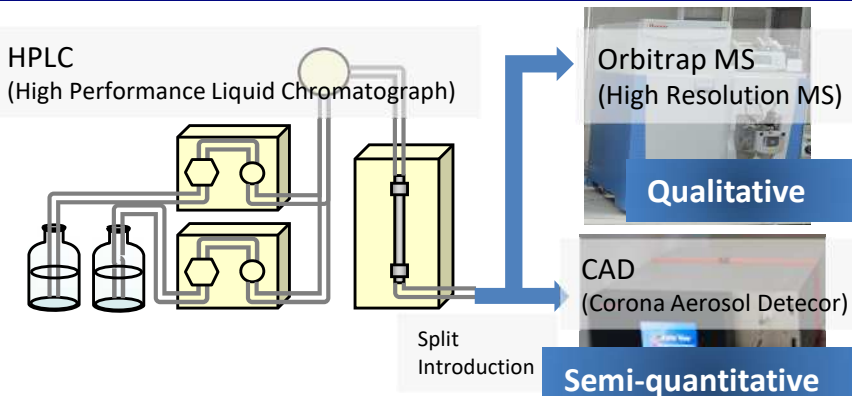# Simultaneous Qualitative and Semi-Quantitative analysis of Trace Compounds by LC/HRMS, CAD

LC/HR (High Resolution) MS and MS/MS are effective for structural analysis of unknown components. CAD (Corona Aerosol Detector), have chemical structure-independent sensitivity, is effective for semi-quantitative analysis of unknown components. Combined with our chromatographic separation technology, simultaneous qualitative and semi-quantitative analysis have become possible.

Equipment configuration for simultaneous analysis using LC/HRMS and LC/CAD (simultaneous qualitative and semi-quantitative analysis)

HPLC
(High Performance Liquid Chromatograph)

Orbitrap MS
(High Resolution MS)

Qualitative

CAD
(Corona Aerosol Detecor)

Split Introduction

Semi-quantitative
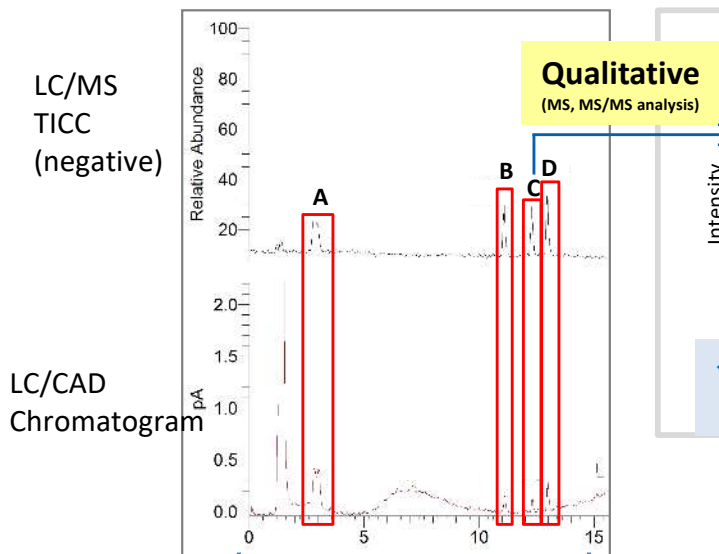
[Cases of simultaneous analyses by LC/HRMS, CAD]
- ✓ Additive degradants, discoloring compounds in the polymer
- ✓ Composition analysis (in the Reverse engineering; difficult to obtain the standard)
- ✓ Trace contaminants adhering to fibers and films
- ✓ Polymer-derived elutes into solvents

Semi-quantitative determination of unknown components (boiling point 350°C or higher) without using the same compound as the standard. Detection limit: About several ug/mL (about several ng) in the measurement solution
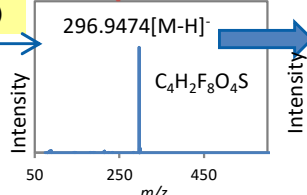
Analytical cases (qualitative and semi-quantitative analysis of polymer degrades)

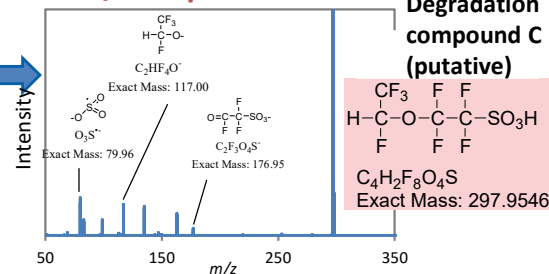Chromatogram of sample solution

LC/MS TICC (negative)

LC/CAD Chromatogram

Sample: Solvent extracted fuel cell electrolyte membrane (Nafion) after operation

Qualitative
(MS, MS/MS analysis)

MS spectrum

$296.9474[M-H]^-$

$C_4H_2F_8O_4S$

MS/MS spectrum

CF_3
$H-C-O-$
$C_2HF_4O^-$
Exact Mass: 117.00

$^-O-\overset{O}{\underset{O}{S}}O$
O_3S^-
Exact Mass: 79.96

$O=\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-SO_3^-$
$C_2F_3O_4S^-$
Exact Mass: 176.95

Degradation compound C (putative)

$CF_3 \quad F \quad F$
$H-C-O-C-C-SO_3H$
$F \quad F \quad F$

$C_4H_2F_8O_4S$
Exact Mass: 297.9546

✓ **Estimate the structure of degradation compounds from high-resolution mass spectra**

Semi-quantitative of degradants by LC/CAD

(Semi-quantitation with alternative standards)

(μg/g)

Degradation compound A

$H \quad CF_3 \quad F \quad F$
$HO-C-C-O-C-C-SO_3H$
$H \quad F \quad F \quad F$
$C_5H_4F_8O_5S$
Exact Mass: 327.9652 **B**

$CF_3 \quad F \quad F$
$H-C-O-C-C-SO_3H$
$F \quad F \quad F$
$C_4H_2F_8O_4S$
Exact Mass: 297.9546 **C**

$H \quad CF_3 \quad F \quad F$
$H-C-C-O-C-C-SO_3H$
$H \quad F \quad F \quad F$
$C_5H_4F_8O_4S$
Exact Mass: 311.9703 **D**

* All putative structure

$CF_3 \quad F \quad F$
$HOOC-C-O-C-C-SO_3H$
$F \quad F \quad F$
$C_5H_2F_8O_6S$
Exact Mass: 341.9444 **A**

Membrane before / Membrane after

[Semi-quantitation results (LC/CAD) of polymer-degraded components]

✓ **Degradation component A was found to be the main component of decomposed products**

[Analysis results of polymer degradation components]

Nafion (Polymer structure)

$F-C-O-CF_2CF_2-SO_3^- H^+$
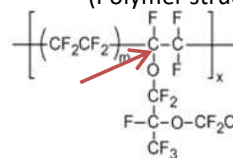
Multiple side-chain-derived components were detected from Nafion membrane in LC/HRMS

(*F^-, SO_4^{2-} were detected in IC)

It was presumed that hydrolysis is caused by the oxygen radical attack on the side chain ether (in addition to the elimination of fluorine and sulfonic acid) as the polymer decomposition mechanism.

Qualitative and semi-quantitative results of polymer degradation components enable consideration of deterioration mechanism

Toray Research Center, Inc.