The matrix effect in organic secondary ion mass spectrometry

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ABSTRACT

Well defined reference materials consisting of Irganox 1010 and either Irganox 1098 or Fmoc-pentafluoro-L-phenylalanine (Fmoc-PFLPA) are described. These have been analysed with time-of-flight secondary ion mass spectrometry (ToF-SIMS) using argon gas cluster ions, 5 keV Ar_{2000}^+, as a sputtering source and 25 keV Bi_3^+ ions as a primary source for analysis. We demonstrate that the binary mixtures of Irganox 1010 and Irganox 1098 demonstrate some weak matrix effects whereas the mixtures of Irganox 1010 and Fmoc-PFLPA demonstrate some strong and unusual matrix effects. A parameter, $\varXi$, is introduced to describe the magnitude of the matrix effect in organic SIMS and a method to correct for the different apparent depths of origin of secondary ions in a depth profile. With some knowledge of the matrix effect magnitude and sign provided by $\varXi$ it becomes possible to select secondary ions for reliable quantitative analysis in binary mixtures. We also indicate how the differences in $\varXi$ between different secondary ions may, in the future, be exploited to assess compositional variation or nanoscale phase separation in materials.

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Introduction

The matrix effect is possibly the most significant unresolved issue in secondary ion mass spectrometry (SIMS). It is well known that the secondary ion intensity of an analyte in SIMS depends upon the material, or matrix, that surrounds the analyte and the effect inhibits the ability to translate secondary ion intensities into quantitative measures of composition. In the analysis of inorganic materials, it is understood that it is necessary to use reference materials of known composition, preferably close to that of the sample, to obtain reliable compositional information from SIMS. For organic materials, the situation is far less simple. There are myriads of organic materials which may be of interest and the bewildering array of combinations of these cannot be practically addressed by reference materials. Therefore the only practical approaches to obtaining reliable quantitative data from SIMS are either: to eliminate or reduce matrix effects or; to understand them and correct for them. The first step in doing either of these is to find suitable materials which display matrix effects so that, following the latter approach, the effects can be classified and described and, in the former case, attempts to mitigate the effects can be verified.

The mechanism of ion formation from organic materials is still rather poorly understood and, although a few models have been proposed [1,2], experimental verification of such models remains elusive. This is at least in part due to the verbal, rather than mathematical, nature of the models. One of the most significant influences on secondary ion intensities from organic materials is thought to be the propensity of secondary species to lose or gain a proton. Indeed, relative gas phase basicities correlate with observations of the enhancement and suppression of secondary ion intensity in mixtures [3]. In the case of codeine and poly(lactide) mixtures, this effect was treated mathematically using a kinetic model and the resulting description found to be in accordance with experimental data [4]. Thus, there is some hope that at least one effect can be accounted for.

Recent advances in organic SIMS analysis has made it possible to begin to address this issue. One of the main problems has been the generation of samples with a known surface composition. Due to segregation, contamination and other effects, the surface composition cannot be known unless an independent, quantitative method, such as XPS is employed. Even then, there are problems in comparing SIMS and XPS data due to the limited sensitivity and specificity of XPS and also differences in the depth of analysed material between and within the two techniques. With the use of argon cluster beams to remove surface layers of organic materials without causing significant chemical damage, it becomes possible to eliminate any surface effects and to understand the influence of the depth from which secondary ions originate. This potential has

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been shown in a VAMAS study on the use of argon cluster beams with layered reference materials [5].

In this work, we describe the production and SIMS analysis of binary mixtures of organic thin films in which the total composition is known with reasonable certainty. We demonstrate how it is possible to establish the magnitude of the matrix effect in such mixtures using thin layers of one material inside another. We also study films of known composition using mixtures consisting of Irganox 1010 and one or another of Irganox 1098 and Fmoc-pentafluoro-L-phenylalanine (Fmoc-PFLPA). In the first mixture a small, but significant, matrix effect is observed and, in the second mixture, very strong effects are found.

Irganox 1010 has been studied extensively by SIMS for many years [5–29]. It is a compound of moderate industrial importance, being employed as an anti-oxidant additive in polymers. The advantage of Irganox 1010 in SIMS studies is that it can be evaporated as a thin, uniform film on a substrate and it provides a reasonably intense pseudo-molecular negative secondary ion at $\sim$1175 Da, $(M_{1010}-H)^{-}$, which is a mass approaching the upper limit of practical organic SIMS analysis. With the advent of cluster ion beams [30–32], it has been shown to be a useful reference material to understand sputtering behaviour, especially when discrete layers of other materials are placed at defined depths within it [5,28,33,34]. From the dose required to reach these marker layers, accurate values of sputtering yields can be obtained, which has contributed to a practical description [24] of cluster ion beam sputtering. There have been some attempts in the literature to understand the shape and width of the secondary ion signals from the marker layers themselves [35–37]. Often, consideration is given only to the effects attributed to mixing, roughening, information depth and statistical issues. These provide some excellent descriptions of the general shape of the experimental curves. However, other effects that may have to be considered are molecular damage and the matrix effect. In this paper, we demonstrate that the latter, at least, can significantly distort the shape of the response curve. Therefore, we should consider depth resolutions in SIMS as having both a physical contribution (mixing, roughening and information depth) and a chemical contribution (matrix effect and damage).

