

Surface Analysis of Insulating Materials by Secondary Ion Mass Spectrometry (SIMS)

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Abstract. For a non-conducting solid sample (TiO_2 powder) the conditions for compensation of the charge build-up at the surface caused by the ion impact in SIMS are experimentally investigated. The compensation is achieved by an additional auxiliary electron beam of low energy. The resolution and the intensities of the secondary ions were measured as a function of the ratio of the current densities of the electron and the ion beams. The compensation for negative secondary ions, and especially for those with higher masses, is more critical than for positive ones. The intensities are influenced by the different values of the mean emission energies and the form of the energy distributions. Examples of mass spectra by SIMS for some insulators are given.

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In the passed years the Secondary Ion Mass Spectrometry (SIMS) has been developed to a widely applicable method for surface analysis [1]. In the SIMS-technique mass spectra of positively and negatively charged atoms and molecules (secondary ions) are measured which have been emitted from the surface of a solid by the impact of high-energized positive primary ions. The application of this method remains in most cases constrained to solids of good electrical conductance, since by the impact of the primary ions insulating material is charged up. This charge will influence or even prevent the emission of secondary ions. An application of SIMS to insulators, therefore, demands a charge compensation. This is of great importance especially when SIMS is used in the field of chemistry because most of the materials are insulators. Important surface problems in chemistry are for example: identification and characterization of the coating of surfaces of fibres, metals, pigments and other materials; examination of catalysts to detect contaminations and poisonings; investigation of surface reactions, for example, adsorption and oxidation or processes of the heterogeneous catalysis.

To overcome the insulator problem different methods have been proposed and also used: evaporation of a conductive mesh onto the solid [2], chopping the primary ion beam [3], heating the sample up to the emission of thermal electrons [4], bombarding the solid with negative primary ions or neutral particles [5], impact of electrons from a separate source simultaneously to the positive primary ions [6].

In this paper the latter method for charge compensation will be examined in detail with a SIMS-apparatus containing a quadrupole mass spectrometer.

1. Mechanism of Surface Charge Build-up and Charge Compensation

The surface of an electrically non-conducting solid will be positively charged if it is bombarded with positive or negative primary ions of energies in the keV-range. This is a consequence of the fact that the primary ions give their charge to the solid and that secondary electrons are emitted due to the ion bombardment.

Using negative primary ions the following conditions are given: Initially the secondary electron yield is greater than one. This means that more secondary electrons leave the target as is necessary to compensate for the incoming negative ions. So the surface rapidly charges positively and the further release of secondary electrons is soon stopped especially for those having lowest energies. Furthermore, a portion of the emitted electrons is drawn back to the sample by the surface potential. A complicated equilibrium is established with a limited constant surface potential which is negligible in comparison to the acceleration potential of the primary ions.

Using as usually positive primary ions the surface potential continuously grows, up to the acceleration potential of the primary ions due to the accumulation of the incoming positive charge of the primary ions, independent of the emission of secondary electrons. If the potential is high enough discharges between the sample holder and the target take place. Because of these surface potential fluctuations continuously changing conditions for the emission of the secondary ions are existing. Furthermore, the surface charge causes a deflection and a deceleration of the primary ion beam. For the mass spectra of the secondary ions this means a drastical deterioration of the resolution and a large decrease of the intensity up to the complete disappearance of the secondary ions (Fig. 2b). Using a magnetic mass analyzer an additional shifting of the mass scale is produced because of changed energy distributions of the secondary ions.

Also negative primary ions will not completely solve the problem, since the remaining equilibrium surface potential will hinder the emission particularly of the negative secondary ions having low energies.

One possibility of charge compensation is the bombardment of the sample with low energetic electrons from a separate external source simultaneously with the impact of the primary ions. The energy of the electrons should be very low (<10 eV) in order to avoid effects as, for example, an electron-induced ion-desorption or a possible electrical stimulation of the surface atoms which could change the secondary ion yield. With electrons of low energy self-focussing takes place. They come easier to places of positive charge, since they are influenced by the lowest charge-up. On the other hand, a negative charge-up of the sample by an overcompensation because of too great an electron current must also be avoided.

The conditions for the charge compensation can be given in an approximation. We consider the values of

the incoming current of the primary ion beam I_i , the current of the electron beam I_e , the corresponding yields of secondary ions and secondary electrons, and the part of secondary electrons which is drawn back to the surface of the insulator [6]. That means there exists an appropriate value of I_e for a given I_i to fulfil the conditions of charge compensation.

