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Three-way principal components analysis for multivariate evaluation of round robin tests

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Introduction

The increasing complexity of analytical investigations promotes the generalization of classical multivariate data sets (with objects and variables) to higher dimensional data arrays. A 3-way data matrix of the so called 'objects – variables – occasions' – type arises e.g. in repeated round robin tests. Here n objects (determinations of a given sample) are characterized by p variables (trace element contents) at k occasions (round robin tests). The set of objects is partitioned into g groups (laboratories). Principal Component Analysis (PCA) is a suitable technique for extracting most parts of the information contained in the data. There are several generalizations of classical PCA to multiway data arrays [1]. In our application to round robin tests we prefer the unfolding technique [2]. This allows us to generalize specific procedures for the valuation of laboratories, which originally were developed for classical multivariate data sets, namely incorporation of the (multivariate) theoretical point [3] and of the generalized bisectrix [4]. The advantage of combining these procedures with multi-way PCA consists in an extreme condensation of large data sets yielding an easy graphically oriented approach for valuating laboratories during several round robin tests. It circumvents a tedious univariate variable by variable or occasion by occasion consideration.

Results

We describe an application to the analysis of waters [5]. Four round robin tests with synthetical solutions of Cd, Cu, Zn, Ni were organized in order to get information on reliability and stable working of 8 laboratories each of which provided 5 repeated estimations. Hence, the 3-way data array we are dealing with, has 'side lengthes' $40 \times 4 \times 4'$. Figure 1 shows the corresponding (unfolded) PCA-plot of the first two principal components. For simplicity only the laboratory centroids (with respect to repeated estimations) are depicted. The multivariate theoretical point (exact contents of the synthetical solutions) is represented by a filled square. There are two laboratories with poor results related to the theoretical point, namely E and G. Obviously laboratories B and I provided most precise results, which are stable with respect to all trace elements and to all tests. The generalized bisectrix (dashed line) represents a generalization of the ordinary bivariate YOUDEN-plot [6] to the multivariate case. Laboratories with positions far from the total centroid (cross) but near to the generalized bisectrix are characterized by systematical errors (always too high or always too low). This seems to be the case for G (and in a smaller extent for C with opposite direction of error). On the other hand, laboratories far from the total centroid as well as far from the bisectrix are characterized by unstable working (sometimes much too high, sometimes much too low). This is true for E. If one is only interested in the relation to the theoretical point then using nonlinear mapping [7] might be superior to PCA. Figure 2 shows the corresponding plot with repeated estimations included but laboratories E and G excluded (since their position is clear from the PCA-plot and in this way a smaller mapping error in nonlinear mapping may be achieved). Obviously, now laboratory B turns out to provide most precise results. The described procedure allows to recognize stable working for laboratories A, B, F, H, I.

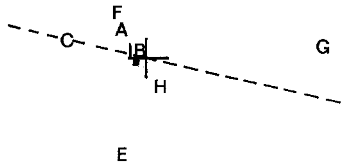

Fig. 1
3-way PCA-plot (unfolded) for the considered data from round robin tests

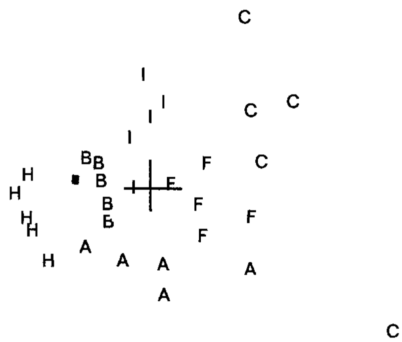

Fig. 2
Non-linear mapping for the same data set

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