ISO Fd Food ERA Chair

Safety Quality Traceability

Selenium and its speciation in plant and animal

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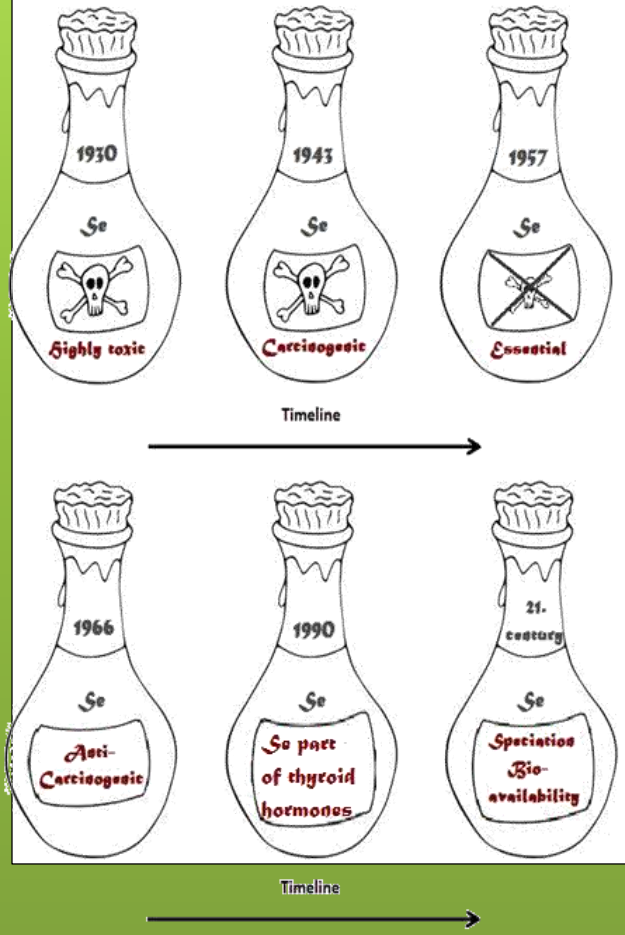
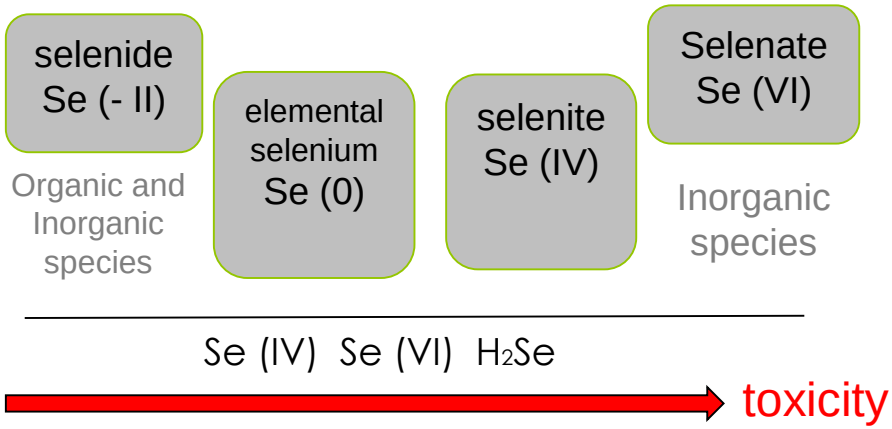
Selenium properties