2. Charge Compensation by Electron Bombardment

Figure 1 shows schematically the arrangement of the target, the primary ion source, the electron source and the quadrupole mass spectrometer with the secondary-ion optics. The target is usually held at ground potential. The electrons are produced by the filament Fi and after acceleration and focusing by the electrodes A and F directed as a beam onto the target, by a x-y-deflection condensator K. The current regulation is achieved by the Wehnelt cylinder W. Using a deflected electron beam has the advantage that the filament brings practically no contamination to the sample and that it represents no thermal or optical load to the target. The secondary ion optic is covered with a screen at ground potential to get a field-free space between optics and target in order to avoid a deflection of the low-energy electron beam. To get higher intensities for the secondary ions it is also possible to apply separate potentials to the diaphragms A and B. In

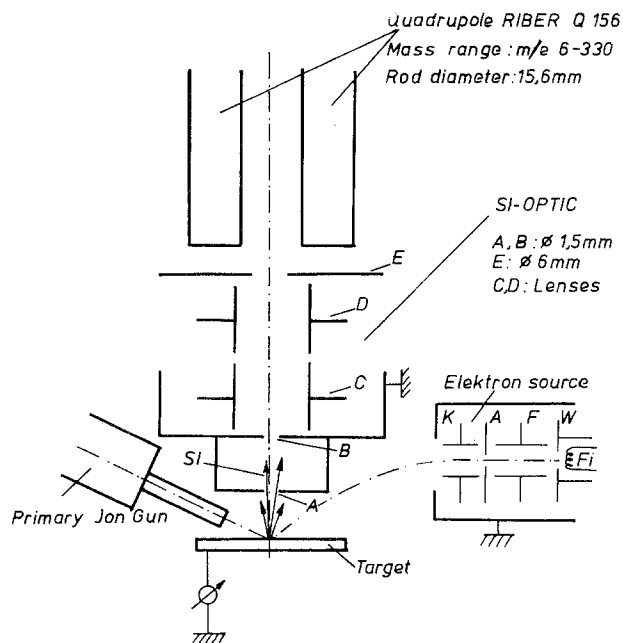


Fig. 1. Scheme of the apparatus in the target region

this mode of operation the potentials of the electron source must be changed to obtain the desired current I_e . The electron beam is adjusted by means of a conductive auxiliary target on the sample holder which is somewhat larger than the focus of the primary ion beam ($\approx 0.1 \text{ cm}^2$); it can be brought into the ion and electron beam. The focus of the electrons covers completely that of the ions. With this source a maximum electron current of $I_e = 5 \cdot 10^{-7} \text{ A}$ and an electron current density of $i_e = 5 \cdot 10^{-6} \text{ A/cm}^2$, respectively, can be

achieved on the target with an acceleration voltage of 5 V. The maximum primary ion current density produced with our ion source is in the same range. With the electron beam alone secondary ions could not be detected.

The experiments for charge compensation have been performed at a TiO_2 pigment which is a powder. The TiO_2 has had no special treatment. To get a plain surface the TiO_2 has been pressed into the sample holder under definite pressure. Figure 2 shows the

