

Workshop on Non-Target Screening  
eawag Dübendorf, September 16<sup>th</sup> - 17<sup>th</sup> 2014



Database **a**ssisted **i**dentification of **o**rganic **s**ubstances

**DAIOS**

Wolfgang Schulz and Rudi Winzenbacher

Landeswasserversorgung Water-supply, Langenau, Germany



## Outline

- Motivation to built DAIOS
- DAIOS
- Example of application
- Conclusion

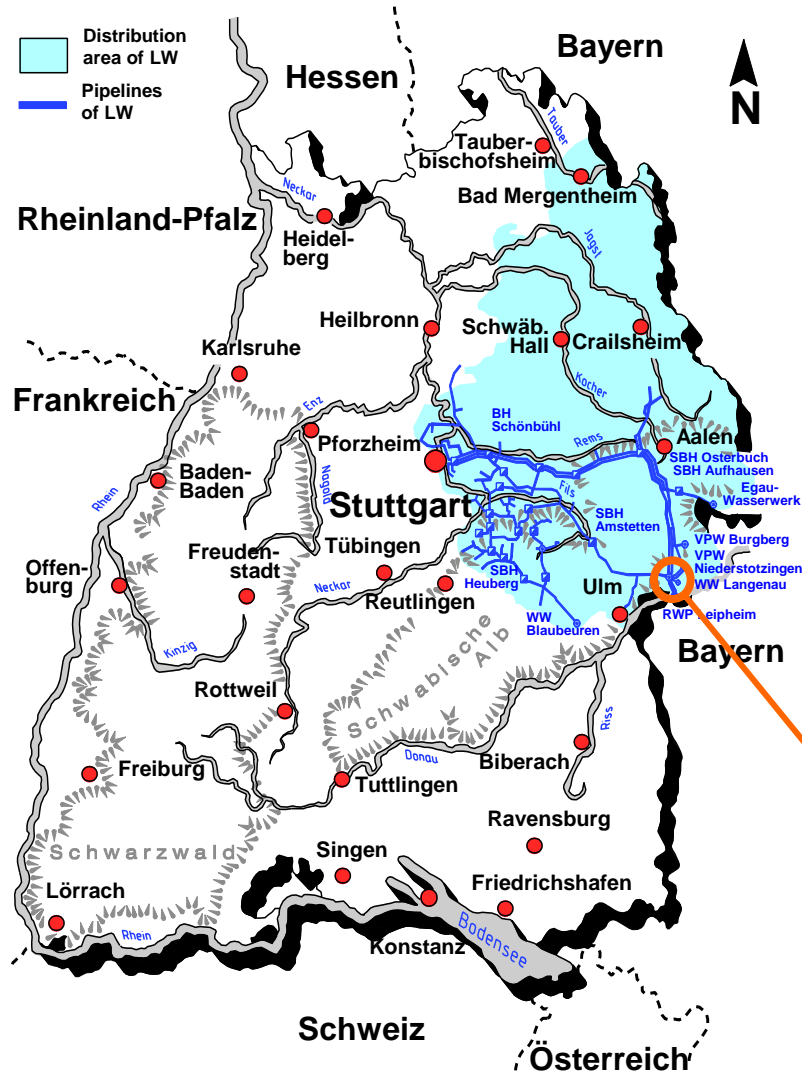


<http://www.daios-online.de>

## Landeswasserversorgung is situated in South Germany



# Distribution area of LW in South West Germany



- Distribution area in South West Germany
- 3 Million customers within distribution area about 95 Million m<sup>3</sup>/Year
- Long-distance water fraction approx. 50%

