Progress in Materials Analysis

Vol. 2

Edited by M. Grasserbauer
and W. Wegscheider

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Preface

Vol. 2 of "Progress in Materials Analysis" contains the lectures of the 12th Colloquium on Materials Analysis, Vienna, May 13–15, 1985. Due to the top level international participation from industry and research institutions the proceedings offer a survey of the present state and current trends in materials analysis of high actuality.

The major topics covered are surface, micro and trace analysis of materials with a special emphasis on metals but also including other materials like ceramics, semiconductors, polymers. According to the strategy of the meeting attention is focussed on an interdisciplinary approach to materials science – combining analytical chemistry, solid state physics and technology.

Therefore progress reports on modern analytical technique like SIMS, SNMS, AES, XPS, Positron Annihilation Spectroscopy, EPMA, STEM, LAMMS, etc. are contained as well as presentations on the development of materials. The majority of the contributions centers on the treatment of important problems in materials science and technology by a (mostly sophisticated) combination of physical and chemical analytical techniques.

Vienna, July 1985

M. Grasserbauer

The following additional papers of this Colloquium will be published in Mikrochimica Acta 1985 II, No. 1–2:

P. Golob: X-Ray Fluorescence Analysis in the Scanning Electron Microscope

J. Linke, H. Hoven, K. Koizlik, K. Schmidt: Quantitative Structural Analysis Using Interference Layer Metallography

M. Mayr, K. Köster, J. Angeli, J. Glocker: Electron Microprobe Investigations on Phase Boundaries Steel-Enamel

B. Vorsatz, Gy. Károly, A. Kirnerné-Kiss: Analytical Possibilities for Determining the Demand for the Optimal Quantity of Deoxidants Influencing Favourably the Morphology of Nonmetallic Inclusions in Steels

J. Forsyt, W. Przybyło: The Effect of the Solidifaction Conditions on Hydrogen Contents in Cobalt

J. Pirs, A. Zalar: Some Results of Investigations Into Relationship Between a Few Elements of Nodular Graphite Cast Iron and Nodular Graphite

G. Kudermann, K.-H. Blaufuß: Analytical Procedures for the Determination of Uranium and Thorium Traces in Aluminium

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Surface Characterization of Thin Organic Films on Metals

By

D. M. Hercules

With 19 Figures

The topic of thin organic films on metals will bring to mind different models for different individuals, depending upon their background and scientific area. For example, one might think of a polymer layer on a metal, such as the coating on the inside of a food can, a protective plastic coating on an automobile bumper, or decorative construction panels used widely in the building industry. On the other hand, one might think of organic contaminants on metal contacts in integrated circuits or contamination of semiconductor processing lines. A third possibility would be layers deposited on metals, such as those used in photo-resist technology. In short, thin polymer films on metals is a topic which covers many areas of materials science.

The area of polymer coated metals is an important area of developing technology. Considerable chemistry is associated with thin polymer layers, and its understanding is important to continued progress in this field. Consider, for example, the chemistry of etched layers. Another very important area is the chemical characteristics of plasma deposited polymer films; these are not identical to the bulk polymer prepared from the same monomer. The whole topic of adhesion is one which relates directly to this area. Thus, chemistry on polymer surfaces is of both scientific and technological interest.

In all of the above, it is the word "polymers" that stands out. Therefore, polymers will represent the major focus of this paper. Indeed, in most cases, organic materials on metals really means polymeric materials on metals.

Thick layers of polymers on metals have been characterized extensively by FTIR, Rutherford backscattering, and similar methods. Thin layers of

polymers, where the thickness of the layer is less than the sampling depth of the technique, have been characterized by conventional surface techniques. For example, ESCA has been used widely to study a variety of polymer layers on metals, polymer surfaces, and even bulk materials. However, characterization of polymeric films by ESCA suffers from the fact that the chemical shifts of carbon, nitrogen, and oxygen for organic functional groups are frequently less than optimum. Also, although some of these techniques can be used for examining small areas on polymers, none of them represents a true microprobe.

The present manuscript has been written to summarize some of our recent work on polymer characterization using mass spectrometry. The mass spectra are generated either by photon or ion beam techniques. There will be four topics discussed here:

1) Comparison of ion and photon techniques for characterizing polymer surfaces.
2) Quantitative characterization of polymers using mass spectrometry.
3) Time-of-flight SIMS studies of polymers.
4) Mapping of organic materials on surfaces using the laser microprobe.

