

Quantitative Atom Probe Analysis of Carbides

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Compared to atom probe analysis of metallic materials, the analysis of carbide phases results in an enhanced formation of molecular ions and multiple events. In addition, many multiple events appear to consist of two or more ions originating from adjacent sites in the material. Due to limitations of the ion detectors measurements generally underestimate the carbon concentration. Analyses using laser pulsed atom probe tomography have been performed on SiC, WC, Ti(C,N) and Ti₂AlC grains in different materials as well as on large M₂₃C₆ precipitates in steel. Using standard evaluation methods, the obtained carbon concentration is 6-24% lower than expected from the known stoichiometry. The results improve remarkably by using only the ¹³C isotope, and calculating the concentration of ¹²C from the natural isotope abundance. This confirms that the main reason for obtaining a too low carbon concentration is the dead time of the detector, mainly affecting carbon since it is more frequently evaporated as multiple ions. In the case of Ti(C,N) and Ti₂AlC an additional difficulty arises from the overlap between C₂⁺, C₄²⁺ and Ti²⁺ at the mass-to-charge 24 Da.

Keywords; Atom probe, Atom probe tomography, Carbides, Quantitative analysis

1. Introduction

Atom probe is the only technique capable of detecting light (boron, carbon) as well as heavy (tungsten, niobium, tantalum) elements with an equal sensitivity. Therefore, already in the early seventies, the method was proposed as suitable and used for studies of carbides in a number of different systems, see for

example [1-6]. However, in many studies the measured carbon content appears to be lower than expected so the question arises, how accurately can carbon be quantified?

Compared to analysis of metallic materials, atom probe analysis of carbide phases results in an enhanced formation of molecular ions and multiple events where more than one ion originating from the same pulse is detected [7]. This may be due to a high ionization energy of carbon [8] and/or because the difference between metallic bonding and the bonding between adjacent carbon atoms or carbon and metal atoms. As a result carbon will evaporate at a higher electric field, which may cause its retention on the specimen surface and stimulate the occurrence of multiple events. The large amount of such events puts high demands on the performance of the detector, in particular on the dead time, and may lower the “detection efficiency” for carbon. This problem was recently also recognized by Yao et al. [9].

We have for a long time corrected individual peaks in the mass spectrum for the detector dead time using the Rolander ion pair correction algorithm in the 1-D atom probe [10]. This was accomplished by a statistical approach making use of multiple events detected, i.e. multiple events separated by a time longer than the dead time, and then calculating the amount of lost ions. In the 3-D atom probe this method cannot easily be used since time and space are coupled. Two ions arriving at the position sensitive detector exactly at the same time can easily be recorded if they are well separated in space. Unfortunately, when several ions are field evaporated during the same pulse, they will most probably be close in space, making detection more difficult. As most of the pulses do not generate any ions, it is unlikely that one pulse causes ions far from each other to field evaporate because they cannot influence each other at a large separation. Here we will present other possibilities of correcting the missing carbon in atom probe analyses.

2. Materials and methods

Five carbide materials are included in this study; Ti(C,N), Ti₂AlC, WC, SiC and M₂₃C₆. The first four materials can be considered as bulk carbides, whereas M₂₃C₆ was found as a relatively large precipitate in a creep resistant steel.

The Ti(C,N) material was produced from Ti(C_{0.7}N_{0.3}) powder that was pressed and sintered at a high pressure and high temperature, around 5 GPa and 1500°C. Chemical bulk analysis has shown the composition to be 33.1 at.% C - 15.9 at.% N - 1.2 at.% O (balance Ti) [11]. Titanium carbonitrides in cermets have previously been analyzed using voltage pulsed 1-D atom probe [4, 12], where the effect of the detector dead time was addressed. In the case of cermets the carbides are surrounded by a metallic binder phase making them easier to analyze.

The analyzed Ti₂AlC is the major phase in bulk Maxthal®211 from Kanthal AB, Sweden. It possesses both metallic and ceramic properties due to its layered structure consisting of Ti₂C layers separated by individual Al layers. This phase has not been analyzed using atom probe before. Further details are presented by Sonestedt et al. in this issue [13].

The WC analyzed is the dominating constituent in a WC-NbC-Co sintered cemented carbide material. NbC additions are made to the powder mixture in order to decrease crater wear when used as a tool material. A detailed description of the material production can be found elsewhere [14]. WC is believed to be a stoichiometric compound. It has previously been analyzed using voltage pulsed 1-D atom probe [5].

