

Hyphenation of On-line EC-ESI-TOF-MS: An Analytical Method for Monitoring FAME Oxidation

Waraporn Ratsameepakai¹, Christianne Wicking¹, Julie Herniman¹, Simon Lambert², G. John Langley¹

¹School of Chemistry, Faculty of Natural and Environmental Sciences, University of Southampton, United Kingdom

²ARC Sciences LTD, Alton, United Kingdom

Introduction

Biodiesel has been used as alternative energy because of the shortage of petroleum fuel resources. Unlike conventional fuel, the nature of biodiesel (FAMEs) makes it more sensitive to oxidation during long term storage. Oxidation products can be formed such as peroxides, hydrogen peroxides and polymers. These compounds may lead to deposits and coking in vehicles. Electrochemical (EC) oxidation has been applied as a surrogate system for monitoring oxidation in very short time (~10 minutes). The EC cell is directly coupled to ESI-TOF-MS for identification of products generated in the electrochemical cell. The purpose of this project is to monitor EC oxidation products of FAMEs.

Method

Electrochemical reaction is based on applying a potential to the auxiliary and working electrodes.

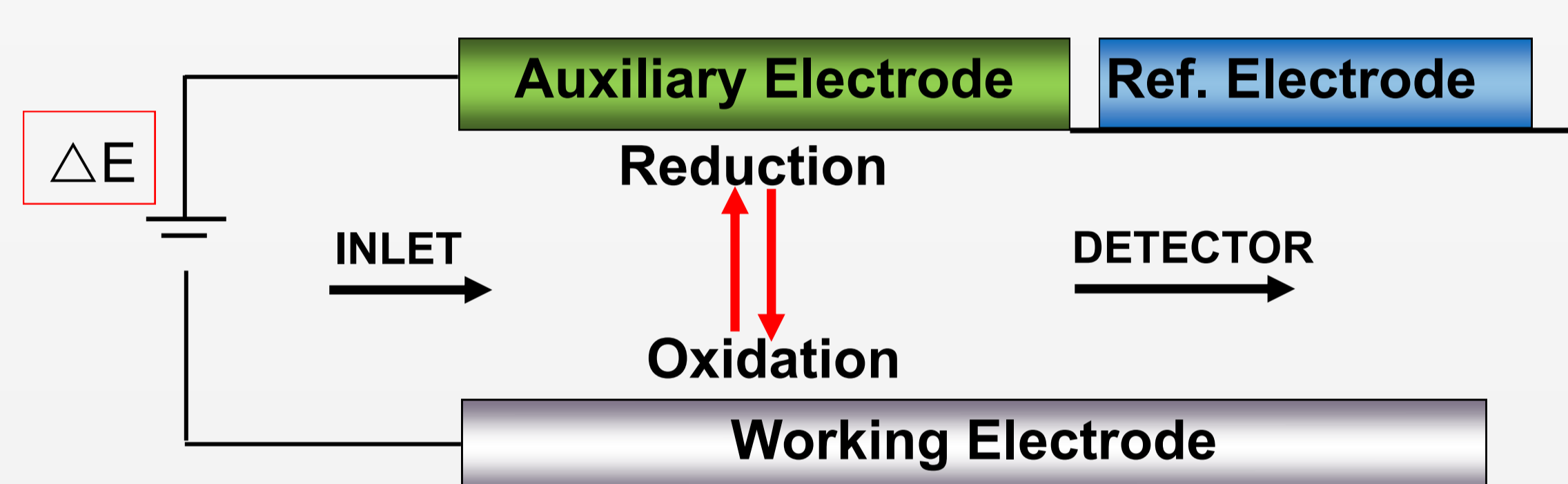


Figure 1. Electrochemical reaction¹.

