Microsaic Systems

On-line batch reaction monitoring using the Microsaic 4000 MiD® mass spectrometer

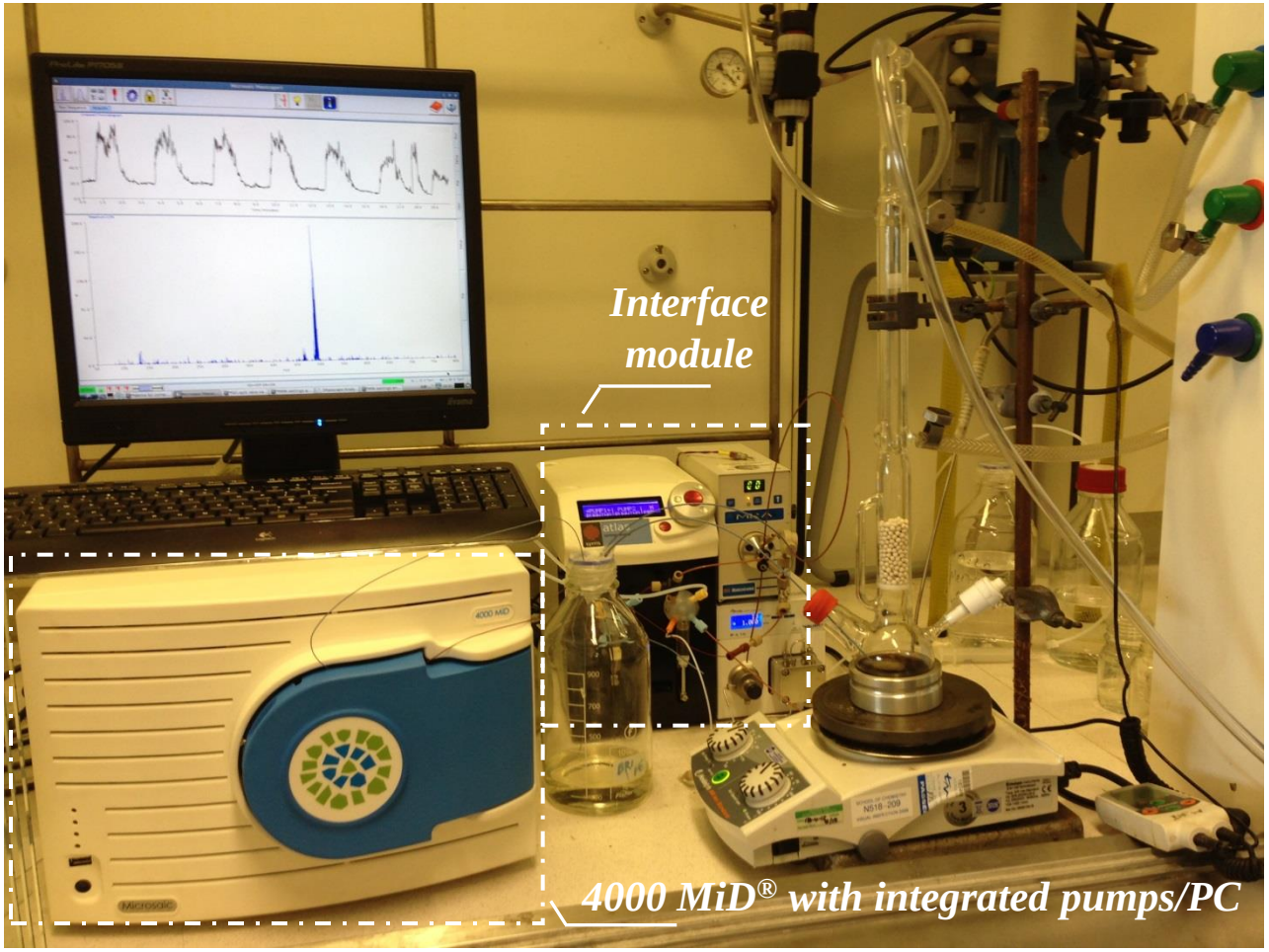
Introduction

- Microsaic Systems set up the new 4000 MiD® mass spectrometer at Bristol University to demonstrate the benefits of using on-line reaction monitoring for reactions in batch and flow mode
- The catalytic conversion of ethanol to an advanced biofuel was carried out at Bristol University in collaboration with Prof. Duncan Wass and Dr. Richard Wingad