The liquid phase sintered silicon carbide ceramic was fabricated with the addition of 3 wt% Al₂O₃ and Y₂O₃ and hot isostatically pressed at 1800°C for 2 h under a pressure of 160 MPa. α -SiC grains, with the 6H or 4H polytype, were surrounded by an yttrium, aluminium and oxygen rich residual glass present as thin (~1.5 nm) grain boundary films merging into pockets at multi grain junctions [15]. Silicon carbide has previously been studied using laser pulsed 1-D [16] and 3-D atom probe [17].

The $M_{23}C_6$ precipitate studied was present in a high-boron (300 ppm) martensitic 10.5% chromium steel containing 0.21% C, 1.5% Mo, 0.24% V and 0.18% Nb (wt%). The steel was austenitized at 1150°C for 1 h and tempered at 700°C for 2 h, and was studied in the as-tempered state. Of course, many atom probe studies have been carried out on carbides in steels [18] using both 1-D and 3-D atom probe, mostly using voltage pulsing. The alloy carbide $M_{23}C_6$ in creep resistant 9-12%Cr steel has for example been studied by Lundin and Andr en [19].

All materials were analyzed using a local electrode atom probe (Imago LEAP 3000X HR) equipped with a reflectron for improved mass resolution. The detection efficiency is about 37% and the dead time of the delay-line detector is less than 3 ns, as stated by the supplier. The analyses were carried out in laser pulse mode with a wavelength of 532 nm. At least in the case of $M_{23}C_6$ and WC voltage pulsing is of course also possible. However, the success rate and the analysis length appear to be clearly higher when using laser pulsing. As a comparison WC was additionally analyzed using voltage pulse mode. The analysis parameters are listed in table 1.

Atom probe samples of Ti(C,N), Ti_2AlC , SiC and $M_{23}C_6$ were prepared using the focused ion beam (FIB) lift-out technique [20]. In the case of $M_{23}C_6$ the steel sample had to be carefully ion milled until a carbide could be observed close to the tip apex. Needle samples of WC were prepared by a combination of electropolishing and FIB [21]. In all cases the final milling was carried out using a lower voltage (5 kV) to limit Ga implantation.

3. Results and Discussion

3.1 Mass spectra

In all cases, except for SiC, the atom probe analyses resulted in mass spectra of high quality. The mass resolving power ranges from 350 to above 700 (FWHM). The usual broad peak tails (towards higher mass-to-charge ratios) are reasonably small and the formation of molecular ions typical for laser pulsing is

not excessive. Results from analyses of all materials are found in table 2. In the case of SiC good analyses have not been achieved. The peaks are very broad and have large tails, see the mass spectrum in figure 1, giving poor values of FWHM and FWTM, similar to values in older 1-D work [16] as well as in very recent analyses [17]. The analysis is, however, still useful, and the measurement of the boron content of the carbide is probably correct. Perhaps improved results can be obtained using lower laser pulse energy or specimen temperature. However, this would increase the already high risk of premature specimen fracture.

Two mass spectra of WC are presented in figure 2, one obtained using laser pulsing and one using voltage pulsing. The effect of an increased evaporation field in the voltage pulsed analysis, despite the 30 K higher base temperature, results for example in the formation of C^{3+} . The mass resolution and background noise level are very good and similar in the two cases.

The evaporation fields in the analyses were estimated from the charge state curves of Kingham [22]. Ti(C,N), Ti_2AlC and $M_{23}C_6$ gave values of 37-38 V/nm using the ratio of Ti^{3+}/Ti^{2+} in the titanium based carbides and the ratio of Mo^{3+}/Mo^{2+} in $M_{23}C_6$. In the case of SiC the evaporation field was estimated using the ratio Ga^{2+}/Ga^+ from FIB implanted gallium. The value obtained was 28 V/nm, which in turn implies that the fraction of Si^+ should be extremely small ($<10^{-4}$) and therefore the peak at 28 Da is perhaps not Si^+ but $SiCO^{2+}$ or CO^+ . The evaporation field of WC was estimated from the W^{4+}/W^{3+} ratio to be 48 V/nm and 50 V/nm for laser pulsed and voltage pulsed analyses, respectively. The applicability of the Kingham curves when using laser pulsing is probably more limited than when using voltage pulsing, as the amount of molecular ions is higher. The molecular ions will behave differently during post-ionization, affecting the charge state distribution (assuming that molecular ions often split during the process and end up as atomic ions).