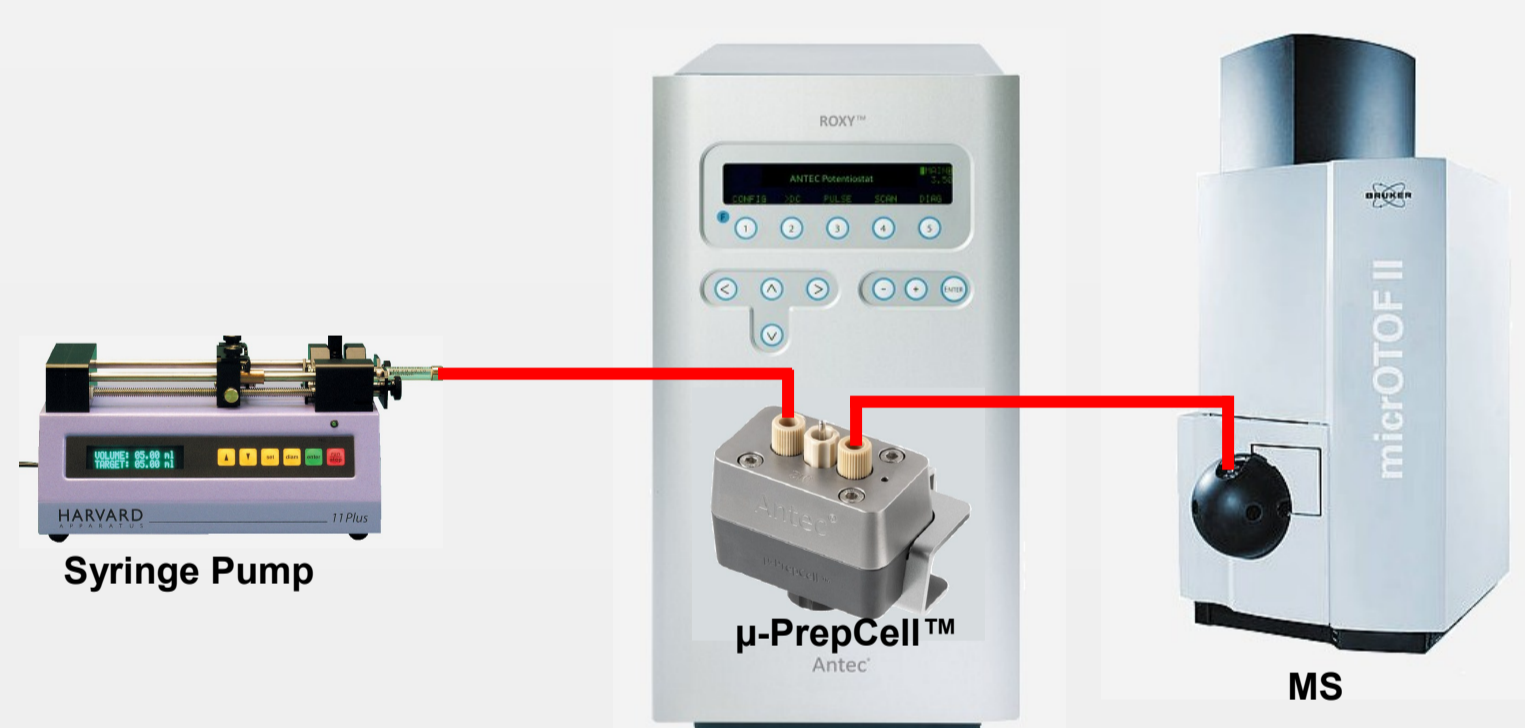


Figure 2. Instrument configuration of on-line ROXY™ EC system (Antec) coupled with mass spectrometer (adapted)^{1,2}.