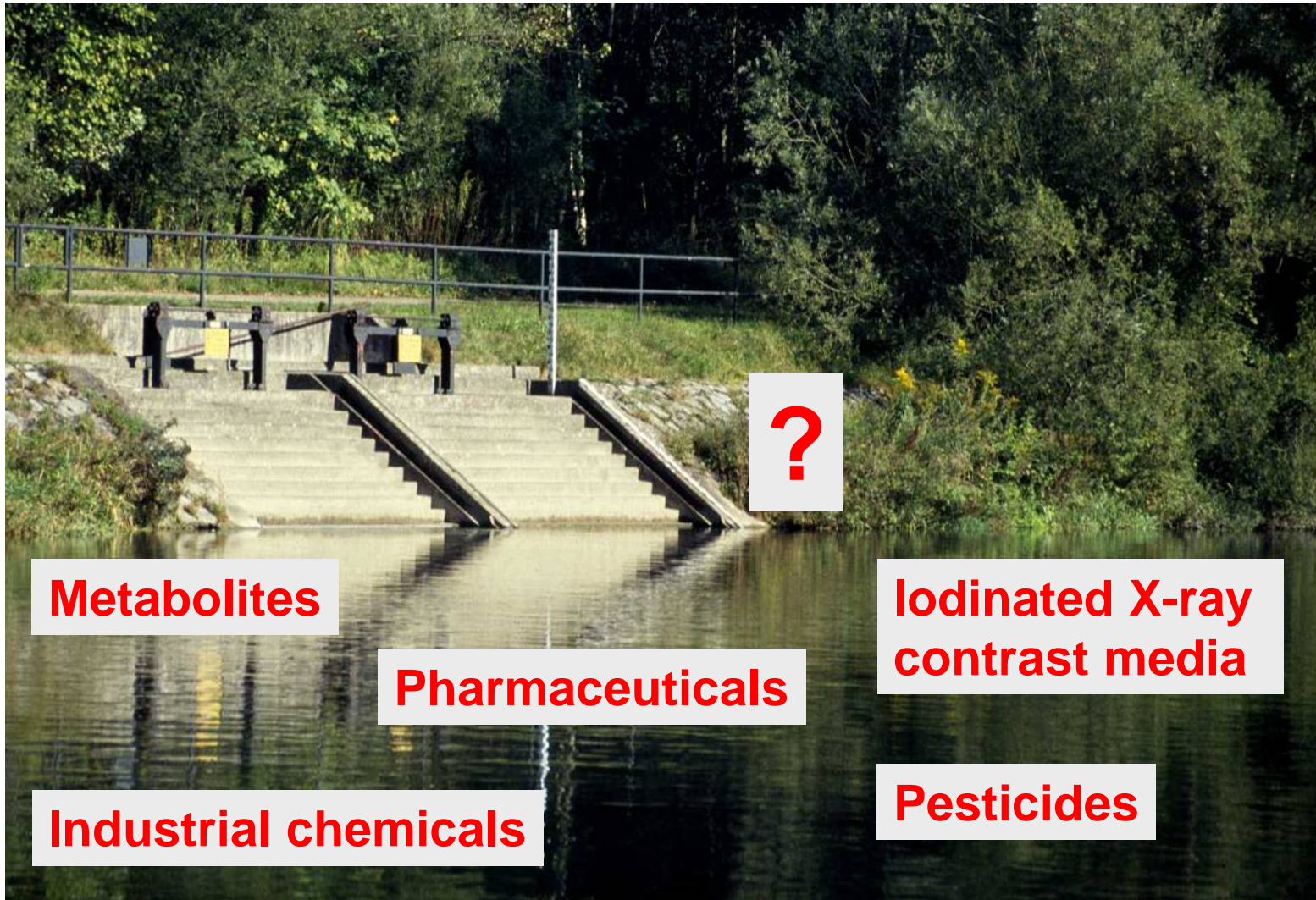
Langenau Waterworks



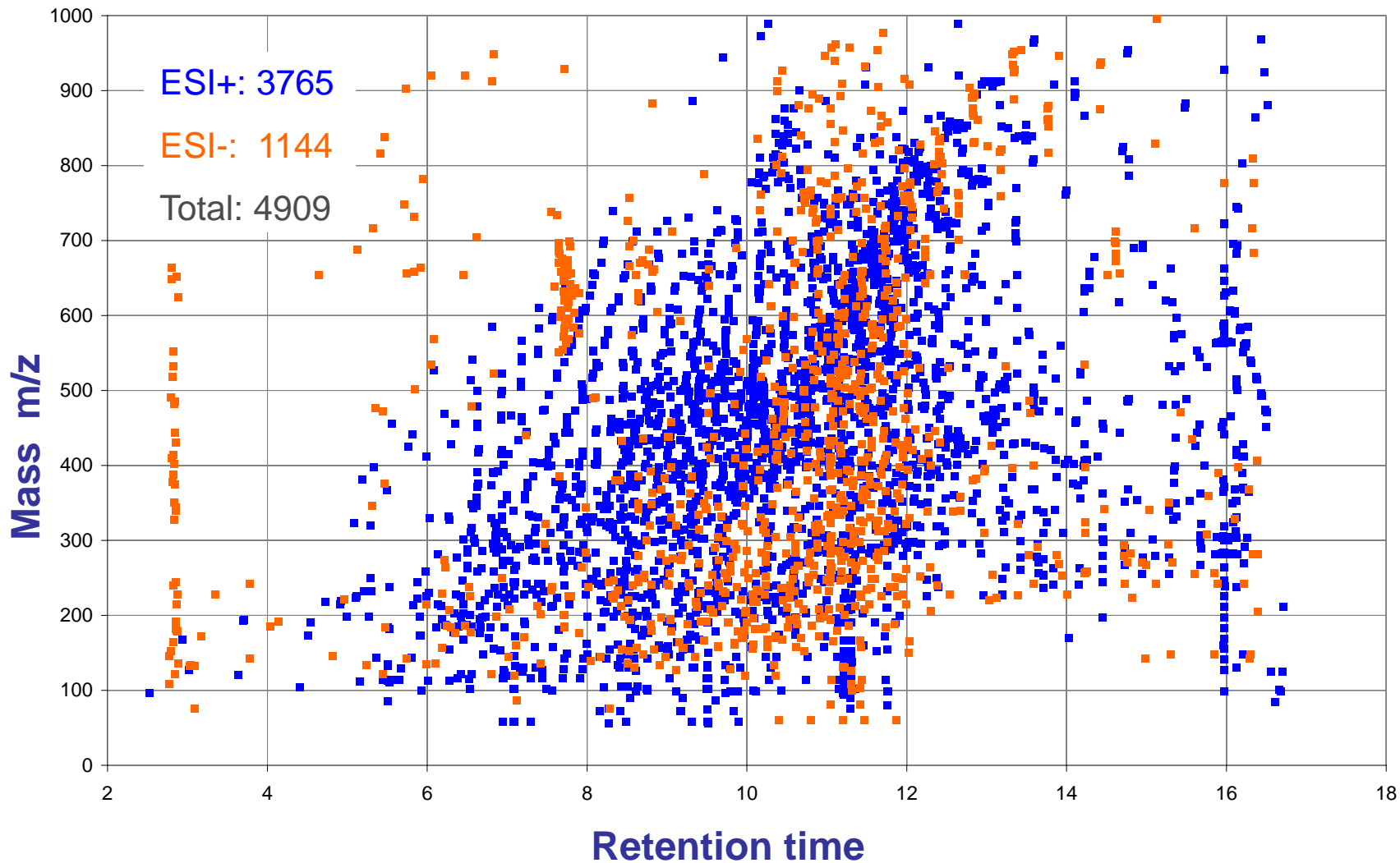
## River Danube in South Germany (Leipheim)



## Direct abstraction of river water (near Leipheim)



# Mass – RT scatter plot (Groundwater industrially influenced)

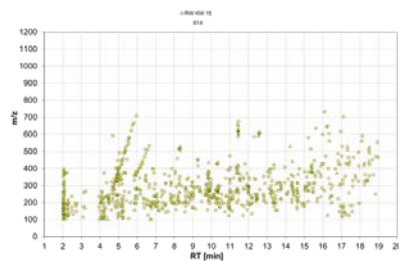
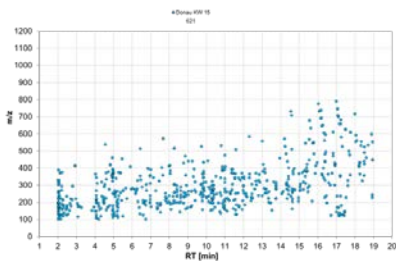
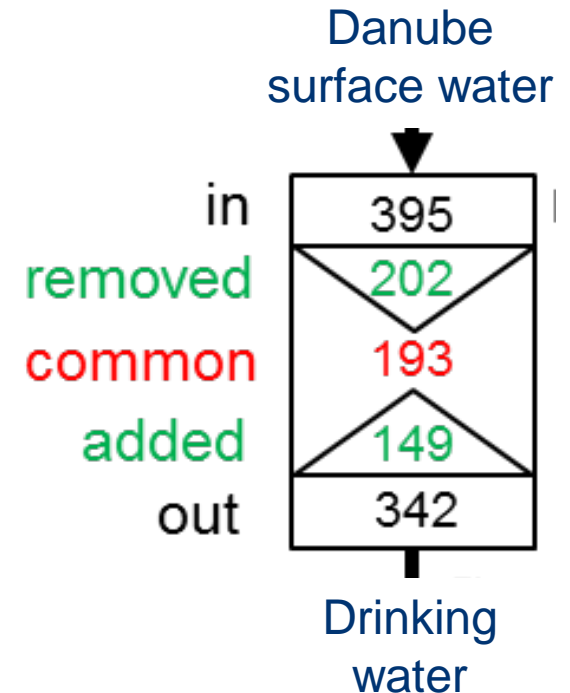




# Removal and formation of organic trace substances during water treatment



Danube Features	Drinking water Features	Question
●	—	removable
●	●	not or partial removable
—	●	transformation product



mass - RT scatterplots

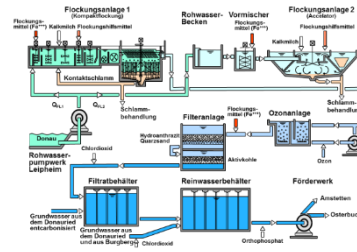


# Non-Target-Screening: Comparison of Danube raw water and drinking water

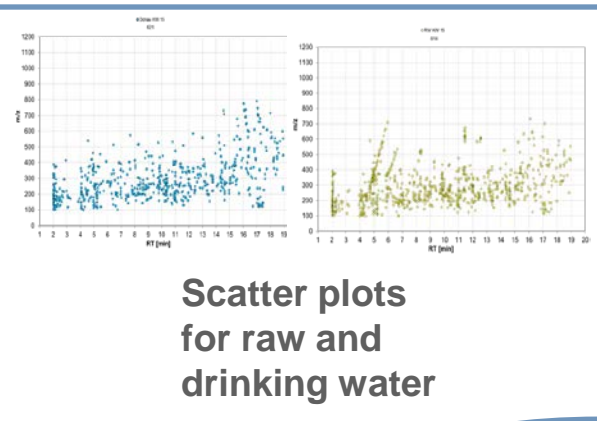
## Danube raw water



## Water treatment



## Drinking water



### Non-target screening

Sample	Number of components (identical)
KW 1	251 / 170 (85)
KW 2	374 / 214 (114)
KW 3	175 / 287 (65)
KW 4	286 / 301 (98)

# DAIOS

Aim: Creating a database to support the Identification of compounds in LC-MS and LC-HRMS

No spectrum library only table of Fragments

2008 DAIOS 1.0

# DAIOS 1.0 2009

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A A A



[» LOGIN - LOGGED OUT](#)

WELCOME TO DAIOS-ONLINE



The word DAIOS is an abbreviation for: DATABASE ASSISTED IDENTIFICATION OF ORGANIC SUBSTANCES.

The database is designed to support Non-Target-Screening research. After your registration you can use this application free of charge. All basic features of the database will then be available for you. In order to participate and generate new data entries you should already be a member of the research group "Non-Target-Screening" of the water

chemical community.

So go ahead and get your free guest user now. Just [» REGISTER](#) here.

To find out more about the concepts of this database please check out the [» ABOUT](#) page.

If you have further questions or suggestions please feel free to [» CONTACT](#) us.

