

Principal Component Analysis Applied to Polymeric Sensing Materials

Alison J. Scott and Alexander Penlidis

*Institute for Polymer Research (IPR), Department of Chemical Engineering,
University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada*

Polymeric sensing materials can be used for the detection and identification of various volatile organic compounds (VOCs). Polymers exhibit good sensitivity and selectivity, allow for room temperature detection, and offer significant potential for product customization.

The suitability of a particular polymeric sensing material for detection of a target analyte (VOC) depends largely on the sensitivity and selectivity of the material. The *sensitivity* is related to the detection limit (lower detection limit = increased sensitivity), while the *selectivity* is related to the detection of the target analyte in the presence of other interfering gases. Using a specialized test set-up (with a highly sensitive GC for detection in the ppm or ppb range), it is possible to evaluate the sensitivity and selectivity of various sensing materials without creating a physical sensor. That is, we are able to evaluate the sorption of target analytes onto polymeric sensing materials without considering the design or mechanics of the sensor itself. This ultimately reduces the experimental work and associated costs; only the best-performing sensing materials are incorporated into sensors for further testing.

Due to the nature of this testing process, experimental data can be collected relatively quickly. Many combinations of individual gases, gas mixtures, and sensing materials culminate into large data sets. Additionally, once responses have been collected from a variety of sensing materials, data sets may be combined to simulate *sensing arrays*. To make physical sense of these large data sets, we turn to multivariate statistics.

Principal component analysis (PCA) is a well-known tool in multivariate statistical analysis. With PCA, it becomes possible to explain the variation of a data set with fewer factors than were originally provided. By reducing the number of factors (components) in the data set, PCA simplifies the analysis while retaining the majority of the statistical information. This allows us to look at the inter-relationships among the observations (here, experimental runs) and among the

variables (here, gases and gas mixtures). Thus, PCA is a valuable tool in evaluating sensing materials for gas analyte detection. Given sufficient experimental data, PCA acts as a filtering algorithm, allowing us to observe useful trends and identify clusters within the data (see Figure 1).

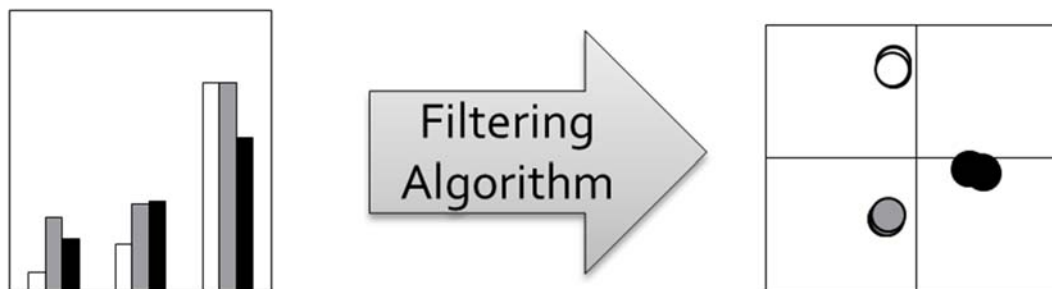


Figure 1. Graphical representation of PCA as a filtering algorithm.

Case Study: Analysis of a Sensor Array

When several sensing materials are analyzed simultaneously (simulating a polymeric sensing array), several target analytes can be detected and identified individually. Plots obtained using principal component analysis can provide information about the relationships between observations (experimental runs), and can identify whether a sensing material (or a sensing array) will be able to distinguish between different gases. Additionally, if there is not sufficient separation of analytes to identify the gases individually, PCA can be used to provide prescriptions for what additional material might improve the sensing performance of the array.

Three polymeric sensing materials were synthesized and then tested to establish the sensitivity and selectivity toward methanol (M), ethanol (E), acetone (A) and benzene (B). Materials were exposed to each individual gas and also to gas mixtures. As shown in Figure 2, the distinction between methanol, ethanol, acetone and benzene was much more obvious when the data only included individual gases (that is, no gas mixtures). The PCA *loadings* plot (Figure 2(a)) indicates good separation between the analytes. Similarly, the PCA *scores* plot (Figure 2(b)) represents each experimental run with a single point. The data points are grouped together according to the analyte used for each run, and their location on the scores plot is aligned with the loadings plot. The scores

plot could subsequently be used as a reference plot for the detection of unknown gases. That is, if the experimental data from an unknown gas (one of M, E, A, B) were added to this plot, it could easily be identified using its relative location.