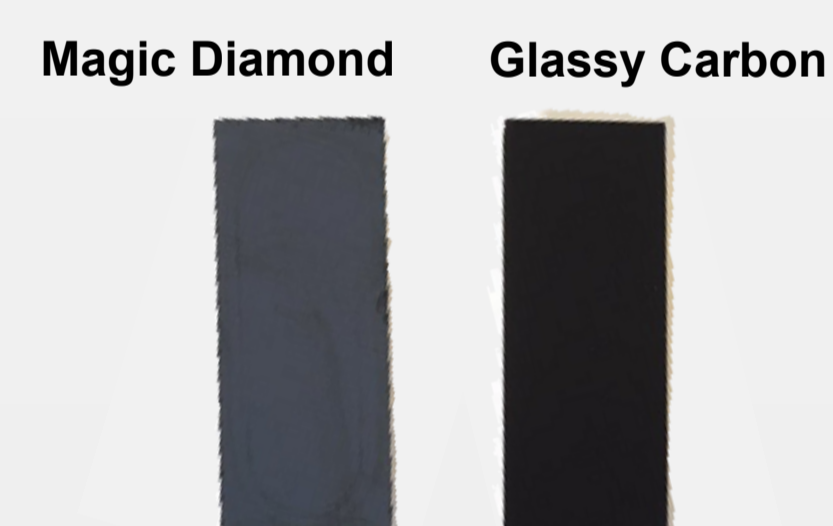


Figure 3. Working electrodes¹.

Table 1. Electrochemical Parameters

Parameter	Value
EC Mode	DC
Reference Electrode	HyREF™ (Pd/H ₂)
Auxiliary Electrode	Titanium
Working Electrode	Glassy Carbon (GC) and Magic Diamond™ (MD)
E cell Potential	500-2500 mV for GC 500-3000 mV for MD
Flow rate	10 μL/min
Solvent	Methanol with Water 10% v/v
FAME standards	Methyl oleate (C18:1), Methyl linoleate (C18:2), Methyl linolenate (C18:3)

Table 2. Mass Spectrometer Parameters

Parameter	Value	Parameter	Value
Ionisation	Electrospray	Nebuliser	1.0 Bar
Ion polarity	Positive ion	Drying gas	4.0 L/min
Mass range	50-1200 <i>m/z</i>	Drying temperature	200 °C
Capillary voltage	-4000 V	Funnel RF	200 Vpp
IS-CID Energy	30 eV	Quadrupole ion energy	4.0 eV

References

- Antec. *Electrochemistry upfront MS*. Available from <http://www.myantec.com/downloads/tutorials/ppt/EC-MS.ppt#35719slide19>. [accessed 17/03/2012].
- Antec. *μ-PrepCell™ User manual 204.0010, Edition 4, 2011*. Available from <http://www.myantec.com/support/docs-and-downloads/user-manuals>. [accessed 05/04/2012].

