

# Arsenolipids from Edible Seaweed by LC-ICP-MS and LC-ESI-MS

## Separation of arsenic species from methanolic extract of the edible seaweed *Alaria esculenta*

Arsenic-containing hydrocarbon:

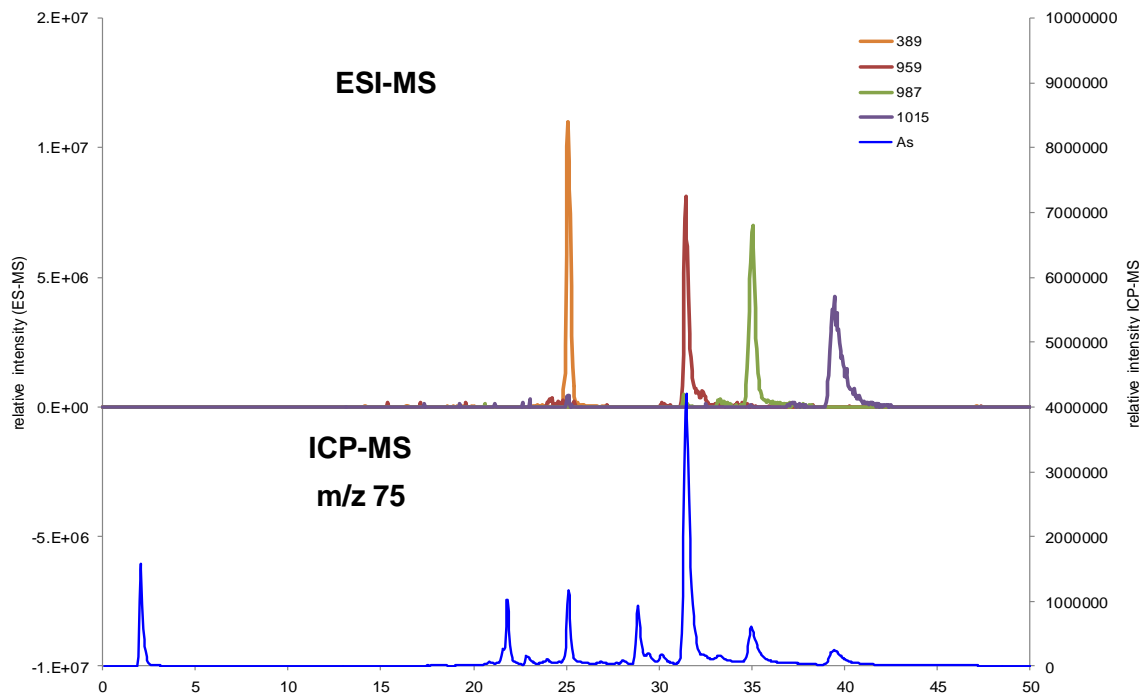
$m/z$  389 [M + H]<sup>+</sup> for C<sub>21</sub>H<sub>46</sub>AsO

Arsenic-containing phospholipids:

$m/z$  959 [M + H]<sup>+</sup> for C<sub>45</sub>H<sub>89</sub>AsO<sub>14</sub>P (C16:0/C16:0)

$m/z$  987 [M + H]<sup>+</sup> for C<sub>47</sub>H<sub>93</sub>AsO<sub>14</sub>P (C18:0/C16:0)

$m/z$  1015 [M + H]<sup>+</sup> for C<sub>49</sub>H<sub>97</sub>AsO<sub>14</sub>P (C20:0/C16:0)



