two parameters, derived from the analysis, are proposed as convenient measures of overall battery performance and stability, allowing a bidimensional graphical representation of the original fourteen-dimensional data matrix.

Keywords Battery performance, Chemometric evaluation, Overcharge

1. Introduction

It has been claimed that in Brazil many car batteries are being submitted to overcharge in actual use, because of the usually poor state of maintenance of Brazilian automobiles, particularly of their charging systems. Indeed, it is very common to find batteries submitted to tensions of 16 or even 17 V. Such an overcharge, combined with the tropical temperatures prevailing in most areas of Brazil, is obviously highly detrimental to battery life. In order to investigate the performance of batteries under overcharge conditions and also to help in the development of batteries more resistant to overcharge, we have performed an experiment in which several batteries were submitted to laboratory overcharge conditions. Since the usual industrial standards for overcharge [1] are not realistic for the conditions mentioned above, we developed a specific testing sequence, which will be described in the experimental section of this article. The multivariate data resulting from such tests were submitted to a principal component analysis, in a search for possible patterns of behavior hidden in the multidimensional structure.

Principal component analysis (PCA) is a well-established chemometric technique that has been applied by one of us to the study of infrared intensity parameters [2–4]. The starting point of a PCA is a data matrix in which each row represents an object (an automotive battery, in the present case) described by a certain number of variables (the overcharge test results), which are ordered by columns. The numerical values of a given row are regarded as the Cartesian coordinates of a point locating the corresponding object in a multidimensional space where each axis represents one variable. The purpose of the analysis is to compress this multidimensional data into a smaller number of dimensions, with a minimum loss of information in the process. This is achieved by rotating the original axes in search of orthogonal directions of maximal variance [5]. As a result, the first principal component axis (PC1) contains the maximum information that can be projected into a single dimension, the second PC axis is orthogonal to the first one and contains as much of the remaining information as possible, and so on. The coordinates of the objects on the new axes are called scores, and the coefficients of the linear combinations defining each PC direction, which are the direction cosines with respect to the original axes, are its loadings. If this information compressing procedure is successful, that is, if most of the original information is found to be represented in the first few principal components, then one may expect that plots of the scores on these PC axes reveal the major patterns implicit in the original, multidimensional data. In the present case, as we shall see, most of the information gathered from the tests can be accounted for by only two parameters that measure a given battery's overall performance and stability. A plot of these two parameters allows instant visualization of the relative quality of a battery, and can therefore be useful for monitoring the manufacturing process.

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Table 1

Average results for battery lots submitted to four overcharge cycles. The tension and the time were also measured before any overcharge tension was applied (cycle zero). Lots A to D come from Brazilian manufacturers. Lots I contain imported batteries. Experimental details are given in the text