Visitors: 805

Users: 49

Substances: 174

Last update: 2009-09-28

# Tab „Search“

SEARCH

Search Parameter


Exact Mass	<input type="text"/>	Tolerance	ppm	10	0,5			
Precursor Mass	<input type="text"/>	Tolerance	ppm	10	0,5			
Fragment Masses	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	Tolerance	ppm	10	0,5
Mass range	<input type="text"/>	<input type="text"/>						
Substance Name	<input type="text" value="Valsartan"/>							

» SHOW/HIDE ADDITIONAL OPTIONS



# Tab „Main“

» HOME » SEARCH » INDEX » NEW SUBSTANCE » ADMIN

A A A 

» LOGOUT » EDIT USER

PHENAZONE

MAIN SECONDARY DATA MISC Ms/Ms CHROMATOGRAPHY TRANSFORMATION TREE


Save changes Reset

Name	<input type="text" value="Phenazone"/>	Exact Mass	<input type="text" value="188.094963"/>
IUPAC	<input type="text" value="1,2-dihydro-1,5-dimethyl-2-phenyl-3H-pyrazol-3-one"/>	Molare Mass	<input type="text" value="188.23"/>
Status	<input type="text" value="green - complete"/>	Nominal Mass	<input type="text" value="188"/>

Chemical Formula	<input type="text" value="C11H12N2O"/>	<input type="button" value="Calculate Masses from Chemical Formula"/>
CAS-Nr.	<input type="text" value="60-80-0"/>	
Synonym	<input type="text" value="Antipyrine"/>	

# Tab „Secondary data“

» HOME » SEARCH » INDEX » NEW SUBSTANCE » ADMIN

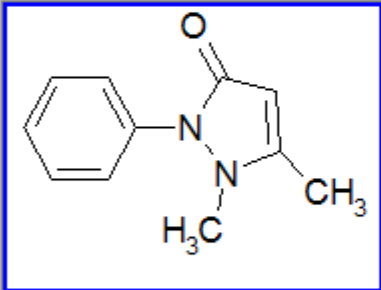
AAA 

» LOGOUT » EDIT USER

## PHENAZONE

**MAIN** | **SECONDARY DATA** | MISC | MS/MS | CHROMATOGRAPHY | TRANSFORMATION TREE

Structure Formula

Cc1cn(c(=O)[n1]c2ccccc2)C

Date of Entry: 2008-08-02

Author (username): mueller  
First name: Alexander  
Last name: Müller  
Email: mueller.a2@lw-online.de

Please upload structure formula as JPG GIF or PNG

# Tab „MS/MS“

VALSARTAN

MAIN SECONDARY DATA MISC Ms/Ms CHROMATOGRAPHY TRANSFORMATION TREE

Precursor Mass

H+  -H+

NH4+  Cl

Na+  Br

K+  HCOO

Other

Fragment Mass

<input checked="" type="radio"/>	436.2343	[M+H] <sup>+</sup>	235.0	291.0	207.0	190.0
			362.0			
<input type="radio"/>	434.2198	[M-H] <sup>-</sup>	178.0	350.0		

## Database for identification

DAIOS Login

provided by

developed by

Zweckverband Landeswasserversorgung

HOCHSCHULE WEIHENSTEPHAN-TRIESDORF UNIVERSITY OF APPLIED SCIENCES

User:

Password:

Don't have an account? [Click here to register](#)

Login

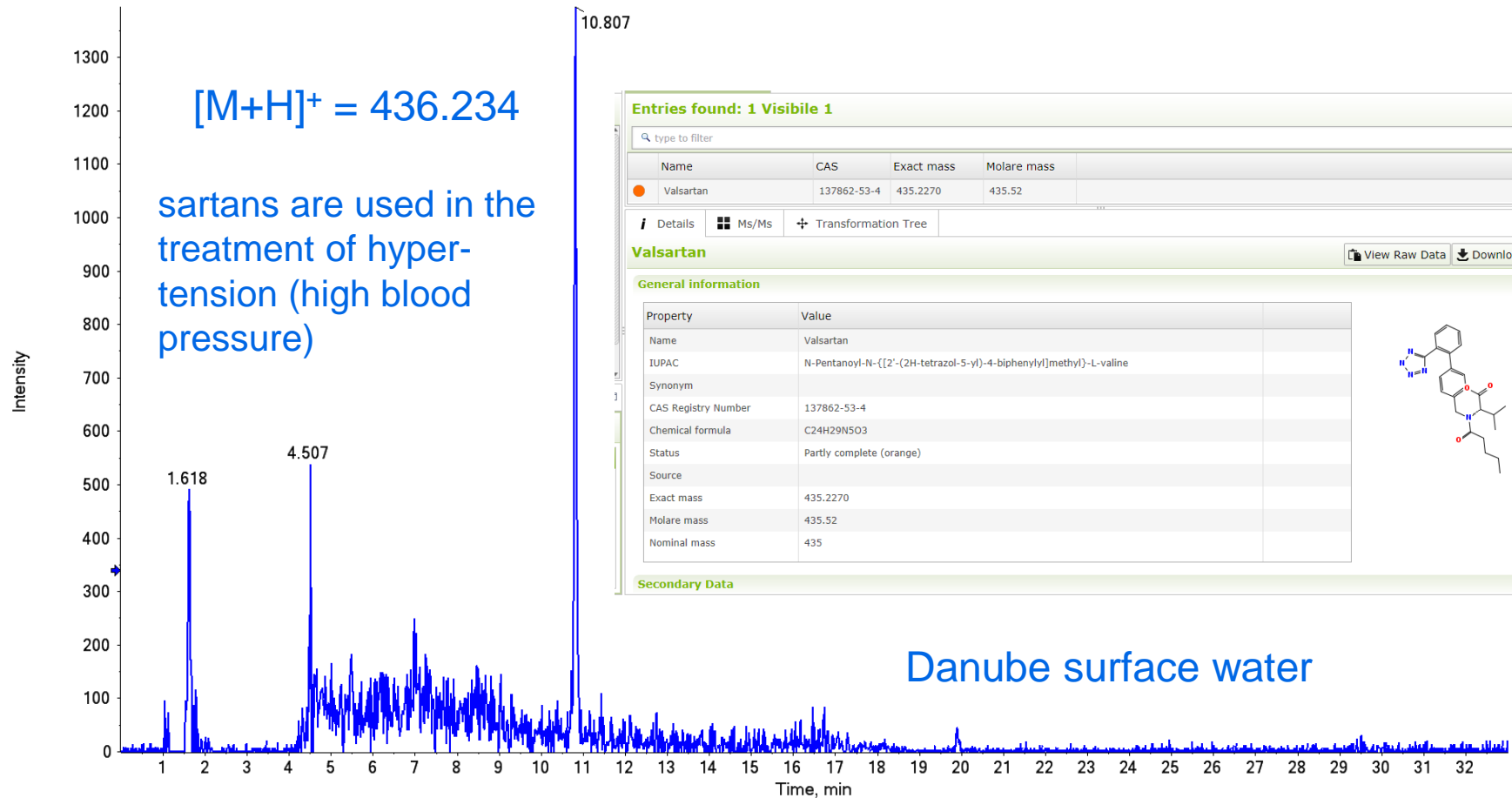
<http://www.daios-online.de>

DAIOS 2.0 built 2013  
by T. Placht and M Luthardt  
University of applied sciences  
Weihenstephan - Triesdorf



# XIC (extracted ion chromatogram) of Valsartan

Valsartan XIC from 14-03-04\_TOF\_BfG\_pos\_2014-KW10\_Donau\_04-03-14\_05.wiff (sample 1) - Donau-direkt\_KW10\_04-03-14, Experiment 1, +TOF MS (100 - 1200): 436.234 +/- 0.025 Da



# Stoff-Ident Database Search with RTI-Calculation (Bavarian environmental Agency)

Hit for mass 436,2343  
Valsartan

The screenshot displays the Stoff-Ident web application interface. The top navigation bar includes links for 'Startseite', 'Wir', 'Stellenangebote', 'Ausschreibungen', 'Kontakt', and 'Impressum'. The main menu features categories like 'Themen', 'Umweltqualität', 'Wirtschaft', 'Kommunen', 'UmweltWissen', 'Publikationen', 'Veranstaltungen', and 'Presse'. A search bar at the top left contains the text 'Suspected target screening'. On the right side, there are buttons for 'Über', 'Kontakt', 'Benutzer', and 'Ausloggen'.