Results

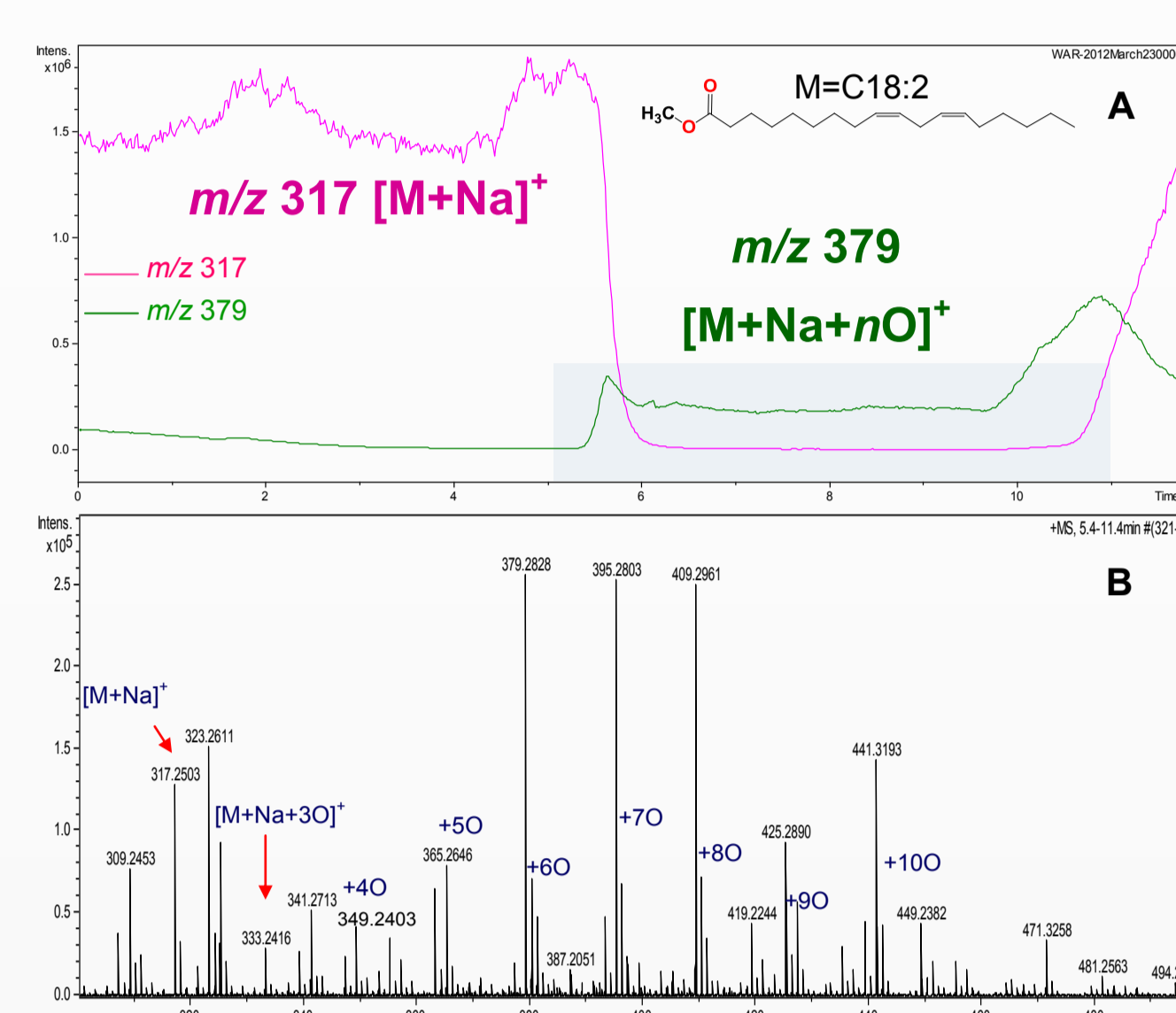


Figure 4 (A): EICs of the sodiated C18:2 (*m/z* 317) and example of their oxidation product (*m/z* 379). (B): Mass spectrum corresponding to the blue area of EICs from A.