- Discovered in 1817

by Berzelius and Gaham



- 4 oxidation states & numerous compounds



DMSe, DMDSe $TMSe^+$ selenocysteine selenomethionine

- Trace element for human and animals

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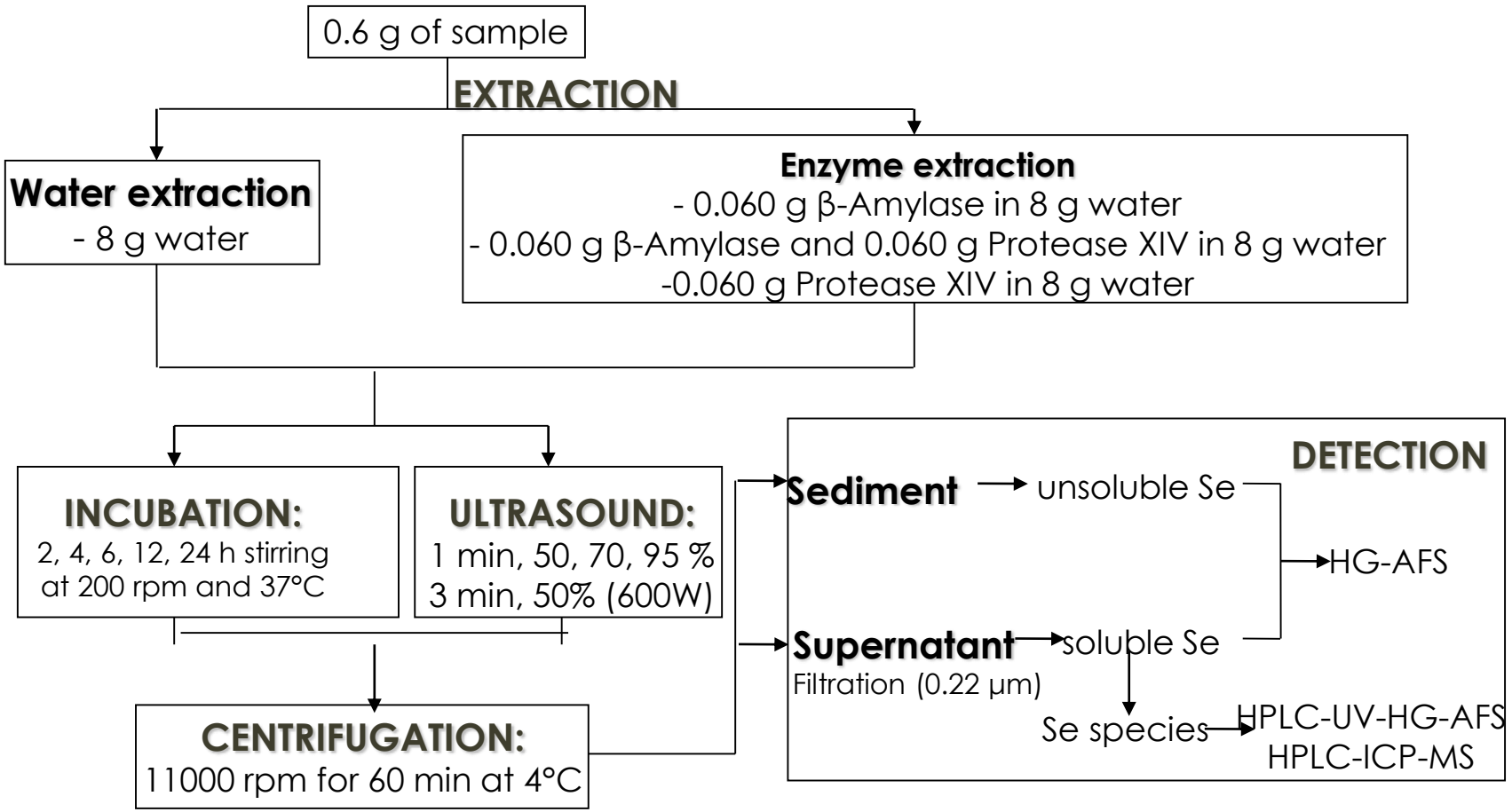
Selenium in plants

- Essentiality of selenium for plants has not yet been proven.
- In the diet vegetables are a poor source of selenium (<0.1 mg/kg wet weight), therefore cultivation of edible plants enriched with selenium could be an effective way to improve the selenium status in men.
- Since the essential nature and toxicity depend not only on the total concentration but also on chemical forms of the element present, investigation of the chemical forms of selenium: **selenite**, **selenate**, **Se-methionine**, **Se-cystine**, **Se-methylselenocysteine** in selenium enriched plants is needed.