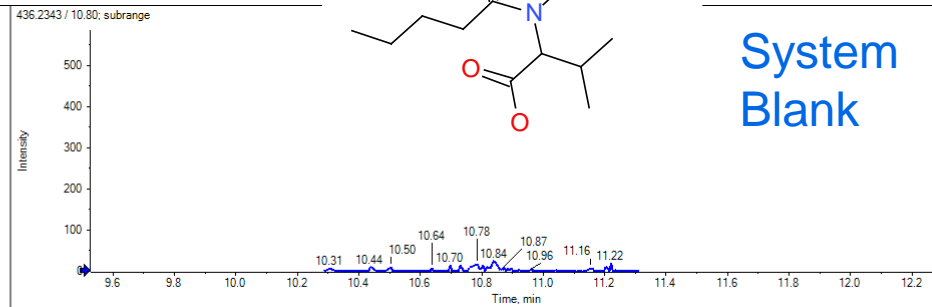
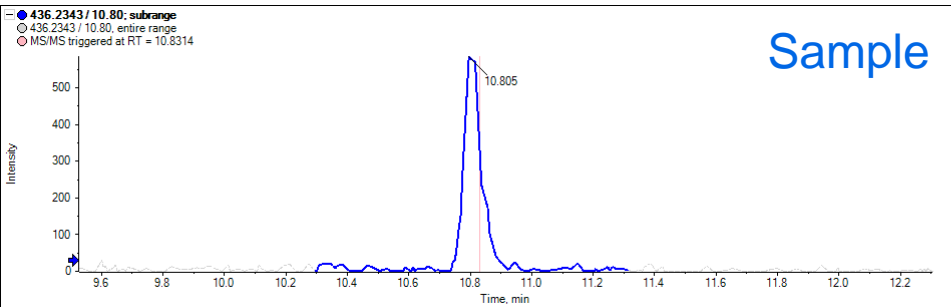
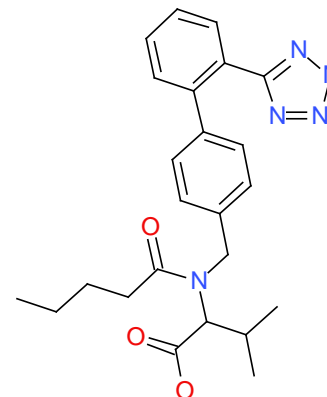
The main content area shows a search results table for 'Compounds for SI.xls'. The table has columns for 'Target identifier', 'Best match', 'Monoisotopic ma: Δ mass', 'logP', 'Δ logP', 'Name', 'CAS', 'EC Number', 'Elemental formula', and 'SMILES'. The first row is highlighted, corresponding to the hit for mass 436,2343, which is Valsartan.

Below the search results, there are two tables: 'Kalibrationsdaten' (Calibration data) and 'Ziele' (Targets). The 'Kalibrationsdaten' table lists various substances with their RTI, logP, and retention times. The 'Ziele' table lists the search targets with their RTI, logP, exact mass, and retention times. A red arrow points from the 'Hit for mass 436,2343 Valsartan' text to the first row of the search results table.

Two blue boxes with white text are overlaid on the image: 'RTI standard' is positioned over the 'Kalibrationsdaten' table, and 'RTI calculation for ALL compounds' is positioned over the 'Ziele' table.

# Identification using DAIOS IDA-MS/MS

## Valsartan



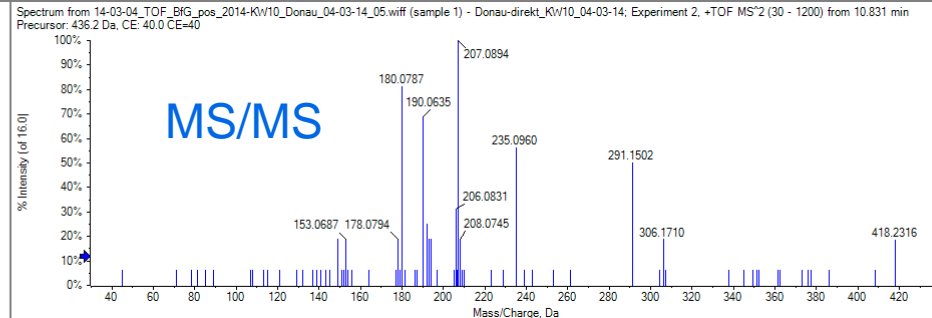
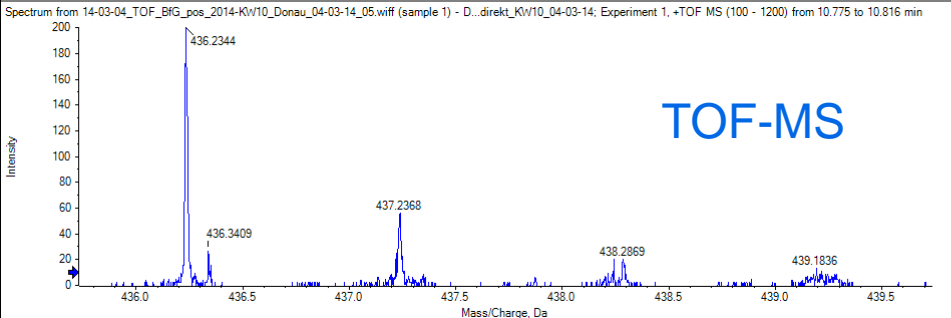
MasterView **New Session**

CTRL	Wiff file Name	Sample Name	Number of positive results
✓	14-03-04_TOF_BFG_pos_2014-KW10_Donau_04-03-14_05	Sample 1	9532
✓	14-03-04_TOF_BFG_pos_2014-KW10_Oul-Injektion_01	Sample 1	7436

