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Secondary ion mass spectrometry for the identification of polymers with noncharacteristic secondary ions using multivariate statistical analysis

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Eleven different, filler-free polymers were depth profiled until all secondary ion signals were stable. Discriminant function analysis and principal components analysis were performed on a dataset containing the intensities of noncharacteristic hydrocarbon secondary ions, measured in this steady state. Discriminant function analysis showed that these secondary ions were sufficient to correctly identify all polymers using leave-one-out correction. Even with principal components analysis, which uses no prior knowledge about the origin of a data point, identification was shown to be possible. © 2004 American Institute of Physics. [DOI: 10.1063/1.1642278]

Secondary ion mass spectrometry is a powerful tool in the analysis of polymer surfaces. However, similarities in chemical composition, as, e.g., in polyethylene and polypropylene, make direct distinction by techniques based on mass spectrometry difficult, if not impossible. Multivariate statistical analysis¹ of static SIMS spectra has already been applied to a multitude of problems, such as classification studies of adsorbed proteins,^{2–5} the study of their conformational changes upon adsorption,^{6,7} and other classification studies.^{8–10} All these studies used mass spectra measured during static sputter conditions. The main reason for this is that for high ion fluences, such as encountered during dynamic SIMS, any characteristic fragments that are most often used for multivariate statistical analysis are unstable.¹¹ Nevertheless, performing SIMS measurements under dynamic conditions may be desirable for the purpose of depth profiling.

However, the secondary ions produced by all common polymers (and hence noncharacteristic), such as the C_n^- and the C_nH^- ions, are usually stable after equilibrium between the primary ions and the substrate has been reached. Although these secondary ions each by themselves do not contain any apparent information, these fragments together could contain enough information about the polymer to be able to identify it, for example the hydrogen to carbon ratio within each polymer, or because of different fragmentation pathways. Hence, it may be feasible to use these noncharacteristic hydrocarbon fragments to differentiate between mass spectra from different depth profiled polymers, with further differentiation from stable fragments containing other elements commonly encountered in polymers, such as oxygen and nitrogen. This study attempts to determine if this can be

achieved using discriminant function analysis and principal components analysis.

Eleven common and filler-free polymers obtained from Goodfellow, shown in Fig. 1, polyethylene terephthalate (PET), polypropylene (PP), polymethylmethacrylate (PMMA), polyetheretherketone (PEEK), polybenzimidazole (PBI), polyethersulphone (PES), high density polyethylene (HDPE), polyamide-nylon 6 (PA 6), polyvinylchloride (PVC), polyimide (PI), and polyamide-nylon 6,6 (PA 6,6), were first cleaned with methylchloride, hexane, acetone and methanol, if they were not soluble in these solvents, to remove possible contamination from prior handling and storage. A thin gold layer of ~ 30 Å was deposited on top of all cleaned polymer samples by sputter coating to facilitate charge neutralization during depth profiling.

Depth profiles of all polymers were measured in a VG Ionex system equipped with a MIG-102 Ga^+ ion source, a LEG 31F electron flood gun and a M12-2 s (< 800 amu) quadrupole, using 10 keV Ga^+ primary ions for all measurements with an on-target current of 5.5 nA. An electronic gate was used that only allowed secondary ions originating from the center 10% of the total sputtered area to avoid crater wall effects. The depth profiles were continued until all secondary ion signals of interest were stable. From the stable part of each depth profile a selection was made of ten consecutive data points, and these were added to the dataset used for discriminant function and principal components analysis.