ACE C18, 3 $\mu$ m 150 x 4.6mm

Gradient analysis

A = 0.1% formic acid in H<sub>2</sub>O

B = 0.1% formic acid in CH<sub>3</sub>OH

Time (mins)	%B
0	0
20	100
45	100

Flow rate: 1 ml/min

Injection volume: 100 $\mu$ l

Split ratio: 75% ESI-MS: 25% ICP-MS

Thermo Scientific Element 2 ICP-MS

Mode: Organic mode

Medium resolution

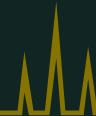
Thermo Scientific Orbitrap Discovery

Positive ESI mode

Spray voltage: 4.5kV

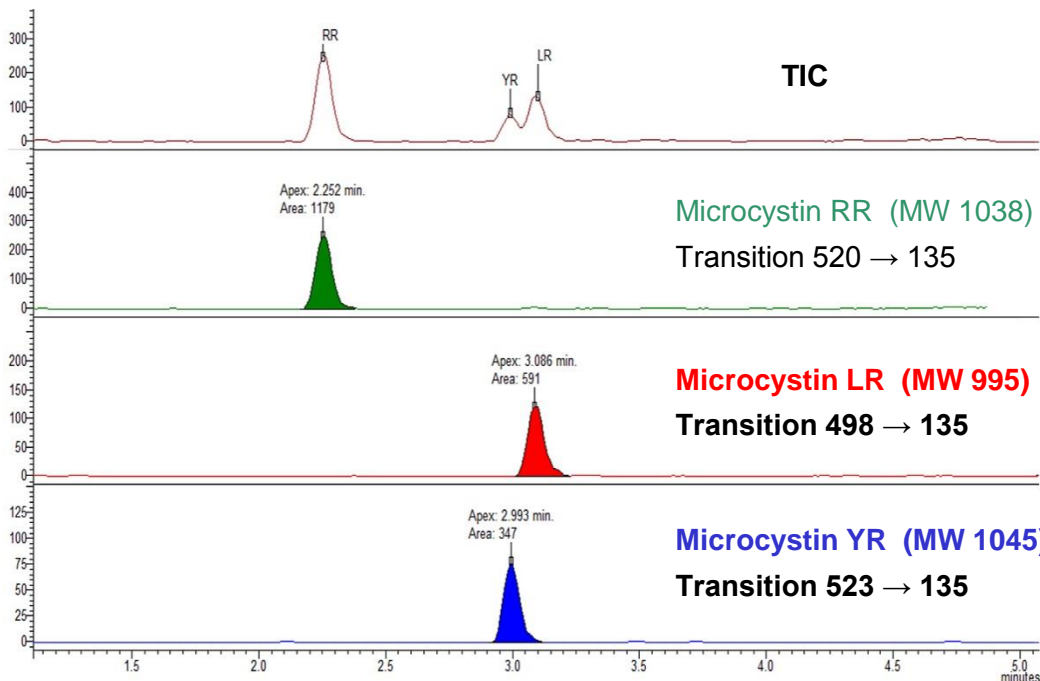
Capillary temperature: 320°C

Capillary voltage: 42V



# Microcystins From Blue/Green Algae In Drinking Water

ACE Excel 2  $\mu\text{m}$  C18, 100 x 2.1 mm



0.05 ppb each

Variants	R	L
MC-LR	Leucine	Arginine
MC-RR	Arginine	Arginine
MC-YR	Tyrosine	Arginine