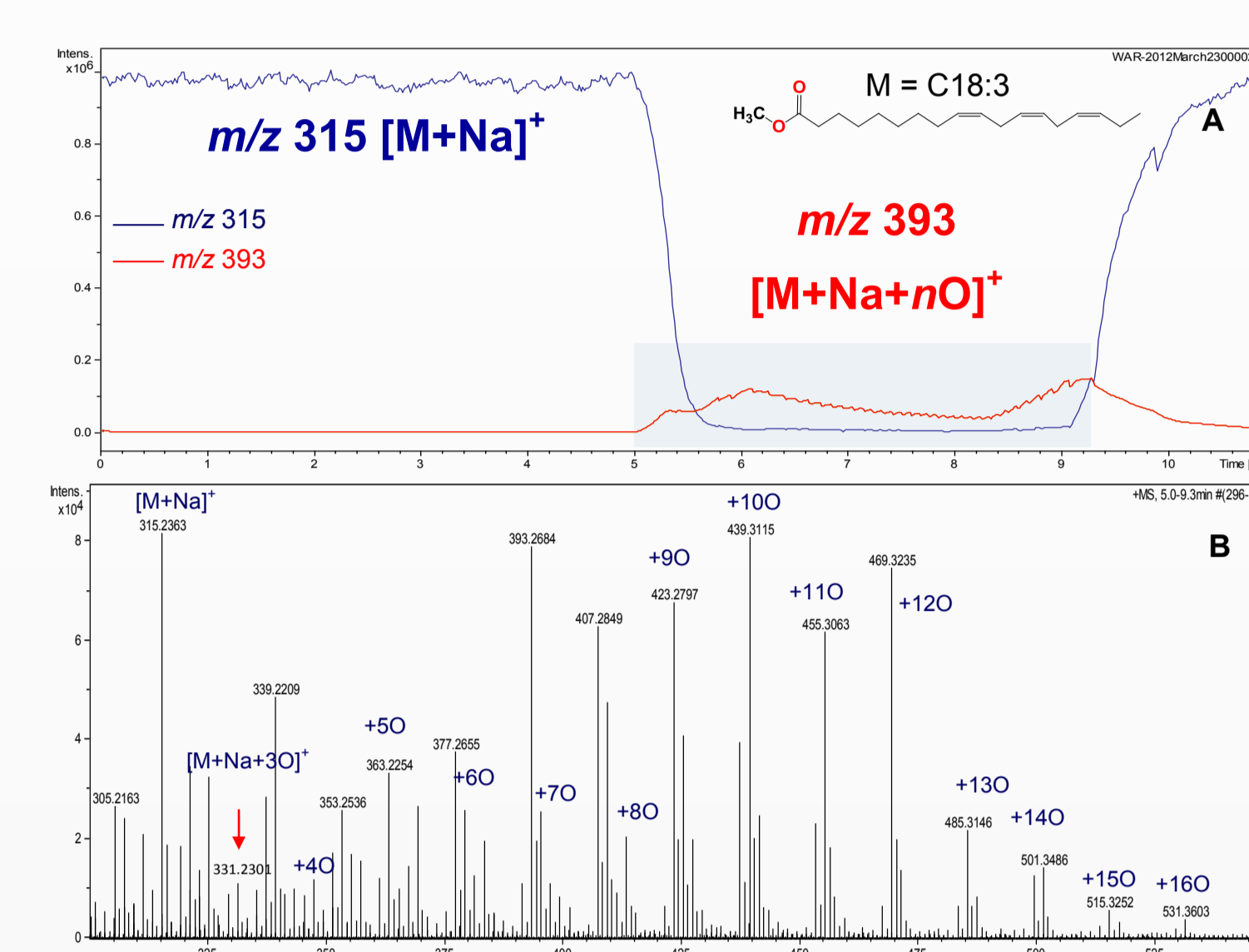


Figure 5 (A) EICs of the sodiated C18:3 (*m/z* 315) and example of their oxidation product (*m/z* 393). (B): Mass spectrum corresponding to the blue area of EICs from A.

