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3 **ANALYTICAL POTENTIAL OF RF-PGD-TOFMS FOR DEPTH PROFILING**  
4 **OF OXIDIZED THIN FILM COMPOSITE**  
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**ABSTRACT**

The capabilities of radiofrequency pulsed glow discharge time of flight mass spectrometry (rf-pulsed-GD-TOFMS) for the analysis of thin film composite membranes have been investigated in this work. These semi-permeable membranes, used for water purification and desalinization, consist of a thin film of polyamide on top of a polysulfone porous layer deposited on a support sheet of polyester. The analysed samples were four oxidized swatches obtained using NaClO or ClO<sub>2</sub> (diluted in seawater) as oxidant agents, and a non-oxidized virgin membrane.

The performance of the rf-pulsed-GD-TOFMS prototype was investigated for the detection of both positive and negative analyte ions. Improved depth profiles turned out to be achieved using an Ar pre-chamber that avoids air entrance in the discharge. The detection of polyatomic ion signals was needed to monitor properly the transition between the subsequent sputtered membrane layers. In particular, NH<sub>3</sub><sup>+</sup> and <sup>12</sup>C<sup>14</sup>N<sup>-</sup> polyatomic ions were mainly found at the polyamide layer (in the positive and negative detection modes, respectively), while <sup>34</sup>S<sup>+</sup> and <sup>33</sup>S<sup>1</sup>H<sup>-</sup> ion signals appeared in the polysulfone layer. Qualitative depth profiles of the oxidized samples showed an intense Br ion signal in the polyamide layer. Moreover, Br ion signal was significantly enhanced when NaClO was used as the oxidant agent, in agreement with previous studies. It is considered that the incorporation of Br to the membranes is consequence of its presence in the seawater and of the oxidation process.

## INTRODUCTION

Thin film composite (TFC) membranes are semi-permeable membranes used for water purification or desalinization.<sup>1</sup> These membranes used in reverse osmosis (RO) are typically made of a thin film of polyamide on top of a polysulfone porous layer deposited on a support sheet.<sup>2</sup> This configuration has the properties needed for high rejection of undesired compounds (e.g. salts), high filtration rate and good mechanical strength. One of the main drawbacks of TFC membranes is their oxidation since it is an irreversible process, which turns into lower salt rejection. This oxidation is caused by substances commonly employed in water treatment such as sodium hypochlorite (NaClO) and chlorine dioxide (ClO<sub>2</sub>). RO membranes degradation by chlorine compounds involves a polymer deformation (produced by N-chlorination and/or ring chlorination) followed by a de-polymerization.<sup>3-5</sup> Furthermore, the water matrix composition has a high influence on the oxidation processes. For instance, bromide ions in seawater in the presence of chlorine based oxidants could lead to the formation of bromine. Therefore, bromine can take the role usually played by chlorine when brackish or feed water is employed and can contribute to the degradation of the polyamide membrane.<sup>6,7</sup>

The Fujiwara test has been traditionally used to check the polyamide membrane degradation by halogen exposure (e.g. a small quantity of a dye solution is dropped on the membrane surface, the dye will adhere to the support material that has been oxidized, and these damaged areas will appear as bright pink spots).<sup>8</sup> Additionally, other techniques, such as ATR-FTIR (Attenuated Total Reflection–Fourier Transform Infrared) and XPS (X-ray photoelectron spectroscopy), have been also employed to determine the oxidation in RO membranes when NaClO acted as the oxidant agent.<sup>5,9</sup> Those studies have demonstrated that these methods are able to detect the membrane degradation process earlier than the Fujiwara test.

In ATR-FTIR, the chemical degradation and structural modifications of the surface active layer can be detected monitoring changes in the characteristic infrared bands of the polyamide. The ratio between the transmittance bands observed for the degraded membrane and the virgin one can be used as a degradation index. The higher this parameter, the greater is the chemical attack to the polyamide layer.<sup>7</sup>

The elemental composition and the chemical state of the elements present on the surface of a solid can be measured by XPS. Therefore, it is possible to determine if the halogens present in the oxidized membrane are attached to the polyamide structure evaluating the

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3 photoelectrons binding energy.<sup>6</sup> Previous XPS studies found that the binding energy of  
4 the photoelectron Cl(2p) measured in membranes oxidized with NaClO or ClO<sub>2</sub>  
5 corresponds to chlorine bonded to C.<sup>10</sup> Nevertheless, the main inconveniences of the  
6 XPS technique are the high instrumental cost, the high vacuum requirements and the  
7 long analysis time necessary for in-depth analysis (e.g. several hours for 100 nm).  
8 Therefore, the evaluation of alternative methods able to provide detailed information  
9 about the degradation of the polyamide layer in shorter times is of great interest today.  
10 In this context, Glow Discharges (GD) coupled to optical emission spectrometry (OES)  
11 or mass spectrometry (MS) are widely employed methods for direct solid chemical  
12 analysis. Moreover, the relatively soft and fast sputtering processes achieved by GD  
13 sources allow fast depth profile analysis with high depth resolution (~ nm).<sup>11,12</sup> An  
14 enormous variety of applications have been developed, including not only the analysis  
15 of conducting samples but also of non-conductive materials when using radiofrequency  
16 glow discharges (rf-GD). In particular, the recent development of a new rf-pulsed-GD  
17 coupled to a time of flight mass spectrometer (TOFMS) has broadened the application  
18 fields of this technique, including the analysis of thin polymer films and the  
19 determination of anions from halogenated compounds.<sup>13-16</sup>

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21 In this work, the analytical potential of rf-pulsed-GD-TOFMS is investigated for the  
22 development of a fast analytical method that allows the characterization of the oxidation  
23 degree of TFC membranes that were immersed in seawater. In particular, depth  
24 profiling of anion and cation species in oxidized TFC membranes is used to evaluate the  
25 membrane degradation as a function of the employed oxidants for water treatments (e.g.  
26 NaClO and ClO<sub>2</sub>).

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**EXPERIMENTAL**

### *Sample description*

The samples used in this work were provided by Acciona Agua S.A. (Barcelona, Spain). The samples were obtained after treatment of a commercially available TFC membrane (SWHR-380, Dow Filmtec) that consists of a thin film of polyamide (200 nm) on top of a polysulfone porous layer (40 μm), which is deposited on a support sheet of polyester (120 μm). Figure 1 shows the sample structure and the layers composition. The virgin membrane (sample 1) was immersed in a solution of sodium bromide (50 mg/L) in milli-Q water and then dried at room temperature. This non-oxidized sample is used as

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3 reference for bromide ions adsorbed on the polyamide network. The oxidized TFC  
4 membranes (samples 2-5) were immersed in a solution of 50 mg/L of NaClO  
5 (Barcelona de Drogas) or ClO<sub>2</sub> (generated using the standard method 4500-ClO<sub>2</sub>-B7,<sup>17</sup>  
6 and its concentration determined by DPD, standard method 4500-ClO<sub>2</sub>-D.<sup>17</sup>) in seawater  
7 for several hours, in order to achieve an accelerated oxidation processes. Table 1 shows  
8 the oxidant agent and the oxidation time for each sample and Table 2 shows the  
9 composition of the seawater solution employed for sample oxidation. Once the  
10 oxidation process was finished the membrane swatches were gently cleaned with milli-  
11 Q water to stop the degradation process and to ensure that all oxidant species were  
12 removed. Further details of about sample preparation are given elsewhere.<sup>7</sup>  
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### 21 *Instrumentation*

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23 The thin film composite membranes were analyzed using a rf-pulsed-GD-TOFMS  
24 prototype developed in the frame of the European project EMDPA.<sup>18</sup> The instrument  
25 has been described elsewhere.<sup>19,20</sup> The GD ion source is a copper-based modified  
26 Grimm-type chamber (EMPA, Switzerland) with a 4 mm diameter anode and a 2.5 mm  
27 inner diameter flow tube to face the gas flow towards the cathode surface. This ion  
28 source is mounted in a GD unit (GD Profiler HR instrument, Horiba Jobin Yvon,  
29 France) and coupled to a fast orthogonal time-of-flight mass spectrometer (Tofwerk,  
30 Switzerland). The rf-GD-TOFMS instrument can record complete mass spectra with a  
31 frequency of up to 100 kHz, and has a mass resolving power of about 3000 (measured at  
32 m/z 208).  
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40 Rf-power is supplied to the plasma through the backside of the sample by an rf-  
41 generator operating at 13.56 MHz. This generator can work either in continuous mode  
42 or in pulsed mode. However, due to the advantages of the pulsed mode,<sup>21</sup> including  
43 reduced thermal effects, enhanced atomization, excitation and ionization by application  
44 of high short-term power, the experiments included in this work were carried out in the  
45 pulsed mode. After optimization a pulse width of 1ms and a duty cycle of 0.25 were  
46 selected for the analysis of TFC membranes.  
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51 Constant pressure (200 Pa) and constant forward power (30 W) were used for all  
52 the measurements. High-purity argon (99.999% minimum purity) from Air Liquid  
53 (Oviedo, Spain) was employed as discharge gas.  
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56 In addition, aiming at minimizing the effect of micro-leaks due to the porous nature  
57 of the samples, a sealed pre-chamber surrounding the sample was employed. Ar gas is  
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continuously flowing through this pre-chamber warranting an Ar atmosphere around the examined sample. A schematic showing the design of this pre-chamber can be seen elsewhere.<sup>22</sup>

## RESULTS AND DISCUSSION

Thin film composite membranes are flexible and porous materials; therefore, it was necessary to fix them to metallic discs using a double face tape in order to gain rigidity and to avoid sample deformation during the GD analysis at low pressure. Moreover, the samples were placed in a pre-chamber purged with continuous flow of Ar to avoid the entrance of air into the plasma region. Figures 2a and 2b show the mass spectra in the range between  $m/z$  13 and 17 obtained for the analysis of virgin TFC membranes by rf-pulsed-GD-TOFMS, without and with using the Ar pre-chamber, respectively. As can be seen,  $^{16}\text{O}^+$  ion signal was strongly reduced when the Ar pre-chamber is used. Similar results were observed for polyatomic ions containing oxygen. For instance,  $(^{16}\text{O}^1\text{H})^+$  ion signal is significantly reduced allowing the determination of  $(^{14}\text{N}^1\text{H}_3)^+$  ion signal, which is used to identify the external polyamide layer. As a result of this study, the Ar pre-chamber was used in all the measurements.