Determination of Se species



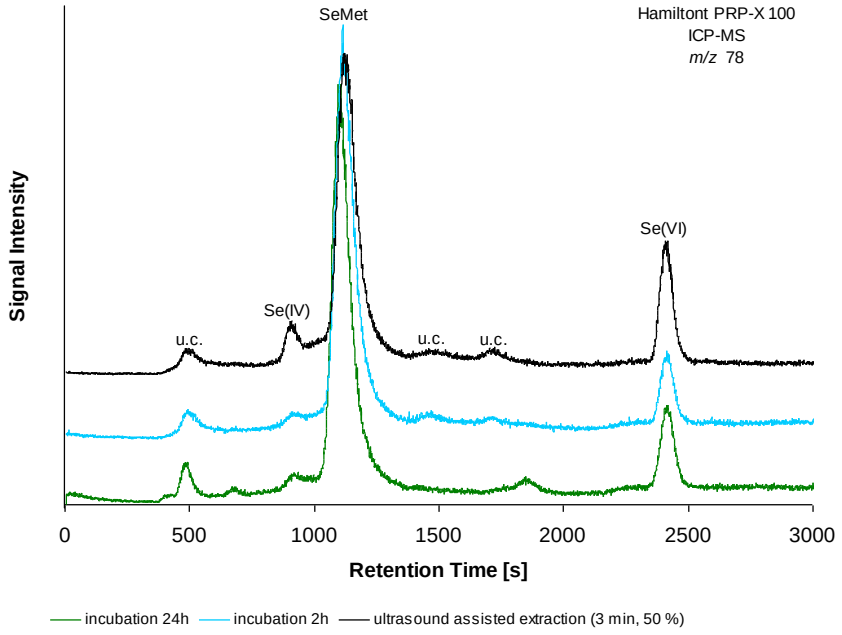
Verification of the method

total Se content (µg Se/g)			SeMet* (µg Se/g)			
	Found value	Certified value	Found value			Literature data[b]
	HG-AFS		HPLC-ICP-MS		HPLC-UV-HG-AFS[a]	
Durum Wheat Flour, RM 8436	1.10 ± 0.11	1.23 ± 0.09	incubation 24h	0.60 ± 0.07	0.57 ± 0.04	0.59 ± 0.04
			incubation 2h	0.58 ± 0.01		
			ultrasound probe 3min, 50%	0.54 ± 0.05		

* Se as SeMet

[a] Smrkolj et al., 2006

[b] Wolf and Goldschmidt, 2004



Soluble Se species in potato

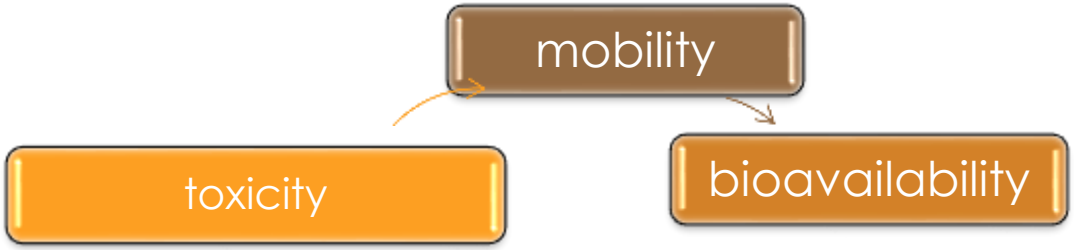
EXTRACTION		anion exchange column				
		Se(VI) [ng/g]		SeMet* [ng/g]		% SeMet* acording total Se
		ICP-MS	HG-AFS	ICP-MS	HG-AFS	
Water	W-	89	64	<LOD	<LOD	-
	W+	321	338	<LOD	<LOD	-
Protease XIV	W-	80	82	124	130	31
	W+	288	338	313	421	28
β-Amylase from barley	W-	87	82	73	61	19
	W+	313	281	113	158	12
Protease XIV + β-Amylase from barley	W-	100	121	115	85	29
	W+	321	341	351	292	29
β-Amylase from sweet potato	W-	98		44		13
	W+	286		<LOD		-
Protease XIV + β-Amylase from sweet potato	W-	103		100		29
	W+	278		284		26
LOD [ng/g sample]		1	60	10	60	

* Se as SeMet
SeMet was confirmed also on cation exchange column (Zorbax SCX-300)
W-,W+ -various growing conditions

CUDERMAN, Petra, KREFT, Ivan, GERM, Mateja, KOVAČEVIČ, Miroslav, STIBILJ, Vekoslava. *Journal of agricultural and food chemistry*, 2008, vol. 59, no. 19, str. 9114-9120,

Selenium in marine and freshwater biota

- Se contents in seafood are higher than in terrestrial foodstuffs
  - Se speciation is more important in defining

