Interactive Demonstration

NORMAN-MassBank
MetFusion

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Contents of Demonstration

- NORMAN MassBank
  - Record Structure and the Record Index
  - Quick Search
  - Peak Search
  - Spectrum Search
  - Substructure Search
  - Administration of NORMAN MassBank

- MetFusion: Compound Database meets Spectral Database!
  - *Michael Gerlich*

Mass Spectral Database Searching

Some Definitions

- Compound Database (e.g. ChemSpider, PubChem):
  - A collection of structures, basic properties and associated information[1]
  - Generally, no spectral data – but >25,000,000 structures

- Mass Spectral Databases (or Libraries)
  - A collection of structures, their mass spectra and associated information
  - NIST and Wiley Mass Spectral Libraries for GC-EI-MS
    - NIST11: >200,000 spectra; Wiley 9th: >660,000 spectra[2]
  - MS/MS databases are growing; none are yet “established”
    - MassBank: 31,140 spectra (mixed origin);
    - METLIN: 52,904 HR-ESI-MS/MS – Agilent TOF-MS
    - NIST MS/MS: ~95,000 LR-MS/MS spectra of ~5,000 compounds
    - Keep an eye on mzCloud.org (Robert Mistrik, HighChem)

[1]http://www.chemspider.com/About.aspx. [2]http://www.sisweb.com/software/ms/wiley.htm

Using NORMAN MassBank

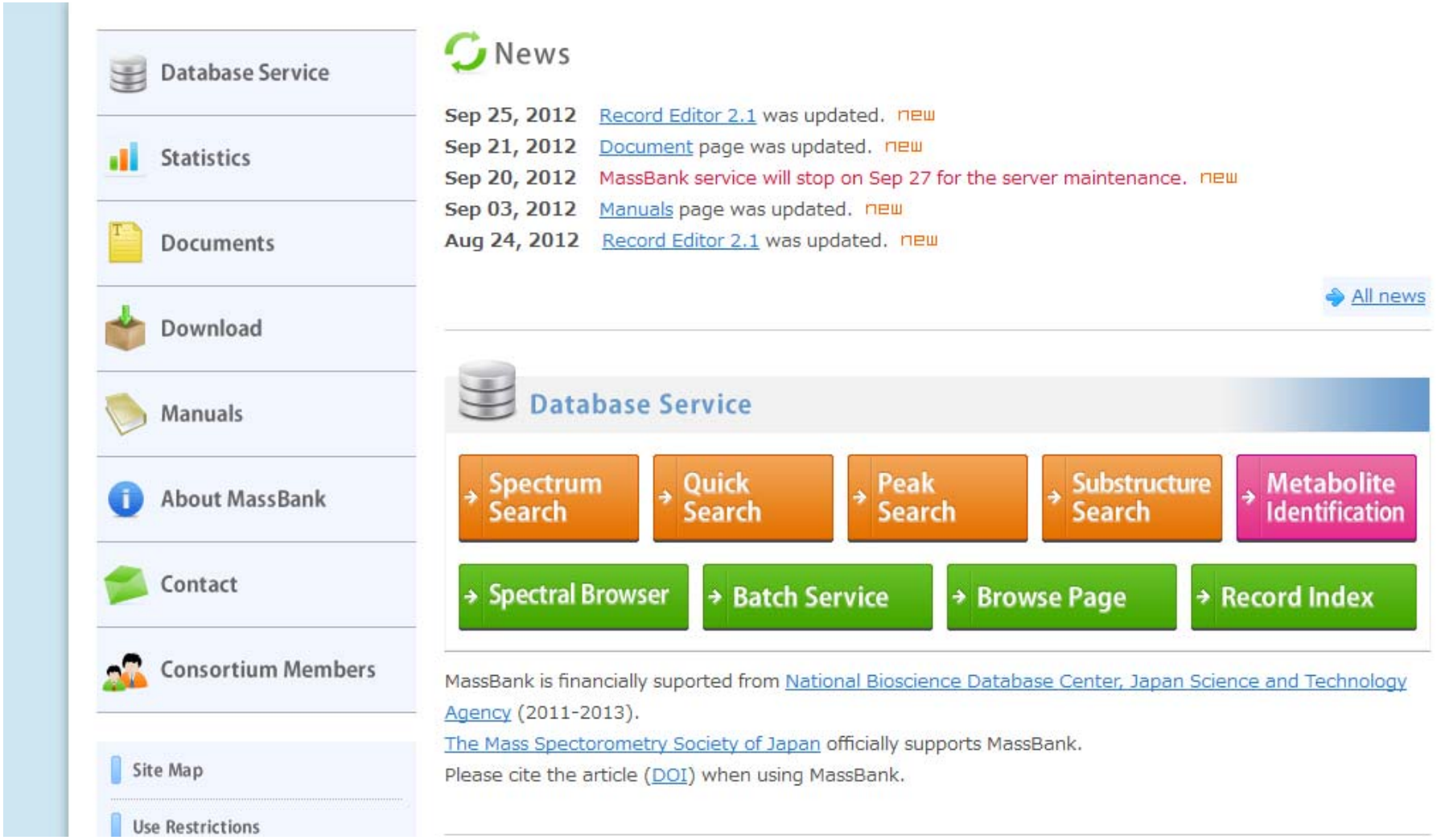
What do you really want to achieve?

- Flexible exchange of data within NORMAN
  - Upload of data from different instruments, different resolutions, …
  - Reduce standard purchase via sharing of data
  - Extension to tentative / unknown spectra

- Purpose of a Mass Spectral Search
  - I have a compound of interest
    - Are there any spectra? What do they look like?
  - I want to identify an unknown
    - Features of MassBank that may be useful
    - Using MetFusion for identification
  - I want to perform routine confirmation and quantification of targets
    - MassBank is not the best stand-alone solution for you (yet?!)
    - *Talk to vendors to value-add instrument software with MassBank*