Before describing these results, it is worth considering the manner in which the distribution of material in a mixture may influence secondary ion intensities. In the following, we assume that the two materials do not chemically react to form a new compound. A mixed material which is phase separated into its pure components on a scale length much larger than the size of an individual primary ion crater should display a linear relationship between composition (expressed as volume fraction, φ) and secondary ion intensity for each of the components. This relationship can be termed 'ideal' behaviour. If the components are intimately mixed on a scale length smaller than the size of an individual primary ion crater, then the linear relationship may not be observed and several effects may be expected. A secondary ion intensity may be higher than the expected ideal behaviour, this is 'enhancement', if it is lower than ideal, it is called 'suppression'. However, if there is a compositional change in depth within the scale length of the primary ion crater we may anticipate another effect, which arises from the different information depth of secondary ions. Secondary ions that originate from a shallow depth (for example, molecular ions) will be characteristic of a different composition than those that originate from a greater depth (for example, atomic ions). Therefore, it is necessary to understand the depth of origin of the secondary ions and correct for it, or to analyse mixtures which are homogenous in composition in the near surface region [38].
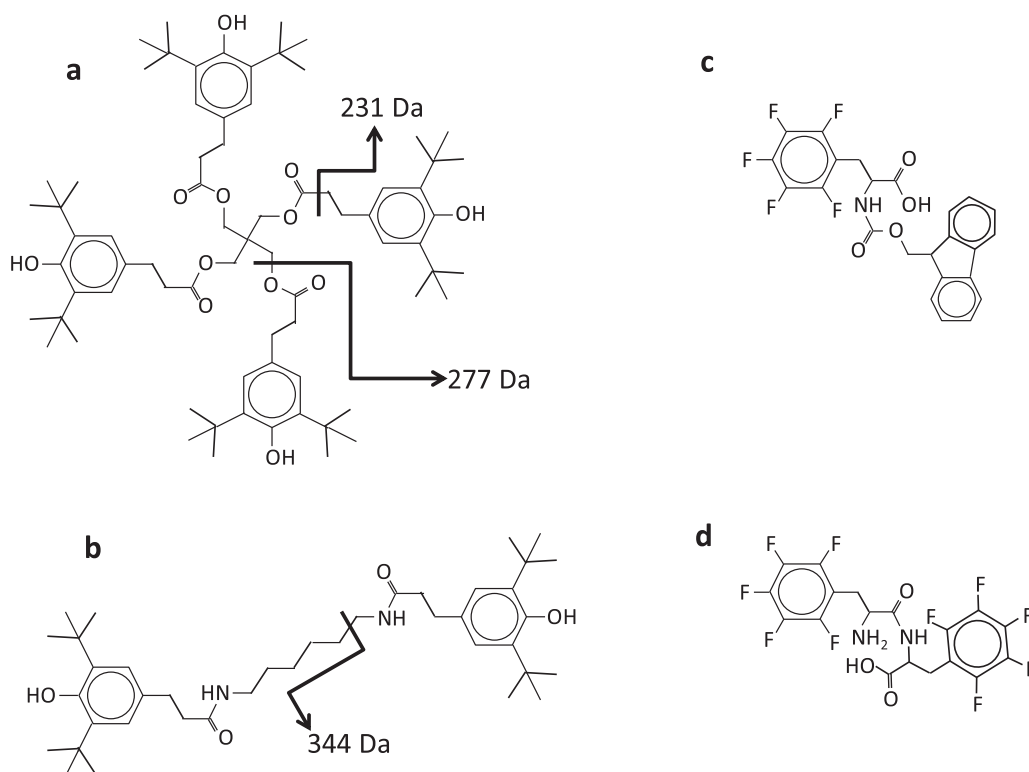

Fig. 1. Chemical structures of the main compounds used in this study. (a) Irganox 1010 showing two of the fragment secondary ions studied here. (b) Irganox 1098 showing one of the fragment secondary ions studied here. (c) Fmoc-PFLPA. (d) Possible contaminant in, or thermal breakdown product of, Fmoc-PFLPA with molecular mass 492 Da.