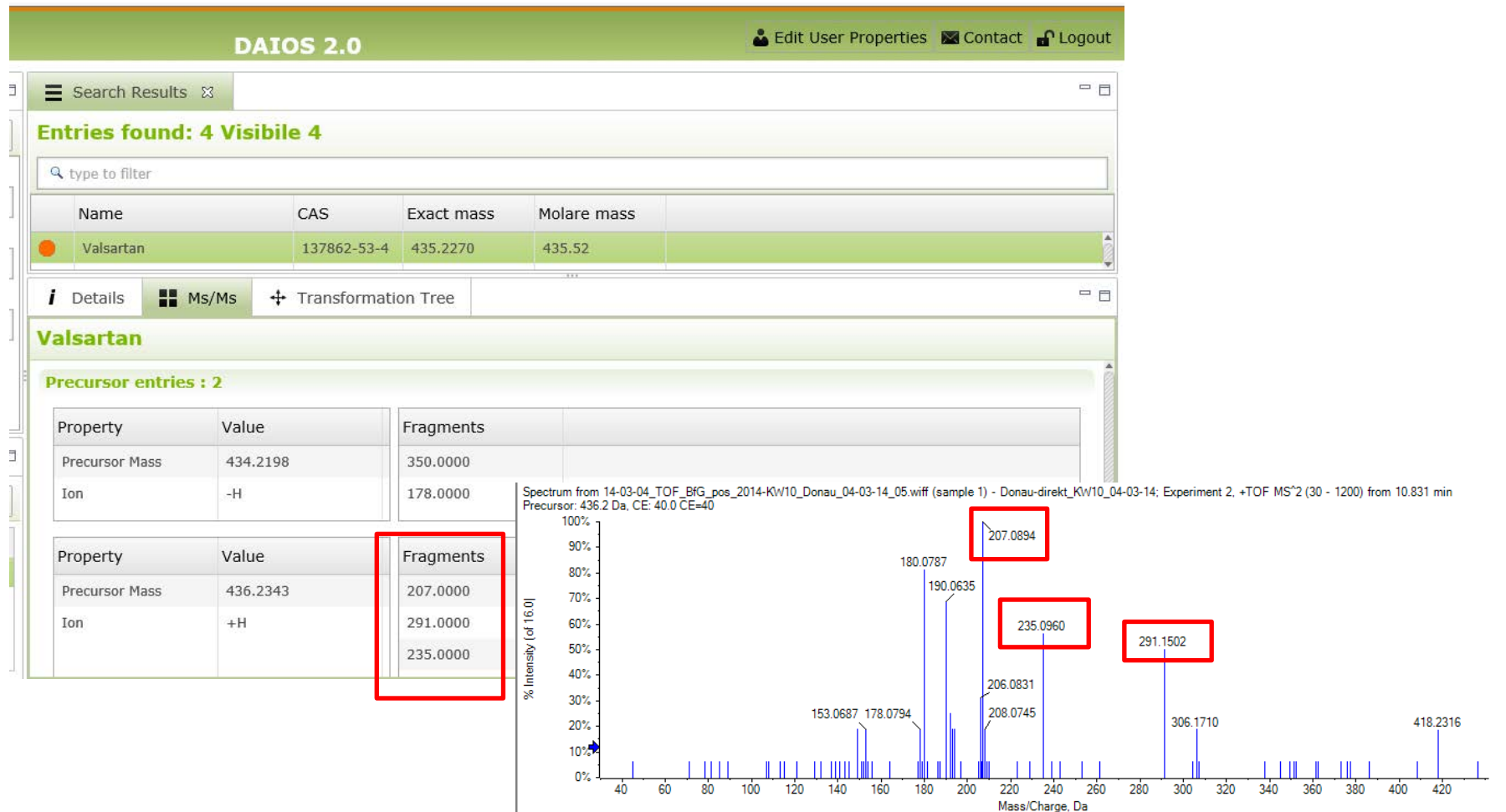
  

Name	Formula	Isotope	Mass (Da)	Adduct	Int. Std.	Extraction Mass (Da)	Width (Da)	Width (ppm)	Found At RT (min)	Formula Finder Result	Fragment Mass (Da)	Expected RT (min)	RT Width (min)	Found At Mass (Da)	Error (ppm)	Isotope Ratio Difference (%)
435.8099 / 17.82		0	435.80992			435.80992	0.005	11.473	17.84	No Formula Found		17.82	1	435.80988	-0.1	
436.0924 / 4.79		0	436.09235			436.09235	0.005	11.465	4.6	C17H25NO6S3		4.79	1	436.09146	-5.3	
436.1248 / 4.90		0	436.12479			436.12479	0.005	11.465	4.69	C25H17N5OS		4.9	1	436.12249	-5.3	
436.1288 / 4.81		0	436.12881			436.12881	0.005	11.465	4.74	C21H25NO5S2		4.81	1	436.12454	-9.8	
436.1636 / 5.16		0	436.16357			436.16357	0.005	11.464	4.99	C23H17N9O		5.16	1	436.16275	-1.9	
436.2343 / 10.80		0	436.23427			436.23427	0.005	11.462	10.81	C24H29N5O3		10.8	1	436.23443	0.4	
436.3413 / 9.61		0	436.34134			436.34134	0.005	11.459	9.61	C26H45NO4		9.61	1	436.34148	0.3	
436.3415 / 2.52		0	436.34151			436.34151	0.005	11.459	2.84	C19H45N7O2S		2.52	1	436.34177	0.6	
436.3416 / 6.08		0	436.34161			436.34161	0.005	11.459	6.13	C19H45N7O2S		6.08	1	436.34239	1.8	

Sample: 14-03-04\_TOF\_BFG\_pos\_2014-KW10\_... Control: 14-03-04\_TOF\_BFG\_pos\_2014-KW10\_... Rows 9720



# Database assisted identification of organic substances





Mass Meta Index

A B C D E  
 F G H I J  
 K L M N O  
 P Q R S T  
 U V W X Y  
 Z

1 2 3  
 4 5 6  
 7 8 9

Search Results

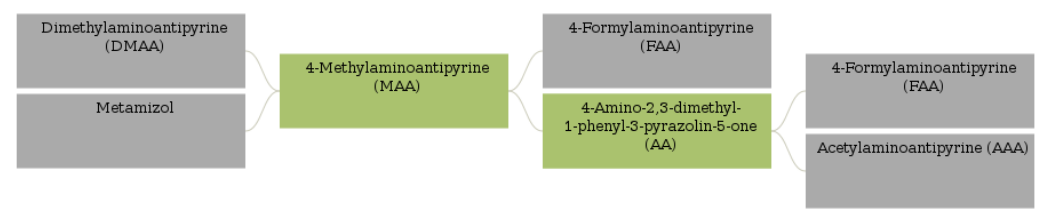
Entries found: 14 Visible 14

type to filter

Name	CAS	Exact mass	Molare mass
1,2-Dihydroxynaphthalene	574-00-5	160.0524	160.17
1,4-Dihydroxynaphthalene	571-60-8	160.0524	160.17
4-Amino-1-Naphthol	2-74-0	159.0684	159.19
5-Amino-1-naphthol	83-55-6	159.0684	159.19
8-Amino-2-naphthol	118-46-7	159.0684	159.19
3-Amino-2-naphthol	5417-63-0	159.0684	159.19
1,6-Dihydroxynaphthalene	575-44-0	160.0524	160.17
2,6-Dihydroxynaphthalene	581-43-1	160.0524	160.17
1,7-Dihydroxynaphthalene	575-38-2	160.0524	160.17