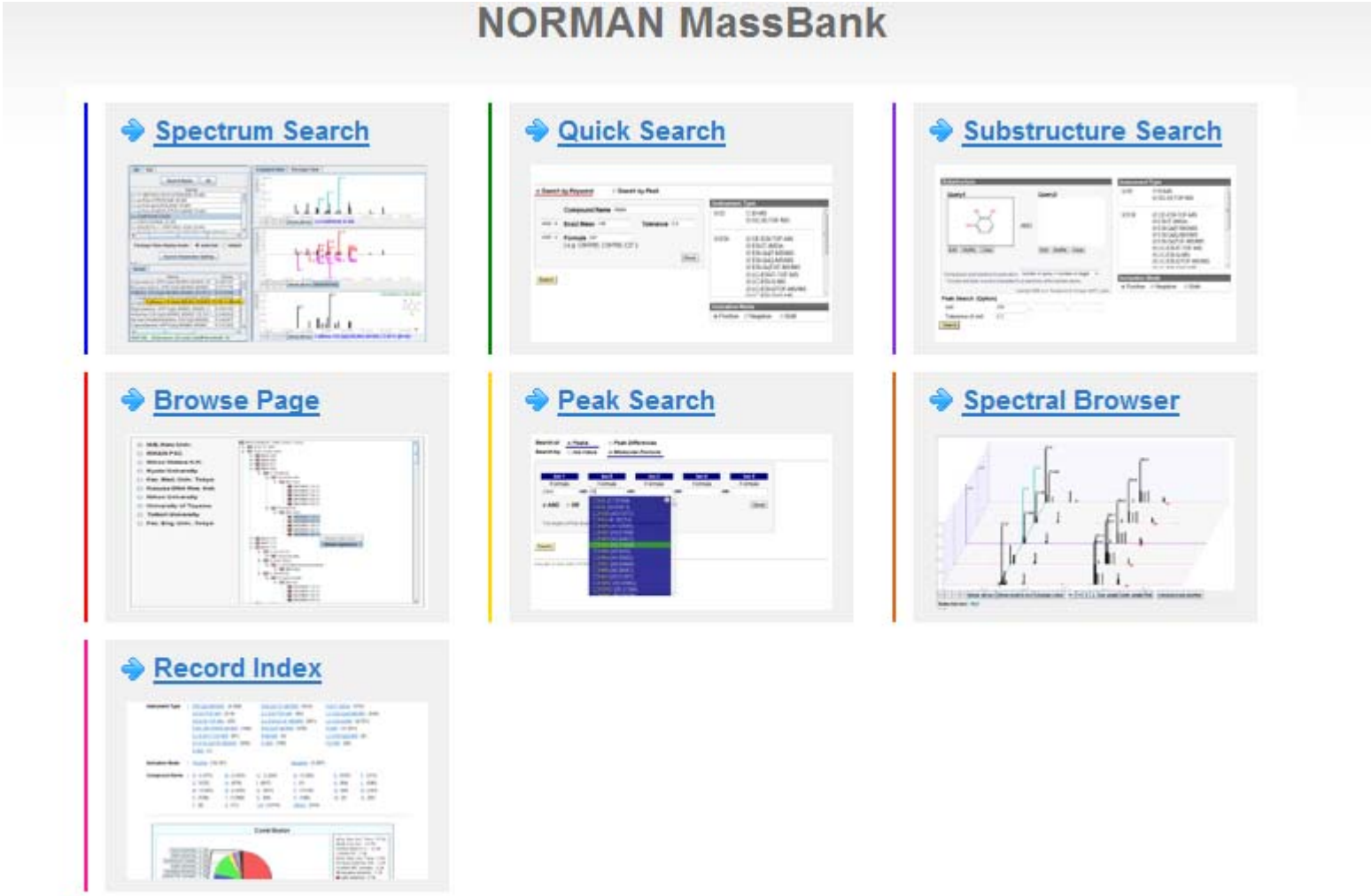
MassBank: www.massbank.jp

Horai et al. 2010: DOI 10.1002/jms.1777



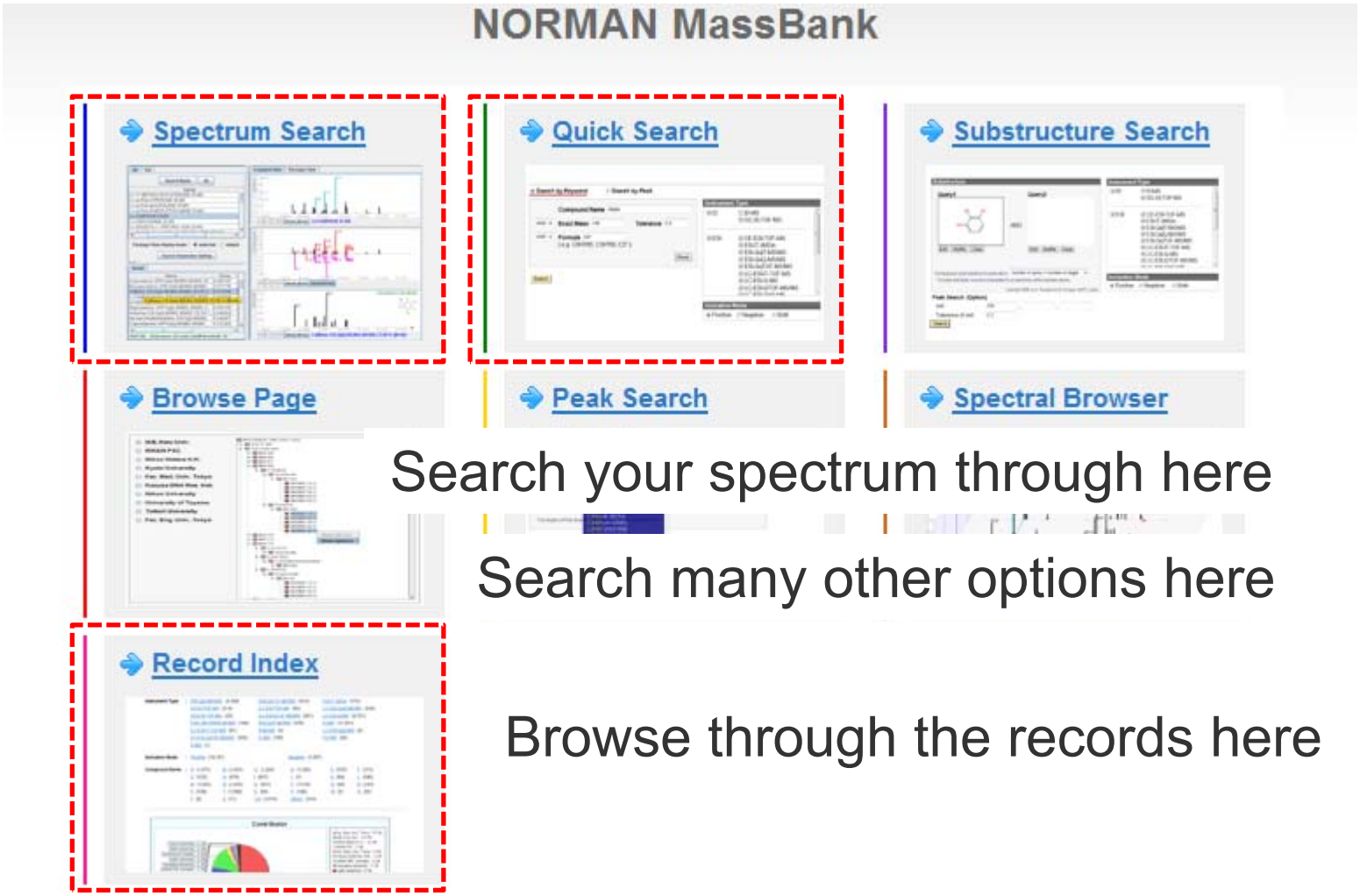
NORMAN MassBank

http://massbank.normandata.eu/MassBank/



NORMAN MassBank

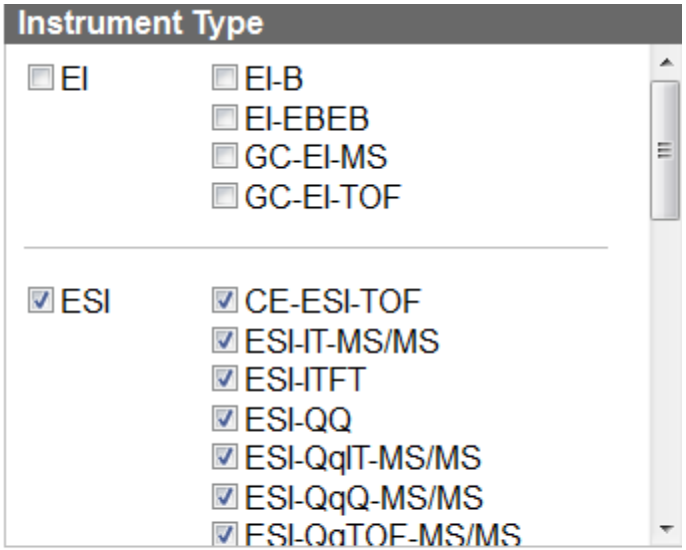
http://massbank.normandata.eu/MassBank/



Searching MassBank

What do you want to achieve?

- MassBank is a mixed database
  - Be careful to pick and mix your settings
  - Adjust the thresholds to the data you have
  - …but also to the data in MassBank
  - Tolerance is in Da (i.e. one mass unit)
- Quality of spectra is quite mixed
  - …as is the information provided in them



More details in the next slides!

MassBank Record Format

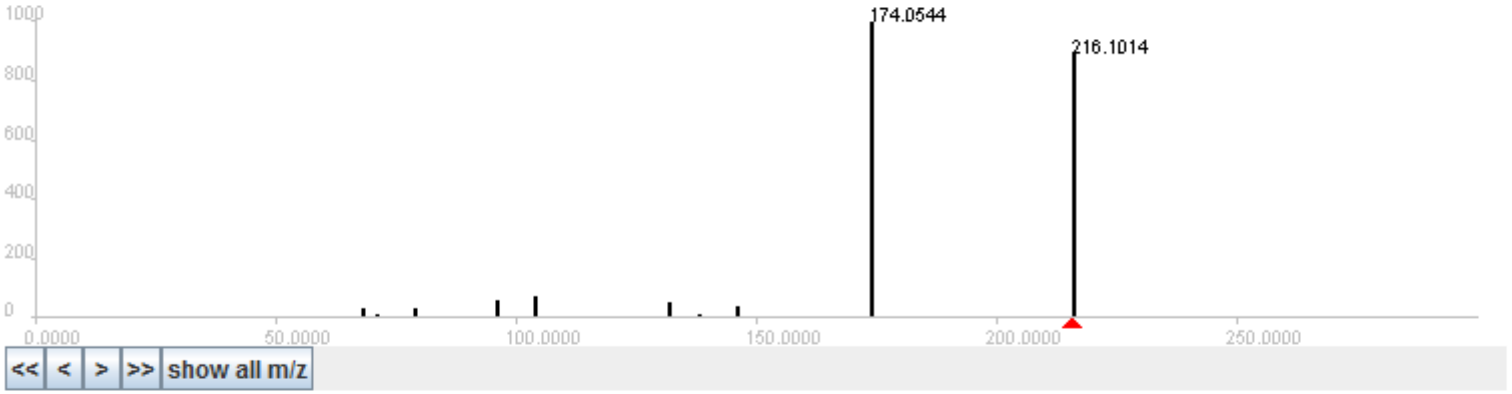
MassBank Record: EA028804

Home | Spectrum | Quick | Peak | Substructure | Prediction | Browser | Batch | Browse | Index

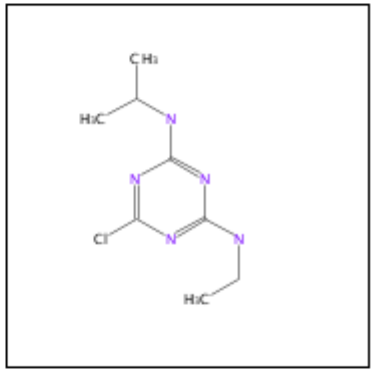
MassBank ID: Go

Atrazine; LC-ESI-ITFT; MS2; 45%; R=7500; [M+H]+

Mass Spectrum



Chemical Structure



```
ACCESSION: EA028804
RECORD_TITLE: Atrazine; LC-ESI-ITFT; MS2; 45%; R=7500; [M+H]+
DATE: 2012.08.02
AUTHORS: Stravs M, Schymanski E, Singer H, Dep
LICENSE: http://massbank.ufz.de/MassBank/files/
COPYRIGHT: Copyright (C) 2011 Eawag, Duebendorf, Switzerland
COMMENT: CONFIDENCE standard compound
COMMENT: EAWAG_UCHEM_ID 288

CH$NAME: Atrazine
```

Authors, licence, copyright, etc

MassBank Record Format

Compound Information

```
CH$NAME: Atrazine
CH$NAME: 6-chloro-N-ethyl-N'-isopropyl-1,3,5-triazine-2,4-diamine
CH$NAME: 6-chloranyl-N4-ethyl-N2-propan-2-yl-1,3,5-triazine-2,4-diamine
CH$COMPOUND_CLASS: N/A; Environmental Standard
CH$FORMULA: C8H14Cl1N5
CH$EXACT_MASS: 215.0932
CH$SMILES: c1(nc(nc(n1)Cl)NCC)NC(C)C
CH$IUPAC: InChI=1S/C8H14ClN5/c1-4-10-7-12-6(9)13-8(14-7)11-5(2)3/h5H,4H2,
CH$LINK: CAS 1912-24-9
CH$LINK: CHEBI 15930
CH$LINK: KEGG C06551
CH$LINK: PUBCHEM CID:2256
CH$LINK: INCHIKEY MXWJVTOOROXGIU-UHFFFAOYSA-N
CH$LINK: CHEMSPIDER 10774593
```

MassBank Record Format

Instrument and Measurement Information

```
AC$INSTRUMENT: LTQ Orbitrap XL Thermo Scientific
AC$INSTRUMENT_TYPE: LC-ESI-ITFT
AC$MASS_SPECTROMETRY: MS_TYPE MS2
AC$MASS_SPECTROMETRY: IONIZATION ESI
AC$MASS_SPECTROMETRY: ION_MODE POSITIVE
AC$MASS_SPECTROMETRY: FRAGMENTATION_MODE HCD
AC$MASS_SPECTROMETRY: COLLISION_ENERGY 45 % (nominal)
AC$MASS_SPECTROMETRY: RESOLUTION 7500
AC$CHROMATOGRAPHY: COLUMN_NAME XBridge C18 3.5um, 2.1x50mm, Waters
AC$CHROMATOGRAPHY: FLOW_GRADIENT 90/10 at 0 min, 50/50 at 4 min, 5/95 at
AC$CHROMATOGRAPHY: FLOW_RATE 200 ul/min
AC$CHROMATOGRAPHY: RETENTION_TIME 8.3 min
AC$CHROMATOGRAPHY: SOLVENT A water with 0.1% formic acid
AC$CHROMATOGRAPHY: SOLVENT B methanol with 0.1% formic acid
```

```
MS$FOCUSED_ION: BASE_PEAK 216.1012
MS$FOCUSED_ION: PRECURSOR_M/Z 216.101
MS$FOCUSED_ION: PRECURSOR_TYPE [M+H]+
MS$DATA_PROCESSING: DEPROFILE Spline
MS$DATA_PROCESSING: RECALIBRATE loess on assigned fragments and MS1
MS$DATA_PROCESSING: WHOLE RMassBank
```