Comparison of ESCA, ISS, and SIMS for Acrylic Polymers

Acrylic polymers represent an excellent set of material for comparison of surface techniques, both qualitatively and quantitatively. These films have been used to compare data obtained using ESCA, ISS, and static SIMS. The polymers investigated include those containing short alkyl chains, isomeric C_4 alkyls, cyclic C_6 alkyls, and long chain alkyls[1].

Fig. 1 shows the ESCA spectra for a set of acrylics in the C1s and O1s regions. The C1s envelopes can be resolved into three peaks assignable to C–H, C–O, and C=O at 285.0, 287.0, and 288.6 eV, respectively. The O1s envelope from all polymers includes peaks due to at least two oxygens and is centered at 532 eV. The ESCA binding energies would not be expected to vary significantly for these polymers, and thus distinction between the various polymers using ESCA chemical shifts is not possible.

Fig. 2 shows a plot of the C1s/O1s intensity ratios versus the number of carbons in the monomer unit for the acrylic polymers studied. There is a linear relationship between these variables. Thus, although ESCA is limited to a sampling depth of 30–50 Å for polymers, this is sufficient to give essentially bulk results. Thus, it would be possible to identify (or come to close to identifying) a polymer on the basis of the C1s/O1s intensity ratio using ESCA.

Fig. 3 shows a comparable plot of the C/O peak height ratios from ISS for the same series of polymers. Although the linear correlation coefficient

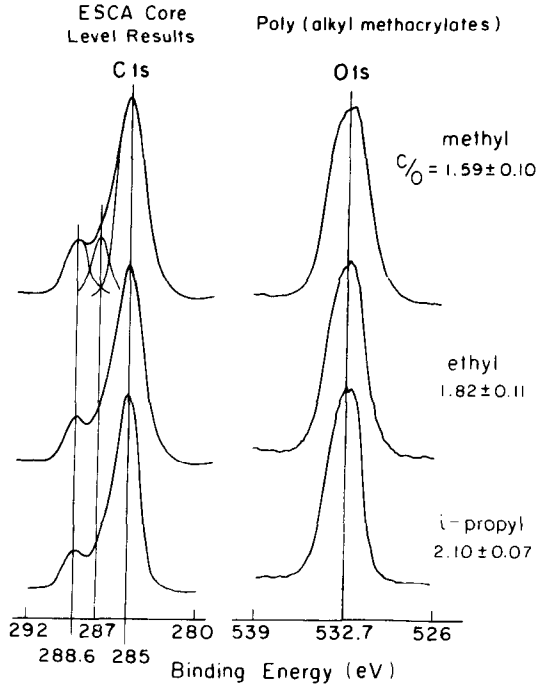


Fig. 1. ESCA core level results for short alkyl ester groups[1]

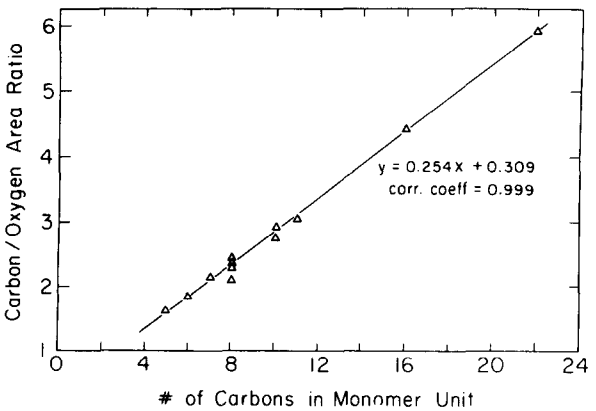


Fig. 2. Plot of ESCA carbon/oxygen peak area intensity ratio vs. the number of carbons in monomer unit (number of oxygens = 2 at all times) for the poly(methacrylate) series[1]

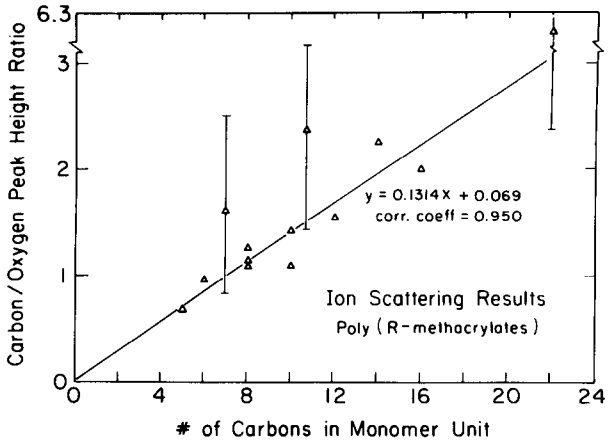


Fig. 3. Plot of ISS (^{3}He) carbon/oxygen peak height intensity ratio vs. the number of carbons in monomer unit (number of oxygens = 2 at all times) for the poly(methacrylate) series[1]