Bruker Advance UHPLC system

ACE Excel 2  $\mu\text{m}$  C18, 100 x 2.1mm

Gradient elution

A = 0.1% formic acid in water

B = Acetonitrile

T (mins) %B T (mins) %B

0 30 7.1 30

1 30 10 30

7 95

Flow rate: 0.4mL/min

Column temperature: 40°C

Injection volume: 50  $\mu\text{L}$

Concentration each microcystin: 0.05ppb

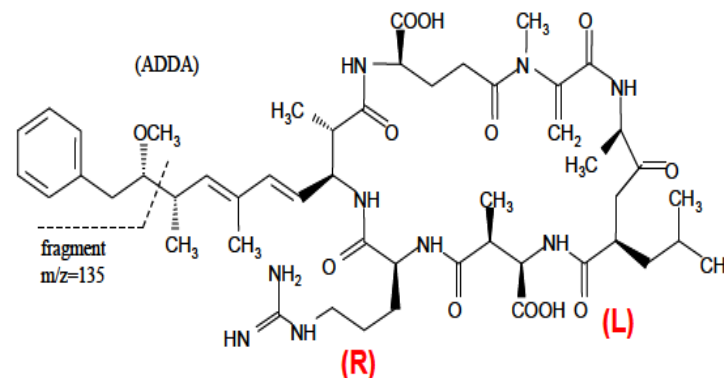
Bruker EVOQ Elite triple quad MS

VIP heated-ESI temperature: 350°C

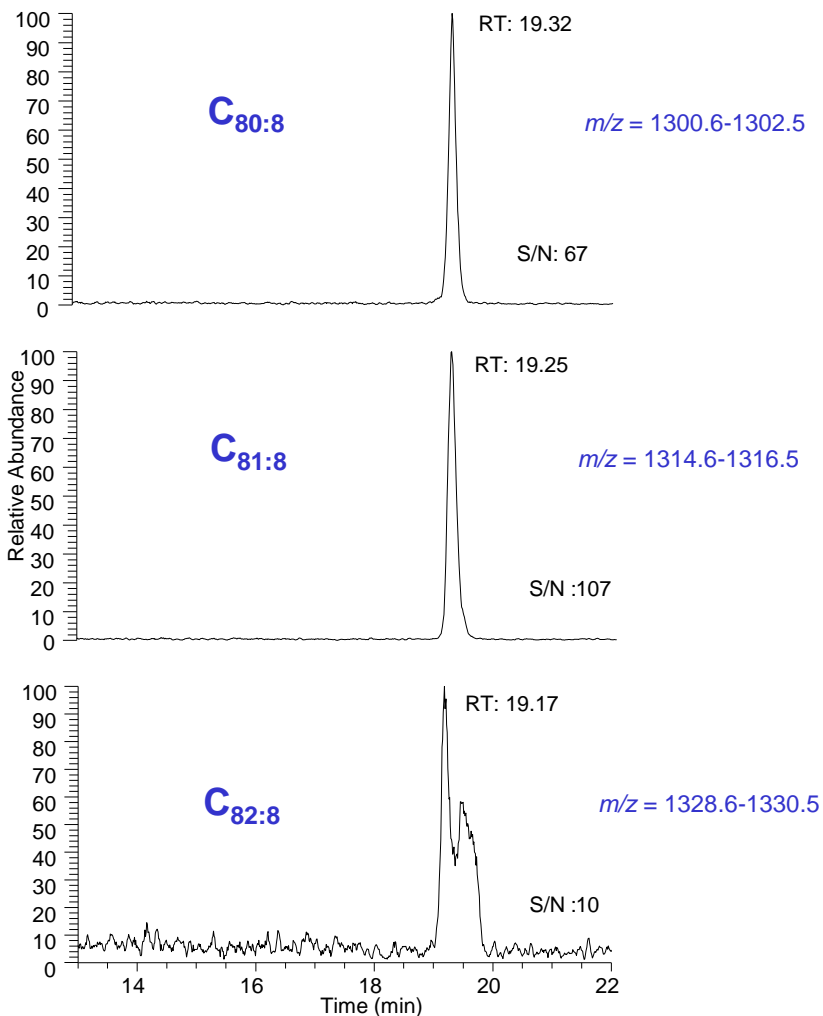
Cone gas temperature: 200°C

Spray voltage: 4500V (+)