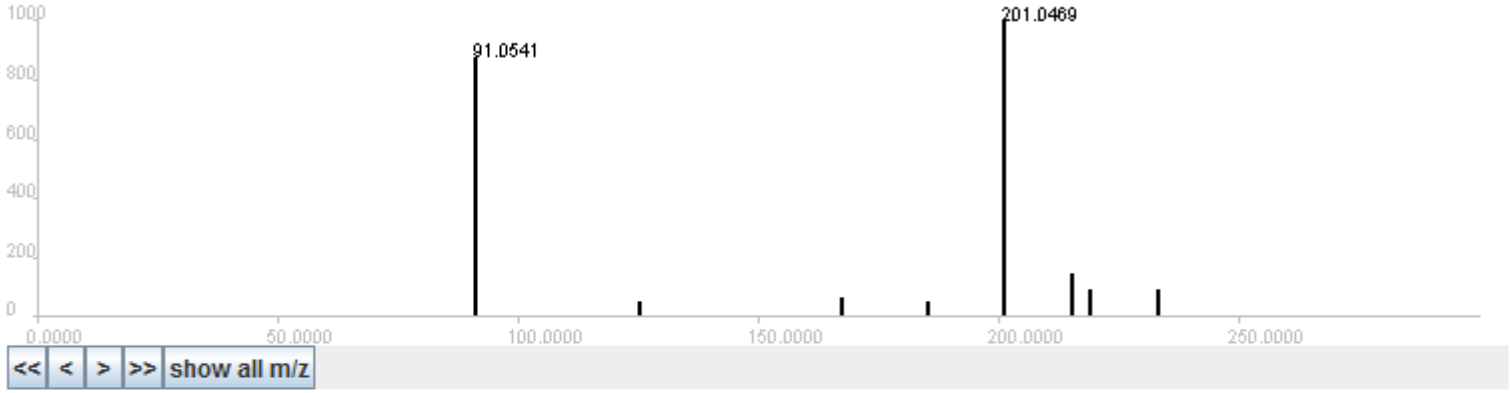
MassBank Record Format - Peaks

```
PK$ANNOTATION: m/z num {formula mass error(ppm)}
  68.0243 1 C2H2N3+ 68.0243 0.24
  71.0603 1 C3H7N2+ 71.0604 -0.35
  79.0058 1 CH4ClN2+ 79.0058 0.35
  96.0557 1 C4H6N3+ 96.0556 0.48
  104.001 1 C2H3ClN3+ 104.001 0.28
  132.0324 1 C4H7ClN3+ 132.0323 0.37
  138.0779 1 C5H8N5+ 138.0774 3.1
  138.1029 1 C7H12N3+ 138.1026 2.36
  146.0228 1 C3H5ClN5+ 146.0228 0.01
  146.0481 1 C5H9ClN3+ 146.048 0.95
  174.0544 1 C5H9ClN5+ 174.0541 1.9
  216.1014 1 C8H15ClN5+ 216.101 1.81
PK$NUM_PEAK: 12
PK$PEAK: m/z int. rel.int.
  68.0243 949141.4 28
  71.0603 167093.1 5
  79.0058 1014555.8 30
  96.0557 1956578 59
  104.001 2256202.5 68
  132.0324 1805661.3 54
  138.0779 349329.9 10
  138.1029 280901.6 8
  146.0228 1313633.2 39
  146.0481 263134.4 7
  174.0544 32958196.3 999
  216.1014 29362258.7 890
//
```

MassBank Record – Example Unknown (so far)

CASMI2012 LC Challenge 13; APCI-ITFT; MS2; CE:45 CID;

Mass Spectrum



Chemical Structure

Not Available

```
ACCESSION: SMI00131
RECORD_TITLE: CASMI2012 LC Challenge 13; APCI-ITFT; MS2; CE:45 CID;
DATE: 2012.08.31 (Created 2012.08.31)
AUTHORS: S. Neumann: IPB-Halle, Germany & E. Schymanski: Eawag, Switzerland
COPYRIGHT: CASMI2012
COMMENT: Unknown
COMMENT: http://casmi-contest.org/challenges-cat1-2.shtml

CH$NAME: CASMI2012 LC Challenge 13
CH$COMPOUND_CLASS: N/A; Unknown for CASMI
CH$FORMULA: N/A
CH$EXACT_MASS: N/A
CH$SMILES: N/A
CH$IUPAC: N/A

AC$INSTRUMENT: LTQ-Orbitrap
AC$INSTRUMENT_TYPE: APCI-ITFT
AC$ANALYTICAL_CONDITION: MODE POSITIVE
AC$MASS_SPECTROMETRY: MS_TYPE MS2
AC$MASS_SPECTROMETRY: ION_MODE POSITIVE

MS$FOCUSED_ION: PRECURSOR_M/Z N/A
MS$FOCUSED_ION: PRECURSOR_TYPE N/A

PK$NUM_PEAK: 8
PK$PEAK: m/z int. rel.int.
  91.0541 2211410.3 873
  125.0152 130666.3 52
  167.0859 161086.1 64
  185.0519 125915.7 50
  201.0469 2531123 999
  215.0626 371698.1 147
  219.0576 223408.9 88
  233.0733 226928.3 90
//
```

MassBank Record Index

Have a look at what is in MassBank:

Contributor:

Instrument Type: (Orbitrap = ITFT)

Compound Name: watch out for numbers…

Contributor :

NORMAN EMPOMASS (2,081)	CASMI (42)	Eawag (944)
UFZ (2,509)	Keio Univ. (5,629)	RIKEN (1,721)
Waters (2,993)	Kyoto Univ. (185)	Chubu Univ. (2,628)
Kazusa (273)	Nihon Univ. (75)	Univ. Toyama (253)
Tottori Univ. (16)	IPB Halle (528)	Fukuyama Univ. (340)
Metabolon (149)	UOEH (35)	NAIST (680)
Osaka MCHRI (20)	Univ. Connecticut (510)	Osaka Univ. (502)
IMM, CAMS & PUMC, China (192)	PFOS research group (365)	MPI for Chemical Ecology (691)

nstrument Type :

GC-EI-MS (2,097)	LC-ESI-QTOF (2,750)	LC-APCI-ITFT (10)
APCI-ITFT (1,206)	LC-ESI-ITFT (4,504)	ESI-ITFT (1,310)
LC-ESI-IT (515)	LC-ESI-QQ (5,038)	CE-ESI-TOF (20)
GC-EI-TOF (1,016)	LC-ESI-Q (2,720)	EI-EBEB (12)
FAB-EBEB (173)	LC-ESI-QIT (378)	EI-B (91)
LC-ESI-ITTOF (253)	FAB-EB (5)	ESI-IT-MS/MS (149)
CI-B (1)	FAB-B (26)	FD-B (3)
MALDI-TOF (17)	ESI-QqTOF-MS/MS (510)	ESI-QqIT-MS/MS (140)
ESI-QqQ-MS/MS (52)	APPI-QqQ-MS (2)	APPI-QqQ-MS/MS (27)
ESI-QQ (78)	LC-APPI-QQ (258)	

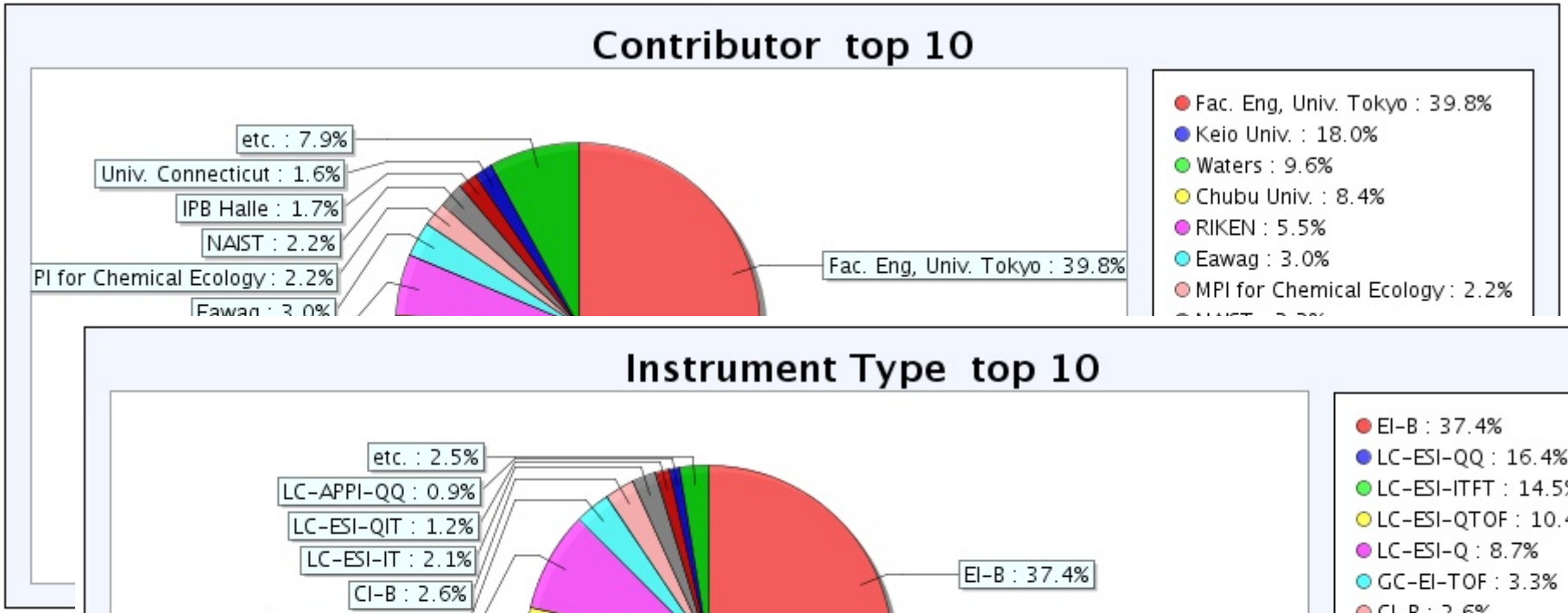
onization Mode : Positive (16,197) Negative (7,164)