Aims of the evaluation:

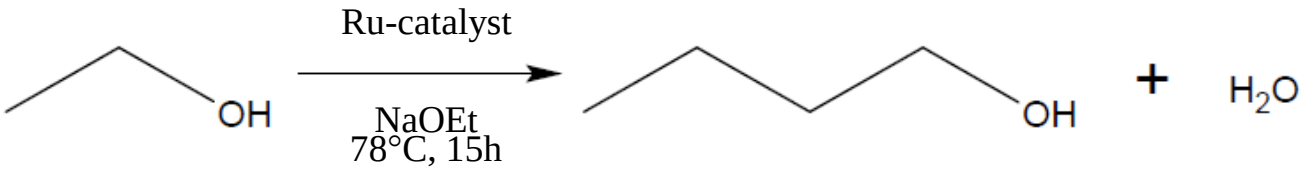
- Obtain more information than conventional off-line method
- Generate instant data reducing sample clean up and off-line analysis associated down times
- Demonstrate the simplicity of setting up on-line reaction monitoring using Microsaic 4000 MiD®
- Overcome reaction solvents incompatibility with conventional MS systems

Experimental set-up for on-line batch reaction monitoring



Monitoring of the catalytic conversion of ethanol into *n*-butanol has been carried out by coupling the Microsaic 4000 MiD® to a three neck round bottom flask under inert atmosphere (N_2) through an interface module

Monitoring the catalytic conversion of ethanol into advanced biofuel using the Microsaic 4000 MiD® mass spectrometer



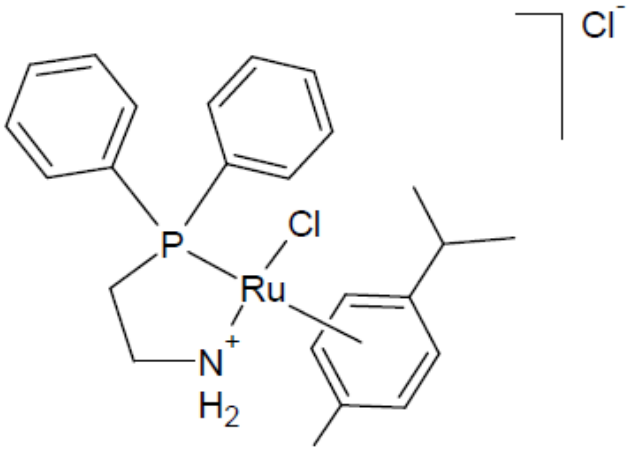
Ruthenium catalysed conversion of ethanol into *n*-butanol

Ruthenium catalyst

Concentration: 12 mg/ml in ethanol

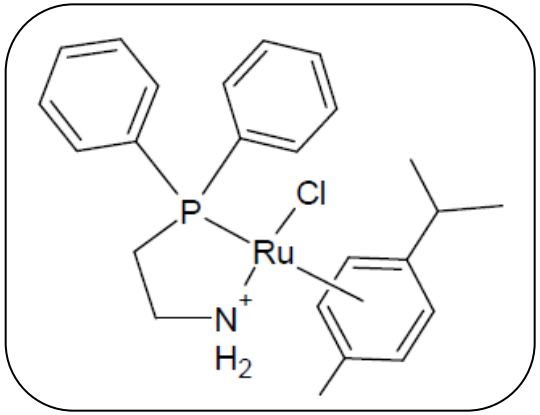
Chemical formula: $C_{24}H_{30}NCl_2PRu$