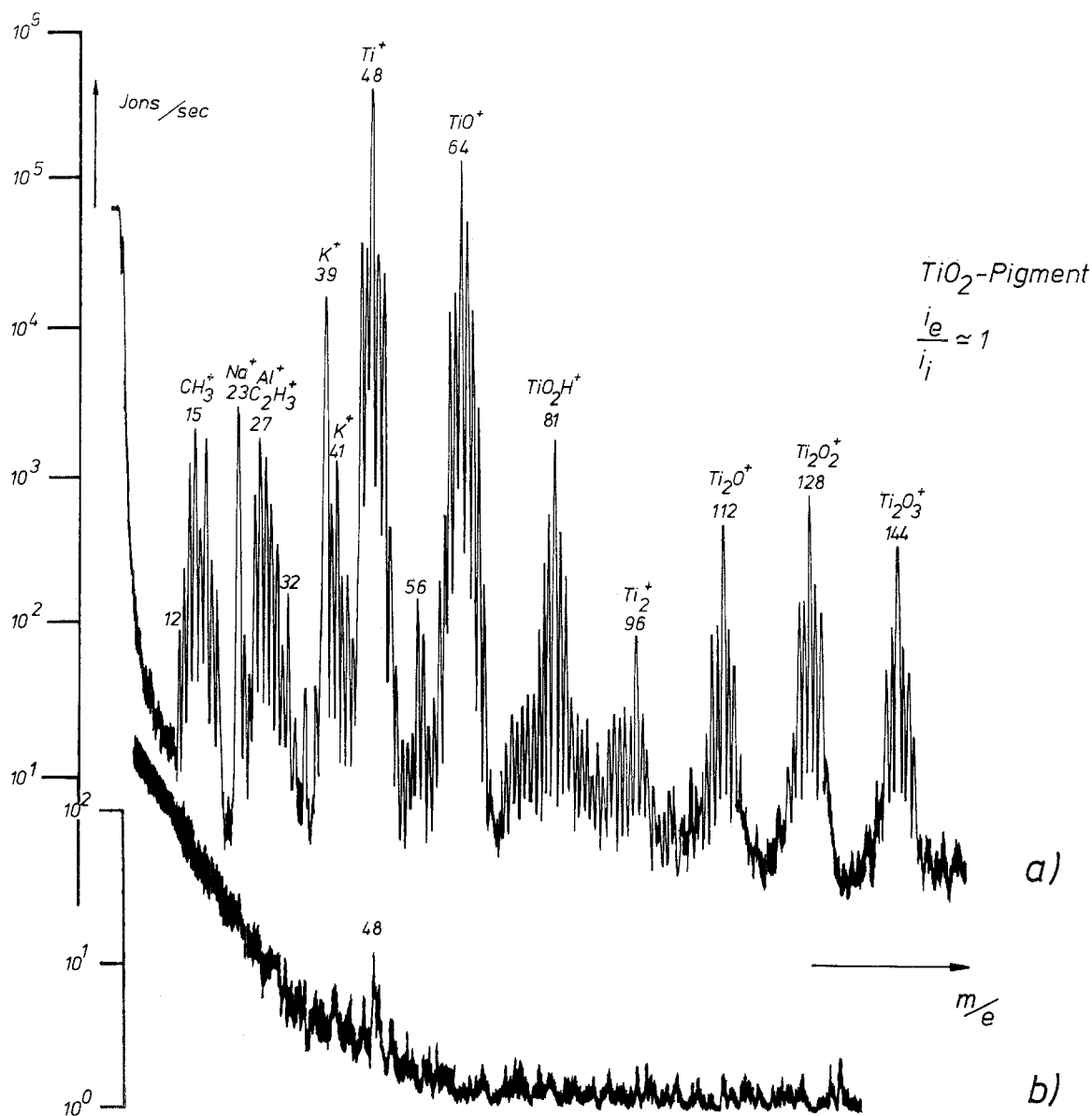


Fig. 2a and b. Mass spectra of positive secondary ions of the pigment TiO_2 in a logarithmic intensity scale. (a) without electron compensation; (b) with electron compensation: $i_e/i_i = 1$

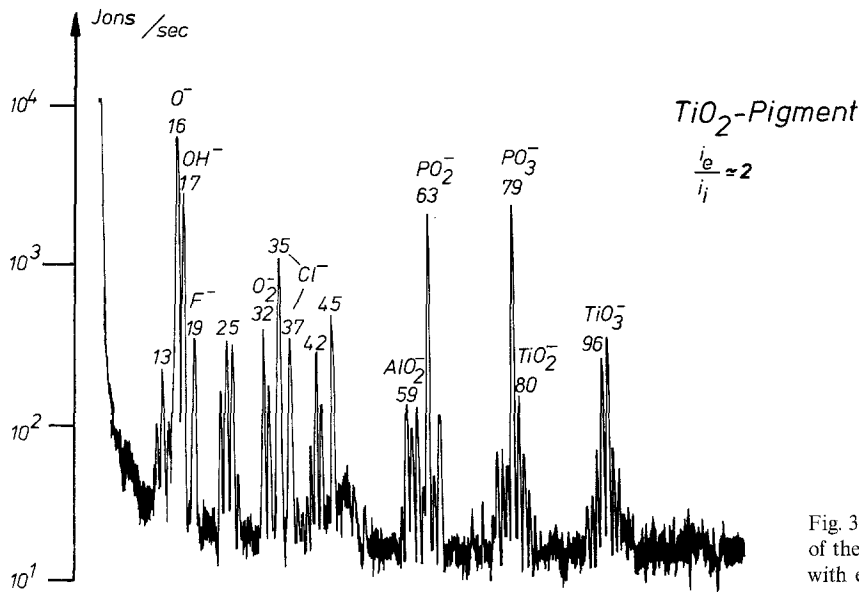


Fig. 3. Mass spectrum of the negative secondary ions of the pigment TiO_2 in a logarithmic intensity scale with electron compensation: $i_e/i_i=2$