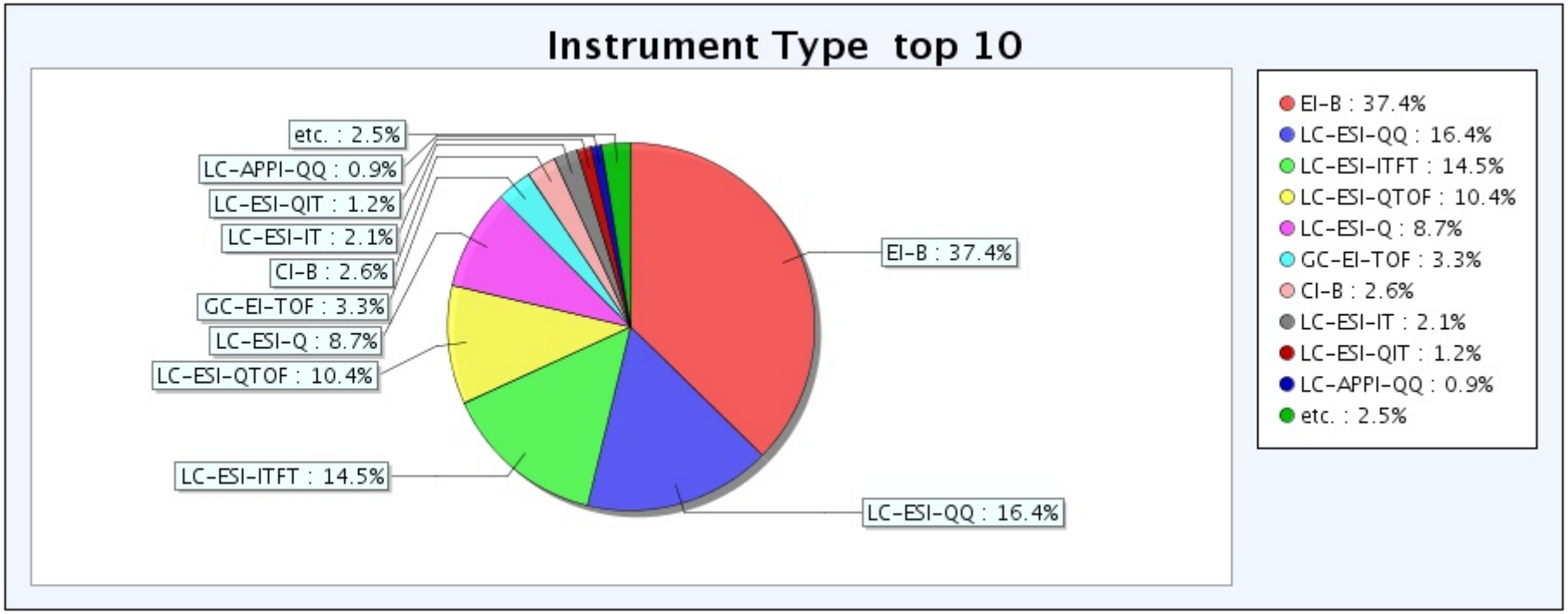
Compound Name :

A (1,185)	B (1,122)	C (1,372)	D (1,559)	E (426)	F (421)
G (793)	H (429)	I (657)	J (2)	K (223)	L (1,254)
M (996)	N (1,005)	O (388)	P (3,687)	Q (184)	R (287)
S (941)	T (1,249)	U (887)	V (128)	W (3)	X (51)
Y (5)	Z (72)	1-9 (3,844)	Others (191)		

MassBank Record Index

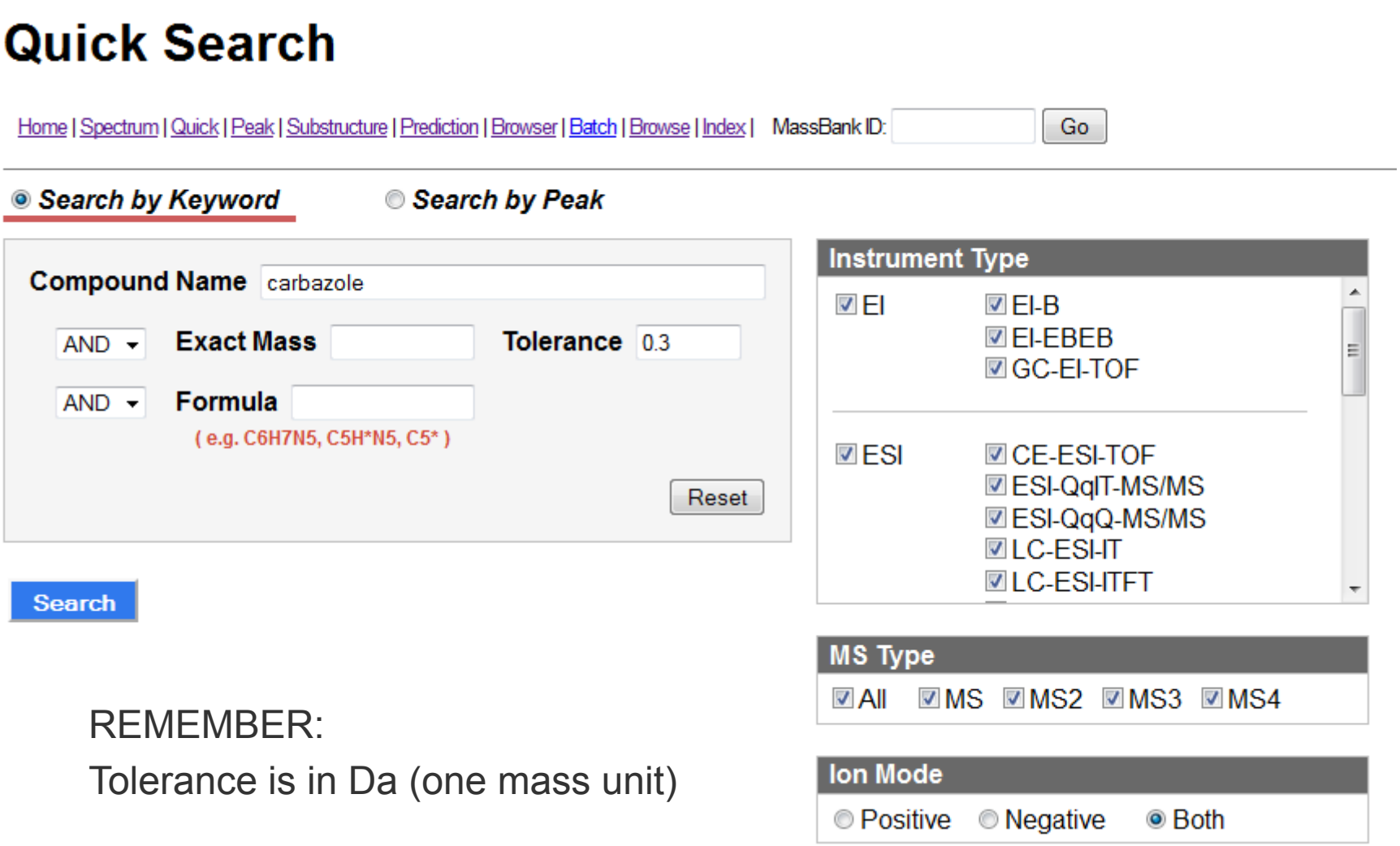
Scroll to see the contents (and see if your institute is in the top 10!)





MassBank Quick Search

Search compounds or peaks



REMEMBER:

Tolerance is in Da (one mass unit)

Quick Search Results

Search Parameters :

Compound Name: **carbazole**

Instrument Type: **EI-B , EI-EBEB , GC-EI-TOF , CE-ESI-TOF , ESI-QqIT-MS/MS , ESI-QqQ-MS/MS , LC-ESI-IT , LC-ESI-ITFT , LC-ESI-ITTOF , LC-ESI-Q , LC-ESI-QIT , LC-ESI-QQ , LC-ESI-QTOF , CI-B , FAB-B , FAB-EB , FAB-EBEB , FD-B , FI-B , LC-APPI-QQ , MALDI-TOF , MALDI-TOFTOF**

MS Type: **All**

Ion Mode: **Both**

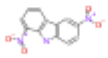
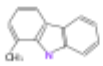
Edit / Resubmit Query

Results : 34 Hit. (1 - 34 Displayed)