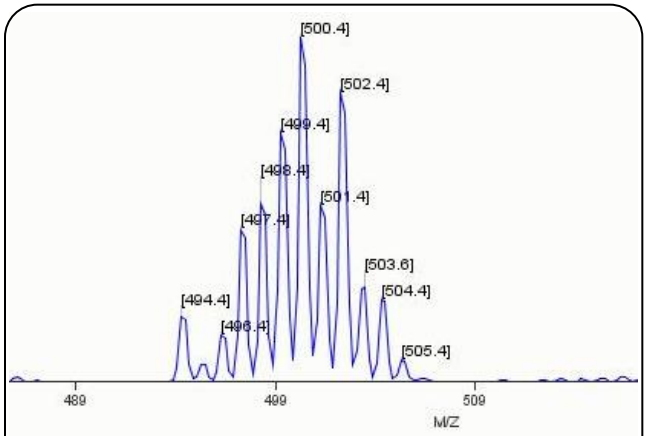
MW: 535.5 g/mol



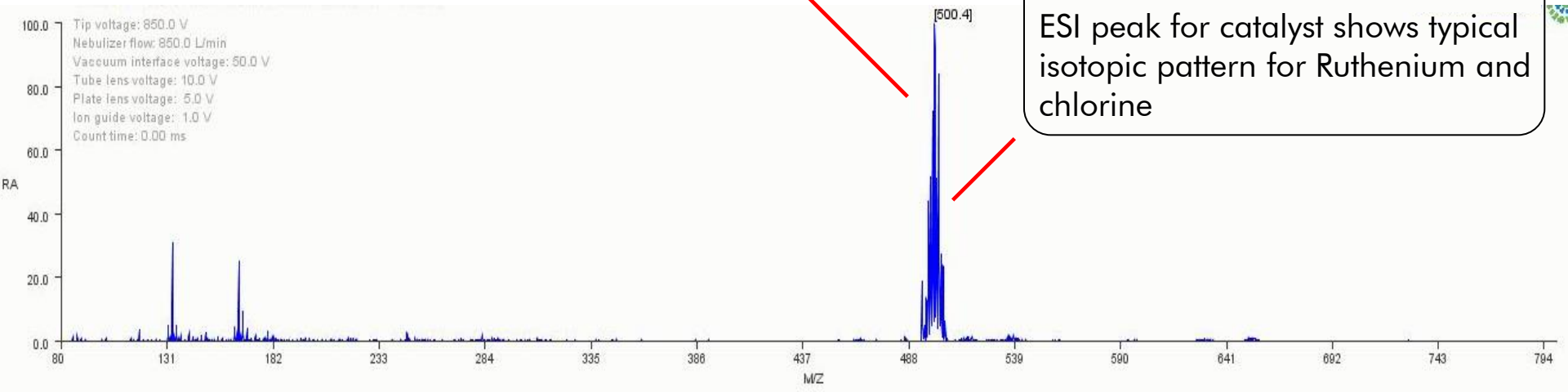
Full scan mass spectrum of ruthenium catalyst in positive ESI before NaOEt addition