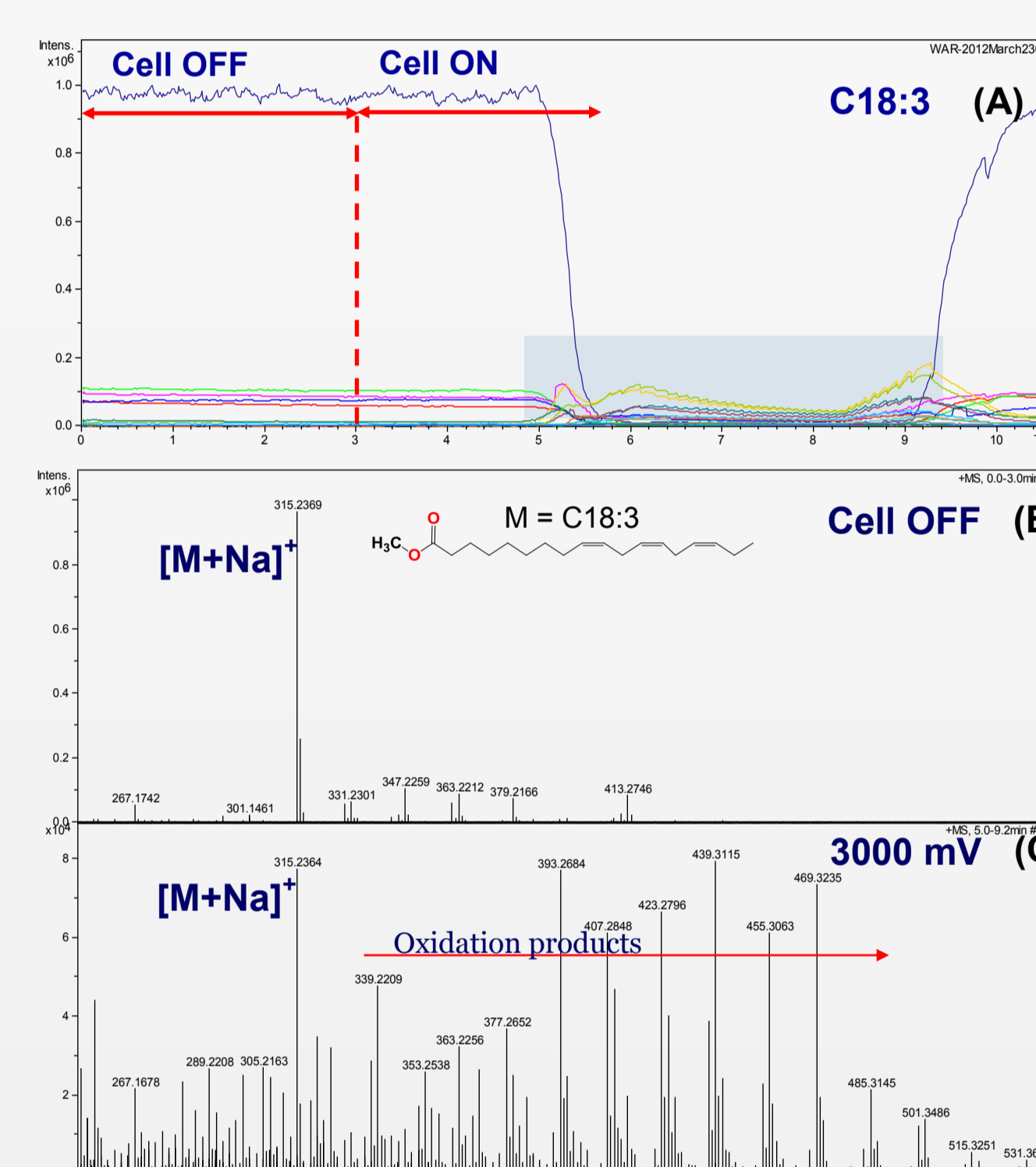


Figure 6. (A): EICs of C18:3 and their oxidation products. (B): Mass spectrum with cell OFF. (C): Mass spectrum corresponding to the blue area of EICs from A. (Magic Diamond electrode).