Open All Tree | Multiple Display | Spectrum Search

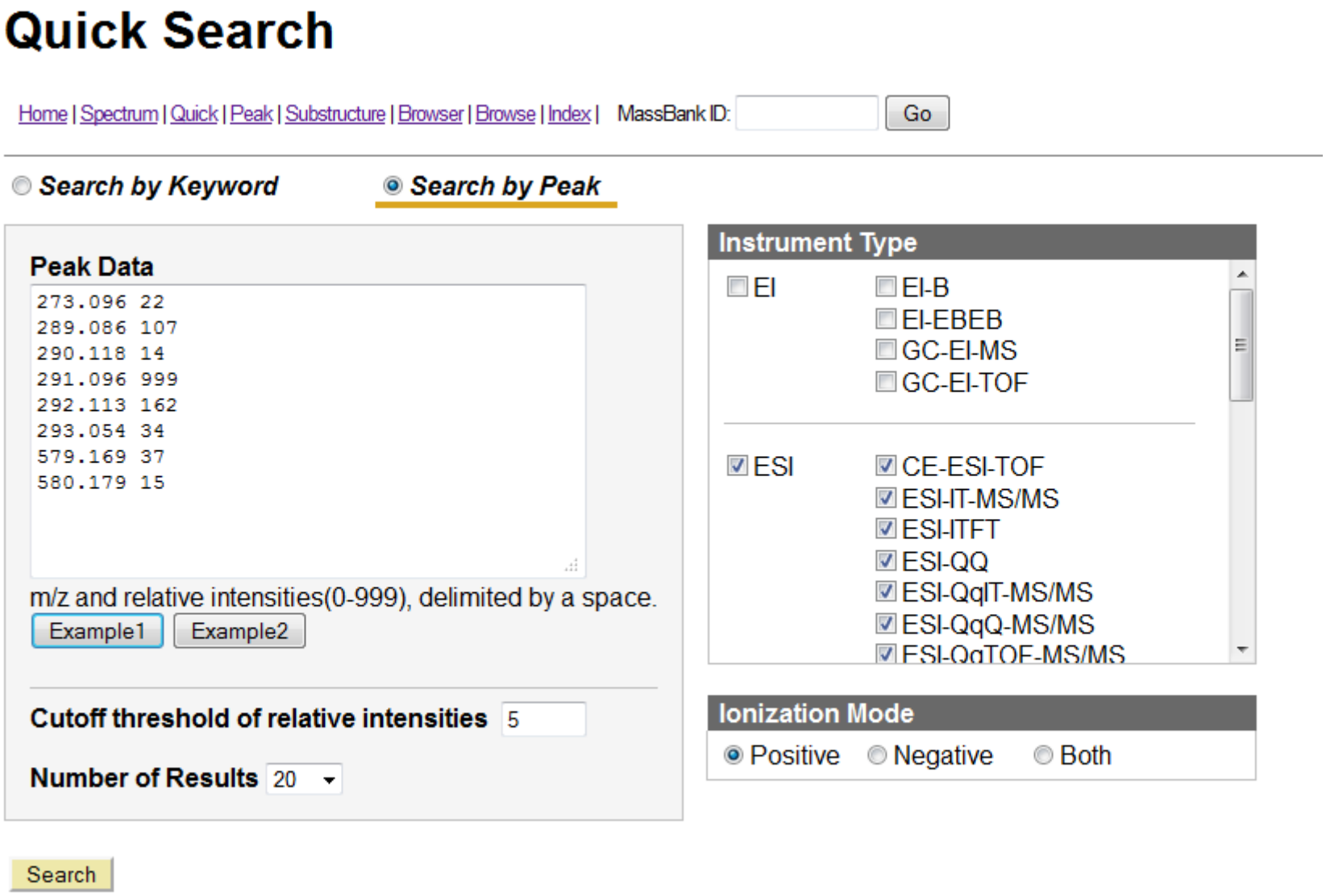
First Prev *1* Next Last (Total *1* Page)

▼ Results End

	Name	Formula / Structure	ExactMass	ID
☐	⊞ 1,6-DINITROCARBAZOLE 1 spectrum	C12H7N3O4 	257.04366	
☐	⊞ 1-METHYLCARBAZOLE 1 spectrum	C13H11N 	181.08915	
☐	⊞ 2-METHYLCARBAZOLE	C13H11N	181.08915	

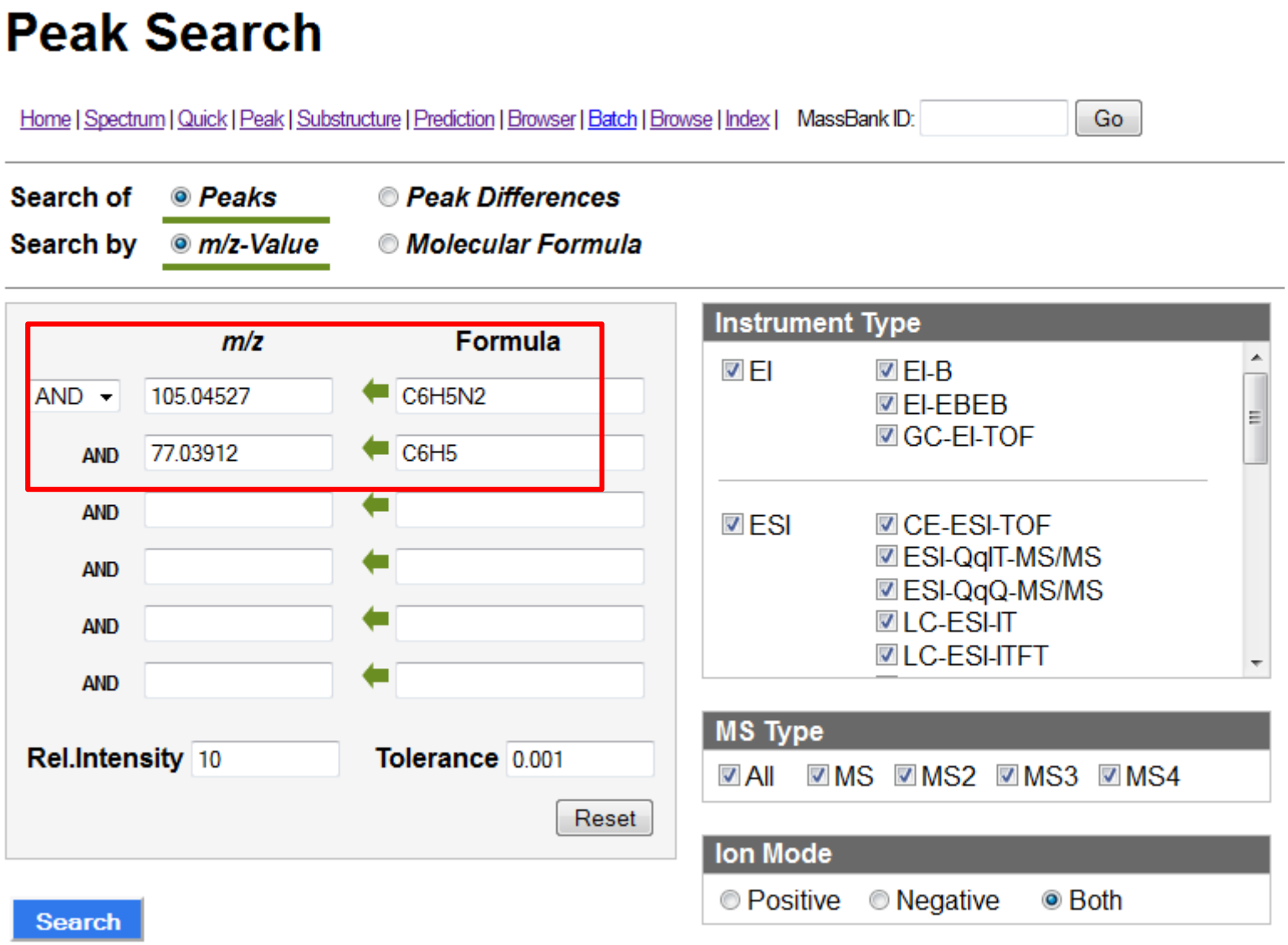
MassBank Quick Search

Search compounds or peaks



MassBank Peak Search

Different to Quick Search → Search by Peak!



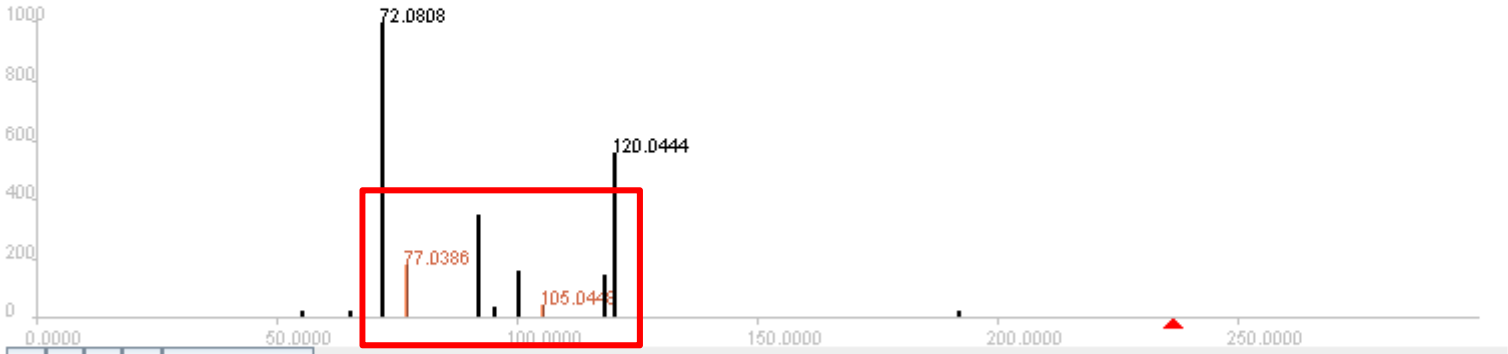
Peak Search Results (Peaks by *m/z* value)

MassBank Record: EA013612

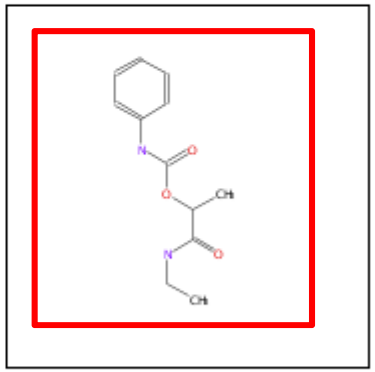
Home | Spectrum | Quick | Peak | Substructure | Prediction | Browser | Batch | Browse | Index | MassBank ID: Go