Ruthenium catalyst positive ion with loss of chlorine at *m/z* 500.4

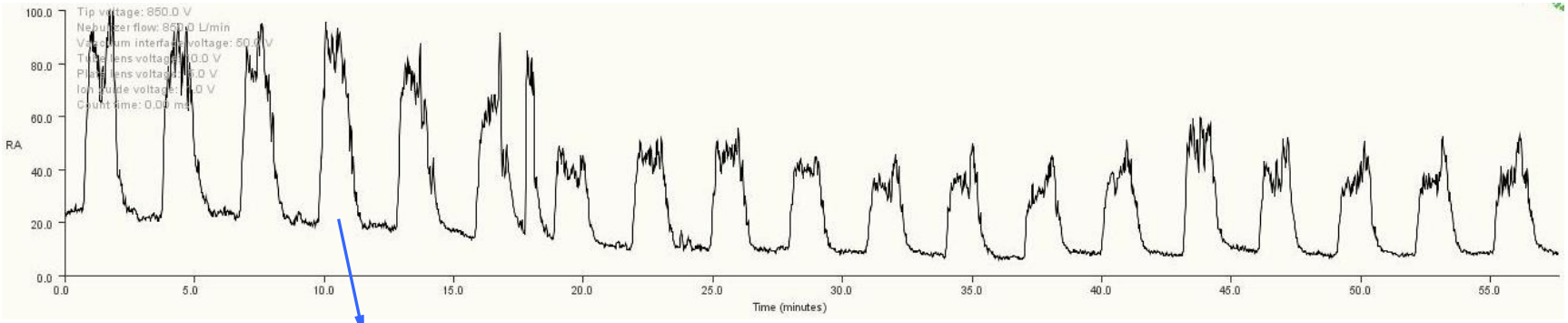


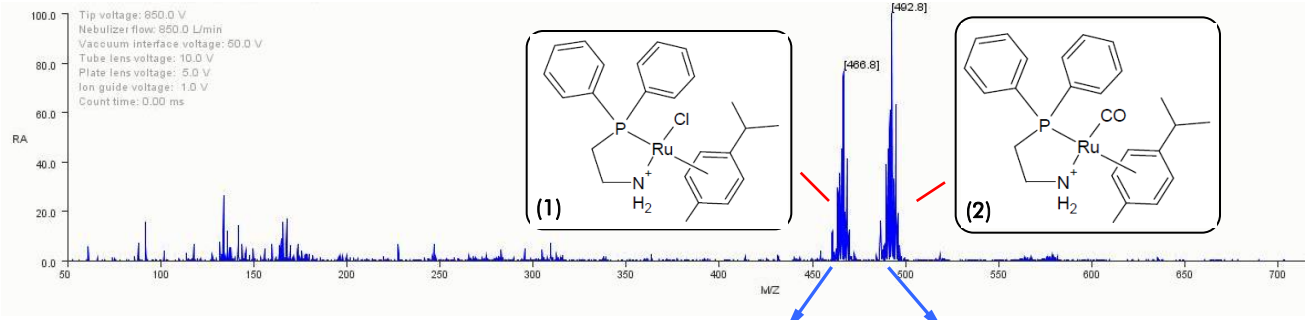


ESI peak for catalyst shows typical isotopic pattern for Ruthenium and chlorine

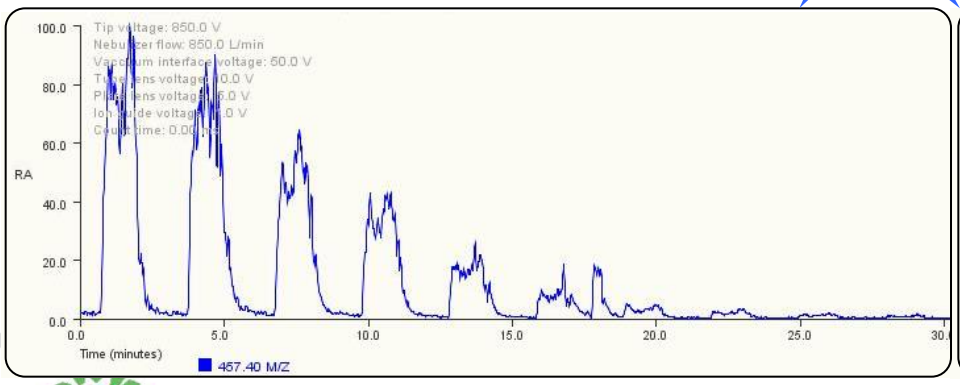


TIC for the ruthenium catalysed conversion acquired in full scan with a sampling rate of ~ 5 min

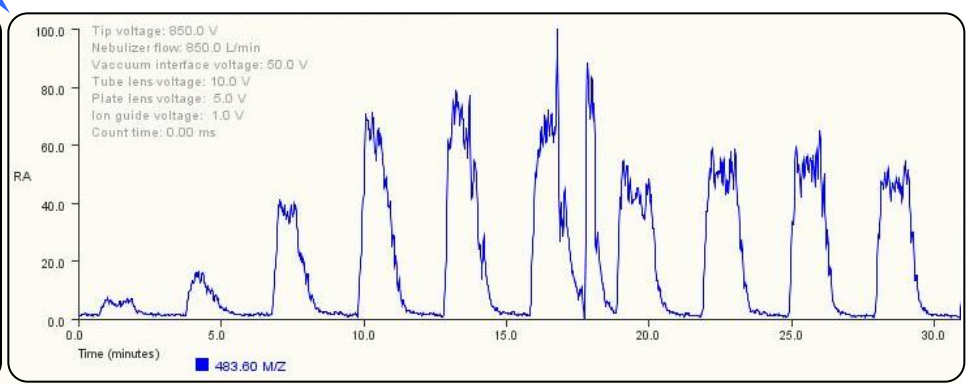




Mass spectrum generated from peak at 10 min. Ru-catalyst reacts with NaOEt to give (1), which is converted over time to (2).