Battery lot	Water consumption (g) Cycle				Tension after 30 s (V) Cycle					Time for 6 V (s) Cycle				
	1	2	3	4	zero	1	2	3	4	zero	1	2	3	4
1I	95.00	77.50	61.25	41.25	10.20	10.96	10.58	10.88	10.81	279.00	395.75	304.00	364.50	361.75
2I	107.50	72.50	32.50	20.00	10.75	10.76	10.76	10.69	10.59	308.00	337.00	314.00	300.50	278.50
3I	102.50	57.50	32.50	5.00	10.87	11.01	10.55	10.28	10.85	305.00	330.00	223.00	148.00	236.00
4B	147.50	145.00	110.00	62.50	10.05	10.49	10.15	10.05	9.86	199.00	220.50	223.00	224.00	200.00
5A	477.50	677.50	585.00	1362.5	10.33	10.22	10.00	9.73	8.24	266.00	224.00	235.00	135.50	42.50
6A	202.50	162.50	342.50	732.50	9.95	10.06	10.08	9.87	9.35	212.00	182.00	170.50	152.00	115.50
7A	312.50	280.00	517.50	752.50	10.05	10.06	9.84	9.02	8.44	250.00	246.50	211.50	165.00	173.00
8A	477.50	427.50	857.50	1027.5	10.05	10.09	9.90	9.90	9.69	223.50	251.00	220.00	219.50	202.00
9A	370.00	457.50	765.00	1015.0	10.13	9.98	10.02	9.92	9.85	234.50	239.50	238.00	207.00	219.00
10C	196.25	95.25	170.00	91.25	10.50	10.84	10.91	11.19	11.04	248.50	307.75	340.75	385.50	391.25
11A	560.00	385.00	842.50	670.00	10.59	10.42	10.64	10.81	10.31	256.50	177.50	210.50	132.50	152.00
12A	477.50	437.50	1002.50	1757.5	10.47	10.49	10.59	10.42	5.24	270.50	217.50	259.00	170.50	114.00
13A	255.00	210.00	460.00	535.00	9.97	10.72	10.27	10.91	10.77	186.00	311.00	218.00	327.00	318.00
14A	397.50	218.75	243.75	493.75	10.54	10.76	10.82	10.51	10.32	291.50	311.00	293.00	212.75	161.00
15I	182.50	135.00	112.50	117.50	10.66	10.88	10.87	10.64	10.65	297.00	347.00	333.00	299.50	296.00
16A	645.00	858.33	1386.67	1065.0	10.36	10.46	10.46	8.83	9.04	242.33	218.67	215.33	93.00	60.33
17A	432.50	642.50	803.00	1524.0	10.56	10.69	10.41	10.29	5.00	348.50	365.50	331.50	297.50	107.50
18I	317.50	127.50	149.00	233.50	10.56	10.74	10.45	10.55	10.66	302.00	343.50	300.00	290.00	309.50
19A	288.75	289.50	370.25	322.50	10.32	10.42	10.51	10.47	10.44	282.50	262.25	213.00	177.50	151.50
20A	237.50	242.50	258.75	217.50	10.30	10.44	10.39	10.09	10.44	299.50	306.00	304.75	226.00	278.25
21A	447.50	520.00	492.50	667.50	9.81	10.11	9.97	10.11	9.67	184.25	265.50	248.25	294.25	179.00
22A	145.00	232.50	245.00	262.50	10.00	10.24	10.18	10.25	10.05	221.50	251.00	238.50	238.00	234.00
23A	135.00	152.00	210.00	287.50	10.05	10.33	10.15	10.31	9.83	227.50	258.50	222.00	252.00	178.00
24A	118.75	152.50	135.00	287.50	10.17	10.17	10.27	10.26	10.30	255.00	244.00	246.75	225.25	188.75
25A	75.00	105.00	100.00	200.00	10.14	10.24	10.28	10.31	10.35	283.25	285.75	302.75	300.75	296.50
26A	125.00	230.00	105.00	875.00	10.02	9.98	10.17	10.19	9.83	229.00	204.50	221.50	199.50	131.50
27D	45.00	52.50	90.00	102.50	10.05	10.01	10.07	10.07	10.06	204.50	185.00	177.50	189.00	189.00

2. Experimental

The overcharge condition was simulated by placing the batteries in a water bath at 40 °C under a constant 16 V tension during 120 h. This is what we called a cycle of overcharge. Battery performance was measured in terms of water consumption (as given by total weight loss after the cycle) and by a room temperature fast discharge. Each battery was submitted to a total of four cycles of overcharge. The initial performance, before any overcharge had been applied, was also evaluated through a fast discharge in 'cycle zero'. The parameters used to evaluate the performance were the weight loss and the room temperature fast discharge performance, expressed by the voltage after 30 s and the time to reach 6 V during the discharge. The batteries selected for this study were all of 45 Ah nominal C_{20}. The current used for fast discharge was 180 A.

3. Results and discussion

The experimental cycles yielded a total of fourteen experimental values (the test results) for each battery. The original data matrix contained these results for a group of seventy batteries coming from several different manufacturers, both Brazilian and foreign. Most of these batteries were taken from normal production lines, while others were especially prepared for the tests. Since some of them originated from the same manufacturing lot, the results of their tests were averaged and the analysis was performed on the average results. This averaging process tends to cancel out random fluctuations, allowing the underlying structures to be more easily discerned. The original 70×14 matrix representing individual batteries was thus compressed into a 27×14 matrix representing battery lots, given in Table 1.