Carbetamide; LC-ESI-ITFT; MS2; 75%; R=15000; [M+H]+

Mass Spectrum



Chemical Structure

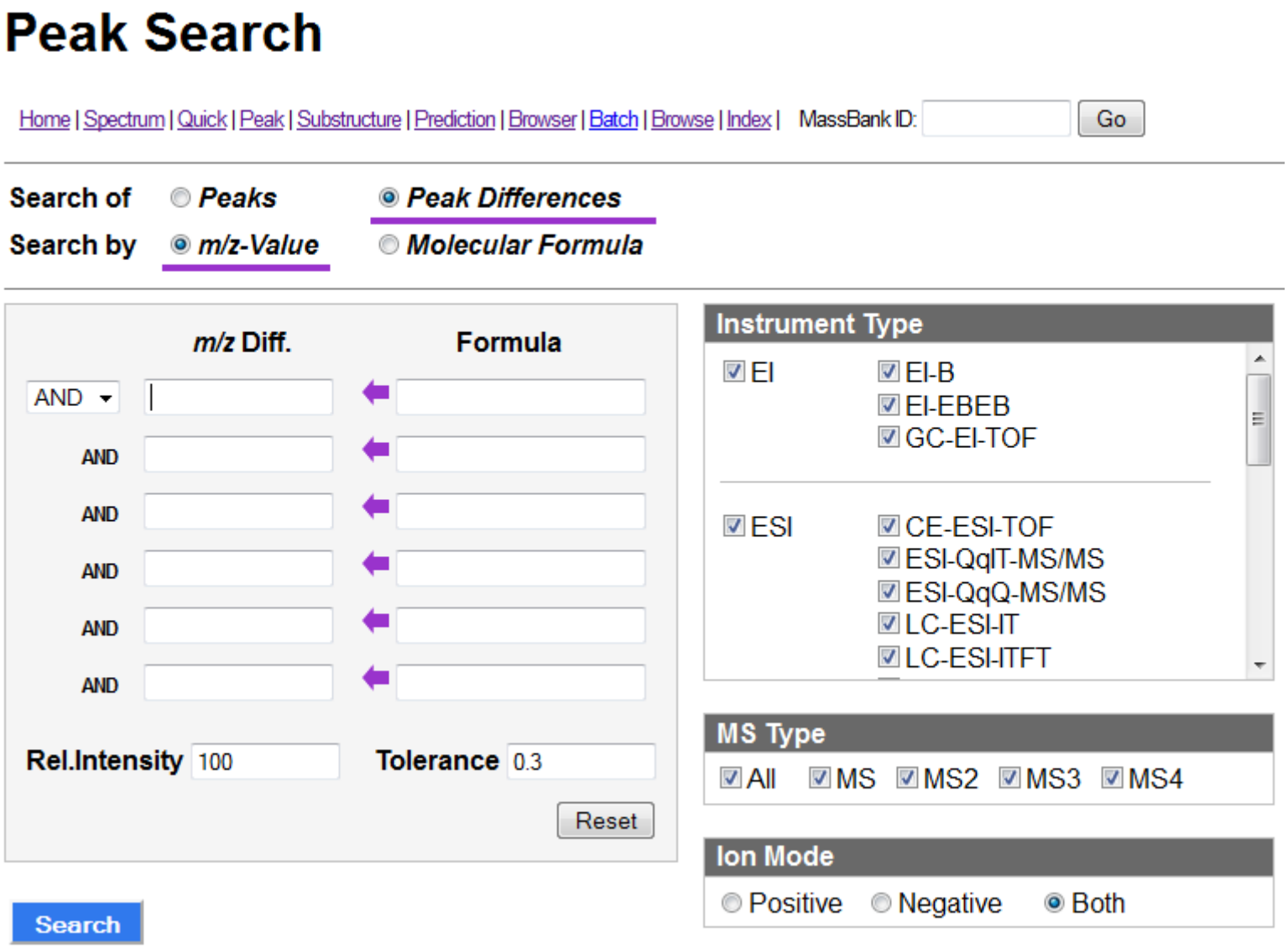


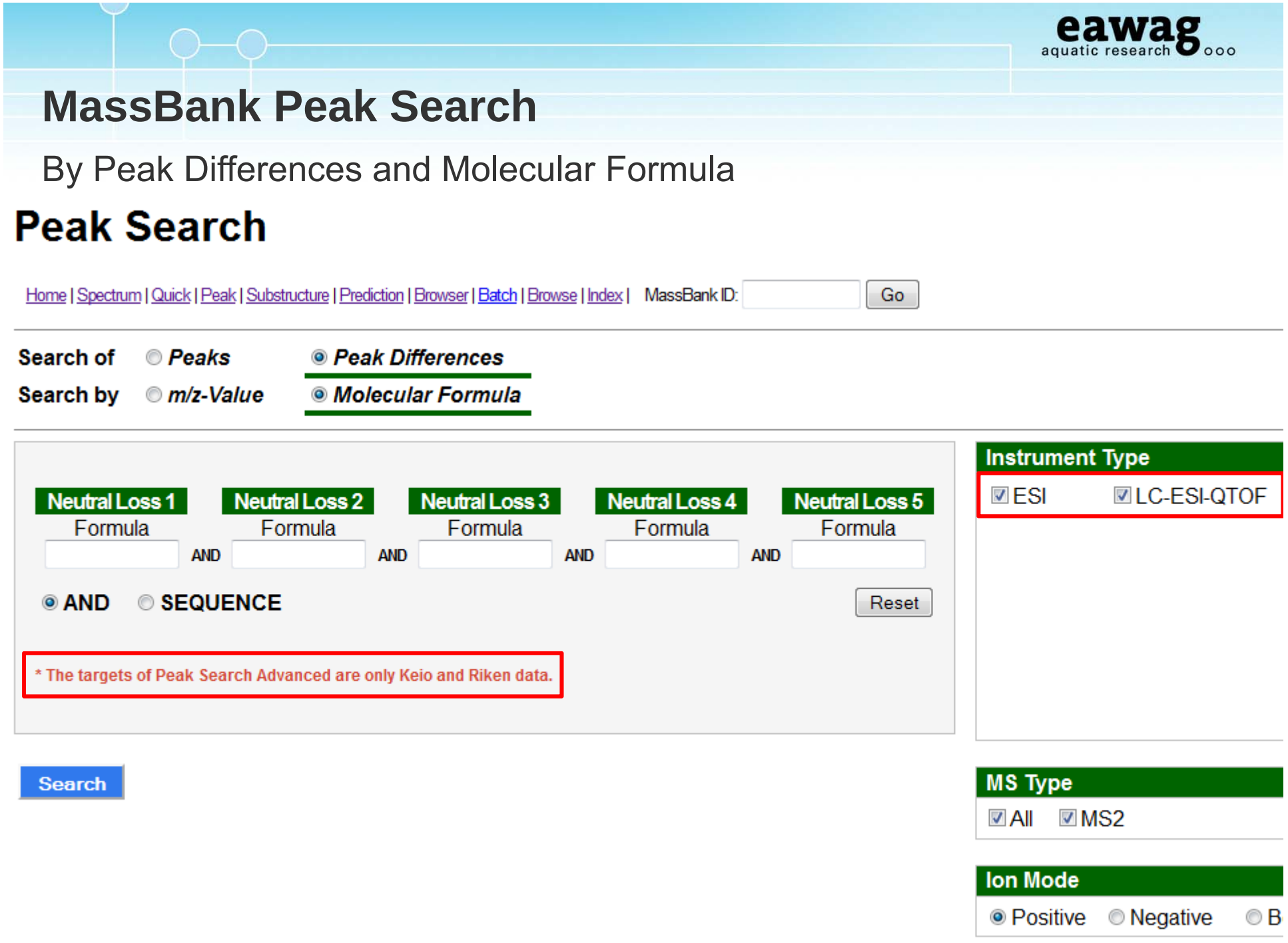
ACCESSION: EA013612
RECORD_TITLE: Carbetamide; LC-ESI-ITFT; MS2; 75%; R=15000; [M+H]+
DATE: 2012.08.02
AUTHORS: Stravs M, Schymanski E, Singer H, Department of Environmental Chemistry, Eawag

☐ ⊞ **Aminocaproic acid** 1 spectrum	**C6H13NO2**	**131.09463**	

MassBank Peak Search

By Peak Differences and m/z value




eawag
aquatic research
MassBank Peak Search
By Peak Differences and Molecular Formula
Peak Search
Home | Spectrum | Quick | Peak | Substructure | Prediction | Browser | Batch | Browse | Index | MassBank ID: Go
Search of Peaks Peak Differences
Search by m/z-Value Molecular Formula
Neutral Loss 1 Formula AND
Neutral Loss 2 Formula AND
Neutral Loss 3 Formula AND
Neutral Loss 4 Formula AND
Neutral Loss 5 Formula
AND SEQUENCE
Reset
* The targets of Peak Search Advanced are only Keio and Riken data.
Search
Instrument Type
ESI LC-ESI-QTOF
MS Type
All MS2
Ion Mode
Positive Negative B

MassBank Spectrum Search

http://www.massbank.jp/sample/sample.txt

```
// Specification of file format
// - A line started by '//' is a comment line.
// - A peak is denoted by its m/z and intensity
     separated by one or more spaces.
// - Delimiter of spectra: one or more empty lines is
     necessary between spectra.
// - A line started by 'ID:' specifies the value of the
     ID column in the spectrum table for each spectrum.
// - A line started by 'Name:' specifies the value of the
     name column in the spectrum table for each spectrum.
// - A "Nist Format" file can be used without any
     modification.
```

If you saved the data before the workshop, you can try this example with “SpectrumSearch_EnvEgs.txt”

MassBank Spectrum Search Results

Spectrum Search

Home | Spectrum | Quick | Peak | Substructure | Prediction | Browser | Batch | Browse | Index | MassBank ID: Go

Browse... File Read sample file sample archive

DB File

No.	Name	ID
1	EA013612	US000001
2	EA008812	US000002

Click on file name to search

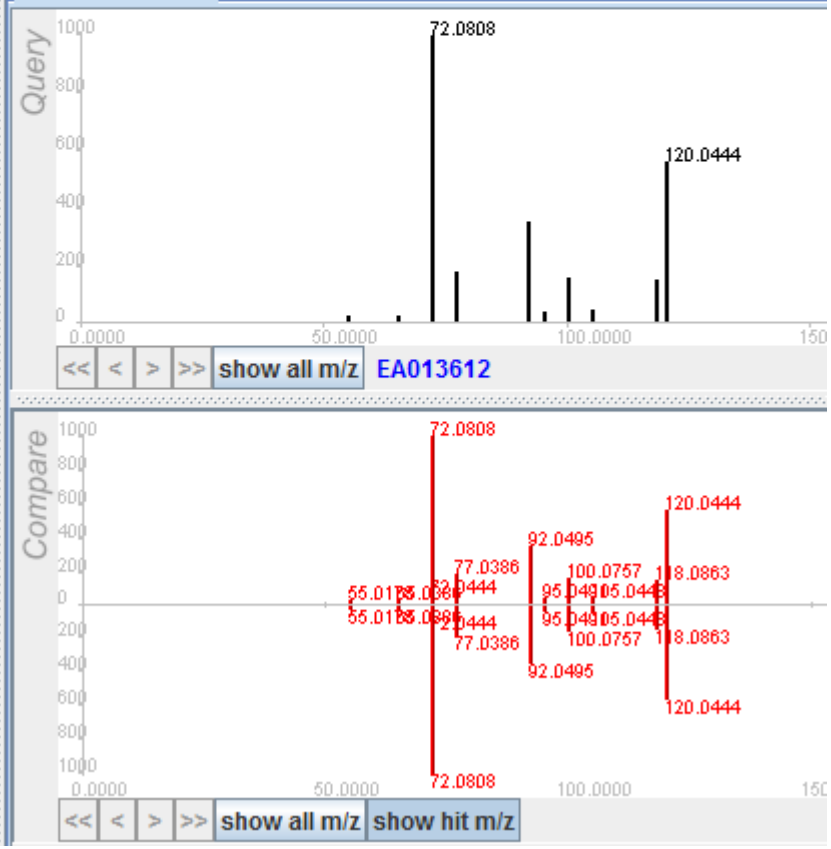
Package View display mode : selected related