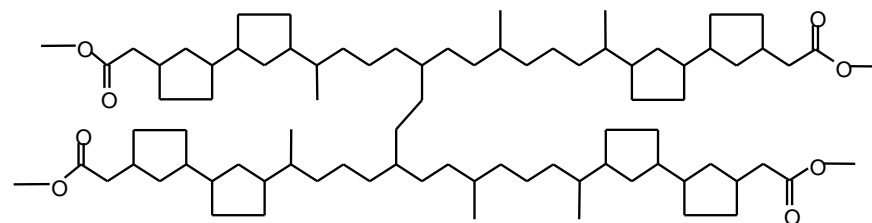
Collision gas: argon 1.5mTorr



# Polycyclic Tetracarboxylic Acids



C80-82 polycyclic tetracarboxylic acids isolated from oilfield deposits



**Tetramethyl ester of C<sub>80:8</sub> ring acid**

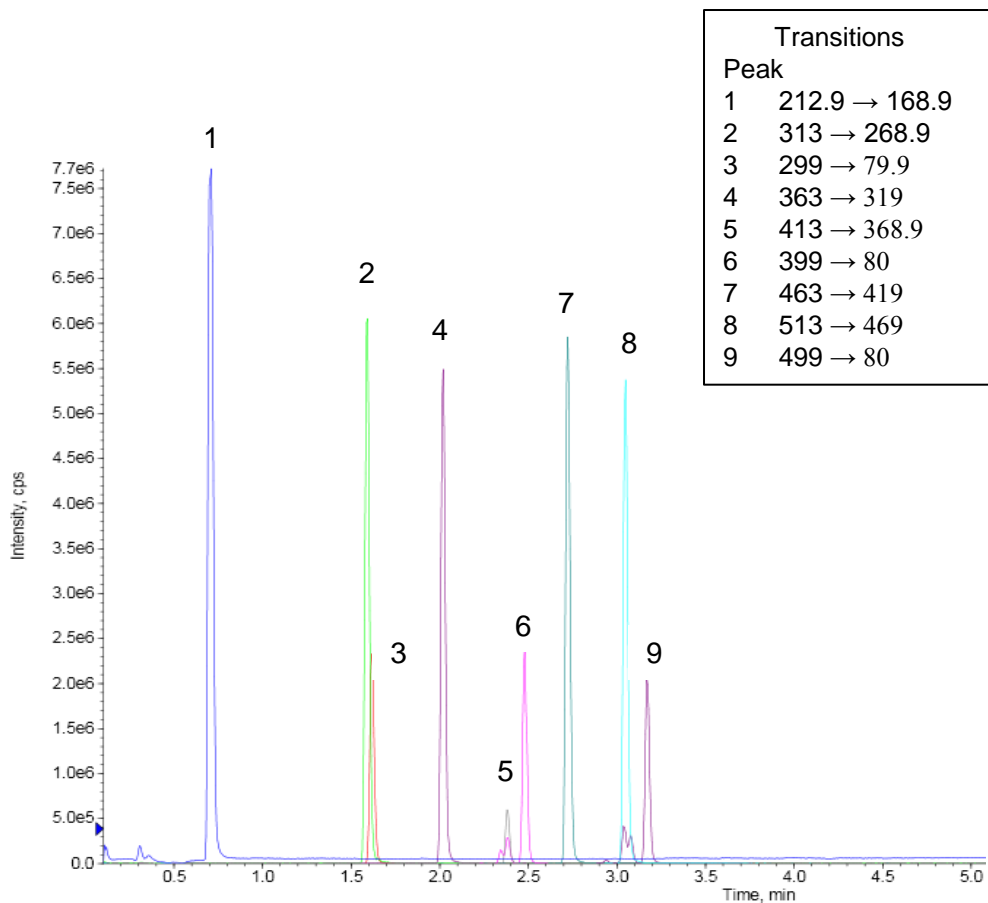
ACE UltraCore SuperPhenylHexyl 2.5µm, 100 x 2.1mm  
Gradient analysis  
A: CH<sub>3</sub>OH – H<sub>2</sub>O (98:2) containing 10mM ammonium acetate  
B: IPA-H<sub>2</sub>O (98:2) containing 10mM ammonium acetate

T (mins)	%B	T (mins)	%B
0	0	15	100
1	0	25	100

Flow rate: 0.15ml/min  
Column temperature: Ambient  
Injection volume: 5µl  
LCQ Ion trap MS  
LC-ESI-MS extracted ion chromatograms  
Compounds detected as ammoniated quasimolecular ions  
[M+NH<sub>4</sub>]<sup>+</sup>  
Detection limit ~ 0.1ppm