mass spectra for the positive secondary ions with and without charge compensation by electrons. The primary ion current density was $i_i=5 \cdot 10^{-7} \text{ A/cm}^2$, and in the case of compensation the ratio of the current densities was $i_e/i_i=1$. Without charge compensation there are no mass resolution and practically no intensity of the secondary ions. But with the electron compensation good resolution and large intensities are achieved. As Ti-containing secondary ions with the corresponding isotopes could be detected: Ti^+ , TiO^+ , TiO_2H^+ , Ti_2^+ , Ti_2O^+ , Ti_2O_2^+ , and Ti_2O_3^+ . The isotope ratios of the oxid-ion in comparison to Ti^+ were partly perturbed by hydroxides. With poorer intensities the alkali ions Na^+ and K^+ from the production process and ions like CH_3^+ , $(\text{CH}_3)_2^+$, C_2H_3^+ from adsorbed hydrocarbons were observed.

Figure 3 shows the corresponding mass spectrum of the negative secondary ions. Again a regular mass spectrum can only be measured when the surface charge is compensated. Besides the ions Ti^- , TiO^- , TiO_2^- , TiO_3^- , O^- , OH^- , and O_2^- originating from TiO_2 ions like PO_2^- and PO_3^- from the production process and F^- and Cl^- as contaminations were detected. The background pulse rate was 10–30 pulses/s for negative secondary ions and <5 pulses/s for positive secondary ions depending on the roughness of the sample.

For an optimal charge compensation two criteria are decisive: the mass resolution of the spectra and the intensity obtained. For that purpose Figure 4 shows the intensities for some selected secondary ions nor-

malized to the maximum obtained value (= 100 %) as a function of the ratio of the current densities i_e/i_i . The secondary ion optic has practically no effect of an energy filter. Ar^+ primary ions of the energy 2 keV are used. The ion current density is $i_i=5 \cdot 10^{-7} \text{ A/cm}^2$. The figure shows great differences for positive and negative ions. The intensities of the positive ions are already increasing with low values of i_e/i_i and reach saturation of 100% at $i_e/i_i=1$. With $i_e/i_i>3$ the intensities decrease slightly probably due to an overcompensation or to a reneutralization of ions by the high electron current. An overcompensation represents a potential barrier for the positive secondary ions. The curves in Figure 4 for the positive ions Al^+ ($m/e=27$) and Ti_2O_2^+ ($m/e=128$), in spite of their quite different masses, are practically identical to the curve of Ti^+ ($m/e=48$). For negative secondary ions this is

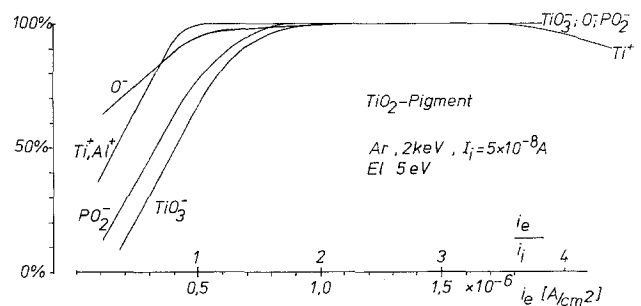


Fig. 4. Intensities of the secondary ions from TiO_2 as a function of the ratio of current densities i_e/i_i , $i_i=5 \cdot 10^{-7} \text{ A/cm}^2$

not longer the case and besides that they reach the saturation of 100% at greater values of i_e/i_i .

The different beginning of the curves can be explained by the different energy distributions of the secondary ions. At values $i_e/i_i \approx 1$ probably a small positive charge remains, which is uncritical for positive ions but appears as a big potential barrier for negative ions having usually lower mean energies. The energy distribution of O^- contains a larger part of ions with higher energy than the distribution of the multi-atomic ion TiO_3^- [7]. The distribution of TiO_3^- probably contains smaller energies so that more of these secondary ions are detected if the compensation is better and the potential barrier is smaller. Successively O^- ,

O_2^- , PO_2^- , TiO_2^- , TiO_3^- reach the 100%-value which is valid for all ions at $i_e/i_i \approx 2$. Between TiO_2^- and TiO_3^- there is practically no difference in the curve of Figure 4. These facts reflect the different energy distributions of the secondary ions. In contrast to the positive secondary ions there exist no decrease in intensity at higher rates of i_e/i_i . For positive and negative ions, Figure 4 shows that, in a wide range of i_e/i_i , the intensity is 100% and that the compensation is uncritical. When the 100%-value is reached there is also no further improvement of the mass resolution.