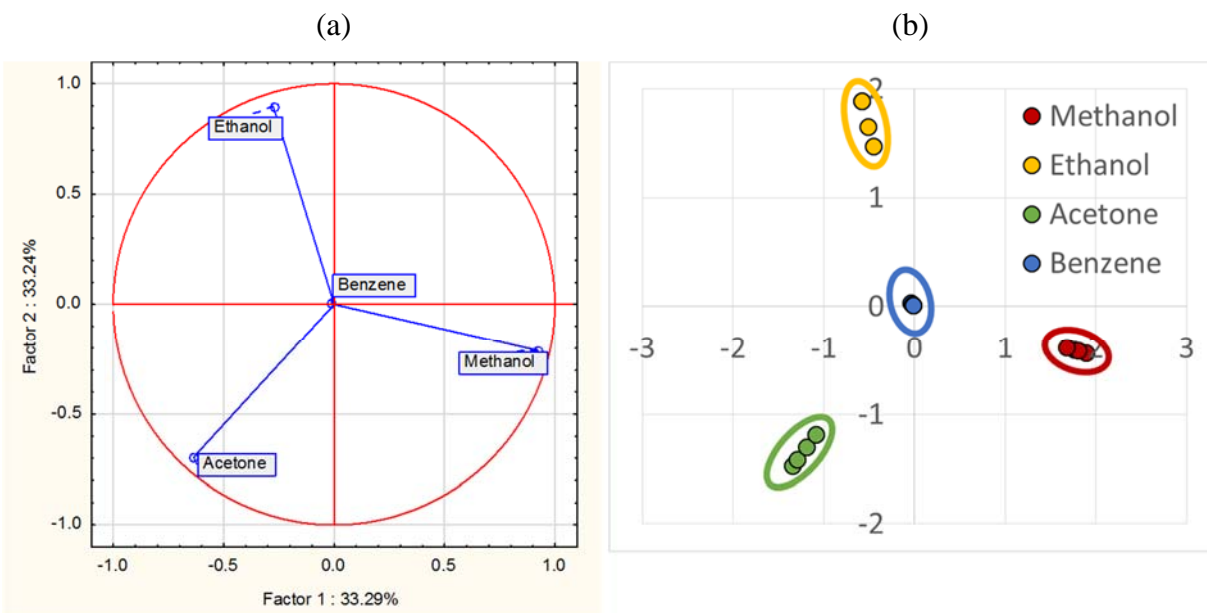


Figure 2. Detection and identification of methanol, ethanol, acetone and benzene.

This is a straightforward example: one sensing material was exposed to four gases (one at a time), and it was possible to distinguish between all four individual gases using PCA. However, this proof-of-concept motivates the next stage: can we reliably distinguish between gases when they are mixed? Can we establish whether we are working with a pure gas or a mixture containing said gas? This is where sensing material arrays become necessary.

The three polymeric materials were again exposed to each of the four gases mentioned previously (M, E, A, B), as well as all possible combinations of these gases (3 sensing materials \times 15 gas combinations, with replicates). This experimental work inevitably produced a much larger data set, further proving the need for a filtering algorithm like PCA. Results showed that gas mixtures were susceptible to interactions, which made it more difficult to distinguish between the four unique gases. However, plots obtained from PCA helped to identify which specific desirable properties could be added to the array to improve sensing performance. For example, if the

loadings plot shows poor separation of benzene, a benzene-sensitive material can (and should) be added to the sensing array to improve performance.

These statistical insights, combined with an understanding of similar sensing materials, made it possible to modify the sensing array in an informed manner. This improved the sensing performance of the array, and we were able to reliably distinguish between methanol, ethanol, acetone and benzene. This proof-of-concept study uses a three-material sensing array to detect four unique gases (and gas mixtures). Not only have we identified potential polymeric sensing materials for future applications, but we have also demonstrated the advantages associated with using principal component analysis to evaluate these sensing materials for gas analyte detection. Additional results and insights will be presented at the time of the IPR conference.

References

- A. J. Scott and A. Penlidis, "Nitrile Rubber Reactor Operation Troubleshooting with Principal Component Analysis," *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, vol. 50, no. 8, pp. 803-811, 2013.
- K. M. E. Stewart and A. Penlidis, "Novel Test System for Gas Sensing Materials and Sensors," *Macromolecular Symposia*, vol. 324, p. 11-18, 2013.
- K. M. E. Stewart and A. Penlidis, "Sensor Array for Volatile Organic Compounds Based on Doped Poly (2,5-dimethyl aniline)," *Macromolecular Symposia*, vol. 370, pp. 120-127, 2016.
- K. M. E. Stewart and A. Penlidis, "Evaluation of Polymeric Nanocomposites for the Detection of Toxic Gas Analytes," *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, vol. 53, no. 10, pp. 610-618, 2016.