Prior to the principal component analysis the data of Table 1 were subjected to autoscaling, a procedure that leaves each variable with zero mean and unit variance [6]. This scaling procedure assigns to each variable the same amount of information (as represented by its variance), compensating for variance differences arising only from differing scales of measurement. In contrast to the original values, shown in Table 1, the autoscaled values are dimensionless.

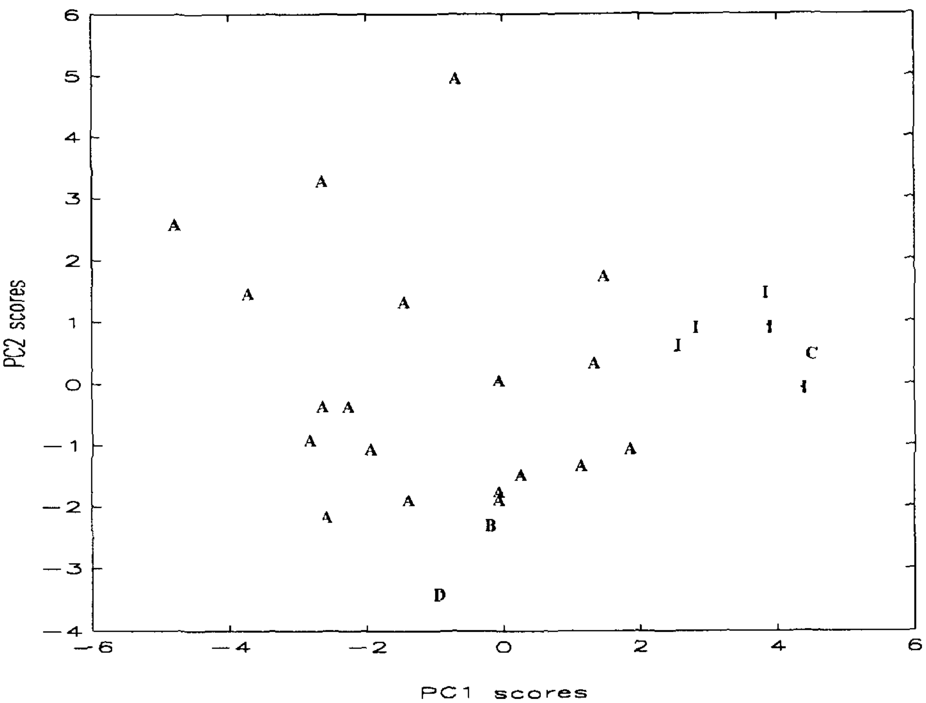

Fig. 1. Plot of the PC2 scores against the PC1 scores obtained in the principal component analysis of the data given in Table 1. The data were autoscaled prior to the analysis. Different letters stand for different manufacturers. The letter 'I' indicates foreign manufacturers.

The principal component analysis was performed with the Ein*sight computer program [7] on a PC486 microcomputer. The loadings of the first three principal components are given in Table 2. Together they explain 79.2% of the original variance, leaving only 20.8% for the remaining eleven dimensions. Four fifths of the original information can therefore be projected into only three dimensions. An examination of the scores of the objects on these three PC axes should reveal most of the underlying structure present in the fourteen-dimensional original data.

Table 2

Loadings for the first three principal components resulting from the analysis of the (autoscaled) data of Table 1. w = water consumption; T = tension after 30 s of fast discharge; t = time for 6 V tension; variance = percent variance explained by each principal component

No.	Variable	PC1	PC2	PC3
1	w, cycle 1	−0.241	0.327	0.088
2	w, cycle 2	−0.288	0.285	0.185
3	w, cycle 3	−0.286	0.276	0.129
4	w, cycle 4	−0.292	0.269	0.231
5	T, cycle zero	0.172	0.381	−0.423
6	T, cycle 1	0.284	0.272	−0 103
7	T, cycle 2	0.257	0.288	−0.258
8	T, cycle 3	0.297	0.033	0 101
9	T, cycle 4	0.214	−0.288	−0.219
10	t, cycle zero	0.166	0.380	−0 201
11	t, cycle 1	0.299	0.204	0.251
12	t, cycle 2	0.266	0.278	0 296
13	t, cycle 3	0.289	−0.022	0.570
14	t, cycle 4	0.332	−0.114	0.237
	Variance (%)	44.83	25 23	9 21