Because these measurements were performed on a quadrupole system, the secondary ions to be used for the discriminant function analysis had to be chosen in advance. To ensure normality of the ion intensity distribution, the intensity of each signal had to be high enough. The C^- , CH^- , O^- , OH^- , C_2^- , C_2H^- , $C_2H_2^-$ or CN^- , C_4^- , and C_4H^- ions were chosen, because of the earlier mentioned hypothesis that the hydrocarbon ions together may contain informa-

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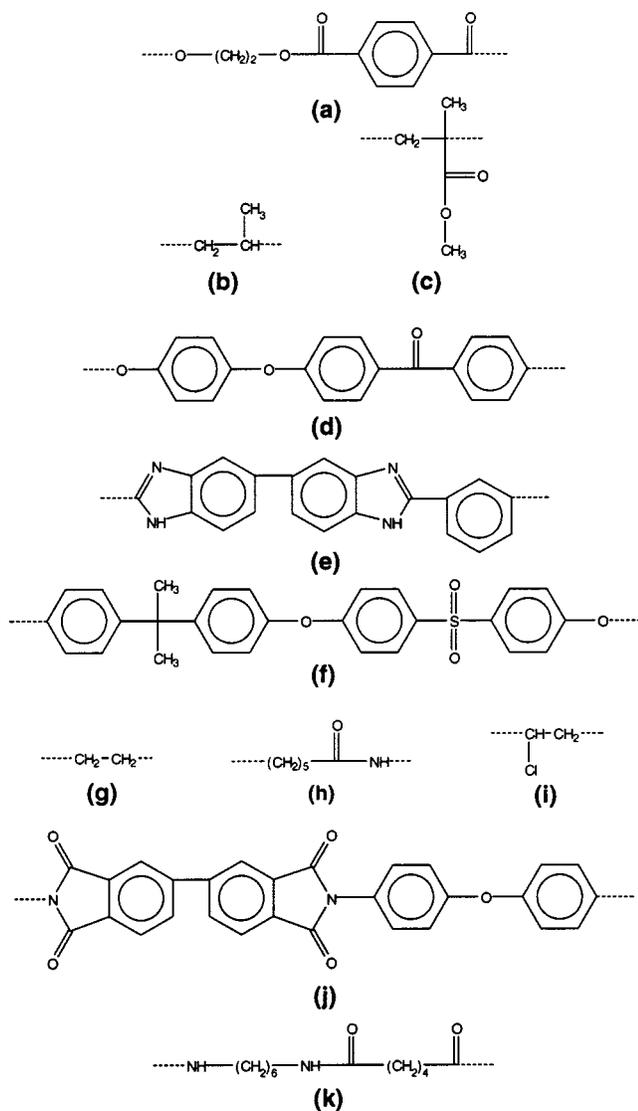


FIG. 1. Polymers used are (a) polyethylene terephthalate (PET), (b) polypropylene (PP), (c) polymethylmethacrylate (PMMA), (d) polyetheretherketone (PEEK), (e) polybenzimidazole (PBI), (f) polyethersulphone (PES), (g) high density polyethylene (HDPE), (h) polyamide-nylon 6 (PA 6), (i) polyvinylchloride (PVC), (j) polyimide (PI), (k) polyamide-nylon 6,6 (PA 6,6).

tion about the hydrogen to carbon ratio or the followed fragmentation pathways in the studied polymers.

It is important to note the essential difference between principal components analysis and discriminant function analysis. The latter emphasizes *only* the differences between different groups of measurements, whereas the former emphasizes the differences between *all* measurements, ignoring any prior knowledge. In both cases the hope is that all variation is captured in some few new variables Z_1 to Z_i .

First discriminant function analysis was performed on the complete dataset (eleven polymers; 110 data points) to see how well the chosen noncharacteristic secondary ions perform in separating the measurements of the different polymers. The first two functions shown captured 78.2% of the between-groups variance. Figure 2 shows that all eleven polymers were well separated using these first two functions, even though 21.8% of the information hidden in the intensities of the secondary ions measured was discarded in this figure. Using one function more would improve the separation only slightly.