It is well-known that rf-pulsed-GD-TOFMS provides a dynamic plasma with different regions (e.g. prepeak, plateau and afterglow). In this sense, Figure 3 shows ion signal profiles of different analytes along the pulse period. It is observed that analyte ion signals are significantly enhanced in the afterglow region, just when the GD power pulse finishes. Therefore, it was selected as the integration region to obtain the analyte intensities.

### *Qualitative depth profile of virgin membranes.*

Figure 4 shows the qualitative depth profile obtained for the virgin TFC membranes by rf-pulsed-GD-TOFMS at the optimized operating conditions. Since the virgin sample had been immersed in a 50 mg/L solution of NaBr,  $^{23}\text{Na}^+$  and  $^{79}\text{Br}^+$  ion signals were selected together with  $^{14}\text{N}^1\text{H}_3^+$  and  $^{34}\text{S}^+$ . It is observed that there is no sharp interface between the polyamide layer (monitored by  $^{14}\text{N}^1\text{H}_3^+$ ) and the polysulfone layer (represented by  $^{34}\text{S}^+$ ). However, an intense  $^{23}\text{Na}^+$  ion signal was detected with its maximum just after the one detected for  $^{14}\text{N}^1\text{H}_3^+$ , indicating that sodium is not adhered on the surface but absorbed in the polyamide layer. Conversely,  $^{79}\text{Br}^+$  ion signal remains

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3 at low levels through all the depth profile, suggesting that the immersion of the virgin  
4 membrane in the bromide solution does not seem to produce a significant incorporation  
5 of this element in the membrane.  
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### 8 9 *Qualitative depth profile of oxidized membranes.*

10 Figure 5 shows the qualitative depth profiles obtained for different oxidized samples  
11 using rf-pulsed-GD-TOFMS. Figure 5(a and b) shows the depth profiles of the samples  
12 that were immersed for 1 and 3 hours, respectively, in seawater containing NaClO;  
13 while Figure 5(c) shows the depth profile of the sample that was immersed for 7 hours  
14 in seawater containing ClO<sub>2</sub>. It is observed that all the oxidized samples present depth  
15 profiles with an intense <sup>79</sup>Br<sup>+</sup> ion signal linked to the external polyamide layer.  
16 However, Cl<sup>+</sup> ion signal was not detected in spite of having immersed the samples in  
17 NaClO or ClO<sub>2</sub>. The appearance of Br instead of Cl in the depth profiles is in agreement  
18 with previous results obtained by R. Sandín et al.,<sup>7</sup> using XPS. In that study membrane  
19 swatches were immersed in two different solutions containing NaClO as oxidant agent.  
20 In one of the solutions Milli-Q water was the solvent while seawater was used in the  
21 other one. XPS spectra showed a peak corresponding to Cl(2p) for the sample oxidized  
22 in the solution with Milli-Q water, but in the other case no peak for Cl was detected and  
23 an intense peak corresponding to Br(3d) was observed. These results showed that Br  
24 came from the seawater. Additionally, it was concluded that when the degradation  
25 process took place in Milli-Q water, chlorination was produced in the polyamide  
26 membrane; however, when seawater was used as solvent, bromination took place  
27 occurred due to the stronger halogenation effect of hypobromite in comparison to  
28 hypochlorite.<sup>23,24</sup>

29 As already mentioned, the oxidation of these membranes is typically checked by the  
30 Fujiwara test, dropping a small quantity of a dye solution on the membrane surface. A  
31 positive result is obtained if the oxidized material in contact with this dye solution  
32 brings about a bright pink colour. Interestingly, Fujiwara tests carried out for the  
33 membrane swatches exposed to seawater solutions containing NaClO or ClO<sub>2</sub> provided  
34 positive results only after exposure times longer than 3 hours in NaClO and after 13  
35 hours in ClO<sub>2</sub>,<sup>25</sup> while the analysis by GD-TOFMS showed that the oxidation takes  
36 place before.  
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38 XPS analysis carried out for the virgin membrane and oxidized samples showed that the  
39 longer the oxidation time the higher the observed Br content; and that Br concentration  
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3 is higher for the samples oxidized with NaClO using the same oxidation exposure  
4 time.<sup>25</sup> Our results using rf-pulsed-GD-TOFMS also show the apparently faster Br  
5 incorporation to the membrane when the oxidation agent is NaClO. To properly  
6 compare the  $^{79}\text{Br}^+$  depth profiles obtained for the different samples Figure 5d shows the  
7 normalized depth profiles resulting of plotting the ratio between the intensities  
8 measured for  $^{79}\text{Br}^+$  and  $(^{14}\text{N}^1\text{H}_3)^+$  versus the sputtering time. These results show clearly  
9 the higher oxidation effect of NaClO as well as the increasing Br content in the  
10 polyamide layer when the samples are subjected to longer oxidation times. This effect is  
11 evident for the profiles of samples oxidized with  $\text{ClO}_2$  solution for 1 and 7 hours. On the  
12 other hand when using NaClO as oxidant agent the maximum value of the normalized  
13 Br intensity is similar for samples oxidized for one and three hours but it seems that Br  
14 penetrates deeper when the oxidation time increase. Although the obtained depth  
15 profiles have shown good reproducibility, it cannot be completely discarded that other  
16 effects, such as for example small changes in the sputtering rates, could also influence  
17 in the resulting qualitative depth profiles. Further analysis of samples oxidized for  
18 different times would be necessary to investigate in detail the relationship between Br  
19 concentration and oxidation time.  
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### ***Qualitative depth profile of TFC membranes in negative mode.***