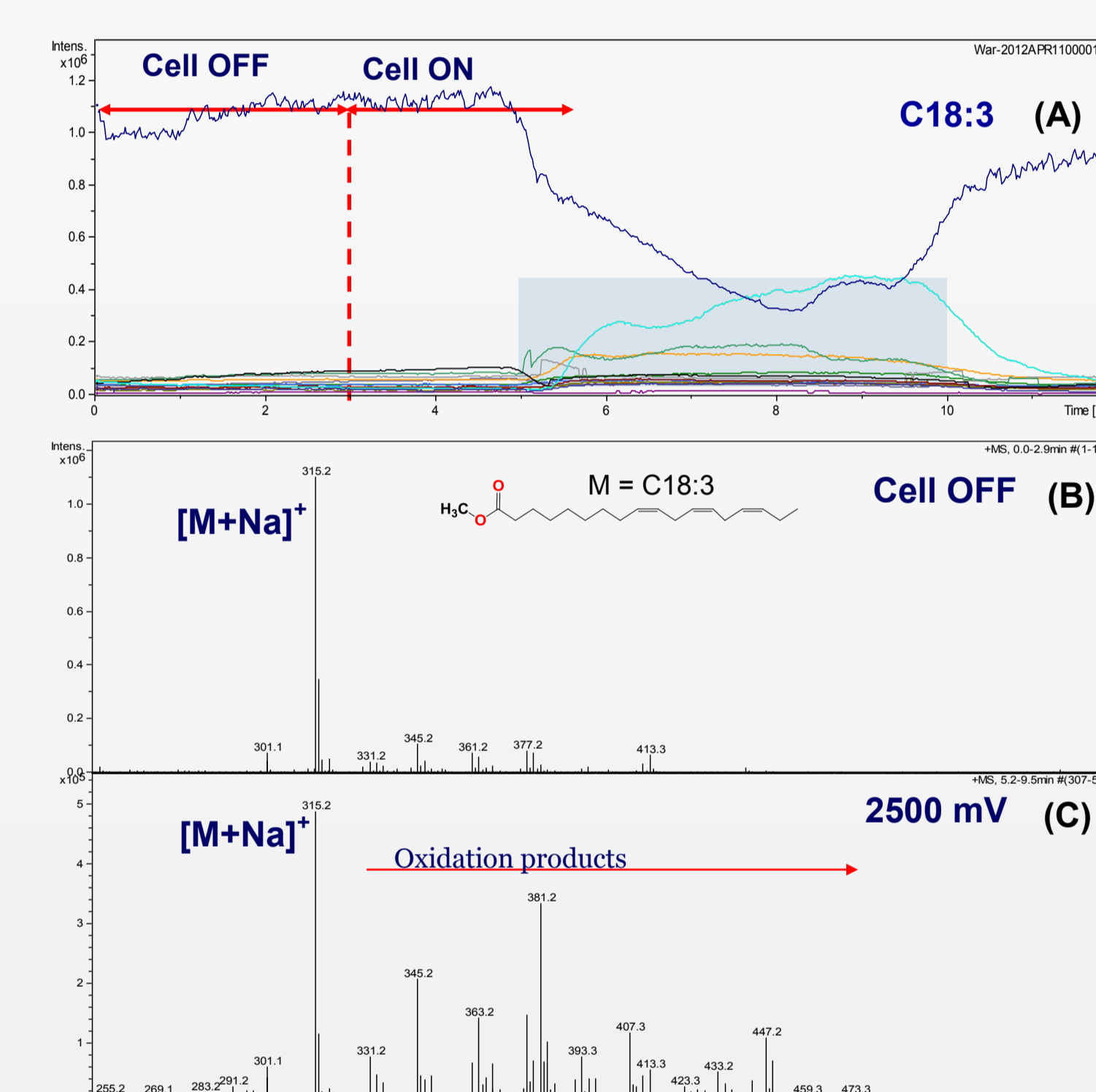


Figure 7. (A): EICs of C18:3 and their oxidation products. (B): mass spectrum with cell OFF. (C): Mass spectrum corresponding to the blue area of EICs from A. (Glassy Carbon electrode).