Details Ms/Ms Transformation Tree

4-Methylaminoantipyrene (MAA) Info



History

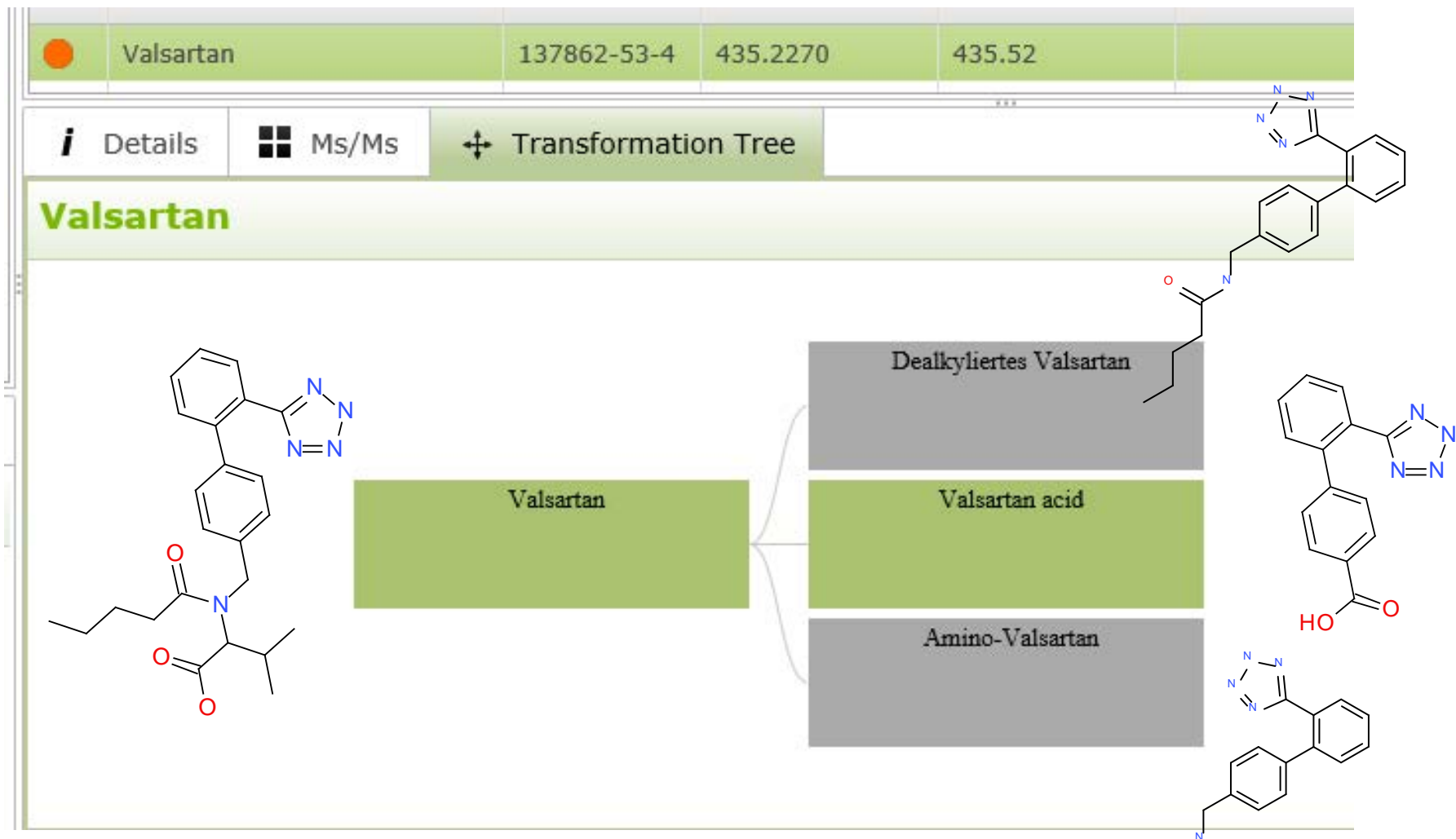
Clear

Index: l  
Isoproturon

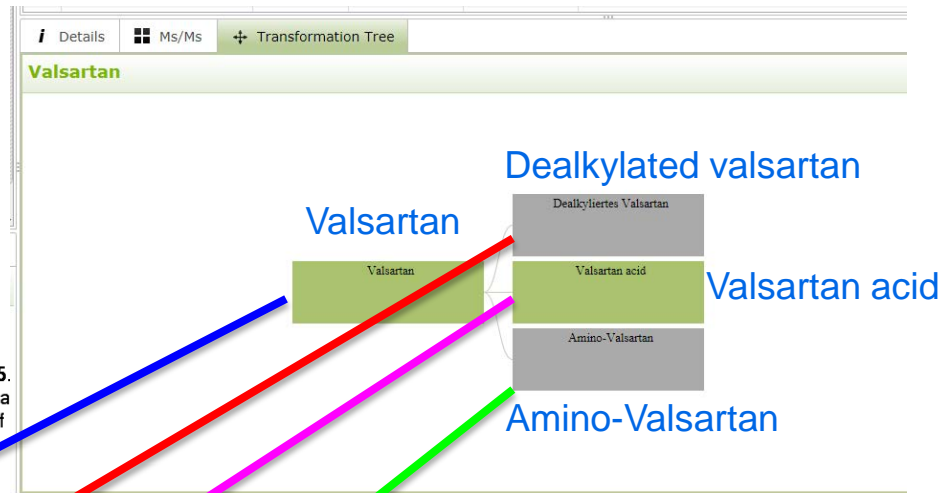
Index: 4

- 4-(Dimethylamino)phenol
- 4-Formylaminoantipyrene (FAA)
- 4-Methylaminoantipyrene (MAA)
- 4-Amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one
- 4-Methylaminoantipyrene (MAA)
- 4-Formylaminoantipyrene (FAA)
- 4-Amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one

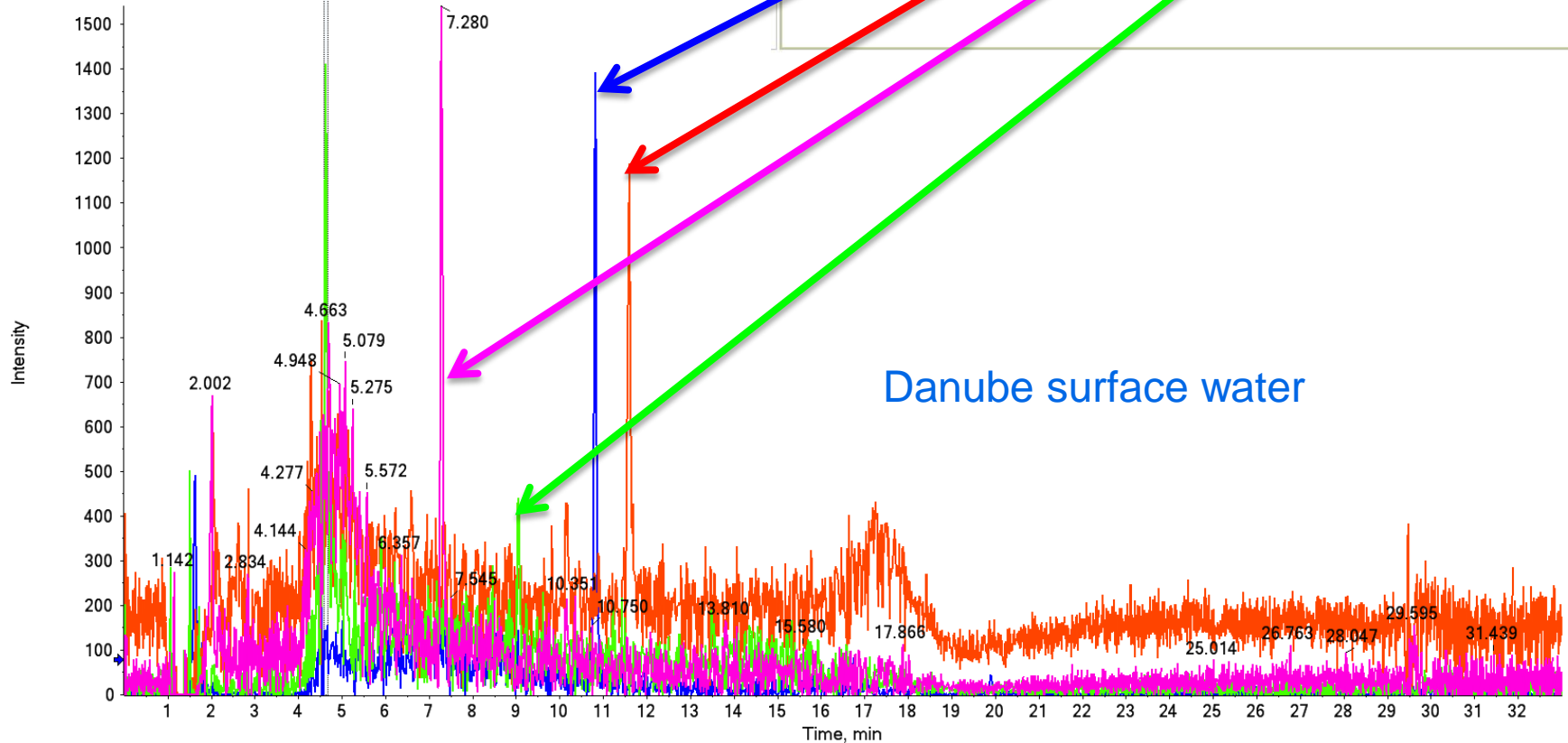
# DAIOS Transformation Tree



# XICs of Valsartan and its transformation products



- Valsartan XIC from 14-03-04\_TOF\_BfG\_pos\_2014-KW10\_Donau\_04-03-14\_05.wiff (sample)
- Valsartansaeure XIC from 14-03-04\_TOF\_BfG\_pos\_2014-KW10\_Donau\_04-03-14\_05.
- Aminovalsartan XIC from 14-03-04\_TOF\_BfG\_pos\_2014-KW10\_Donau\_04-03-14\_05.wiff (sa
- desalkyl. Valsartan XIC from 14-03-04\_TOF\_BfG\_pos\_2014-KW10\_Donau\_04-03-14\_05.wiff