The mass resolution obtained with our apparatus is demonstrated with the spectra in Figures 2 and 3 (logarithmic intensity scale). It is comparable to that

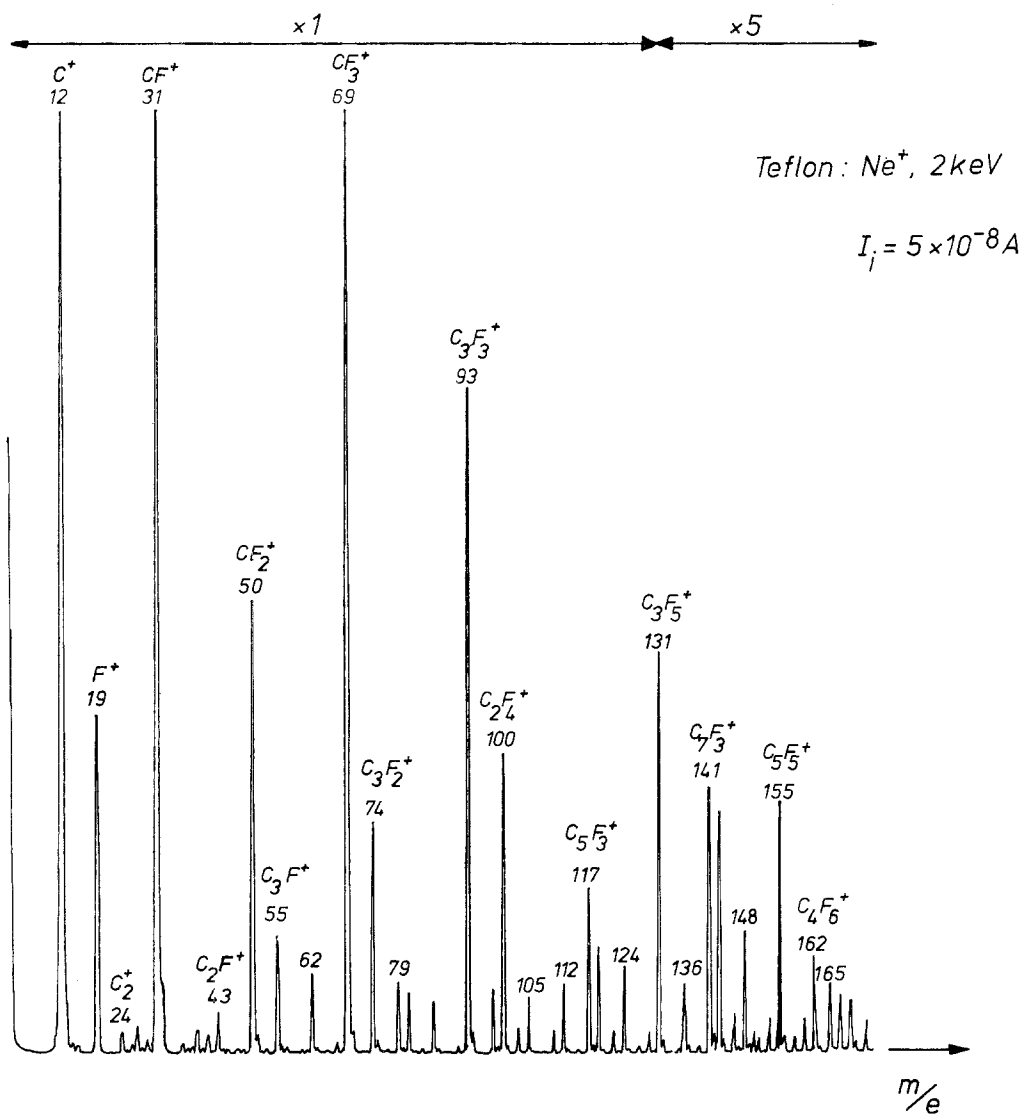


Fig. 5a. Mass spectrum (linear scale) for the positive secondary ions from Teflon up to mass $m/e = 170$. Intensity of CF_3^+ : $2 \cdot 10^6$ ions/s

achieved for conducting material (e.g. for an oxidized Ti-metal). For compact insulating samples the results are similar. But for negative ions slightly smaller values of i_e/i_i are necessary to compensate the surface charge. These higher values for a powder may be caused by the more fissured surface. As far as the charge compensation method is concerned, in the range of the plateau (Fig. 4) the intensities for the different secondary ions prove to be stable and reproducible. A control of the target current is not unconditionally necessary but can be simply done by a regulation of the Wehnelt bias in the electron source.