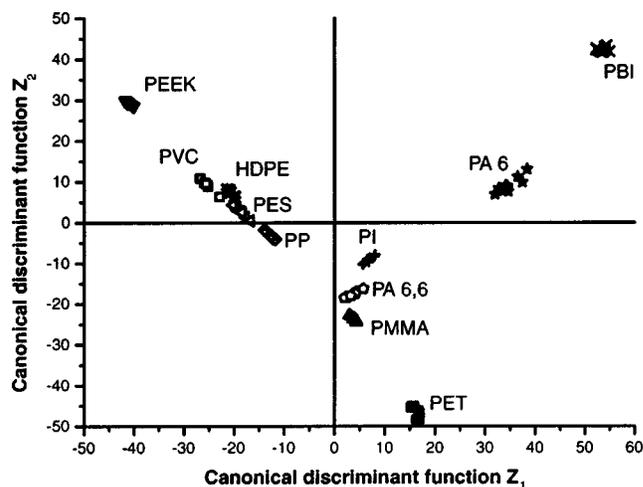


FIG. 2. Discriminant function analysis of the stable part of dynamic SIMS measurements of polymers a–k. The first two functions shown captured 78.2% of the between-groups variance.

To classify each measurement to one of the eleven groups, the so-called leave-one-out classification method was used. In this method each data point is classified by the functions derived from the complete dataset except that data point or case number, so that it cannot influence its own classification. All data points were correctly classified to the polymer they originated from, which proves that the chosen nonspecific secondary ions were together capable of distinguishing between the measured polymers.

Of course, the question is whether measurements can still be classified when no prior knowledge is assumed about the polymer they originate from. Principal component analysis was performed on the same dataset as used for the discriminant function analysis, using object principal normalization to normalize the dataset. This method optimizes distances between data points, which is useful when the differences or similarities between the data points are of interest. Figure 3(a) shows that even when no prior knowledge is used, most polymers can still readily be identified, with 74.6% of the total variance captured with the first two principal components. However, due to the nature of the principal components analysis, the groups of measurements that are rather different from the rest of the measurements influence the analysis rather much, so that polymers with near-identical sub-datasets are grouped together. When PCA is performed on the dataset of only the six closest polymers in Fig. 3(a), these polymers can also be separated completely except for PP and PES, as shown in Fig. 3(b), with 73.4% of the total variance captured. This proves that using nonspecific secondary hydrocarbon ions can be used to differentiate between different polymers even if no prior knowledge about the polymers is available.

The assumption that separation is based on the hydrogen to carbon ratio cannot be correct, because the polymers with more or less the same ratio are not close together in Figs. 2 and 3.

The assumption that different fragmentation pathways are at least partly responsible for the separation seems to have more merit. The purely aliphatic/vinylc polymers, i.e., HDPE, PP, and PVC, are consistently clustered together in both Figs. 2 and 3. Also, when the loading of the first two