Carbon is present in the mass spectrum at a number of peaks, as summarized in table 3. In all cases C^{2+} is the largest, and the only other non-molecular ion, C^+ , also accounts for a large fraction of the detected carbon. In the laser pulsed

analyses the ratio C^{2+}/C^+ ranges from 1.2 for Ti(C,N) to 2.0 for WC. The ratio is still higher for voltage pulsed WC (2.8), which is also the only case where C^{3+} is observed in any significant amount, in agreement with the field being higher. Regarding molecular ions, they account for about half the detected carbon for Ti(C,N), SiC and $M_{23}C_6$, whereas only 16% originate from molecular ions in Ti_2AlC . In analyses of WC the molecular ions constitute a very small fraction, in particular in the voltage pulsed analysis. By comparing the different materials, no simple conclusion can be made as far as the fraction of molecular carbon ions is concerned. Probably the tendency to form molecular ions decreases with increasing evaporation field and decreasing carbon concentration. However, these effects do not fully explain the observed distributions, which indicates that the chemical bonding and/or the carbon sites in the carbide lattice are also of importance.

In all analyses the number of multiple events is very high. This means that more than one ion originating from the same pulse are detected. The fraction of multiple events range from 30% in the material of lowest carbon content ($M_{23}C_6$) to 60% in voltage pulsed WC. This behavior is typical of carbides, which field evaporate in an irregular fashion [4]. The effect of multiple events together with detector dead time is largest if there is only one (or a few) dominating peaks of an element. Hence, the situation improves if there are several charge-states and many isotopes of reasonable abundance. In the case of carbon there are usually several charge-states and some molecular ions, but there is only one dominating isotope ($98.93 \pm 0.08 \% \text{ }^{12}\text{C}$ and $1.07 \pm 0.08 \% \text{ }^{13}\text{C}$ [NEW]). Furthermore, it could be concluded from comparing mass spectra of single events and multiple events that carbon is much more common in the multiple events than other elements, as shown in figure 3. The effect of the dead time obviously gets more severe when the mass resolution is high, as the time spread between two ions of the same mass-to-charge ratio coming from the same pulse is small (in particular it is smaller than the dead time). This also implies that the loss of carbon atoms becomes higher when the voltage increases during an analysis.

The chemical compositions obtained using standard mass spectrum evaluation are presented in table 2. It is clear that in all cases the carbon concentration is too low.

3.2 ¹³C-Method

It was observed in all analyses that the ¹³C peaks at mass-to-charge ratios 6.5 and 13 Da were larger than what is expected from the natural abundance. This can be understood because the effect of the dead time is much stronger for large peaks (¹²C) than for small peaks (¹³C). Hence, the ¹³C isotope can be used to calculate how much carbon should be present at m/q 6 and 12 Da, assuming that the dead time has negligible influence on the ¹³C peaks. The number of counts detected at m/q 6.5 Da is multiplied by 92.5 to give the corrected number of counts at m/q 6 Da. In the same way the number of counts detected at m/q 13 Da is multiplied by 92.5 to give the corrected number of counts at m/q 12 Da. When performing this correction it is very important to make a careful background subtraction, so that the background is not being multiplied. In the examples shown in figure 2, the signal to noise ratios of the ¹³C peaks are larger than 100. The resulting carbon concentrations, after background subtraction and correction of the C⁺ and C²⁺ peaks using ¹³C, are given in table 4. Obviously the corrected carbon concentrations are much closer to the expected values. Unfortunately, the method could not be applied to SiC because of the large peak tails.