33 Although chlorine is the element introduced in the oxidant agents, the main change  
34 observed in the membrane when oxidized is the presence of Br in the polyamide layer  
35 coming from the seawater. These two elements have high ionization potential and  
36 therefore its detection as positive ions is not efficient in an Ar plasma ( $\text{IP}_{\text{Cl}}=12.97$  eV,  
37  $\text{IP}_{\text{Br}}=11.81$  eV,  $E_{\text{Ar}}^{\text{m}}=11.55$  and  $11.72$  eV). Nevertheless, their detection in negative  
38 mode could be analytically useful. Consequently, the performance of rf-pulsed-GD-  
39 TOFMS operating in negative mode for the analysis of the virgin and oxidized  
40 membranes was also investigated. To carry out such analyses in the negative mode, the  
41 glow discharge was operated at the same optimized experimental conditions (200 Pa, 30  
42 W, 1 ms pulse width and 0.25 duty cycle.  
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51 Figure 6 shows the mass spectra obtained for the virgin membrane in the polyamide  
52 layer using both detection modes (e.g. positive and negative) of the rf-pulsed-GD-  
53 TOFMS. It is observed that high ion signals of  $\text{Cl}^-$  and  $\text{Br}^-$  are detected in the negative  
54 mode, even in the virgin membrane. In the particular case of  $\text{Cl}^-$ , this signal was  
55 detected not only in the mass spectrum of the polyamide layer but also when the  
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3 polysulfone layer was sputtered. These results and previous evidences when analyzing  
4 other samples in negative mode indicated that Cl ions were coming from other parts of  
5 the GD source (e.g. background from o-rings or spacers used in the instrument).  
6 Moreover, it is noticed that different analytes dominate the mass spectra in the negative  
7 mode when comparing with the positive one. For instance, in positive mode  $^{14}\text{N}^1\text{H}_3$  ion  
8 signal was used to depict the polyamide layer. However in negative mode at  $m/z=17$  it  
9 is only observed the presence of  $^{16}\text{O}^1\text{H}$  (see inlet of Figure 6). Both ion signals  $^{14}\text{N}^1\text{H}_3$   
10 and  $^{16}\text{O}^1\text{H}$  can be resolved due to the high mass spectral resolution of the rf-pulsed-GD-  
11 TFMS system (Figures 2 and 6). Therefore, different ion signals than those used in  
12 positive mode were selected to identify the different layers of the TFC membranes:  
13  $^{12}\text{C}^{14}\text{N}^-$  was selected to monitor the polyamide, and  $^{32}\text{S}^1\text{H}^-$  was selected to monitor the  
14 polysulfone (see inlet of Figure 6).  
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18 Figure 7a shows the depth profile obtained in the negative mode for the virgin  
19 membrane. In this profile, the in-depth distribution of the interface between the  
20 polyamide and the polysulfone as is similar to that obtained in positive mode (see  
21 Figure 4) and, as expected, it presents a low  $^{79}\text{Br}^-$  intensity. Figure 7b compares the  
22 normalized -depth profiles of  $^{79}\text{Br}^-$  (ratio between the intensities measured for  $^{79}\text{Br}^-$  and  
23  $(^{12}\text{C}^{14}\text{N})^-$  versus the sputtering time) measured for the virgin sample and for the  
24 different oxidized membranes. It is noticed that  $\text{Br}^-$  ion signal is significantly increased  
25 for the oxidized membranes and that higher intensities are again observed for the  
26 samples oxidized by  $\text{NaClO}$ . The results are in complete agreement with those obtained  
27 by rf-pulsed-GD-TOFMS in positive mode (Figure 5d): the Br content increases with  
28 the oxidation time, which is particularly clear when membrane oxidation took place in a  
29  $\text{ClO}_2$  solution while the effect of longer immersion in  $\text{NaClO}$  solution gives as a result  
30 the deeper penetration of Br inside the polyamide.  
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34 According to XPS analysis, Cl is present at the surface of the virgin membranes  
35 probably due to post-treatment that is used to change the membrane hydraulic properties  
36 (i.e. permeate flux and salt rejection). Moreover, oxidized sample had similar Cl content  
37 independently of the oxidation time or oxidizing agent.<sup>25</sup> Unfortunately, reliable  
38 information about Cl could not be extracted from the rf-pulsed-GD-TOFMS analysis  
39 due to its high background (e.g. background from o-rings or spacers used in the  
40 instrument). In consequence it is not possible to discern if Cl measured in the membrane  
41 analysis comes really from the samples or there are other contributions.  
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3 The potential of rf-pulsed-GD-TOFMS to collect complete mass spectra (up to  $m/z =$   
4 250) at high repetition rates was used to detect the presence of relevant ion signals at  
5 high masses. For instance, Figure 8 shows the mass spectra obtained at the surface of  
6 the membranes in the interval between  $m/z=125$  and  $m/z=131$  for all the samples. It is  
7 observed that, for the virgin membrane, there is a prominent ion signal at  $m/z=127$ . This  
8 ion signal has not been assigned to any polyatomic ion because different combinations  
9 could be considered. This signal could correspond to a fragment sputtered from the  
10 polyamide layer but also could be the result of the recombination among smaller ion  
11 fragments present in the plasma. Surprisingly this ion signal is not so prominent in the  
12 mass spectra of the oxidized samples as can be seen in the Figure 8. Figure 9 shows the  
13 depth profile (e.g. first 25 s) of  $m/z=127$  ion signal measured for the virgin sample and  
14 for the different oxidized membranes. Ion signal from  $m/z=127$  is only present during  
15 the first seconds of the analyses while the maximum of the polyamide layer is obtained  
16 at around 50 s in the depth profile, so it seems that a very thin layer is formed in the  
17 surface of the membrane, which gets degraded when the sample is oxidized. Moreover,  
18 this degradation seems to be progressive with the oxidation time and also more effective  
19 when the oxidant agent is NaClO instead of ClO<sub>2</sub>. The possible presence of a thin  
20 coating over the polyamide layer was investigated by C. Y. Tang et al. concluding that  
21 some commercial membranes contained an aliphatic coating layer rich in -COH groups  
22 over the polyamide layer.<sup>26</sup> Moreover studies carried out by A. Antony *et al.* showed  
23 that this coating could be lost during the oxidation.<sup>9</sup>

## 38 39 CONCLUSIONS

40 This work has shown that the rf-pulsed-TOFMS is a powerful tool for the fast analysis  
41 of flexible and porous thin film composite membranes. In particular, appropriate  
42 operating conditions can be achieved for the analysis of these membranes using a proper  
43 rigid support and an Ar pre-chamber that avoids the air entrance in the discharge.

44 The positive and the negative detection modes of the rf-pulsed-GD-TOFMS system  
45 provided adequate depth profiles of the TFC membranes (e.g. virgin and oxidized),  
46 showing that Br is incorporated in the whole polyamide layer and not only in the  
47 surface. Moreover, a higher content of Br is observed in the samples oxidized with the  
48 stronger oxidant agent (e.g. NaClO versus ClO<sub>2</sub>).

49 In both positive and negative modes, it has been possible to confirm a correlation  
50 between the oxidation time and the normalized Br intensity in the profile. Moreover, the  
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3 detection of the negative polyatomic ions at  $m/z=127$  seems to show that there is a  
4 certain “degradation” in the more external region of the polyamide caused by the  
5 oxidation process. In this case, a negative correlation between the oxidation time and  
6 the intensity of this signal is observed being this effect more pronounced when the  
7 oxidant agent is NaClO.  
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18 rf-pulsed-GD-TOFMS prototype.  
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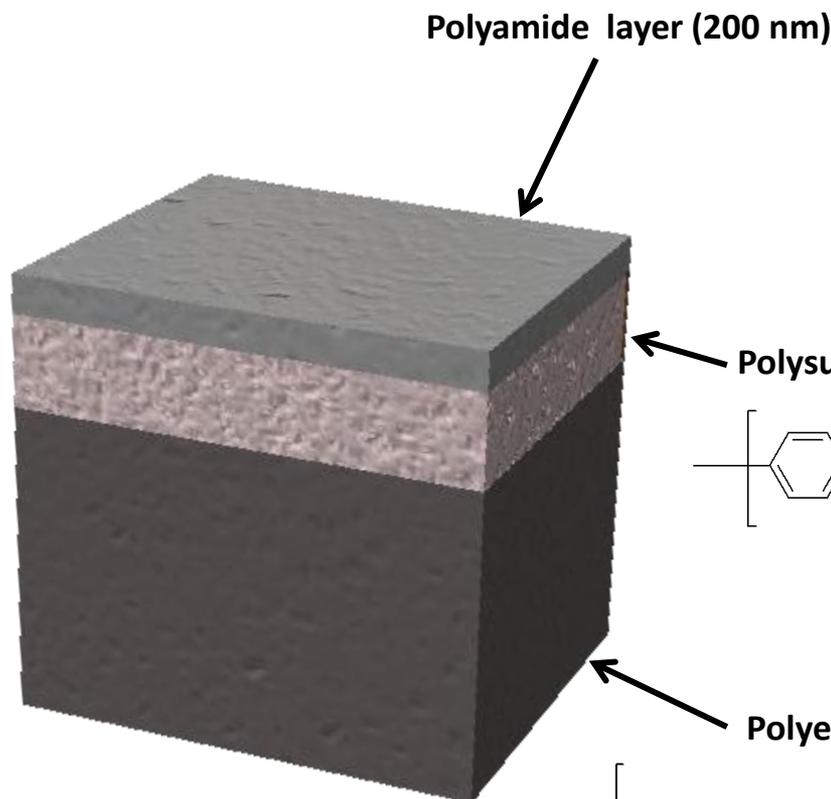
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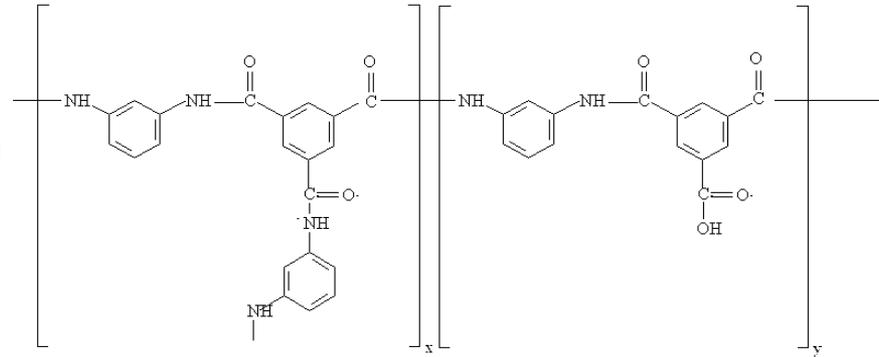
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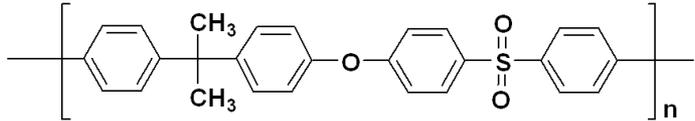
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**Polyamide layer (200 nm)**