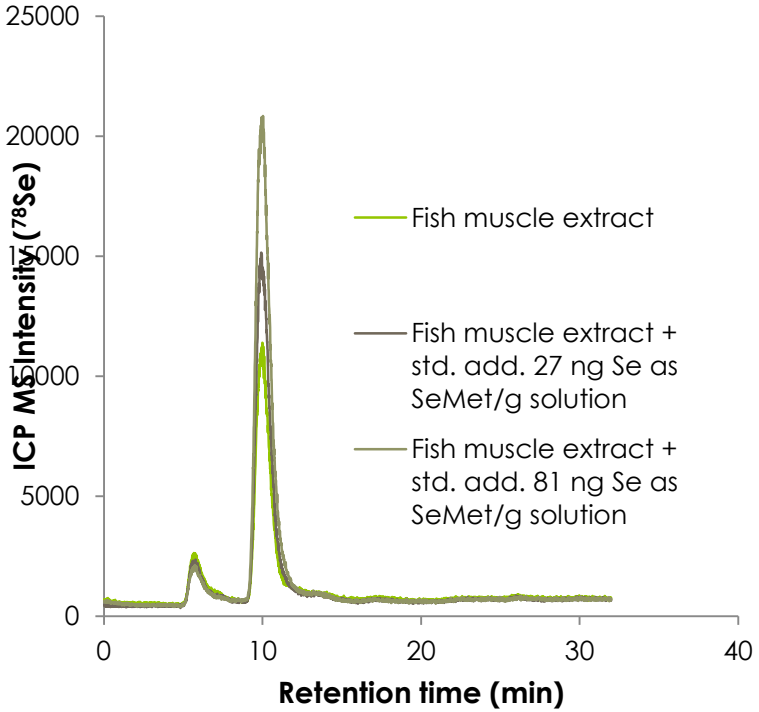


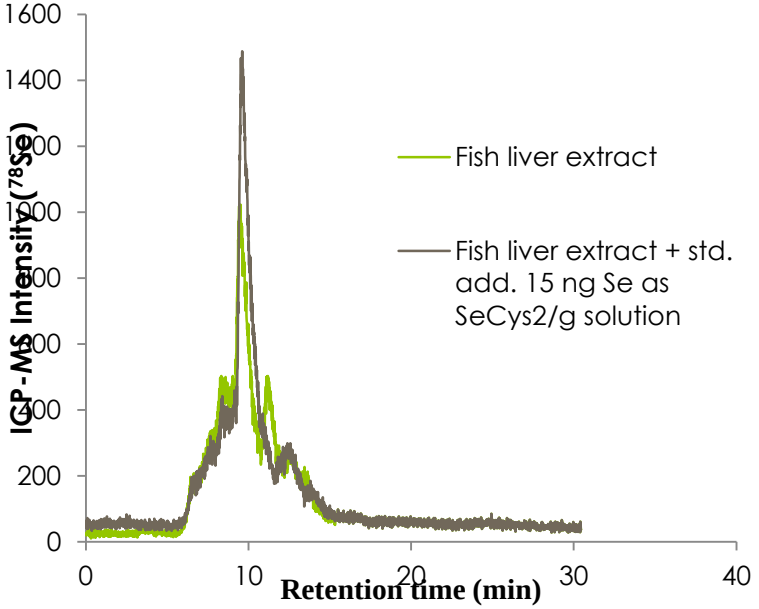
- understanding the absorption of Se from fish to humans
  - **little is known about the chemical forms of organoselenium compounds in seafood**

Se species identified

Typical chromatograms for the separation of Se species in the extract of muscle fish tissue on a Hamilton PRP - X100 anion exchange column.

Chromatograms of liver fish enzymatic extracts on a ZORBAX 300-SCX cationic column, spiked with selenocystine selenium standard.





KRISTAN, Urška, ARRIBÉRE, Maria, STIBILJ, Vekoslava. *Biological trace element research*, 2013, vol. 151, issue 2,p. 240-246,

Selenium and Se species content in muscle fish tissue

Sample (n)	Muscle tissue [a]				
				Se species identified [b]	
	Total Se µg g^{-1} (DM)	Soluble Se µg g^{-1}	Average solubility (%)	SeMet µg Se g^{-1}	W[d] µg Se g^{-1}
brown trout (10)	1.30 ± 0.38	0.65 ± 0.24	47 (37-70)	0.52 ± 0.19 (88.2)	0.13 ± 0.05 (19.1)
	(0.66 – 1.55)				
rainbow trout (11)	1.24 ± 0.40	0.55 ± 0.27	47 (31-66)	0.60 ± 0.34 (86.9)	0.09 ± 0.01 (15)
	(0.72 – 1.61)				
brook trout (5)	1.37 ± 0.35	0.66 ± 0.31	52 (41-60)	0.76 ± 0.35 (75.8)	0.08 ± 0.02 (14.1)
creole perch (4)	1.69 ± 0.73	0.96 ± 0.40	55 (47-62)	1.32 ± 0.72 (88.8)	0.06 ± 0.01 (11.9)