# Perfluoro acids by LC-MS/MS



Peak ID	Analyte
1	Heptafluorobutyric acid
2	Perfluorohexanoic acid
3	Perfluorobutylsulphonic acid
4	Perfluoroheptanoic acid
5	Perfluorooctanoic acid
6	Perfluorohexylsulphonic acid
7	Perfluorononanoic acid
8	Perfluorodecanoic acid
9	Perfluorooctanesulphonic acid

ACE Excel 2 C18 2 $\mu$ m, 50 x 2.1mm

Gradient analysis

A = 2mM NH<sub>4</sub>OAc, 0.1% acetic acid/CH<sub>3</sub>CN (95:5)

B = 2mM NH<sub>4</sub>OAc, 0.1% acetic acid/CH<sub>3</sub>CN (5:95)

T (mins)	% B	T (mins)	% B
0	25	7.5	95
0.5	25	8.0	25
5.5	95	10.0	25

Flow rate: 0.5ml/min

Column temperature: 40°C

Injection volume: 20 $\mu$ l

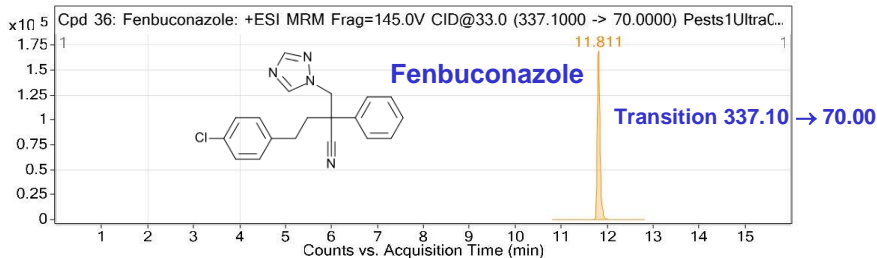
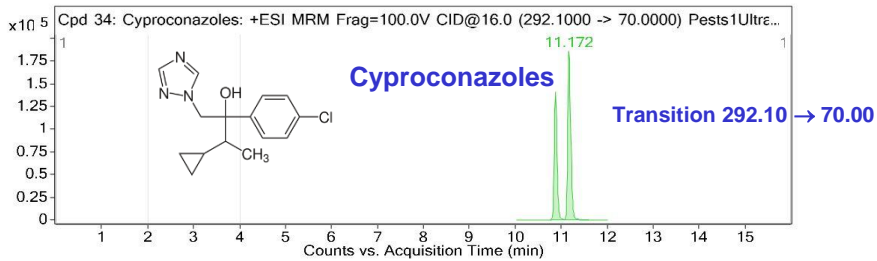
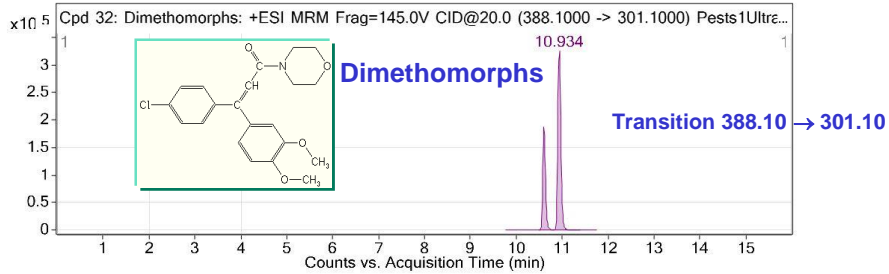
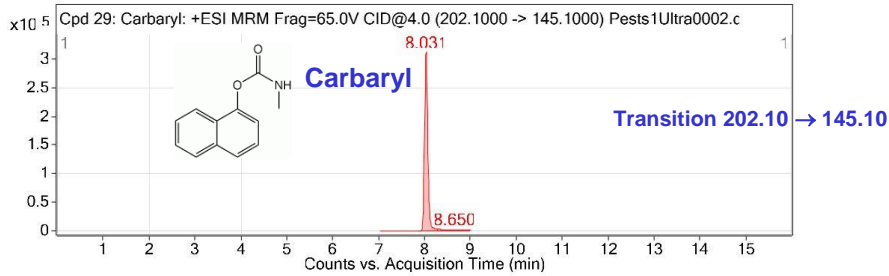
AB SCIEX triple quad 5500