**Polysulfone layer (40 μm)**



**Polyester**

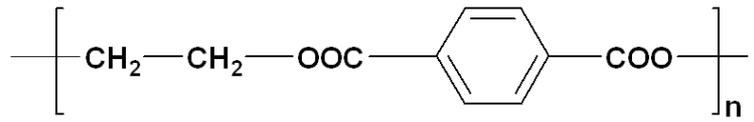
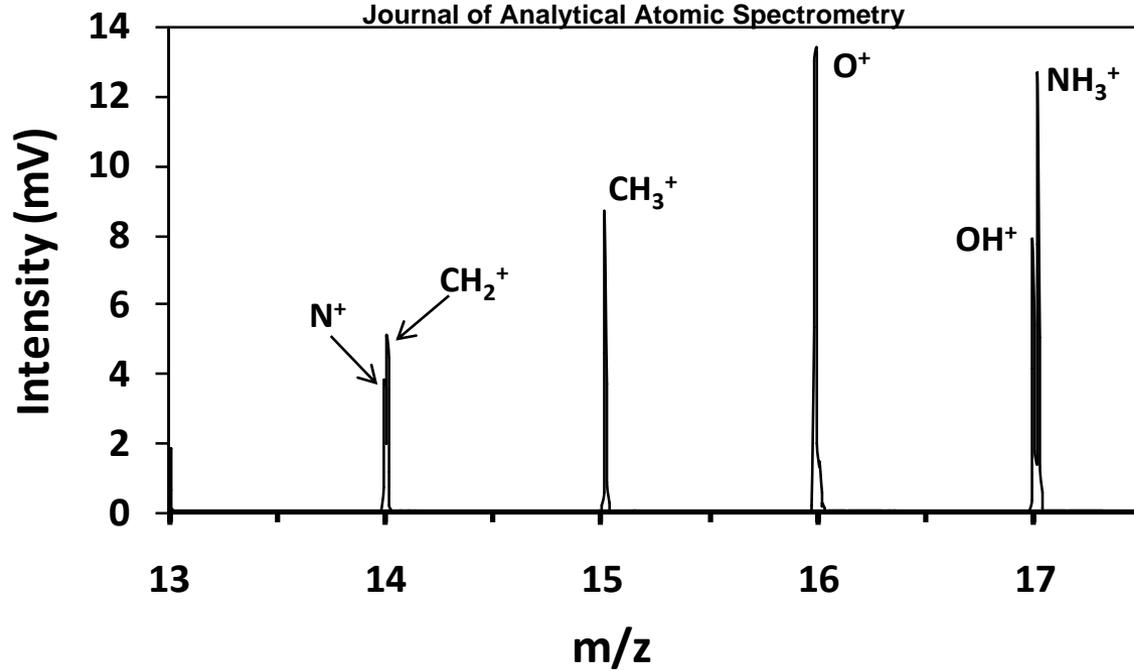


Figure 1

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b)