As just mentioned, the ¹³C-method gives a more correct carbon concentration. On the other hand the uncertainty increases. Firstly, the uncertainty from the counting statistics is studied using C⁺ in the relatively short analysis of Ti₂AlC. The concentration of C⁺ changes from 8.01±0.05 at.% to 11.56±0.55 at.%, when applying the ¹³C-method. Hence, the uncertainty originating from the counting statistics is increased by a factor of 10. It is clear that the analysis must contain a sufficient number of ions for the method to be useful (say 100,000 or so). Secondly, the uncertainty arising from the terrestrial variation in isotope abundance gives a substantial standard deviation of 0.9 at.% for the C⁺ peak in this example. Thirdly, the importance of the background subtraction becomes

much more important when using the ^{13}C peaks for quantification. In the previous example about 8% of the ions in the m/q 13 Da peak were taken as background. In order to make a first rough estimate of the sensitivity of the method, a background of 7% could be used. This would give the concentration of C^+ as 11.66 at.%. If instead the background level is halved (which would clearly be an incorrect background correction), the concentration of C^+ gets 12.1 at.%. All in all, the effect of counting statistics, terrestrial variation in isotope abundance and background subtraction on the uncertainty are tolerable. When adding the uncertainty in the example above the result becomes 11.6 ± 1.7 at.%. The relatively large uncertainty originating from the variation in isotope abundance will be a systematic uncertainty within one material or production lot. In principle, a way to decrease the uncertainty would be to determine the isotope distribution of the bulk of the material to be investigated using mass spectrometry.

A further effect that could potentially be severe would be the formation of hydride molecular ions, such as CH^+ and CH_2^+ . If there would be an appreciable amount of these ions the carbon concentration could be strongly overestimated. However, no cases have been encountered where the ^{13}C method has given unrealistically high C concentrations in this work, suggesting that CH is not a problem.

3.3 The 24 Da peak

In the titanium containing carbides, the isotope correction scheme does not work for the peak at 24 Da, consisting of Ti^{2+} and C_2^+ and perhaps also C_4^{2+} . When performing peak decomposition using the natural abundance of the four minor titanium isotopes, the result is that there is no carbon in the 24 Da peak. In fact, the peak is too small even if the carbon is zero. This is most certainly a consequence of multiple events and the dead time of the detector, strongly affecting the 24 Da peak. The amount of C_2^+ (24 Da) is larger than the amounts of both C_3^+ (36 Da) and C_3^{2+} (18 Da) in laser pulsed analyses of the titanium free carbides WC, SiC and M_{23}C_6 , see table 3. Therefore, it is almost certain that the analyses of $\text{Ti}(\text{C},\text{N})$ and Ti_2AlC should contain significant amounts of carbon at 24

Da (probably a few at.%). A method for estimating the amount of carbon at 24 Da based on comparison of peaks in single event and multiple event spectra has been proposed by Angseryd et al. [11]. After applying the ^{13}C method, Ti(C,N) lacks about 3 at.% C, which is probably attributed to C_2^+ or C_4^{2+} ions, whilst the carbon concentration of Ti_2AlC is not too low and if carbon is further added from the 24 Da peak the apparent carbon concentration becomes too high. The reason for this is probably that also the aluminum concentration is too low, because of multiple events and the dead time. As Al only has one isotope and a majority of Al is field evaporated as Al^{2+} it could easily be affected by the dead time. This is further dealt with in a paper by Sonestedt in this issue [13].

The peak at 24 Da, in the absence of Ti, is usually assigned to C_2^+ but it has also been reported that a large part of the peak may be C_4^{2+} [23]. In the latter case there will be a small peak at 24.5 Da, corresponding to one of the four C atoms being ^{13}C . The size of the 24.5 Da peak will then be $4/92.5$ of the 24 Da peak. From the analysis of M_{23}C_6 , where there is virtually no Ti, the mass resolution is high and the 24 Da peak is large, the amount of C_4^{2+} can be estimated. The number of counts at 24 Da and 24.5 Da were 4903 and 115, respectively, giving the fraction $\text{C}_4^{2+}/\text{C}_2^+$ ions at 24 Da as large as 1.2, and in terms of atoms the ratio is doubled. This is similar to what has been reported for martensitic steel [23]. This topic is further treated in reference [24]. The carbon deficit in the analysis of SiC can perhaps be attributed to C_4^{2+} , even though at the low field doubly charged molecular ions are less likely.

4. Conclusions

Five carbide materials have been investigated using laser pulsed APT. The carbon concentration obtained by standard mass spectrum evaluation was in all cases lower than expected due to multiple events and detector dead time. Improved results could be obtained using the minor isotope ^{13}C and, for titanium containing carbides, using a correction for the 24 Da peak.

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Table 1 . Experimental parameters used for LEAP analyses.