The scores on the first two PCs are plotted in Fig. 1. This plot corresponds to 70% of the information contained in Table 1. No separate well-defined groups are apparent, but it is evident that most of the spread is due to the lots produced by Brazilian manufacturers (A–D), while the imported batteries (I) form a relatively compact cluster scoring high on the first PC axis (PC1). An analysis of the PC1 loadings (Table 2) shows that the first principal component is calculated to be essentially an average of all the fourteen original variables, the water losses being given negative signs. This means that a battery presenting low values for the water loss and high values for the time and the tension will have a high score on the PC1 axis. Since these are all desirable qualities, the PC1 score may be interpreted as a single measure of overall battery performance, summing up the evidence furnished by all fourteen tests. The location of a given battery along the PC1 axis will give an indication of its performance, better performing batteries being expected to appear farther to the right.

It may be seen from Fig. 1 that the foreign batteries perform better than their Brazilian counterparts, on the whole. Not only that, they also exhibit a more uniform behavior, as indicated by the relative tightness of their cluster. The exception is the lot from Brazilian manufacturer C, which is on a par with the foreign batteries.

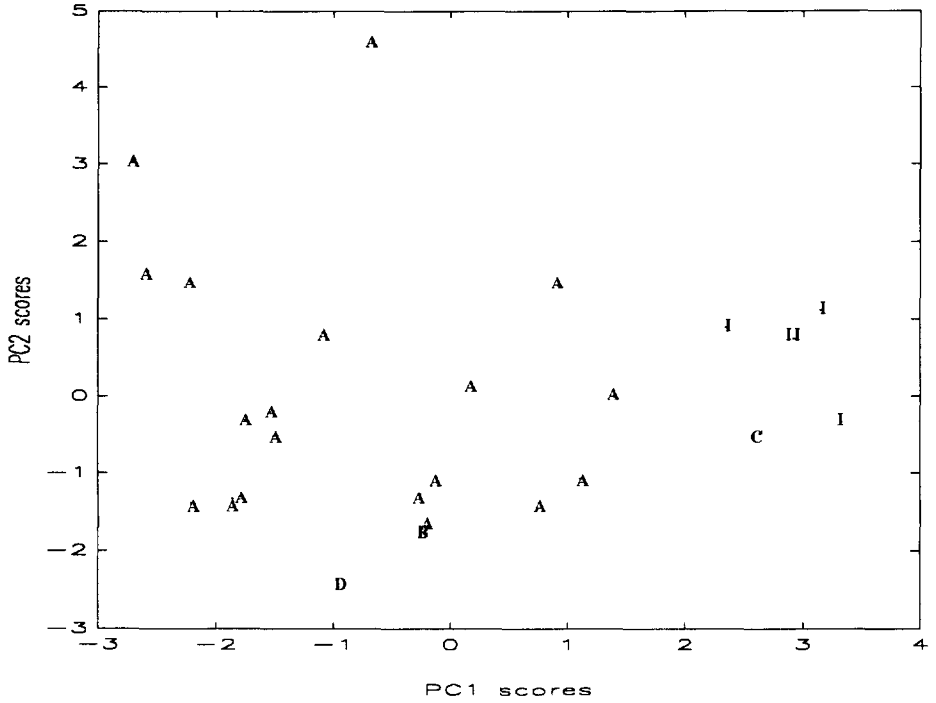

Fig. 2. Plot of the PC2 scores against the PC1 scores obtained in the PCA of the data given in Table 1, excluding the results for the second and third overcharge cycles Notation as in Fig. 1.