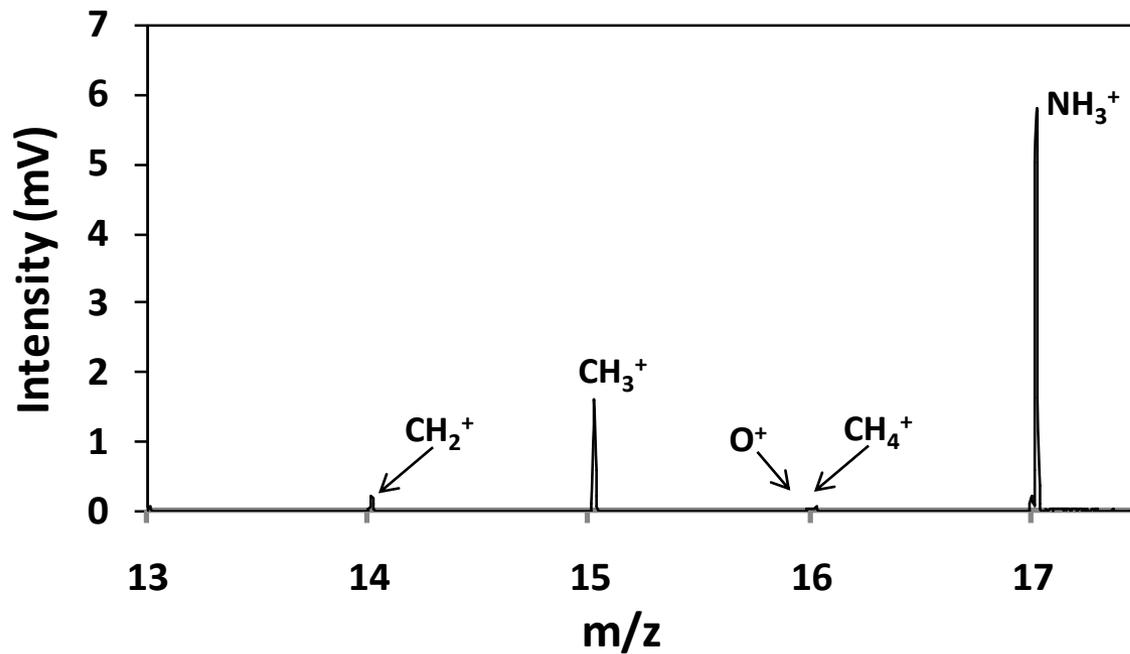


Figure 2

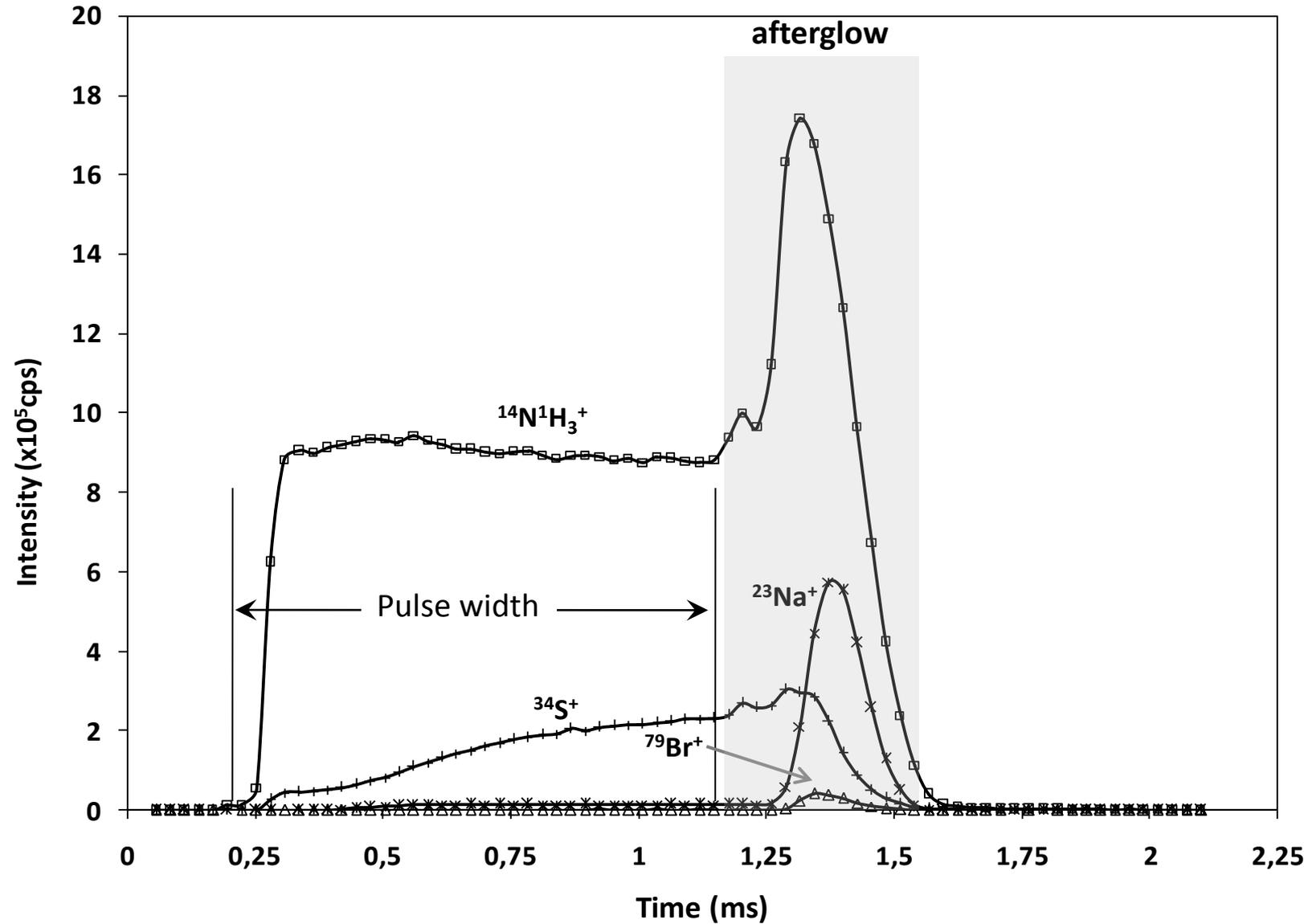


Figure 3

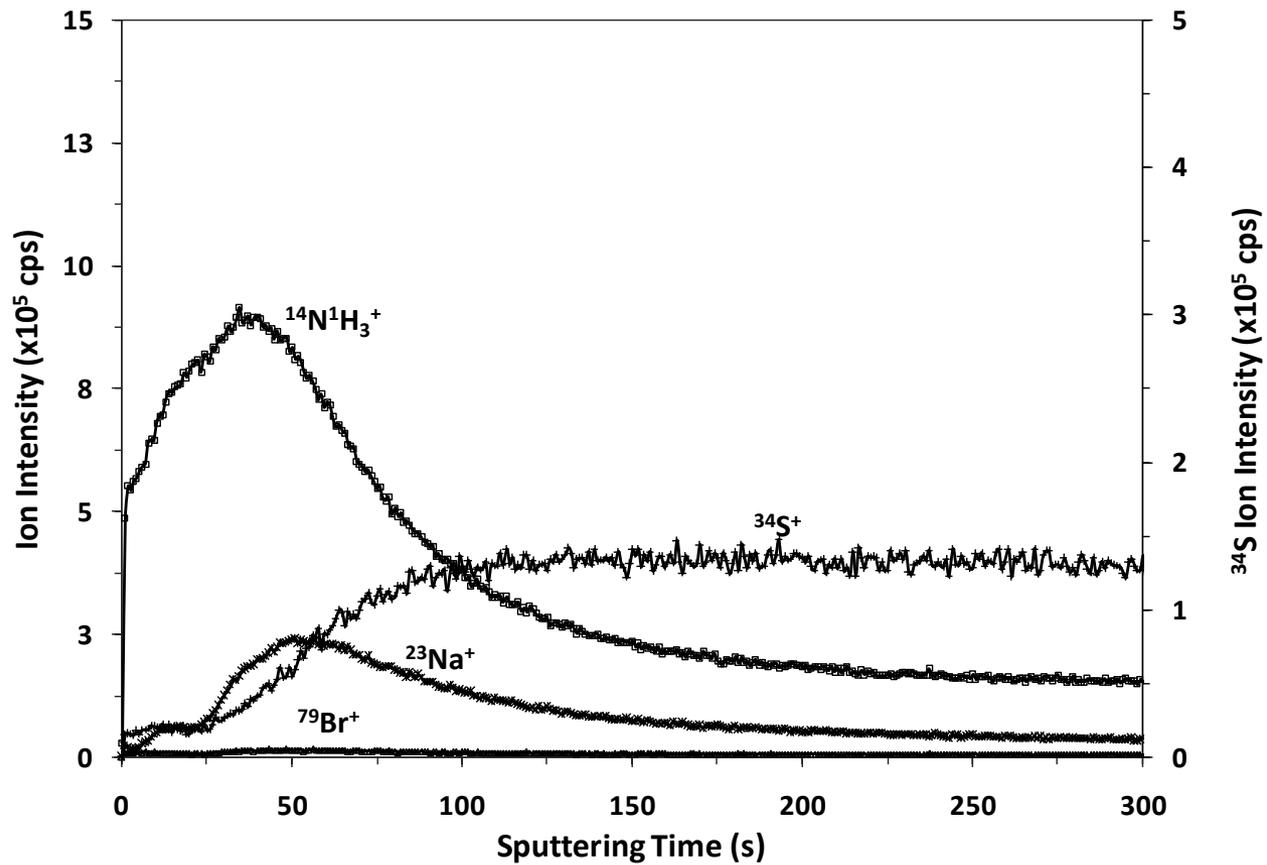
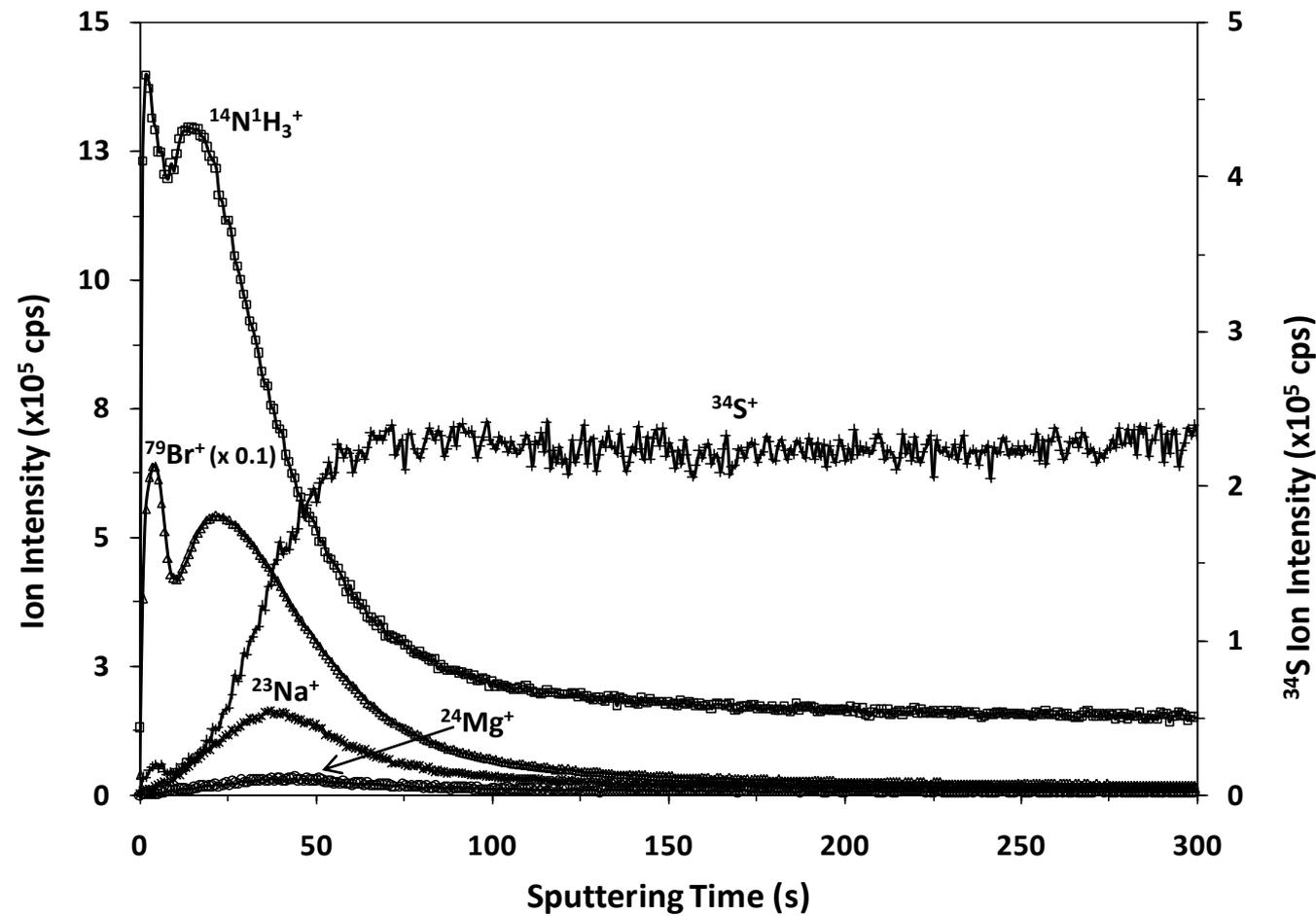