for the ISS data is not as good as for the ESCA data, there is a linear response, and a good correlation between the ISS intensity ratio and the number of carbon atoms in the monomer unit. Three polymers deviated significantly from the plot: isopropyl, benzyl, and octadecyl methacrylates. At the time the data were obtained, it was thought that steric effects may be responsible for this behavior; it has been confirmed subsequently that stereo-irregularity of polymers can have a significant effect on the ISS intensity data[2].

Fig. 4 shows the ESCA data obtained for the isomeric butyl methacrylates. The C1s/O1s intensity ratios are: 2.42, 2.38, 2.10, and 2.28 for the n-butyl, sec-butyl, iso-butyl, and t-butyl isomers, respectively. Given that the relative standard deviation for the intensity ratios is ±0.12 (abs.), one cannot distinguish between the four isomers on the basis of the ESCA intensity measurements. Similarly, the ISS intensity ratios are closely grouped, as indicated by the four closely spaced data points for the C_4 isomers in Fig. 3.

Fig. 5 shows the static SIMS spectra for the four butyl isomers. There are two spectral features which can be used to differentiate among the various isomers; these are the intensity of the m/z 57 peak (due to the butyl cation) relative to the base peak, and the relative intensities of peaks due to ions from bond breaking events involving the butyl ester group. The relative intensities of the m/z 57 peak (to the base peak) are 12% for the n-butyl, 22% for the iso-butyl, 41% for the sec-butyl, and 100% (i.e., base peak) for the t-butyl isomers, respectively. Given that the relative standard deviations for relative intensity measurements using SIMS are better than ±20%,

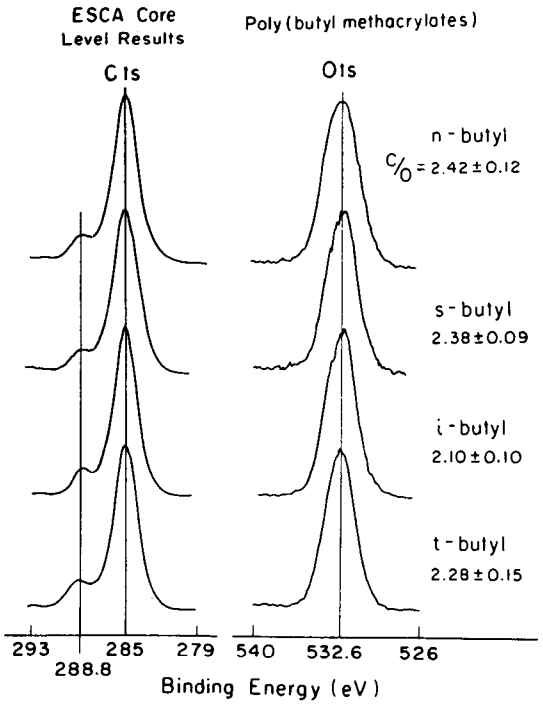
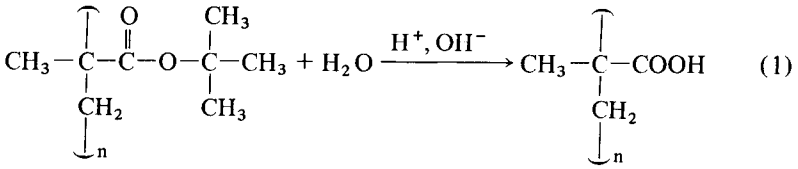


Fig. 4. ESCA core level results for butyl isomer ester groups[1]

the relative intensity of the m/z 57 peak should be sufficient to distinguish between the isomers. In addition, the relative intensities for the m/z 27, 29, 39, and 41 peaks vary for the four isomers. The base peak for the n-butyl isomer is 27, for the s-butyl isomer it is 29, and for the isobutyl isomer, 27 and 41 are essentially base peak. The base peak for the t-butyl isomer is m/z 57. Thus, by combining the relative intensity of the m/z 57 peak and the intensities of the 27, 29, and 41 peaks, it is possible to distinguish among these polymers using SIMS.