	Ti(C,N)	Ti ₂ AlC	WC	WC ^a	SiC	M ₂₃ C ₆
Laser pulse energy (nJ)	0.3	0.4	0.35	-	0.5	0.35
Voltage pulse fraction (%)	-	-	-	20	-	-
Pulse frequency (kHz)	200	200	200	200	200	200
Evaporation rate (%)	0.2	0.6	1	0.5	0.5	0.5
Temperature (K)	65	50	66	96	65	60

^aVoltage pulsing.

Table 2. Composition obtained using standard evaluation (including peak decomposition and background subtraction) together with some other parameters.

	Ti(C,N)	Ti ₂ AlC	WC	WC ^a	SiC	M ₂₃ C ₆
C	26.6	19.9	47.1	46.2	45.3	15.2
N	15.2	0.52	0.018	0.041		
Ti	57.8	54.1				
W			53.4	52.9		
Si					53.3	
Al		22.5				
O	0.15	3.0			1.4	
Nb			0.06	0.48		
B					0.06	2.1
Cr, Fe, Mo, Mn, V, Ni						81.7
C (expected)	33.1	25 ^b	50	50	50	20.7 ^c
No. of ions (×10 ⁶)	2.0	0.34	3.3	0.97	0.46	0.084
FWHM	452	358	604	629	40	720
FWTM	214	173	226	248	18	318
Single events (%)	45	59	48	40	55	70
Multiple events (%)	55	41	52	60	45	30

^aVoltage pulsing.

^bIncluding N and O.

^cIncluding B.

Table 3. Distribution of carbon in mass spectra in at.%, normalized to 100%. The mass-to-charge ratios (m/q) given relate to the ^{12}C isotope and the most abundant isotope of B, N, Si, Ti and Mo, respectively.

	m/q (Da)	Ti(C,N)	Ti ₂ AlC	WC	WC ^a	SiC	M ₂₃ C ₆
C ³⁺ (%)	4	0	0	0.01	0.11	0	0
C ²⁺ (%)	6	30.9	49.6	64.3	73.8	31.9	29.5
C ⁺ (%)	12	24.8	34.4	32.5	26.1	18.9	17.8
C ₃ ²⁺ (%)	18	2.7	5.0	0.52	0	8.4	13.0
C ₂ ²⁺ (%) ^b	24	0 ^c	0 ^c	2.7	0.1	13.5	21.0
C ₃ ⁺ (%)	36	5.2	5.6	0.01	0	12.5	14.9
C ₄ ⁺ (%)	48	2.7	0.37	0	0	6.4	0
C ₅ ⁺ (%)	60	0.42	0.06	0	0	2.1	0
BC ⁺ (%)	23	-	-	-	-	-	0.7
CN ⁺ (%)	26	8.8	0	-	-	-	0
SiC ₂ ²⁺ (%)	26	-	-	-	-	5.7	-
TiC ₂ ⁺ (%)	30	24.4	5.0	-	-	-	-
SiC ⁺ (%)	40	-	-	-	-	0.19	-
SiC ₂ ⁺ (%)	52	-	-	-	-	0.34	-
MoC ₂ ⁺ (%)	55	-	-	-	-	-	3.1
SiC ₃ ⁺ (%)	64	-	-	-	-	0.15	-
Total		100	100	100	100	100	100

^aVoltage pulsing.

^bPartly also C₄²⁺.

^cOverlap with Ti²⁺.

Table 4. Isotope ratios and carbon concentration obtained using only ^{13}C for C^+ and C^{2+} compared to the result obtained using standard evaluation and the expected concentration. In the case of $\text{Ti}(\text{C},\text{N})$ a correction of the 24 Da peak was also made [11].

	Ti(C,N)	Ti ₂ AlC	WC	WC ^a	SiC	M ₂₃ C ₆
$^{13}\text{C}^{2+} / ^{12}\text{C}^{2+}$ (%) (1.08 ± 0.08 expected) ^b	1.65	1.62	1.21	1.34	-	1.87
$^{13}\text{C}^+ / ^{12}\text{C}^+$ (%) (1.08 ± 0.08 expected) ^b	1.73	2.16	1.25	1.19	-	1.44
Standard method (%)	26.6	19.9	47.1	46.2	45.3	17.3 ^c
^{13}C -method (%)	29.6	26.2	48.9	50.1	-	20.4 ^c
^{13}C and 24 Da correction [11]	31.6	-	-	-	-	-
Expected (%)	33.1	25 ^d	50	50	50	20.7

^aVoltage pulsing.