Figure 4

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Figure 5a

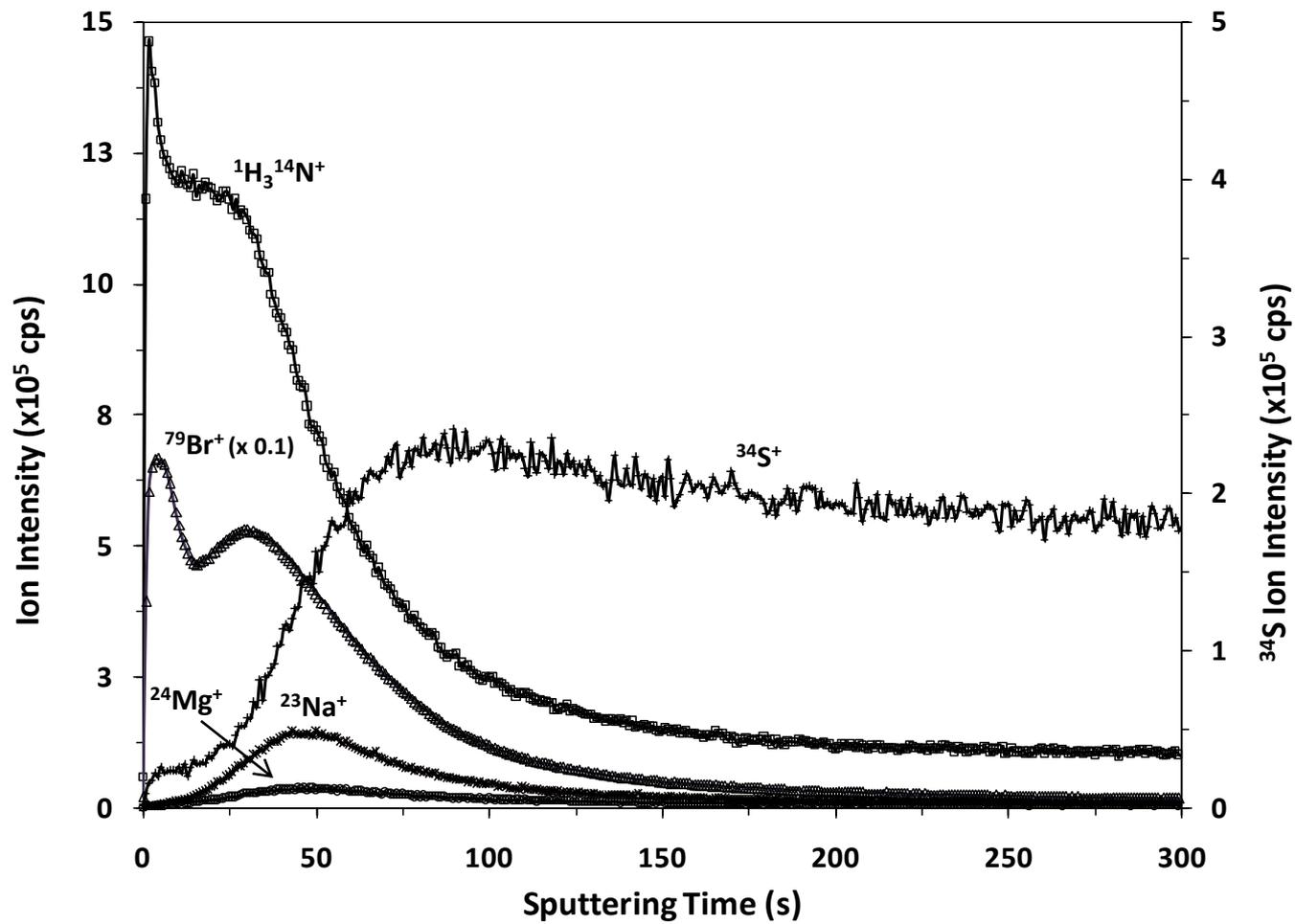
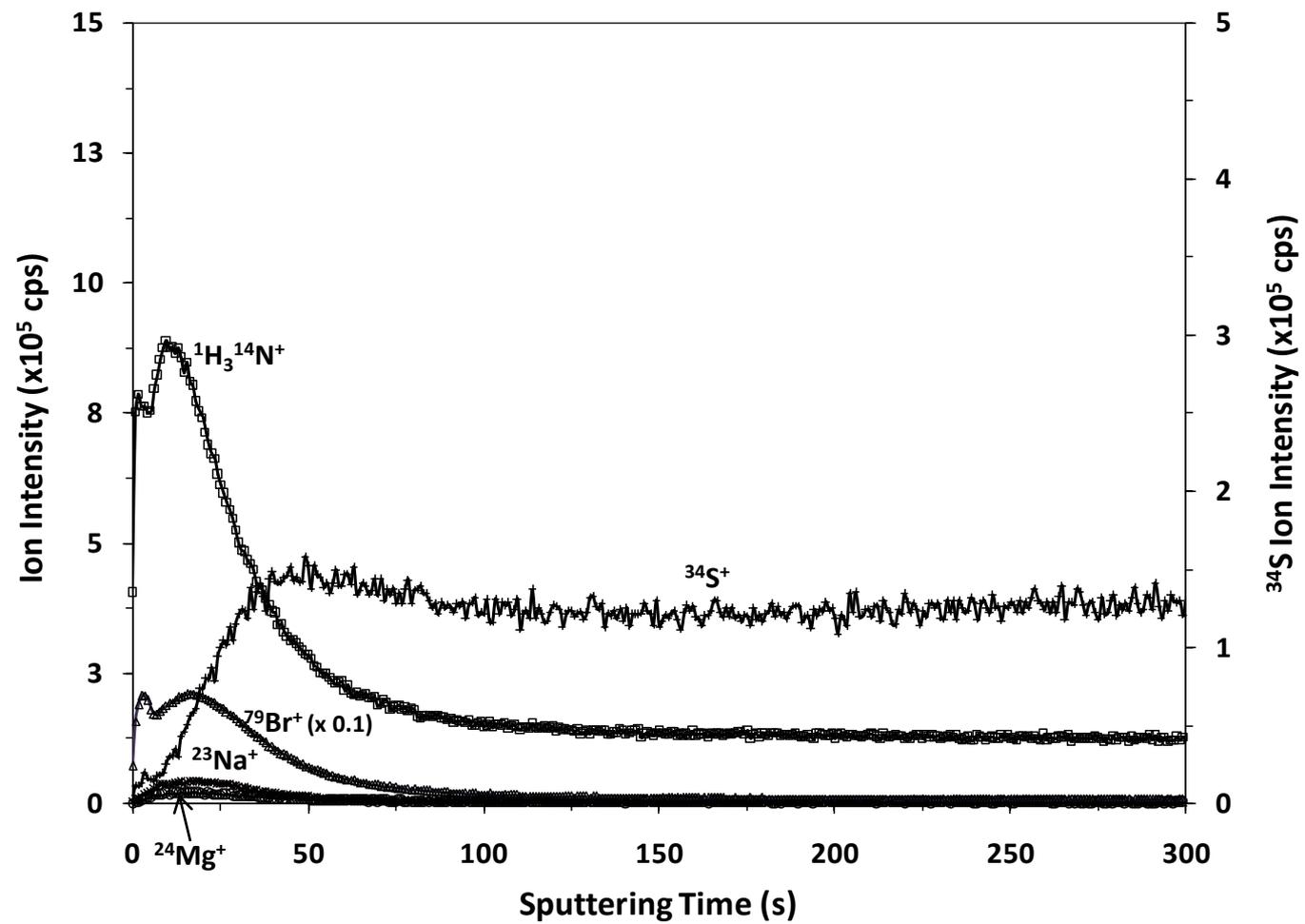