The main result is that the intensities obtained for the secondary ions depend on their energy distribution which can also be changed by the charge. Because of their lower energies negative secondary ions and especially those with higher masses, or the multiatomic ones, react strongly upon an insufficient compensation. It is only possible to detect secondary ions which are able to surmount the remaining potential barrier. This fact is clearly demonstrated in the negative mass spectra where negative ions with high masses have often smaller intensities or were completely absent. With higher energies of the primary ions the mean energies of the secondary ions can be

increased. This may be a possibility to a further increase of the intensities of negative secondary ions.

3. Application to a Polymer

Figures 5a, b, and 6 show as an example the positive and the negative mass spectra (linear intensity scale) of a compact organic polymer (Teflon: $[-F_2C-CF_2-]_n$). The compensation parameter is $i_e/i_i=1$ and 2, respectively, 2 with $i_i=5 \cdot 10^{-7}$ A/cm². It was possible to resolve peaks of positive secondary ions up to the mass of $m/e=330$ and of negative ions up to $m/e=150$. The intensities will decrease with higher masses firstly because of smaller secondary ion yields of greater compounds and secondly because of the mass discrimination of the quadrupole mass spectrometer. With negative secondary ions a small remaining charge on the surface can easily distort the mass spectrum. All the peaks can be interpreted as fragments of general composition $C_mF_n^+$ with $m, n=0, 1, 2, \dots$. In Figure 5 and 6 only the outstanding ones are denoted. The maximum values of the indices in the mass range covered with the quadrupole are $m=15$ and $n=12$ for positive, and $m=10$ and $n=5$ for negative ions. The

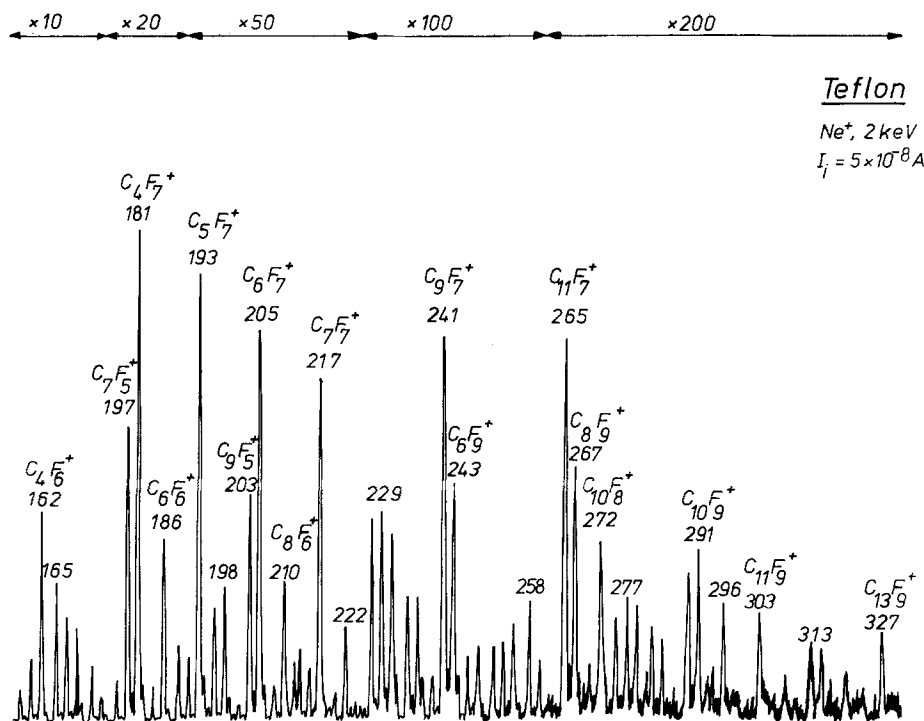


Fig. 5b. Mass spectrum (linear scale) for the positive secondary ions from Teflon up to $m/e=330$