Table 3
Loadings for the first three components resulting from the PCA of the data of Table 1 after the results for the second and third overcharge cycles were excluded. Notation as in Table 2

No	Variable	PC1	PC2	PC3
1	*w*, cycle 1	−0.289	0.358	0.206
2	*w*, cycle 4	−0.400	0.346	−0.271
3	*T*, cycle zero	0.272	0.451	0.514
4	*T*, cycle 1	0.407	0.286	0.008
5	*T*, cycle 4	0.305	−0.397	0.491
6	*t*, cycle zero	0 255	0.472	0.054
7	*t*, cycle 1	0.418	0.213	−0.518
8	*t*, cycle 4	0.428	−0.200	−0.325
	Variance (%)	43.9	32.0	7.8

The second principal component has very small loadings for the tension and the time in the third testing cycle, indicating that these variables contribute almost nothing to define the PC2 axis. On the other hand, the contributions of the first and second cycles to both PC2 and PC1 are quite similar for all the tests, suggesting that there is some redundance in keeping both cycles in the analysis. These considerations led us to perform a new PCA, discarding the values referring to the second and third cycles.

The new loadings are given in Table 3, and the corresponding scores for PC1 and PC2 are plotted in Fig. 2, which represents 76.2% of the total information contained in the eight starting variables. There is some rearrangement of the objects, but the general appearance of the plot and the conclusions that can be drawn are the same as in Fig. 1. Most of the spread is due to the batteries manufactured in Brazil, whereas the points representing the foreign lots are clustered towards the right-hand side. As before, the scores on PC1 can be interpreted as a measure of overall performance. The higher a battery scores on the first principal component, the better its performance is expected to be.

In the second principal component the loadings of the first and fourth cycles have opposite signs for the tension and the time, indicating that for these two variables PC2 can be regarded as a contrast between the first and last testing cycles and therefore can furnish a measure of the stability of battery performance with respect to time. For the water loss this contrast is observed instead on the third component.

These considerations suggest that most of the information contained in the tests can be summarized by two parameters describing essentially battery overall performance and the stability of this performance with time. These parameters are linear combinations of the eight results on which the PCA was done. The precise values of the coefficients defining each combination will fluctuate somewhat, depending on which particular set of batteries is subjected to analysis. To avoid these fluctuations and also to provide more easily interpretable parameters, we propose, instead of an expression based

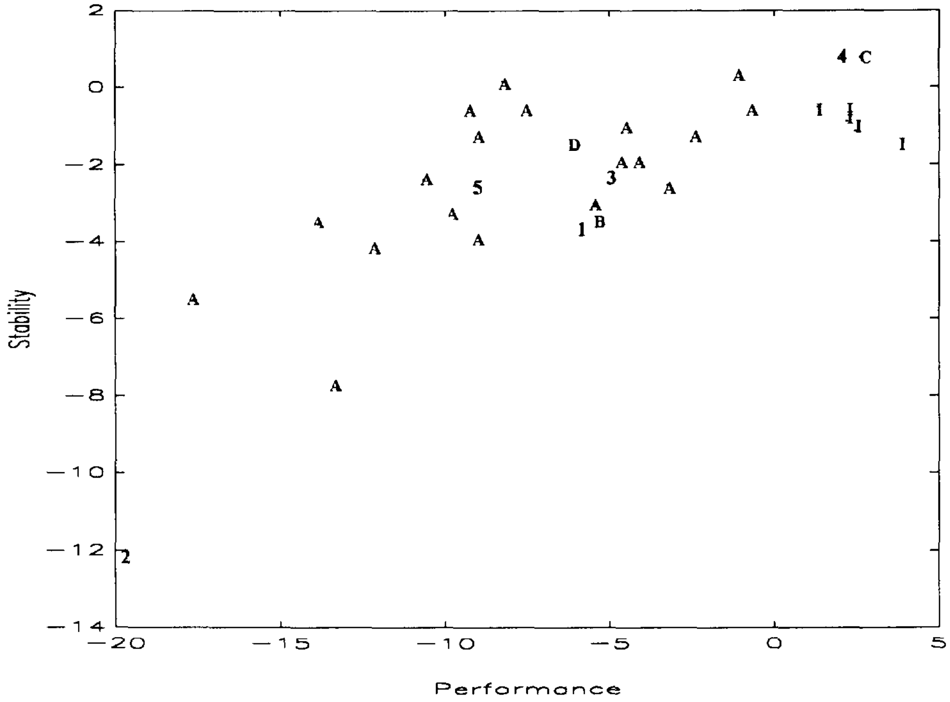

Fig. 3. Plot of the stability parameter S against the performance parameter P for the 27 battery lots in Table 1 plus five new lots, numbered 1 to 5.