The C_4 acrylic isomers have been used in another way to demonstrate the value of SIMS for studying events which occur in layers sufficiently thin that they cannot be detected by ESCA. The hydrolysis of poly(t-butylmethacrylate (PTBMA) occurs as shown eq. 1.



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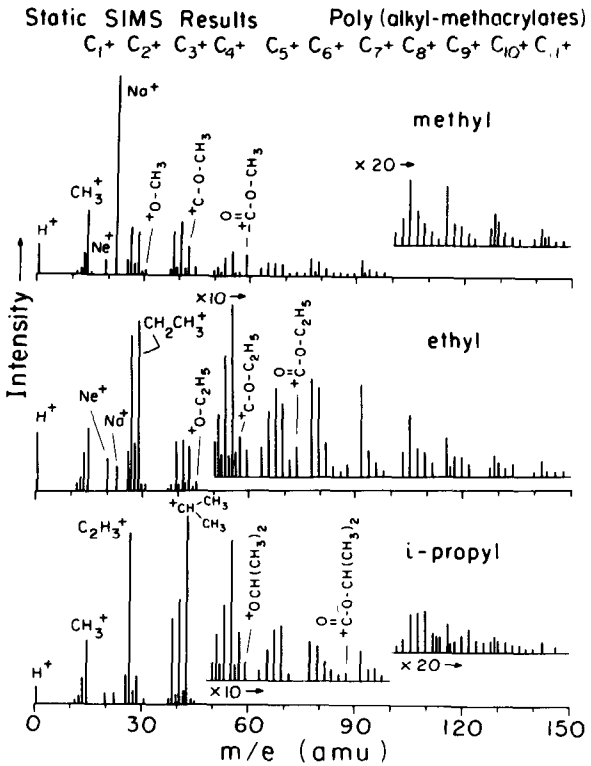


Fig. 5. Static SIMS results for short alkyl ester groups: methyl, base peak = 15 amu; ethyl, base peak = 29 amu; isopropyl, base peak = 43 amu[1]

The t-butyl carbonium ion at m/z 57 is the base peak in the static SIMS spectrum of the untreated polymer. It is clear that as hydrolysis occurs on the surface of this polymer, one will see a decrease in the m/z 57 peak relative to peaks which are characteristic of the polymer backbone. Therefore, t-butyl acrylic polymer films were exposed to mild conditions of hydrolysis, namely, treatment at pH 4.0, 7.0, and 10.0, for 5 min at 23 °C. The ESCA spectra of the treated polymers are qualitatively similar; the C1s/O1s intensity ratios measured for the polymers after treatment are 2.0 ± 0.1; the untreated polymer is 2.25 ± 0.14[3]. Thus, there is no clear statistical difference among the treated samples and no significant difference from the untreated polymer.

The static SIMS spectra for the PTBMA blank and samples treated at pH's 4, 7, and 10, are shown in Fig. 6. There is a distinct difference in the relative intensities of the m/z 57 peaks in the treated and untreated samples. To