Search Parameter Setting

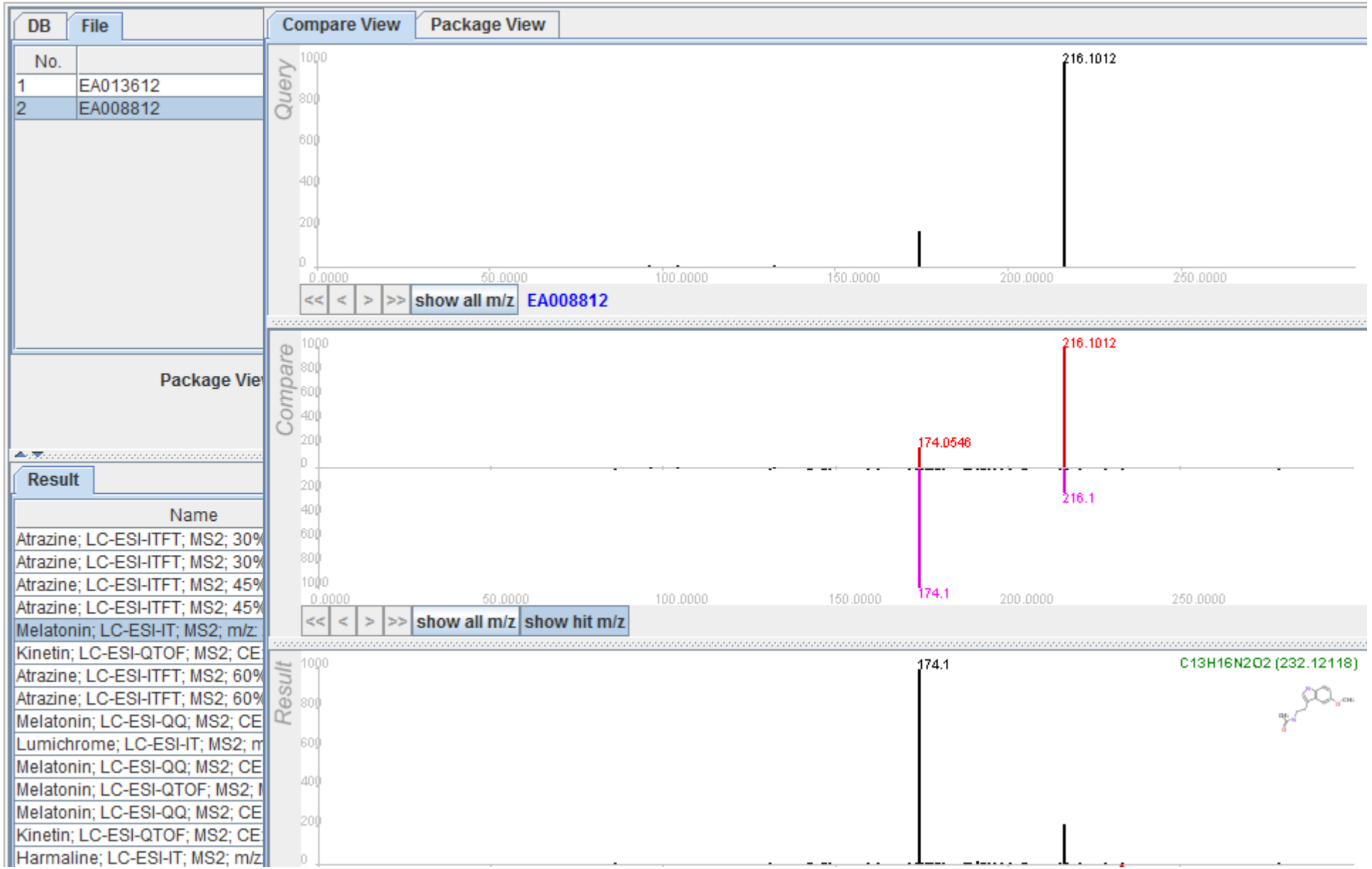
Result

Name	Score	Hit	ID	Ion	Contributor
Carbetamide; LC-ESI-ITFT; MS2; 75%; R=1...	0.941860...	12	EA013612	P	Eawag
Carbetamide; LC-ESI-ITFT; MS2; 75%; R=7...	0.937374...	12	EA013606	P	Eawag
Carbetamide; LC-ESI-ITFT; MS2; 60%; R=7...	0.908825...	11	EA013605	P	Eawag
Carbetamide; LC-ESI-ITFT; MS2; 60%; R=1...	0.903718...	10	EA013611	P	Eawag
Carbetamide; LC-ESI-ITFT; MS2; 90%; R=3...	0.893760...	12	EA013613	P	Eawag