^bBackground corrected counts.

^cIncluding 2.1% B.

^dIncluding N and O.

Figure caption

Figure 1. Mass spectrum of SiC displaying wide peak tails. a) Entire spectrum. b) Lower part of spectrum. The peak shape is composed of a sharp peak at the correct position and a broad tail displaced towards higher mass-to-charge ratios (longer flight-times). Note the small boron peaks at 5, 5.5, 10 and 11 Da.

Figure 2. Mass spectrum of WC. a) Laser pulsed. b) Voltage pulsed. The mass spectra are similar. The mass resolution is slightly better in the voltage pulsed analysis. The C^{3+} peak at 4 Da is larger when using voltage pulsing. Note the high signal-to-noise ratio of the ^{13}C peaks at 6.5 and 13 Da.

Figure 3. Mass spectra constructed using single and multiple events, respectively, from Ti(C, N) obtained using a laser pulse energy of 0.2 nJ. The amount of carbon is significantly larger in the multiple spectrum. Detailed mass spectra of this analysis can be found in Angseryd et al. [11].

Figure 1.

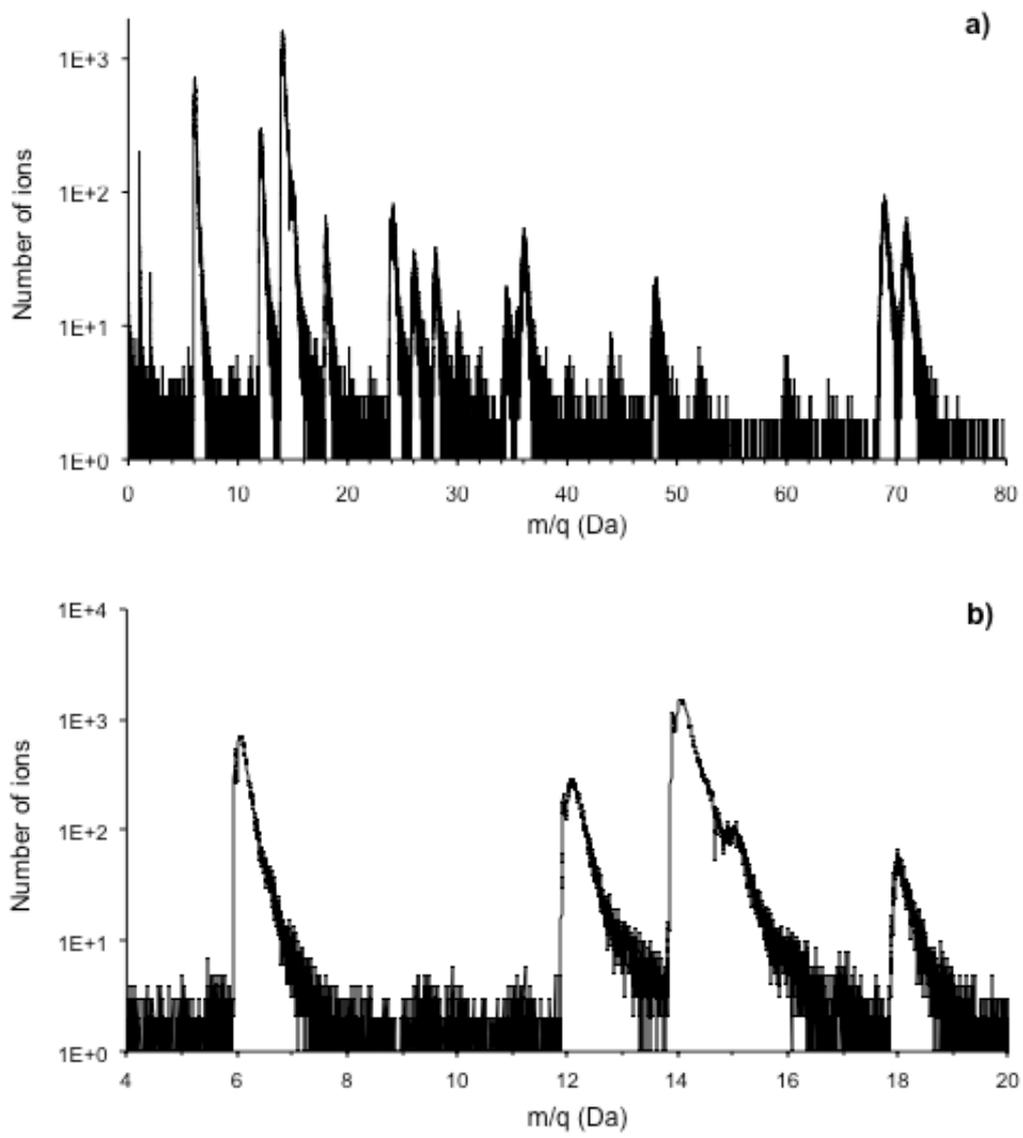


Figure 2.