Negative ESI MRM

Source temperature: 450°C

IonSpray voltage: -2400V

# Pesticides by LC-MS/MS



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ACE UltraCore SuperC18, 2.5µm, 50 x 2.1mm  
Gradient analysis

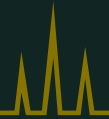
A = 0.1% HCOOH + 5mM NH<sub>4</sub>CO<sub>2</sub>H in 9:1 v/v H<sub>2</sub>O: MeOH  
B = 0.1% HCOOH + 5mM NH<sub>4</sub>CO<sub>2</sub>H in 1:9 v/v H<sub>2</sub>O: MeOH

Flow Rate: 0.4ml/min      Gradient conditions  
Temperature: 40°C      Time (mins) 0 1 15 18 18.05 20  
Injection volume: 20µl      %B 0 0 100 100 0 0

Agilent 6420 Triple Quadrupole MS, +ve mode ESI  
Dynamic MRM

Also analysed under same conditions:

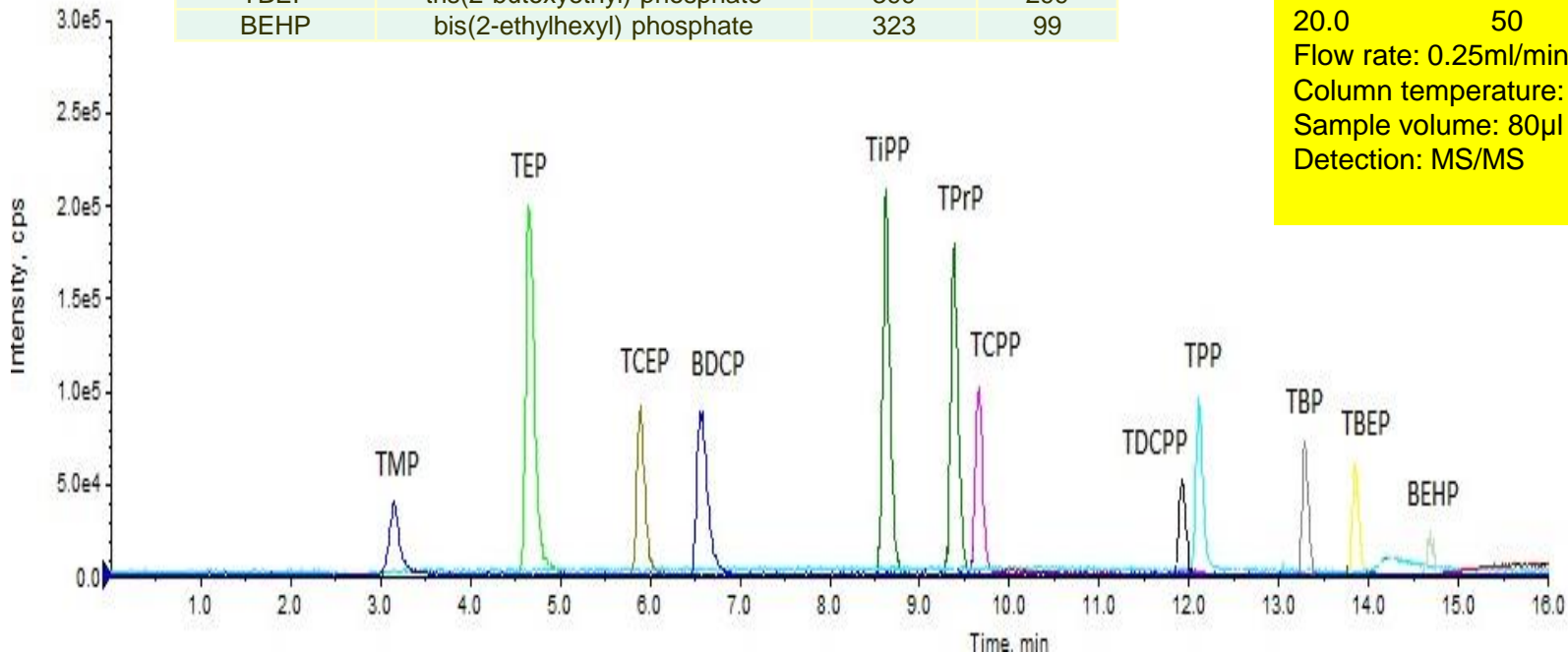
- |                            |                    |
|----------------------------|--------------------|
| Acephate                   | Hexaconazole       |
| Acetamiprid                | Hexaflumuron       |
| Aldicarb                   | Imidacloprid       |
| Aldicarb sulphone          | Indoxacarb         |
| Aldicarb sulphoxide        | Mandipropamid      |
| Benomyl                    | Methamidophos      |
| Carbendazim                | Methomyl           |
| Carbofuran                 | Monocrotophos      |
| Clofentezine               | Nicotine           |
| Clothianidin               | Omethoate          |
| Cyfluthrin                 | Oxamyl             |
| Demeton S-methylsulphone   | Pencycuron         |
| Demeton S-methylsulphoxide | Prochloraz         |
| Dicrotophos                | Propargite         |
| Dimethoate                 | Thiabendazole      |
| Dinotefuran                | Thiacloprid        |
| DMA                        | Thiamethoxam       |
| DMPF                       | Thiodicarb         |
| Flubendiamide              | Thiophanate methyl |
| Folpet                     | Triforine          |
| Formetanate                |                    |