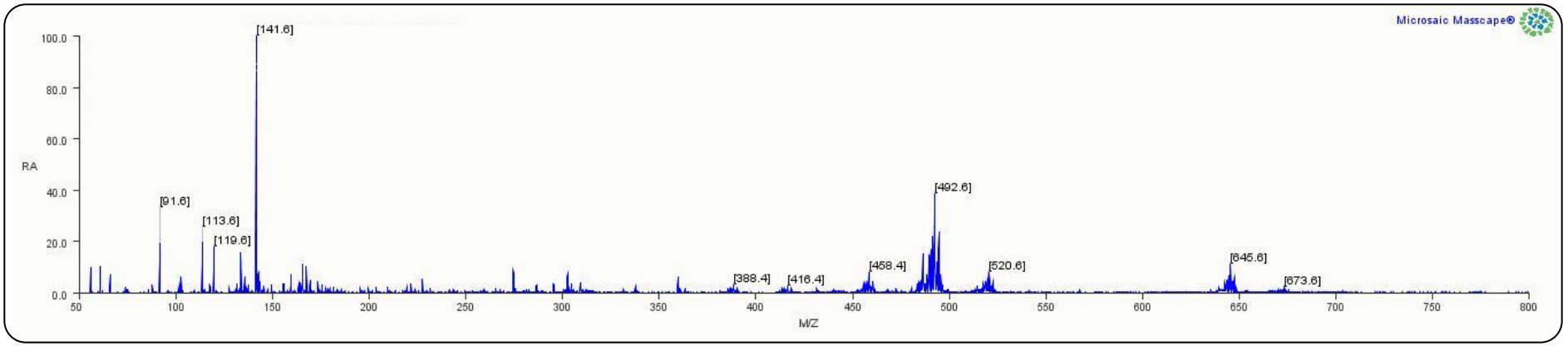


Extracted ion chromatogram of species (1) *m/z* 466.8



Extracted ion chromatogram of species (2) *m/z* 492.8

Mass spectrum for ruthenium catalysed conversion after 15 hrs of analysis



Product species generated after 15 hours reaction at 78 °C:

- *m/z* 91.6 $(C_4H_{11}O_2)^+$
- *m/z* 113.6 $(C_4H_{10}O_2Na)^+$
- *m/z* 119.6 $(C_6H_{15}O_2)^+$
- *m/z* 141.6 $(C_6H_{14}O_2Na)^+$

$C_4H_6O_2$ is 1-ethoxyethan-1-ol
$C_4H_6O_2$ is 1,1-ethoxyethane
$C_4H_{11}O_2$ is 1,3 butandiol

Catalyst species generated after 15 hours reaction at 78 °C:

- m/z 388.4 $[Ru(Ph_2PCH_2CH_2NH_2)(CO)_2H]^+$
- m/z 416.4 $[Ru(Ph_2PCH_2CH_2NH_2)(CO)_3H]^+$
- m/z 458.4 $[Ru(Ph_2PCH_2CH_2NH_2)(CO)_3CH_3CHO]^+$
- *m/z* 520.6 $[Ru(Ph_2PCH_2CH_2NH_2)(cymene)CO_2]^+$
- *m/z* 645.6 $[Ru(Ph_2PCH_2CH_2NH_2)_2(C_4H_6O_2)]^+$
- *m/z* 673.6 $[Ru(Ph_2PCH_2CH_2NH_2)_2(C_4H_6O_2)(CO_2)]^+$

Benefits of on-line batch reaction monitoring using Microsaic 4000 MiD® reported by Dr. Richard Wingad

Did Bristol University achieve the aims of the evaluation?

- Observed previously unseen catalyst species where NMR and other off-line MS techniques gave none or limited data
- Sample analysed instantly rather than sent as a batch to the centralised MS service
- No sample clean up required prior to analysis
- From initial experimental set up to data acquisition in less than 1 hour
- Full compatibility with all common reaction solvents

Summary of using Microsaic 4000 MiD® for on-line flow reaction monitoring

- Provides the 'gold standard' of analytical chemistry for real-time reaction monitoring.
- Less time consuming than conventional off-line analysis without the associated costs in money and time.
- Real-time analysis of the reaction material, enabling transformation optimisation, improved yield, purity and reaction selectivity.
- Determine reactions steady state condition and monitor the presence of transient and reactive intermediates.
- Electrospray source and vacuum interface easily removed and cleaned with less than 1 hour downtime.
- Less than 20 μL reaction mixture consumed per sample
- Easily deployable into a fume hood next to the batch reactor system.

*http://www.purdue.edu/discoverypark/caid/programs/mms.php

Contact details

- Microsaic systems

Jeremy Reddish
E: jreddish@microsaic.com
M: 07808 645810
W: microsaic.com

- University of Bristol

Richard Wingad
E: Rich.Wingad@bristol.ac.uk