on the PCA loadings, the following definitions:

$$P=\frac{-[(w_1-100)+(w_4-100)]}{329.08}+\frac{(T_0-10.3)+(T_1-10.3)+(T_4-10.3)}{0.696}+\frac{(t_0-300)+(t_1-300)+(t_4-300)}{63.04} \qquad (1)$$

$$S=\frac{w_4-w_1}{329.08}+\frac{(T_0-10.3)+T_4-T_1}{0.696}+\frac{(t_0-300)+t_4-t_1}{63.04} \qquad (2)$$

where w, T and t stand for water loss, tension and time, respectively, and the index refers to the overcharge cycle in which these variables are measured. Since the PC analysis was performed on autoscaled data, the proposed parameters P (for performance) and S (for stability) were also scaled by centering the variables on a reference battery with standard values $w_r=100$ g, $T_r=10.3$ V, and $t_r=300$ s, and dividing by the respective standard deviations calculated from the data of Table 1. As a result of this transformation, the parameters P and S are dimensionless quantities. Their interpretation is straightforward. A perfectly stable battery operating with the reference values for w, T and t would have an S value of zero. On the other hand, an exceptional battery, exhibiting high tensions and times and low water losses, would come out with a very positive value for P.

Eqs. (1) and (2) were used to calculate P and S values for the battery lots of Table 1 and five more lots which were tested after the PC analysis had already been made. The results are given in Table 4 and plotted in Fig. 3. On this plot the better batteries are expected to lie close to the zero level of the S parameter and towards the right side of the P axis.

Fig. 3 confirms the conclusions reached in the two PC analyses, regarding the general spread of the data and the relative location of the imported batteries. It is interesting to note that the P and S parameters show a positive correlation ($r=0.69$), which is reflected in the tilt of the data cloud. This may be interpreted as meaning that a poorly performing battery (located on the left side of the plot) also tends to show a less stable behavior, becoming worse with increasing use (negative values for S). The five battery lots that had not been included in the modeling phase (numbered 1 to 5 in Fig. 3) were all produced by Brazilian manufacturers. They are found to span the whole plot. Battery no. 2 is the poorest of all the batteries that were studied, whereas battery no. 4 is very good, performing on a level with the imported lots, together with lot C. The remaining batteries, nos. 1, 3 and 5, present an intermediate behavior.

Table 4
Performance (P) and stability (S) parameters calculated for twenty-seven battery lots P and S are dimensionless quantities, defined by Eqs (1) and (2)

Lot	P	S
1I	3.8964	−1.3950
2I	2.3172	−0.6647
3I	2.4504	−1.1190
4B	−5.1983	−3.4500
5A	−13.8448	−3.5309
6A	−10.6406	−2.3633
7A	−9.6614	−3.3088
8A	−9.0483	−1.2534
9A	−8.2352	0.1648
10C	2.6140	0.7633
11A	−7.5075	−0.5017
12A	−17.6639	−5.5190
13A	−2.3366	−1.2488
14A	−3.2314	−2.5092
15I	2.1841	−0.8673
16A	−12.0896	−4.1043
17A	−13.2639	−7.8082
18I	1.3288	−0.5043
19A	−4.0795	−1.8744
20A	−0.6304	−0.5089
21A	−8.9655	−3.8760
22A	−4.5765	−1.8619
23A	−5.4112	−3.0412
24A	−4.3672	−1.0775
25A	−1.0194	0.2128
26A	−9.2825	−0.6230
27D	−6.0611	−1.5641

4. Conclusions

Most of the information contained in the fourteen experimental variables determined in the overcharge tests reported here can be projected in only two dimensions, according to the principal component analysis performed on the autoscaled data. Following an examination of the PC loadings, we suggest that a convenient way to summarize the experimental results is to represent them by means of two easily interpretable parameters, defined by Eqs. (1) and (2), measuring overall battery performance and stability. We believe that this representation can be profitably employed as the basis of a quality control chart, allowing one to compare at a glance the performance of a group of batteries, or to track the evolution of a given manufacturing process towards improved products.

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