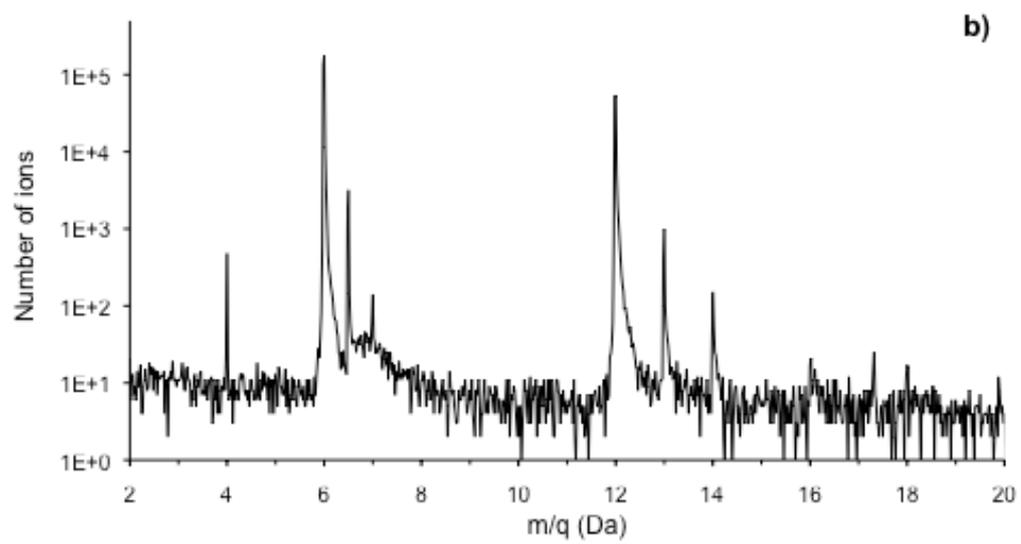
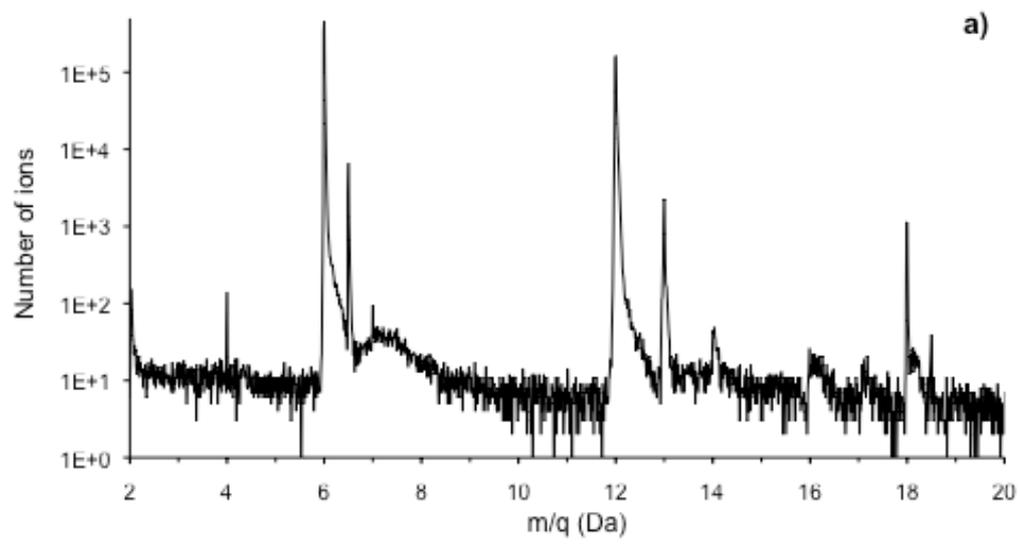


Figure 3.