Compare View Package View

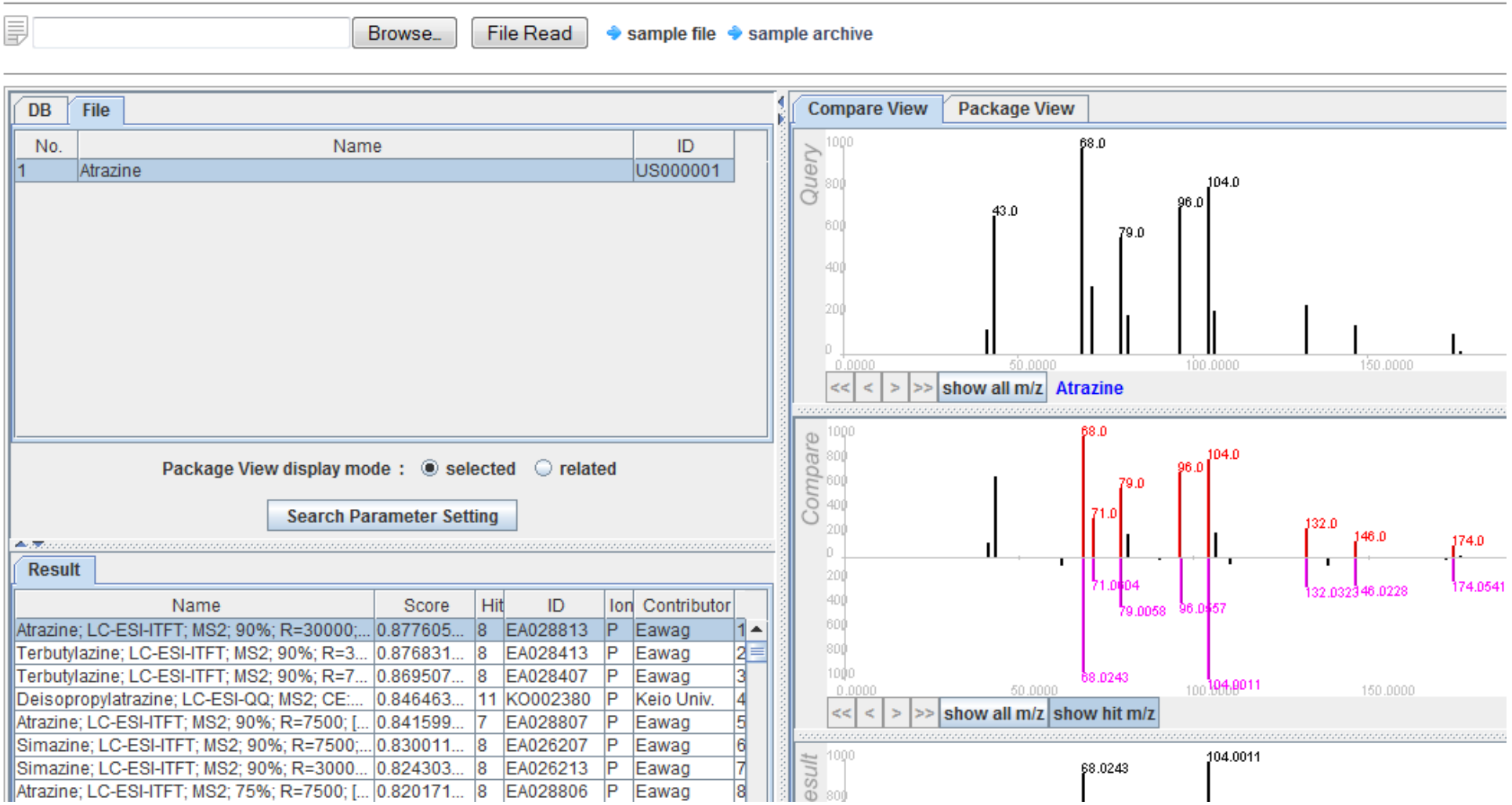


MassBank Spectrum Search Results



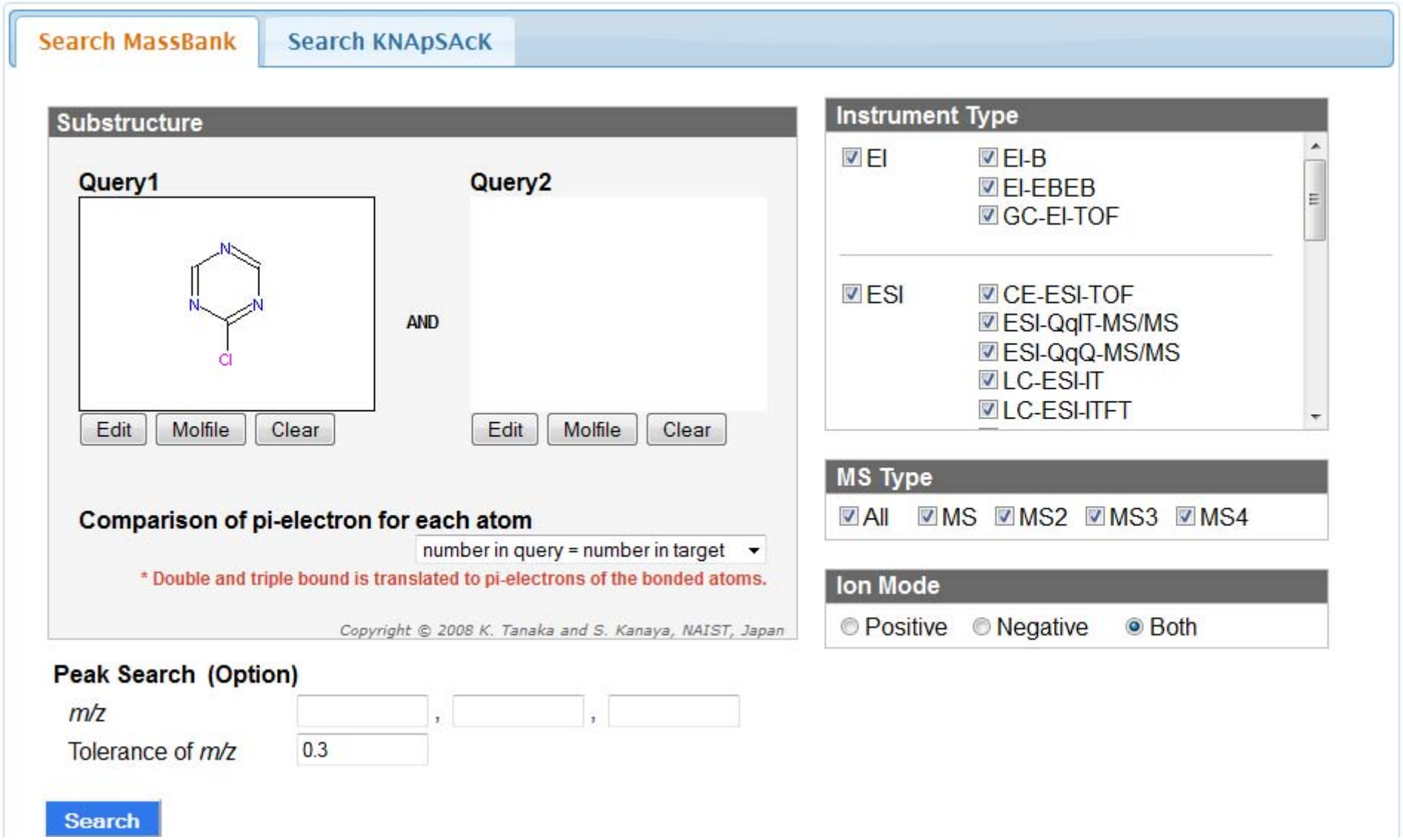
MassBank Spectrum Search with NIST Format

Example Spectrum “atrazine_msms_1563.msp”

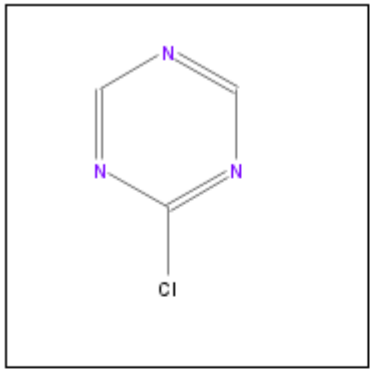


MassBank Substructure Search

How many spectra in MassBank have the atrazine backbone?



Query1



MassBank Substructure Search Results

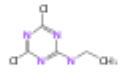
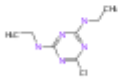
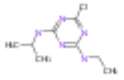
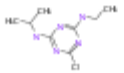
Edit / Resubmit Query

Results : 59 Hit. (1 - 59 Displayed)

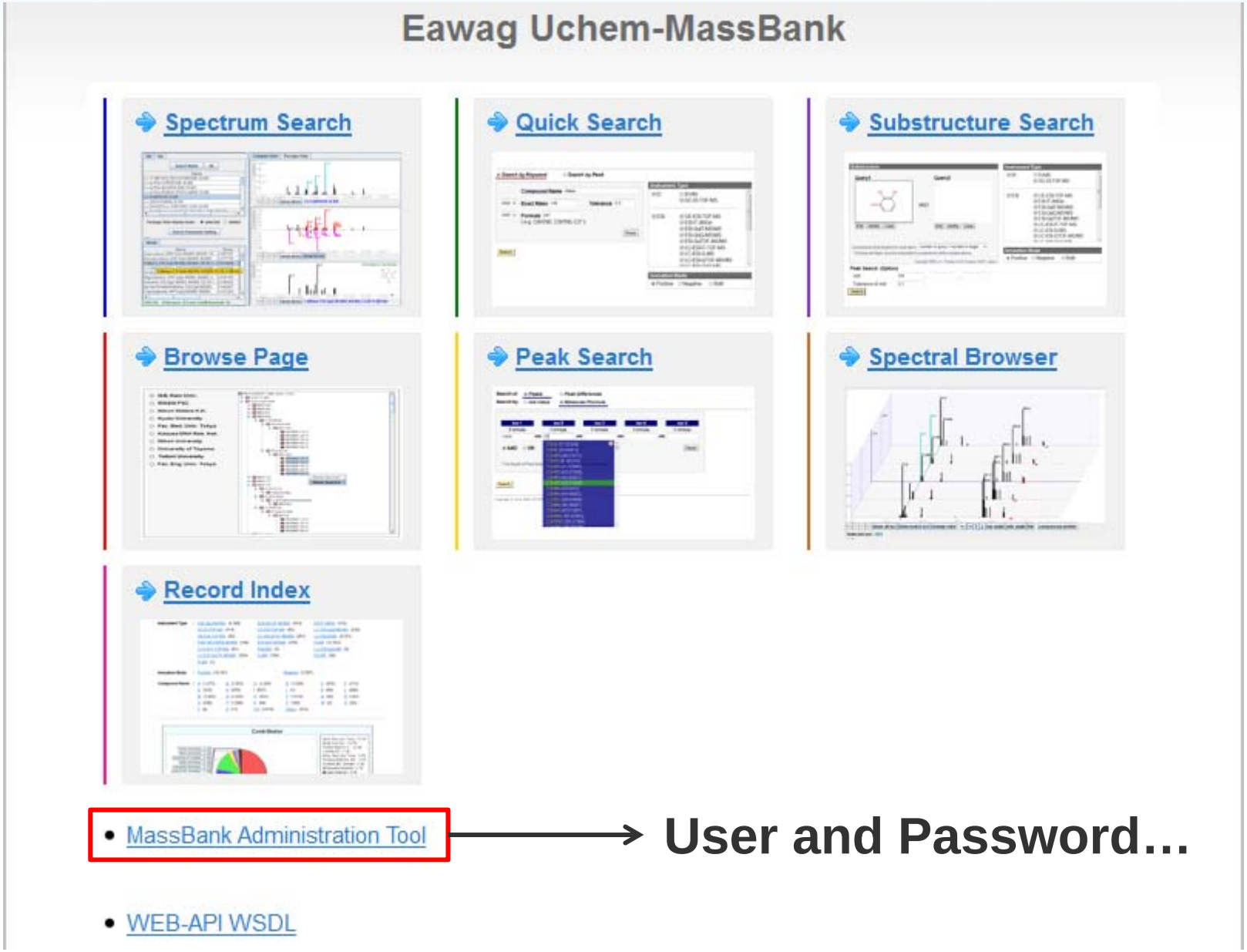
Open All Tree | Multiple Display | Spectrum Search

First Prev **1** Next Last (Total **1** Page)

▼ Results End

Name	Formula / Structure	ExactMass	ID
2,6-DICHLORO-4-(N-ETHYL)AMINO-1,3,5-TRIAZINE 1 spectrum	C5H6Cl2N4 	191.99695	
2-CHLORO-4,6-BIS(ETHYLAMINO)-1,3,5-TRIAZINE 1 spectrum	C7H12ClN5 	201.07812	
6-CHLORO-N-ETHYL-N'-(1-METHYLETHYL)-1,3,5-TRIAZINE... 1 spectrum	C8H14ClN5 	215.09377	
Atrazine 15 spectra	C8H14Cl1N5 	215.09320	
Deisopropylatrazine	C5H8ClN5	173.04682	

Internal MassBank Administration



Internal MassBank Administration

MassBank Administration Tool

Main Menu

Record Validator | **Validator**

ADMIN MENU: Record Validator | Record Registration | Structure Registration | File Upload | Sql File Generator | Version Information
Instrument Editor | Record List | Structure List | Validator | Record List Generator | Dababase Manager
HOME

Record Validator

Database : ---------- **Record Version :** 2 1 *(old record version)*

Record Archive : Browse... Validation

** please specify your [**recdata.zip**] or [*.msbk].*

Internal MassBank Administration

Database Manager

No.	DB Name	Short Label	Long Label
2	UchemA	Eawag Uchem Adducts	Uchem EZ records of adduct spectra

URL Type: (•) internal ( ) external

URL: http://uchem-massbank/MassBank/

Add | Edit | Delete

26 database (20 external database)

No.	DB Name	URL	Short Label	Long Label	Status	Details
0	MassBank	*http://uchem-massbank/MassBank/*	EQ Uchem Q Ex	Eawag Uchem-MassBank	ok	
1	UchemEZ	*http://uchem-massbank/MassBank/*	EA Uchem Orbi Test	Annotated Uchem Standard Spectra for Approval	ok	
2	UchemA	*http://uchem-massbank/MassBank/*	Eawag Uchem Adducts	Uchem EZ records of adduct spectra	ok	
3	EA	*http://uchem-massbank/MassBank/*	EA Uchem Orbi	Annotated Uchem Standard Spectra	ok	
4	Waters	*http://www.massbank.jp/*	Waters	Nihon Waters K.K.	ok	external database.
5	Kyoto	*http://www.massbank.jp/*	Kyoto Univ.	Kyoto University	ok	external database.
6	MassBank	*http://157.110.6.77/MassBank/*	Chubu Univ.	College. Life and Health Sci, Chubu U	ok	external database.

Thank you for listening

Any Questions?

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