# Database assisted identification of organic substances

**DAIOS 2.0** [Edit User Properties](#) [Contact](#) [Logout](#)

Search Results

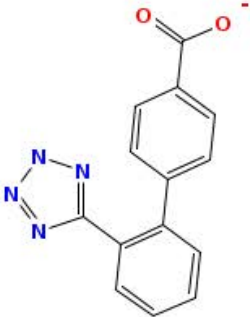
**Entries found: 4 Visible 4**

**Details**  Ms/Ms  Transformation Tree

**Valsartan acid** [View Raw Data](#) [Download Molfile](#)

**General information**

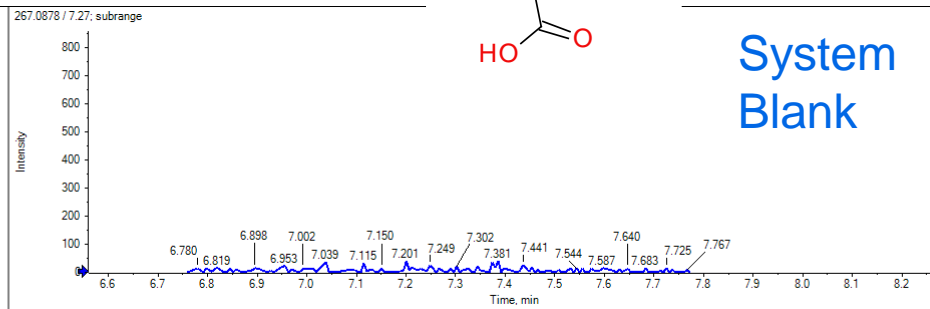
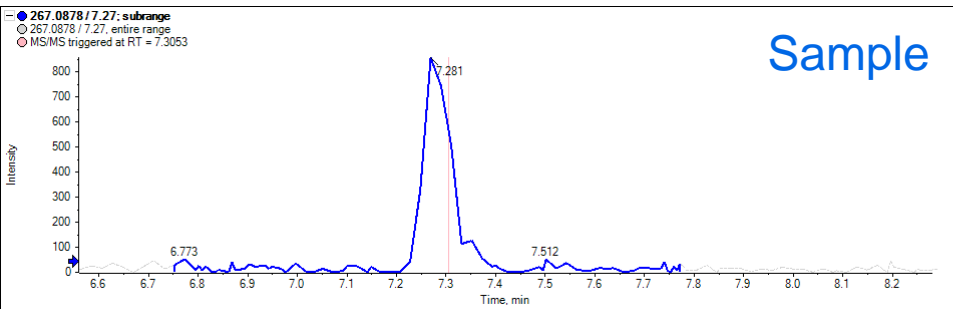
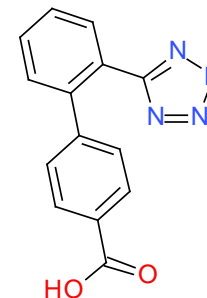
Property	Value
Name	Valsartan acid
IUPAC	
Synonym	
CAS Registry Number	
Chemical formula	C <sub>14</sub> H <sub>10</sub> N <sub>4</sub> O <sub>2</sub>
Status	Incomplete (red)
Source	
Exact mass	266.0803
Molare mass	266.26



The chemical structure of Valsartan acid is shown as a 2D ball-and-stick model. It features a central benzene ring substituted with a 1,2,4-triazole ring at the 1-position and a 4-carboxyphenyl group at the 4-position. The carboxylate group is shown with a negative charge on the oxygen atom.

# Identification using DAIOS IDA-MS/MS

## Valsartan Acid



MasterView New Session

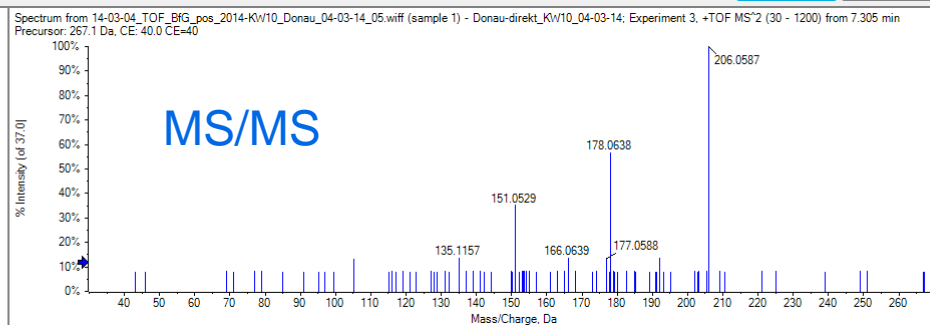
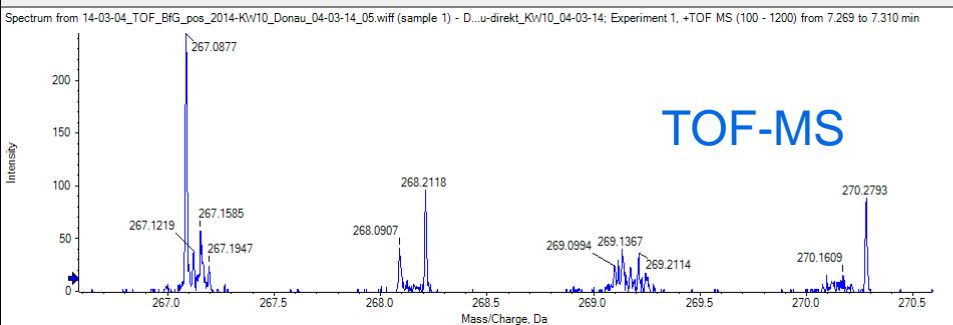
CTRL	Wiff file Name	Sample Name	Number of positive results
✓	14-03-04_TOF_BFG_pos_2014-KW10_Donau_04-03-14_05	Sample 1	9532
✓	14-03-04_TOF_BFG_pos_2014-KW10_OuL-Injektion_01	Sample 1	7436

Name	Formula	Isotope	Mass (Da)	Adduct	Int. Std.	Extraction Mass (Da)	Width (Da)	Width (ppm)	Found At RT (min)	Formula Finder Result	Fragment Mass (Da)	Expected RT (min)	RT Width (min)	Found At Mass (Da)	Error (ppm)	Isotope Ratio Difference (%)	F (r)
266.9974 / 3.52		0	266.99742			266.99742	0.005	18.727	3.73	C8H10O6S2		3.52	1	266.9992	6.7		
266.9985 / 2.50		0	266.99849			266.99849	0.005	18.727	2.84	C12H24N4O2S		2.5	1	266.99752	-3.6		
266.9998 / 4.24		0	266.99977			266.99977	0.005	18.727	3.75	C8H10O6S2		4.24	1	266.99877	-3.7		
267.0867 / 4.90		0	267.08666			267.08666	0.005	18.721	4.96	No Formula Found		4.9	1	267.08571	-3.6		
<b>267.0878 / 7.27</b>		<b>0</b>	<b>267.08779</b>			<b>267.08779</b>	<b>0.005</b>	<b>18.72</b>	<b>7.28</b>	<b>C14H10N4O2</b>		<b>7.27</b>	<b>1</b>	<b>267.08768</b>	<b>-0.4</b>		
267.1209 / 6.52		0	267.12094			267.12094	0.005	18.718	6.16	C10H22N2O2S2		6.52	1	267.12168	2.8		
267.1210 / 5.20		0	267.12102			267.12102	0.005	18.718	5.29	C10H14N6O3		5.2	1	267.12009	-3.5		
267.1215 / 5.95		0	267.12151			267.12151	0.005	18.718	5.95	C14H18O5		5.95	1	267.12157	0.2		
267.1308 / 4.65		0	267.13075			267.13075	0.005	18.717	4.65	No Formula Found		4.65	1	267.13172	3.6		

Positive result: equal or better ✓✓●●●● 0

Sample: 14-03-04\_TOF\_BFG\_pos\_2014-KW10\_... Control: 14-03-04\_TOF\_BFG\_pos\_2014-KW10\_... Rows 9720