Figure 5 b



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Figure 5 c

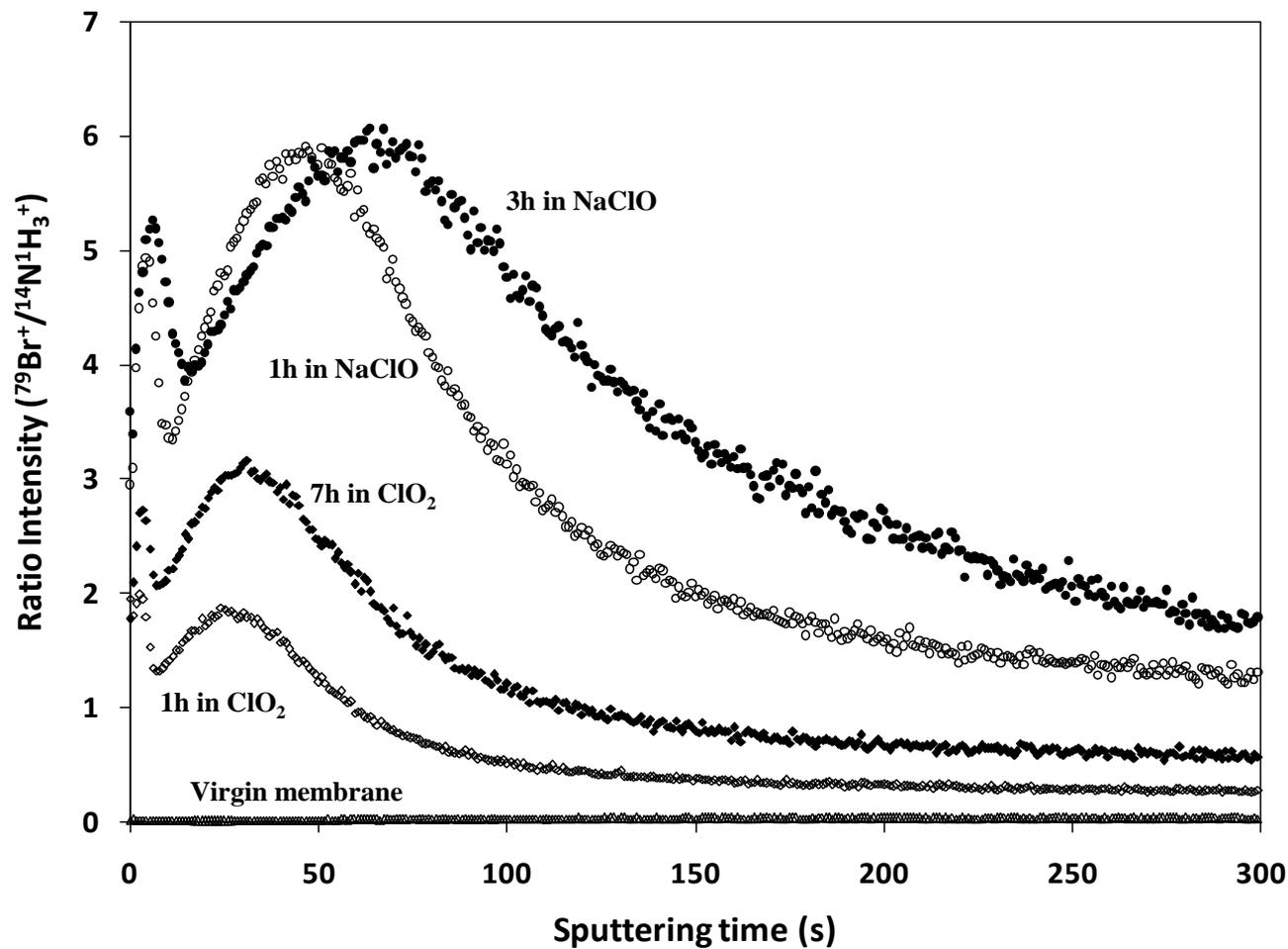
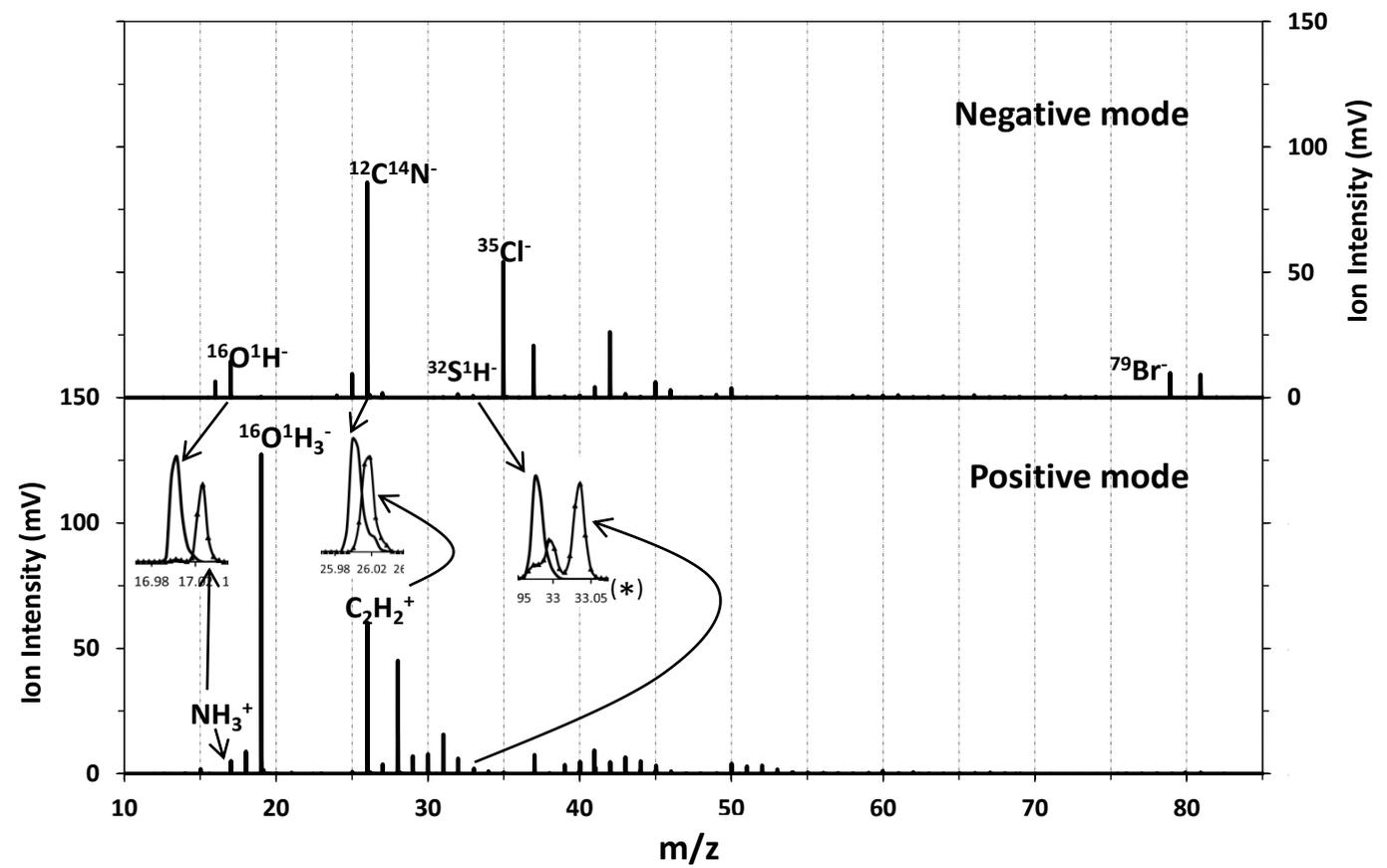