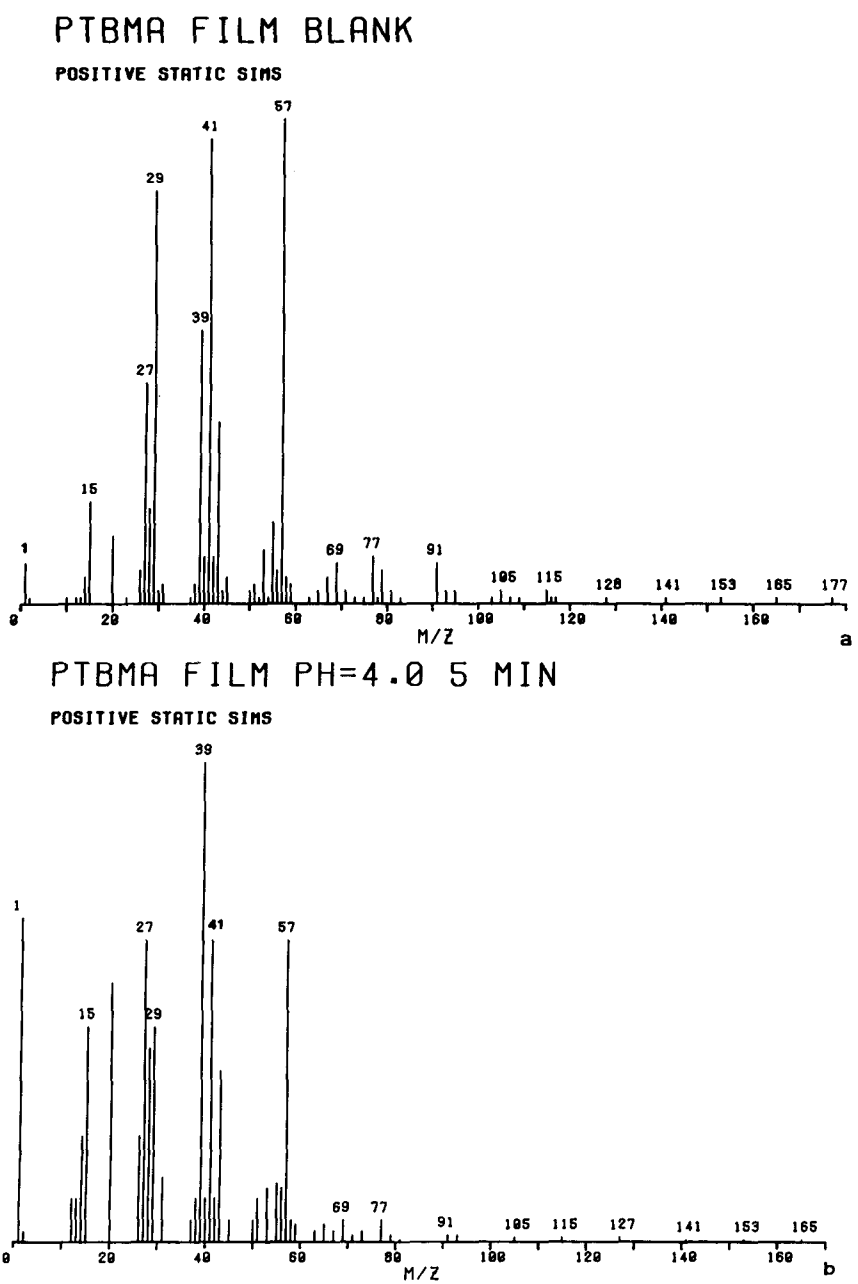
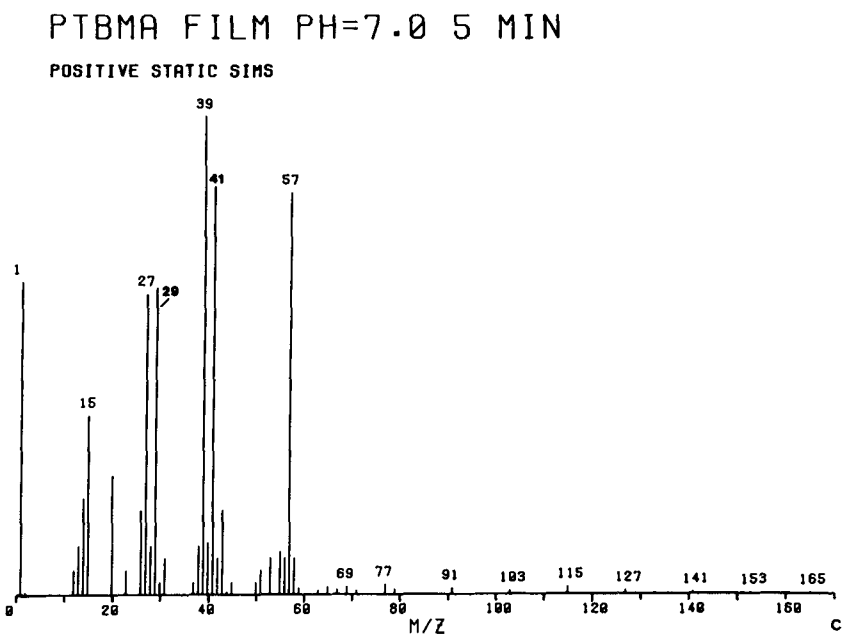


Fig. 6. Static SIMS spectra for PtBMA intensity (arbitrary units) vs. m/z (for conditions see text): a) blank; b) pH = 4.0; c) pH = 7.0; d) pH = 10.0