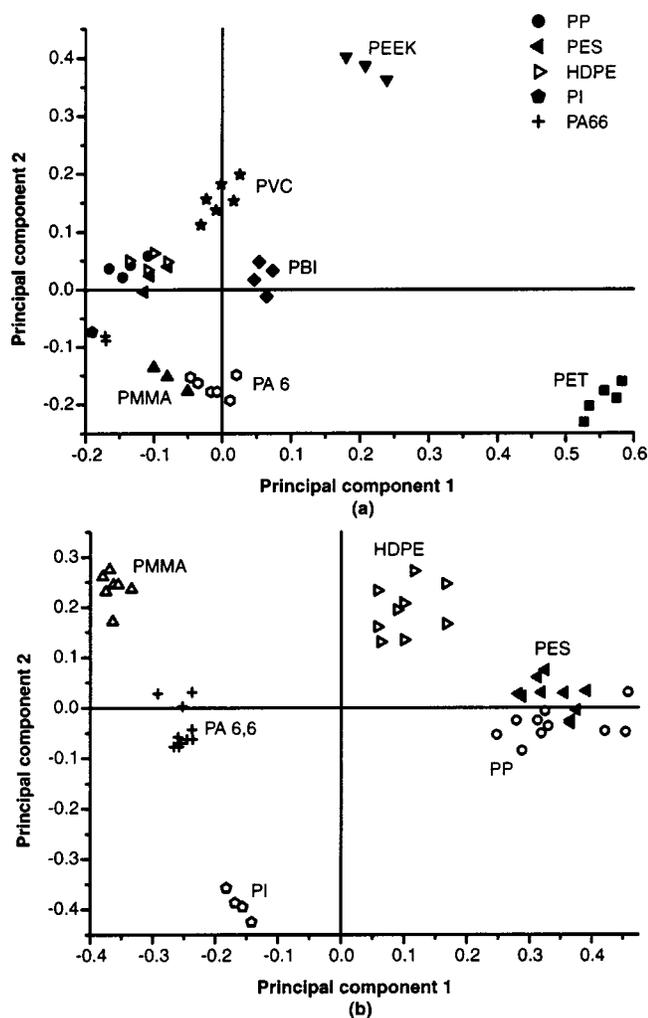


FIG. 3. (a) Principal components analysis of the stable part of dynamic SIMS measurements of polymers a–k. The first two principal components captured 74.6% of the total variance; (b) principal components analysis of the stable part of dynamic SIMS measurements of polymers b, c, f, g, j, and k. The first two principal components captured 73.4% of the total variance.

principal components of the principal components analysis from Fig. 3(a) is studied, shown in Fig. 4, the higher-order hydrocarbon fragments, notably C_2 and C_2H but also C_4 seem to contribute more to the second principal component, whereas the lower order fragments, such as CH and C contribute more to the first principal component, which could also suggest that the separation takes place on the basis of different fragmentation pathways.

In conclusion, a test on eleven common polymers showed that it is possible to distinguish between polymers by analyzing the intensities of nonspecific secondary hydrocarbon ions with discriminant function analysis or principal components analysis, if these secondary ions are measured after a steady-state between the primary ions and the polymer has been reached. Possibly these statistical methods could be used to identify fractions of polymers in depth profiles of binary polymer blends, which would mean a large advance in the depth profiling of polymers.

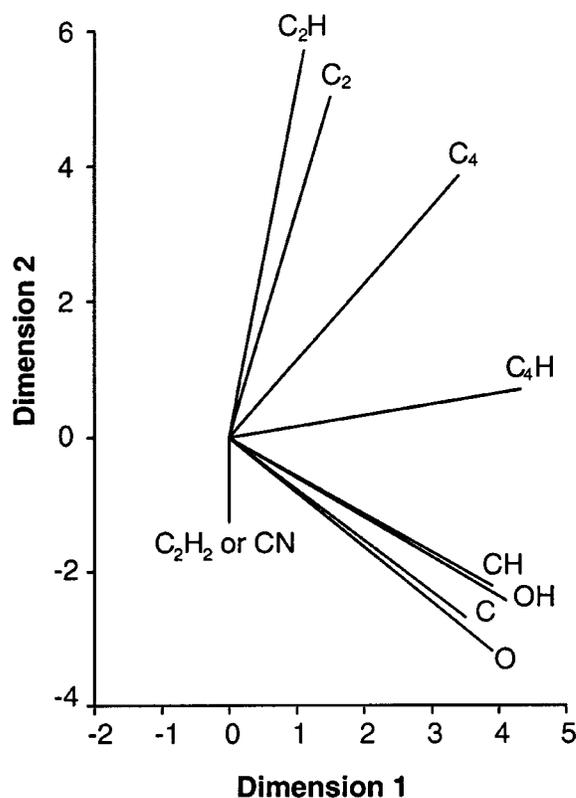


FIG. 4. Loading of the first two principal components.

However, the robustness of both methods needs to be studied, because for example a mass channel that shows a low intensity for all studied polymers may influence the statistical analysis unduly. The exact basis of the separation also remains unclear, although there is some indication that differences in fragmentation pathways play a role. UsingToF-SIMS measurements will probably yield better results, because more and better resolved secondary ions can be used in the analysis.

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