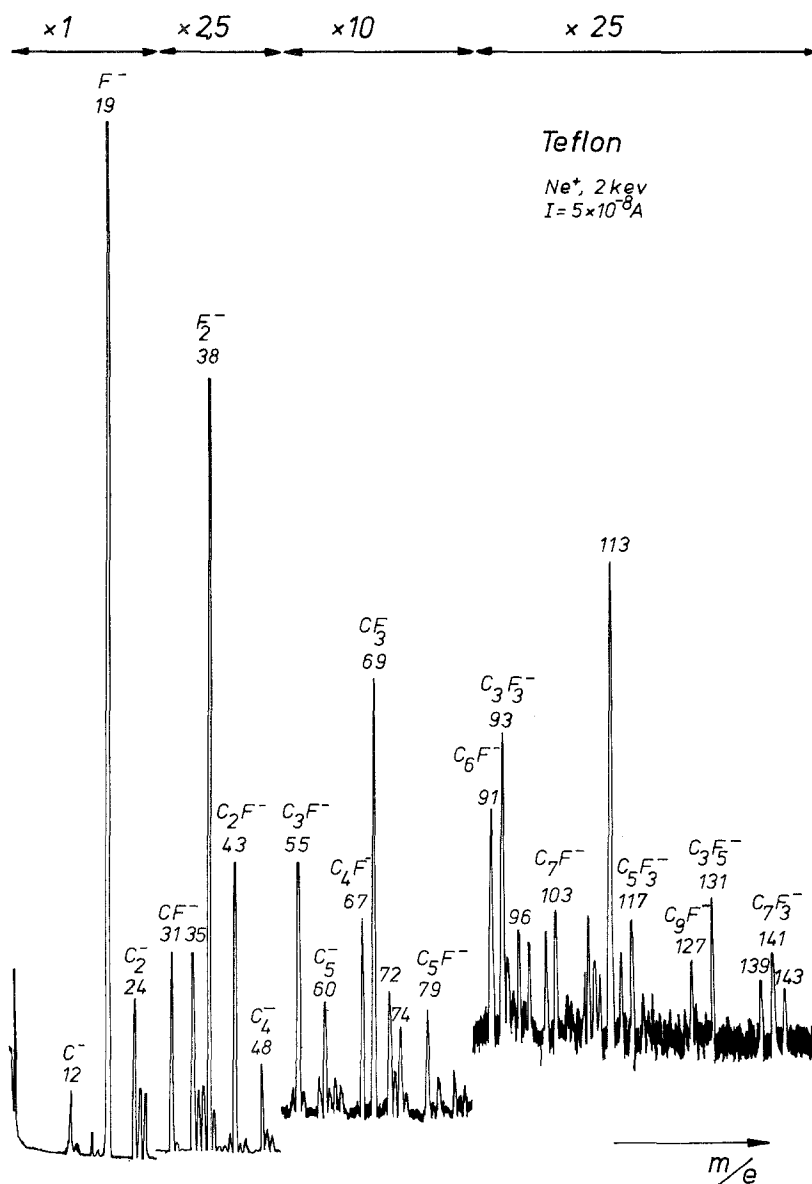


Fig. 6. Mass spectrum (linear scale) for the negative secondary ions from Teflon. Intensity of F⁻: 1 · 10⁴ ions/s