(n) Number of samples analysed, ()- range
[a] Results are given as the average ± standard deviation (range)
[b] (% of identified soluble Se)
[d] Unknown Se species with the same retention time as SeCys2 (6 min), obtained on Hamilton PRP-X 100, estimated as Se in SeCys2

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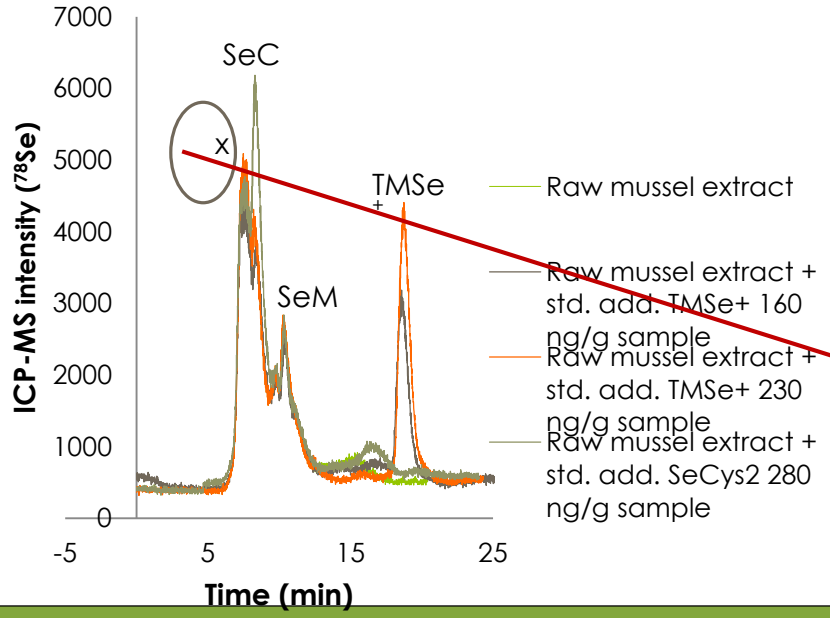
Se species in wild and fish farm fish

	Total Se	Soluble Se	Selenium species		
			SeMet	Se as $SeCys_2$	
	ng/g	ng/g extract	ng/g extract		%
Fish farm trout, foreign (2)	200 ± 130	188 ± 24	106 ± 40 (47–135)	103 ± 2 (102–104)	**88–120**
Fish farm trout, Slovenia (10)	180 ± 20	164 ± 38	83 ± 17 (89–109)	121 ± 27 (75–151)	**95–115**
Salmo marmoratus (1)	1800	1332	840	547	**104**
Salmo trutta (3)	340 ± 110	184 ± 60	78 ± 12 (56–91)	100 ± 25 (74–119)	**90**
Onchorynchus mykiss (1)	280	162	94	51	**89–95**
Fish farm seabass (2)	190± 30	Sample (n)	81 ± 12 (68–96)	46 ± 10 (35–57)	**97–100**
Wild seabass (1)	530	477	144	205	**87**

Mytilus galloprovincialis mussels

- Mussels were collected from 3 different locations:
  - **Slovenia** (Bay of Koper, Piran & Strunjan) in 2009 & 2010; 2 times per year March & Sepetmebr
  - **Italy** (March, 2012)
  - **NE Pacific** (March, 2012)

TMSe+ was not found in mussel



	Se	Soluble Se %	Se as $SeCys_2$	Se as SeMet	Sum
	µg/g				%
Slovenia, March	4.4-7.1	54-74	0.6-0.7	0.09-0.2	**10-16**
Slovenia, September	1.9-2.8	63-80	0.3-0.5	0.06-0.1	**13-25**
Italy	8.3±0.34	68	0.4+0.03	0.3±0.03	**11 (16)**
NE Pacific	3.2±0.04	63	0.5±0.04	0.3±0.02	**24**

	X (unknown)	%
Italy	0.25 ±0.01	5

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FUTURE WORK

- various enzymes and/or different extraction media for Se extraction in plant and fish samples
- identification or and isolation of Se compounds
- Se species in liver from various fish
- Se species in Se and I enriched plants

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