PTBMA FILM PH=7.0 5 MIN
POSITIVE STATIC SIMS
39
41
57
1
27
29
15
69
77
91
103
115
127
141
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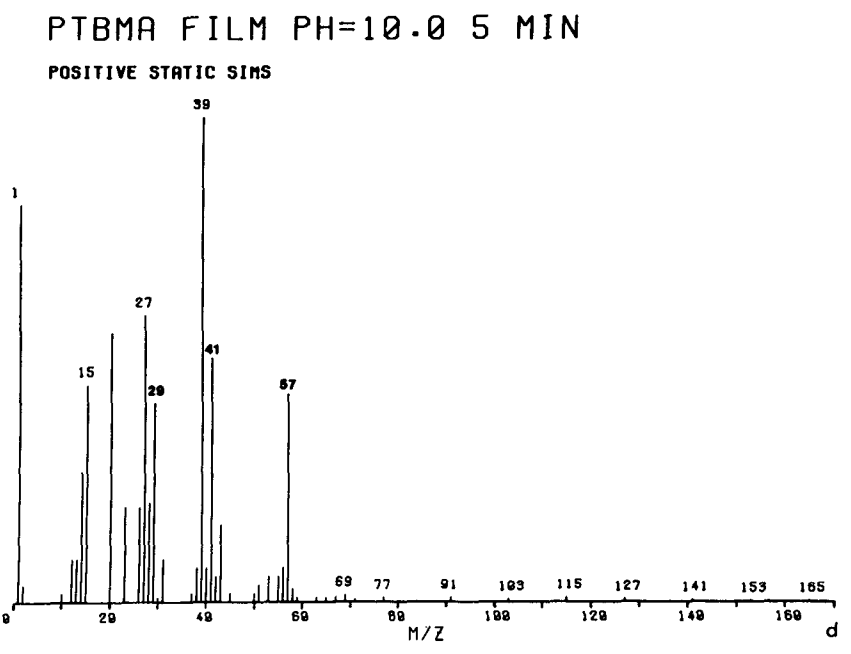
0
20
40
60
80
100
120
140
160
M/Z
c


PTBMA FILM PH=10.0 5 MIN
POSITIVE STATIC SIMS
39
1
27
41
15
29
57
69
77
91
103
115
127
141
153
165
0
20
40
60
80
100
120
140
160
M/Z
d

make the comparison more quantitative, three peaks were investigated which are characteristic of bond breaking events involving the side chain: m/z 57, 41, and 29. Similarly, three peaks were monitored which are due to ions from bond breaking within the backbone: m/z 39, 27, and 15. Peak intensity ratios were compared to test the consistency of the ratios within each set. Thus, ratios were obtained for sets of sidechain/backbone, backbone/backbone and sidechain/sidechain peaks. These data are plotted in Fig. 7. First, observe the plots of I(57)/I(29) (sidechain/sidechain) and I(15)/I(39) (backbone/backbone). These are essentially constant for the three treatments and not significantly different from the ratio in the untreated sample. In contrast, plots of I(57)/I(39), I(57)/I(27), and I(29)/I(27) (all sidechain/backbone) all show a maximum at pH = 7, which is significantly lower than the untreated sample but significantly higher than either the pH = 10 or pH = 4 samples. These results are readily interpreted by considering ester hydrolysis is both acid and base catalyzed. Thus, in highly acid or highly basic media the reaction rate will be faster than at a neutral pH; one would

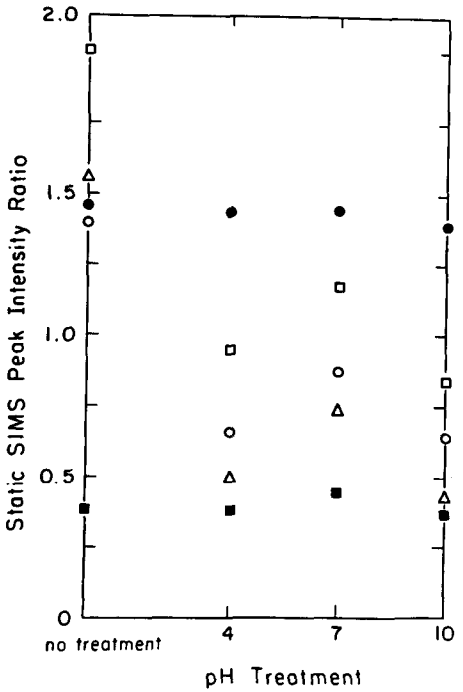


Fig. 7. Plot of static SIMS peak height intensity ratio vs. sample treatment pH (5 min) for mild reaction conditions. Values are given in Table 2. Key: Δ, I_{57}/I_{39} (S/B); □, I_{57}/I_{27} (S/B); ○, I_{29}/I_{27} (S/B); ■, I_{15}/I_{39} (B/B); ●, I_{57}/I_{29} (S/S) (3)