# Organophosphorus Flame Retardants in Water by LC-MS/MS

Symbol	Compound Name	Q1 Mass	Q3 Mass
TMP	tri-methyl phosphate	141	109
TEP	tri-ethyl phosphate	183	127
TiPP	tri-iso-propyl phosphate	225	99
TPrP	tri-n-propyl phosphate	225	99
TBP	tri-n-butyl phosphate	267	211
TCEP	tris(2-chloroethyl) phosphate	285	223
TCPP	tris((2R)-1-chloro-2-propyl) phosphate	327	99
TDCPP	tris(1,3-dichloro-2-propyl) phosphate	431	99
BDCP	bis(1,3-dichloro-2-propyl) phosphate	321	99
TPP	triphenyl phosphate	327	215
TBEP	tris(2-butoxyethyl) phosphate	399	299
BEHP	bis(2-ethylhexyl) phosphate	323	99

ACE C18 3µm, 100 x 2.1mm  
 Gradient analysis  
 A = 0.05mM NH<sub>4</sub>CO<sub>2</sub>H + 0.005% HCO<sub>2</sub>H in water  
 B = CH<sub>3</sub>OH/CH<sub>3</sub>CN (95:5)  
 Time (mins) %B Curve  
 0.1 50 -3  
 12.0 90  
 13.0 100  
 15.0 100  
 15.1 50  
 20.0 50  
 Flow rate: 0.25ml/min  
 Column temperature: 25°C  
 Sample volume: 80µl  
 Detection: MS/MS





# ACE UltraCore SuperC18: Impurity Profile of a Herbicide

ACE UltraCore SuperC18, 2.5 $\mu$ m, 150 x 4.6mm

Gradient analysis

A = CH<sub>3</sub>CN – H<sub>2</sub>O – TFA (5:95:0.05 v/v/v)

B = CH<sub>3</sub>CN – TFA (99.9:0.05 v/v/v)

Time (mins)	%B	Time (mins)	%B
0	10	55	100
3	10	56	10
35	100	60	10

Flow rate: 0.60ml/min

Column temperature: 25°C

Injection volume: 10 $\mu$ l

Detection: UV, 240nm

Sample: Technical Grade Herbicide