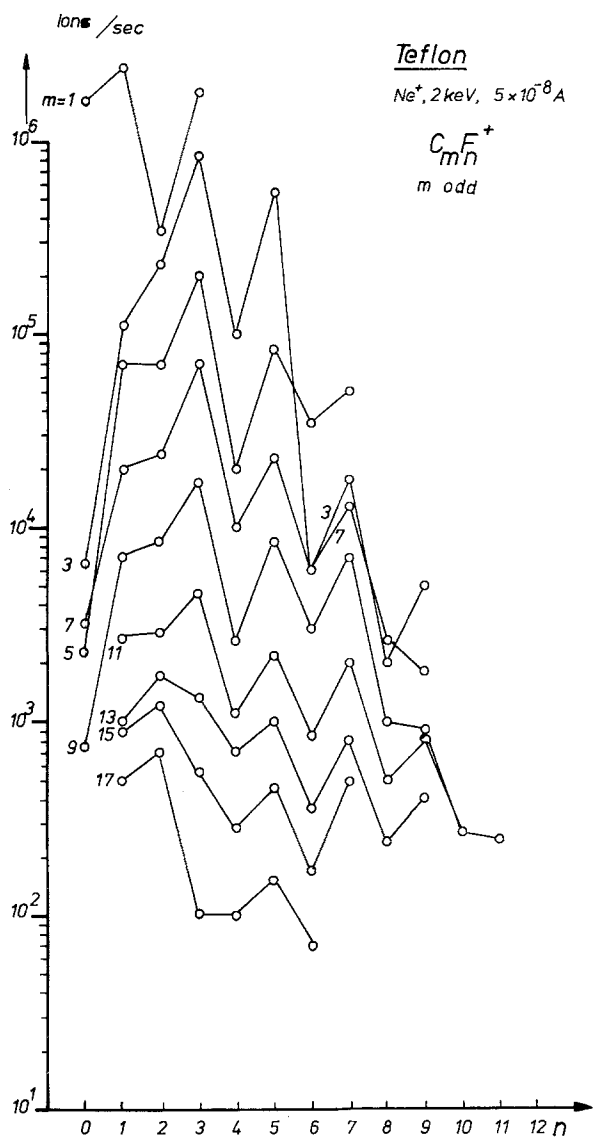
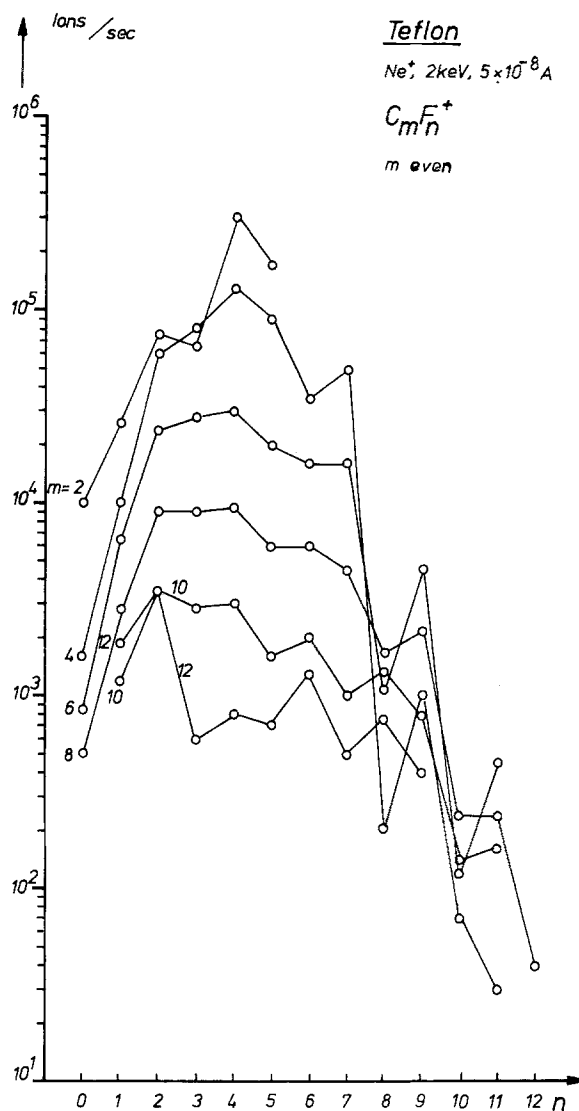
intensities of the peaks have quite a clear system. Especially for positive ions which looks different for m odd and for m even. For a definite m odd alternative maxima of intensity appear for n odd and minima for n even (Fig. 7).

For m even no distinct maxima or minima are obtained for the intensity but for each m even at $n=4$ a smooth maximum is found (Fig. 8).

For negative secondary ions such a system cannot so clearly be recognized. The highest intensities are found for F⁻, F₂⁻ and for all C_{*m*}⁻. For m odd relative maxima and minima are again to be seen. The maxima cor-

respond to n odd and minima to n even. For m even the intensities decrease with increasing n . An important fact is that negative secondary ions C_{*m*}F_{*n*}⁻ can be detected up to high values of m ($m=10$) but only with a small number of F atoms ($n=5$).

For both positive and negative secondary ions it may be possible that a part of the great number of mass peaks are not fragments out of the polymer chain but products of secondary reactions caused by reactive F-ions or F-radicals after the ion bombardment. Secondary reactions have already been detected by examinations of organic compounds [7], with SIMS.

Fig. 7. Ion fragments $C_m F_n^+$ of Teflon for m oddFig. 8. Ion fragments $C_m F_n^+$ of Teflon for m even

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