Figure 5 d

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Figure 6

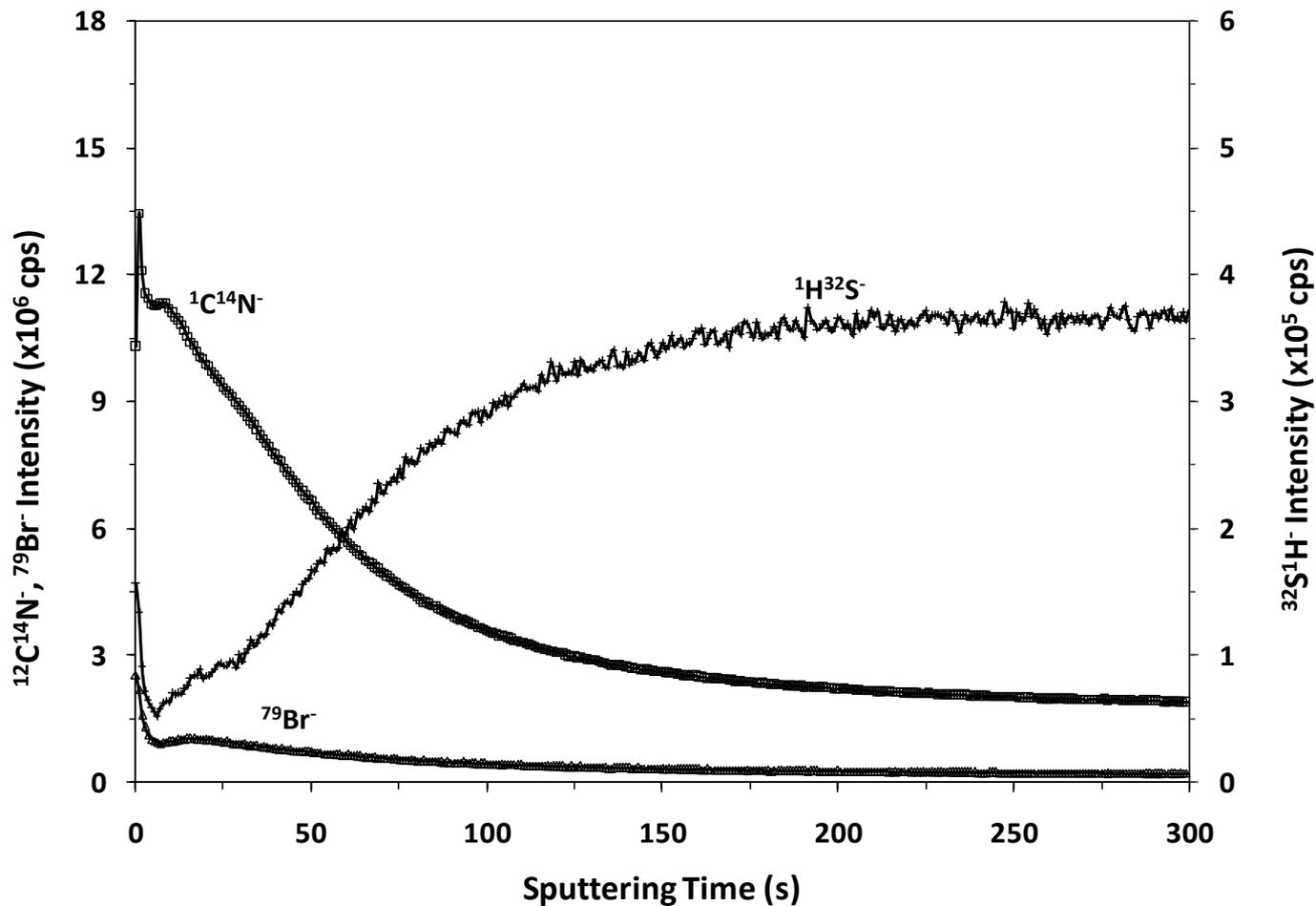


Figure 7a

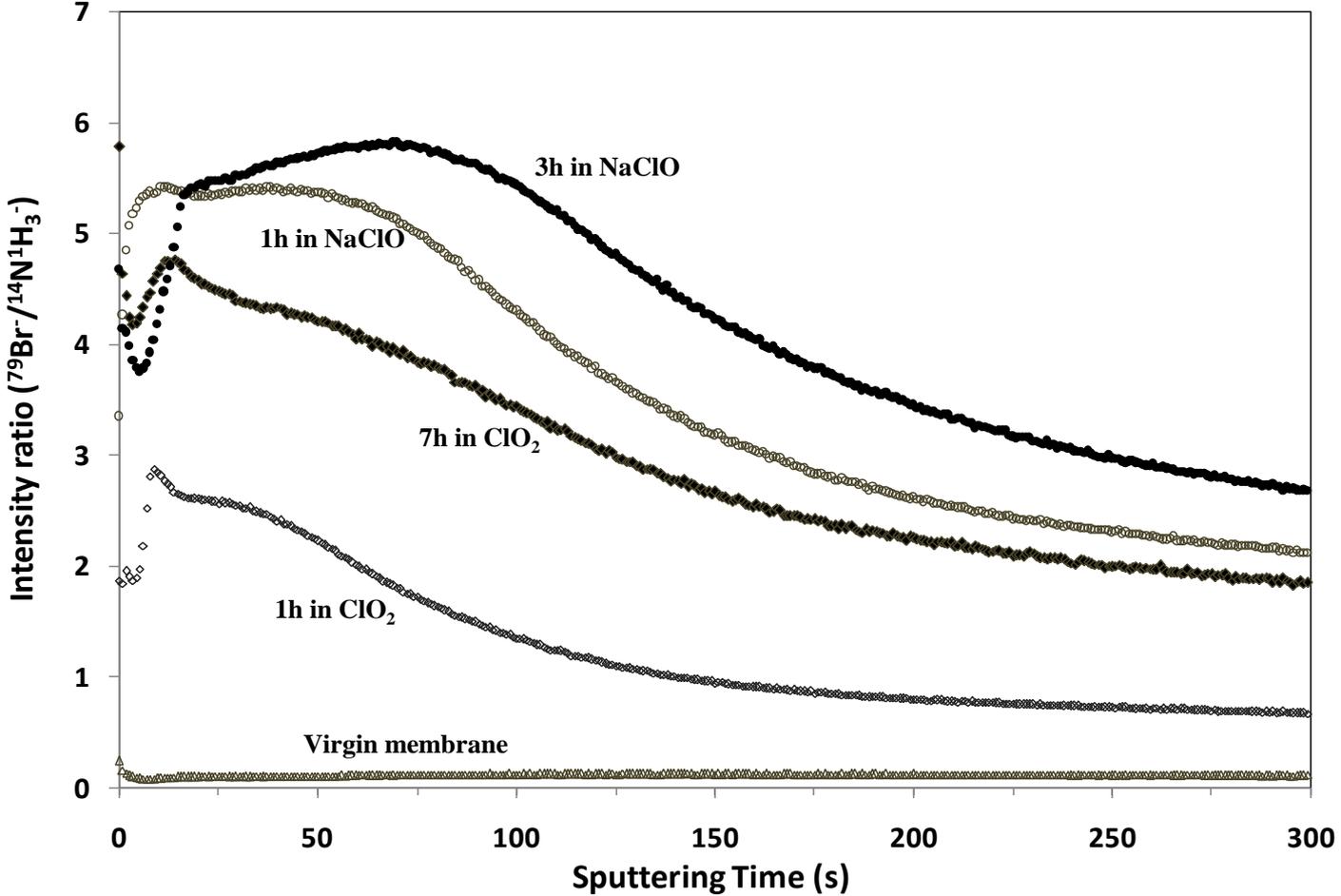


Figure 7b

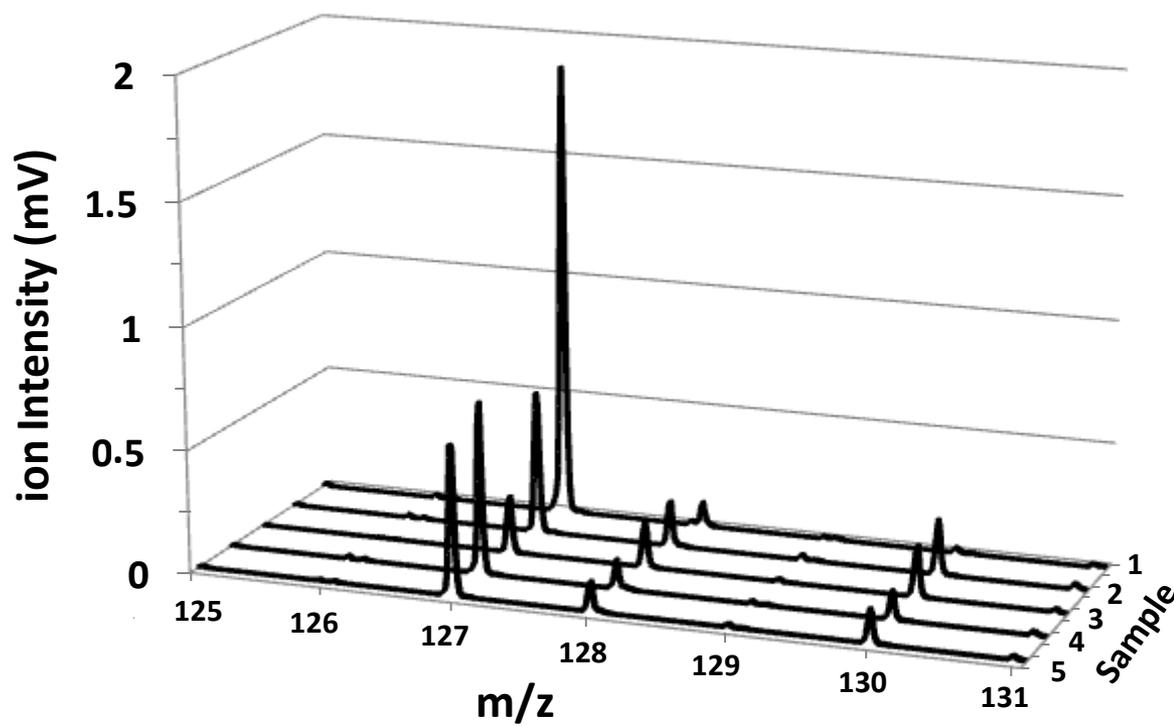


Figure 8

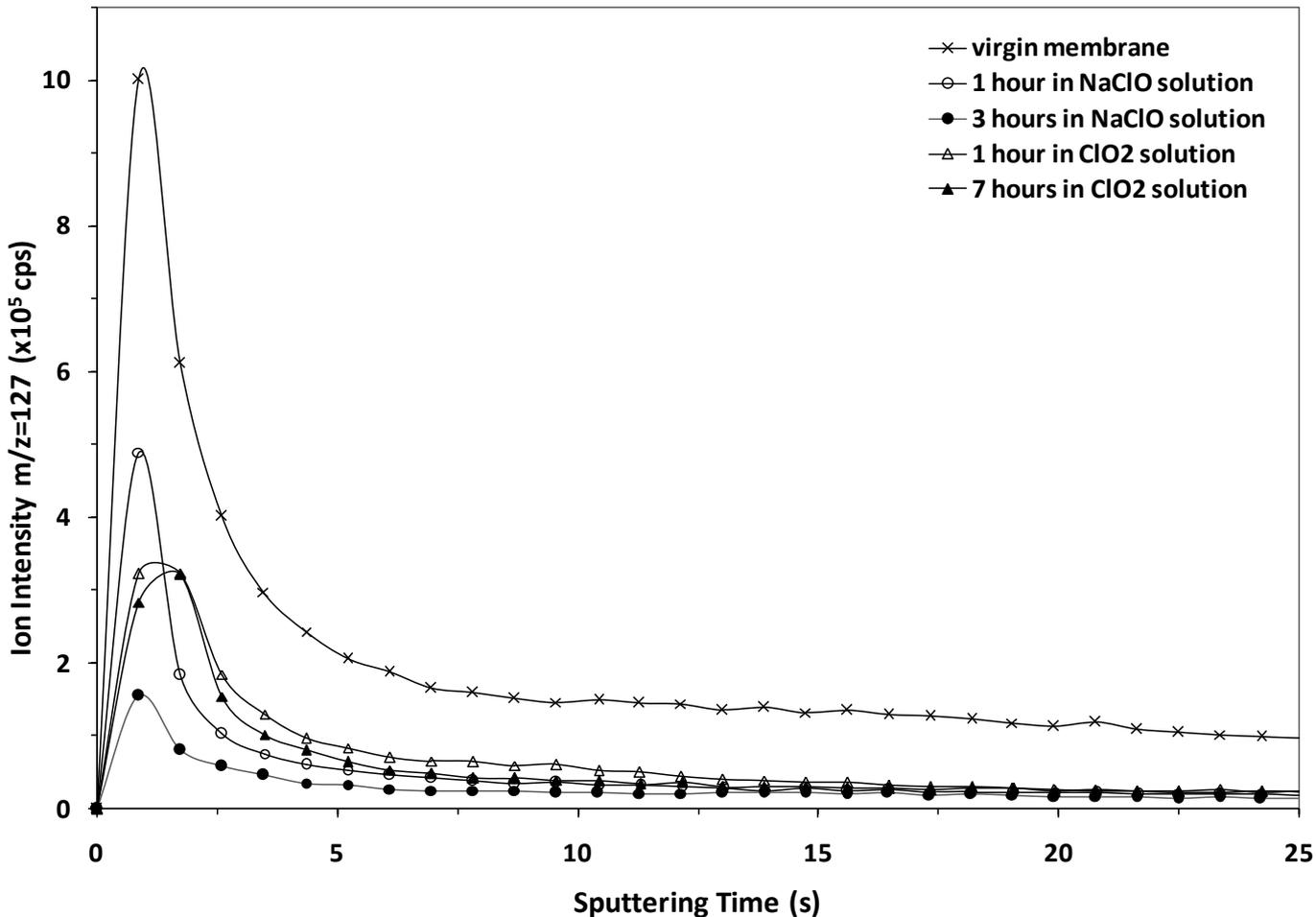


Figure 9