# Identification of valsartan acid with DAIOS

DAIOS 2.0

Edit User Properties Contact Logout

Search Results

Entries found: 4 Visible 4

type to filter

Details Ms/Ms Transformation Tree

Valsartan acid

Precursor entries : 2

Property	Value
Precursor Mass	265.0731
Ion	-H

Fragments

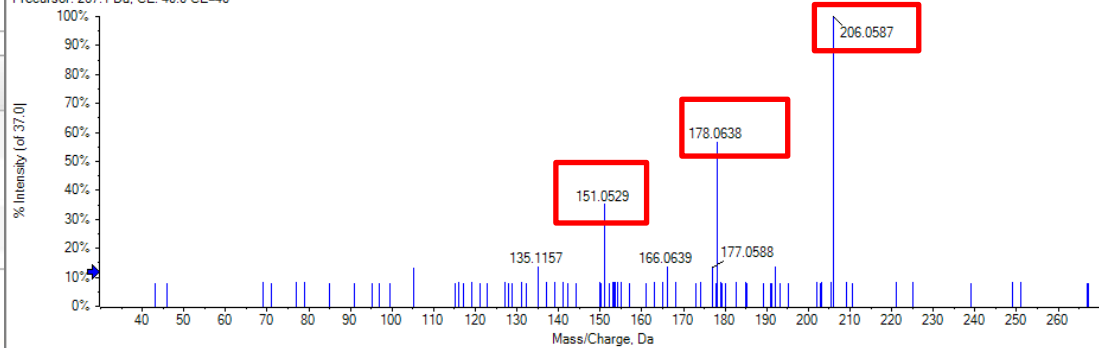
165.0000  
193.0000

Property	Value
Precursor Mass	267.0876
Ion	+H

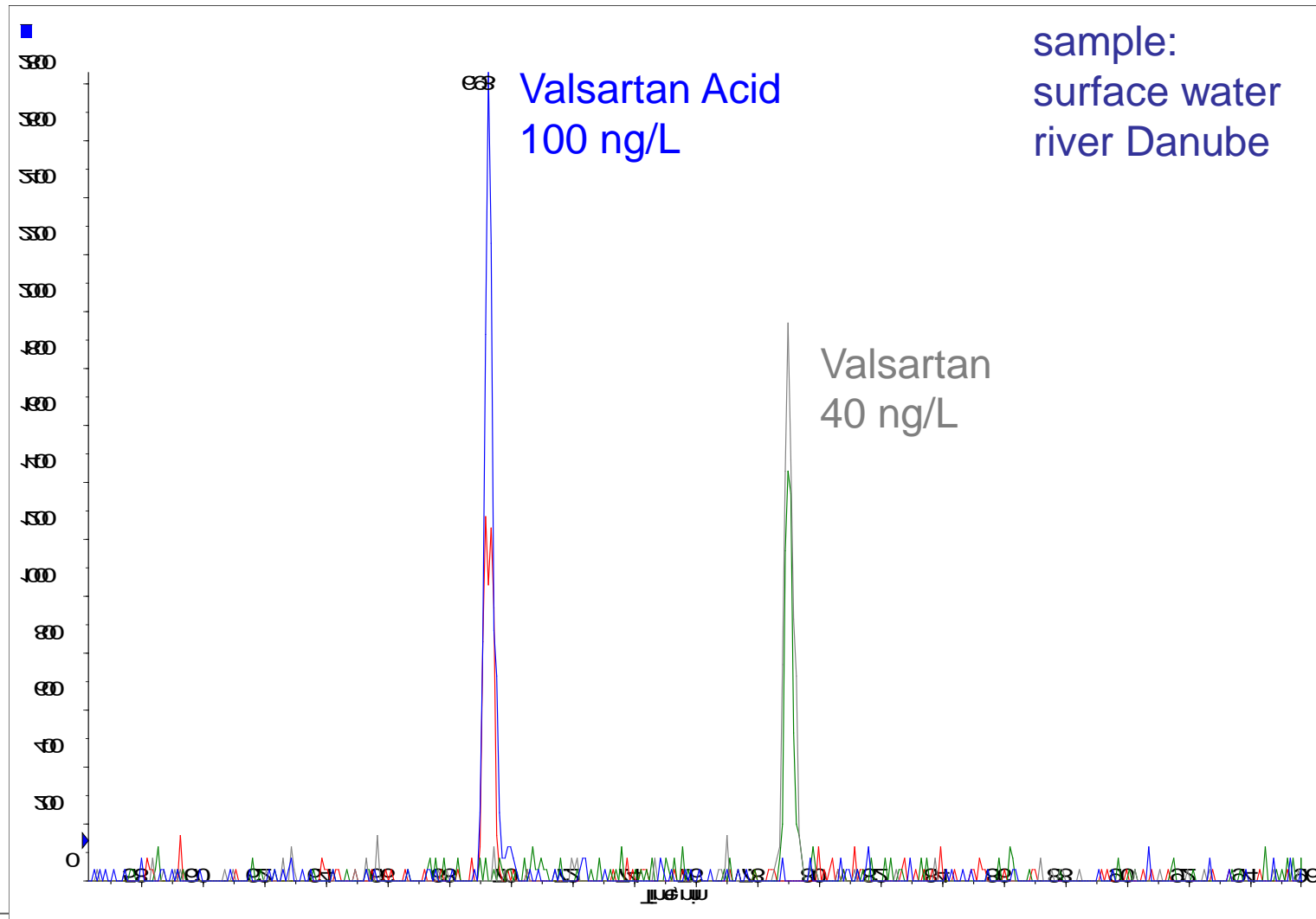
Fragments

206.0000  
178.0000  
151.0000

Spectrum from 14-03-04\_TOF\_BFG\_pos\_2014-KlW10\_Donau\_04-03-14\_05.wiff (sample 1) - Donau-direkt\_KlW10\_04-03-14; Experiment 3, +TOF MS<sup>2</sup> (30 - 1200) from 7.305 min  
Precursor: 267.1 Da, CE: 40.0 CE=40

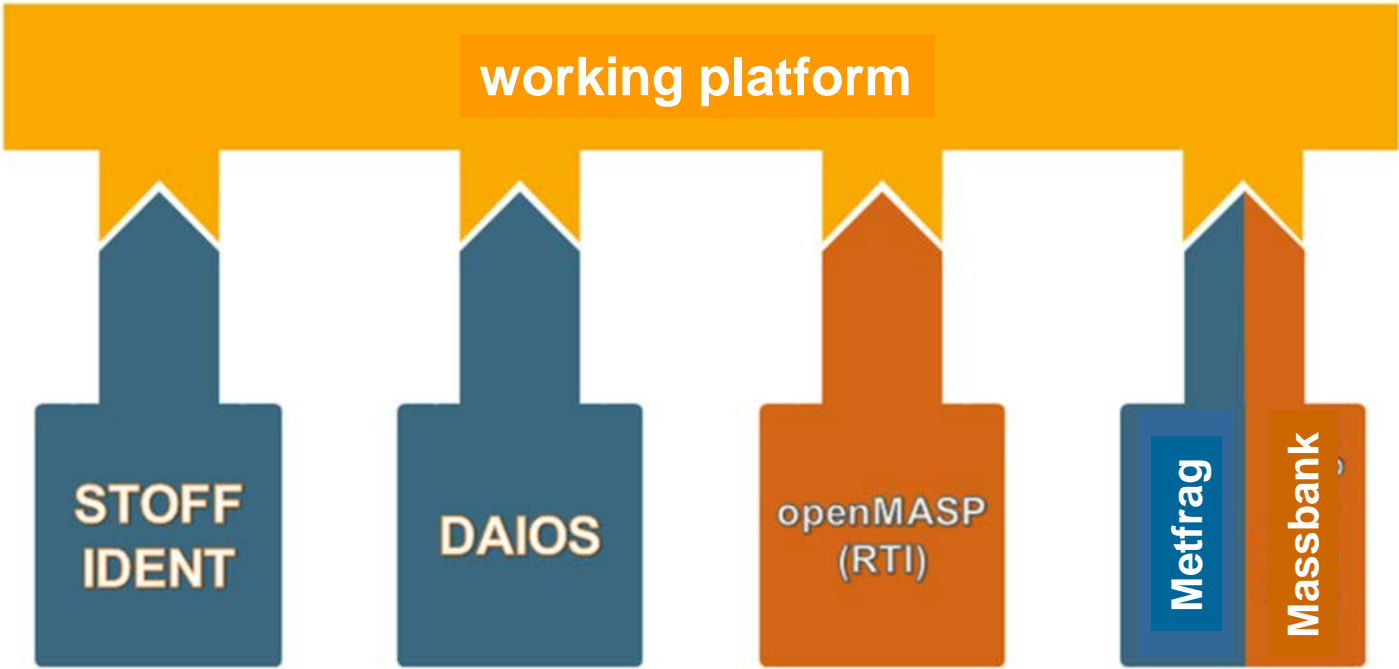


# Quantification of Valsartan and Valsartan Acid





# Concept for the identification



**Thank you**