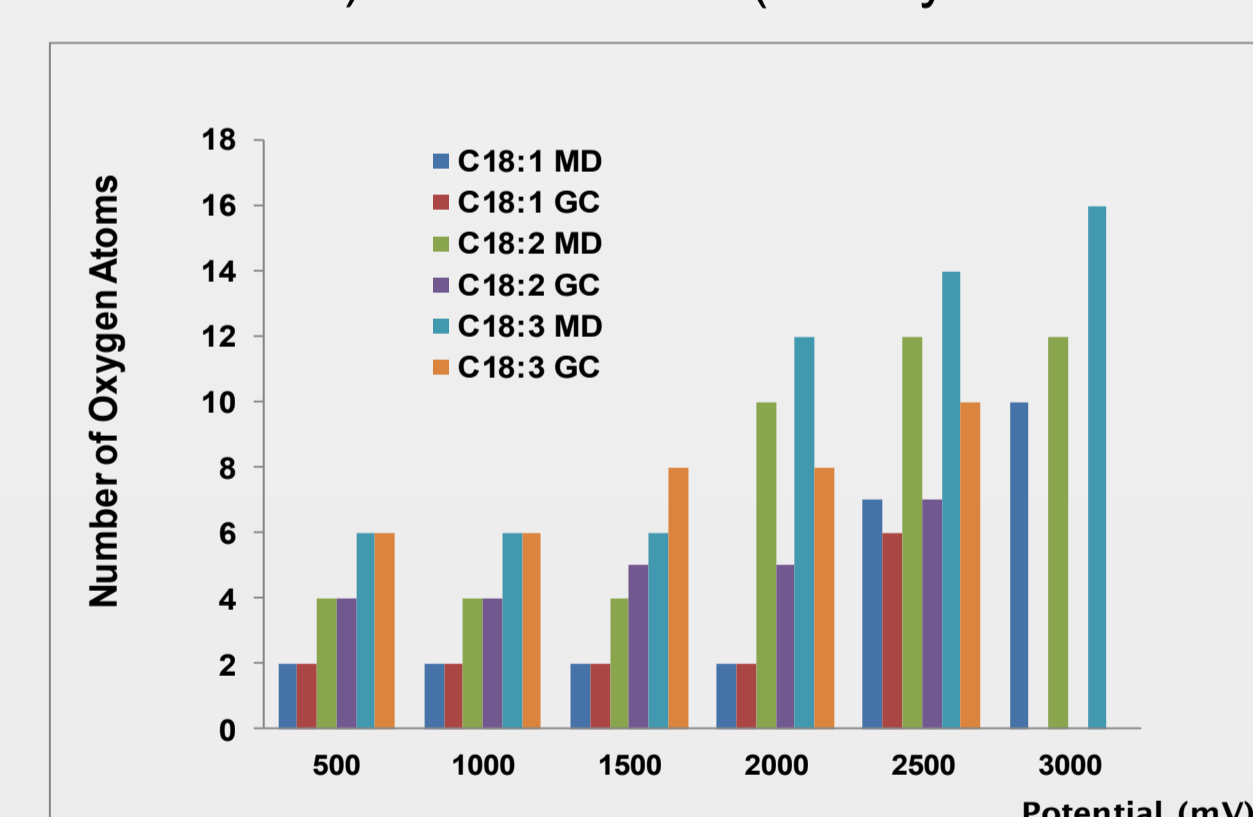


Figure 6. FAME + number of oxygen atoms were obtained from MD and GC electrodes;

The efficiency of GC and MD electrodes was compared. Increasing the potential in the GC electrode up to 2500 mV generated oxidation products of C18:1, C18:2 and C18:3 with up to +6O, +7O, and +10O, respectively, whereas the maximum number of additional oxygen atoms for C18:1, C18:2 and C18:3 up to +10O, +12O, and +16O respectively were obtained from the MD electrode at 3000 mV. Both electrodes well suited for generating FAME oxidation products with the MD electrode affording higher oxidation products cf. the GC electrode. The potentials of oxidation increased in the order methyl esters of C18:3 < C18:2 < C18:1 for both MD and GC electrodes.

Conclusions

EC-ESI-TOF-MS has proved to be an excellent technique for monitoring oxidation in FAME within short time period (~10 minutes), without pre-treatment of samples and no need for separation.

Acknowledgement

We acknowledge the Royal Thai Government for financially supporting this study.