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Safety Quality Traceability

# Selenium and its speciation in plant and animal

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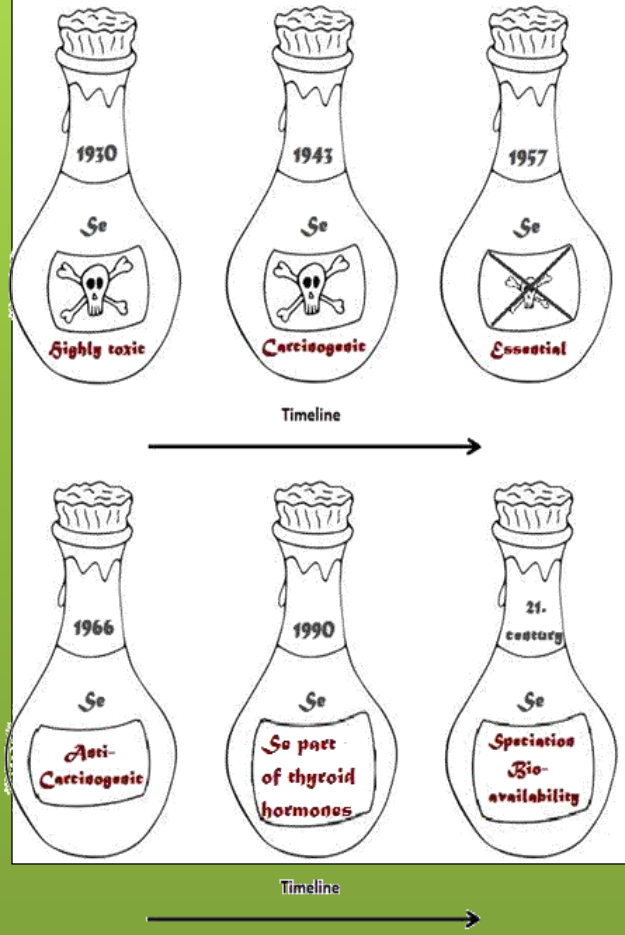
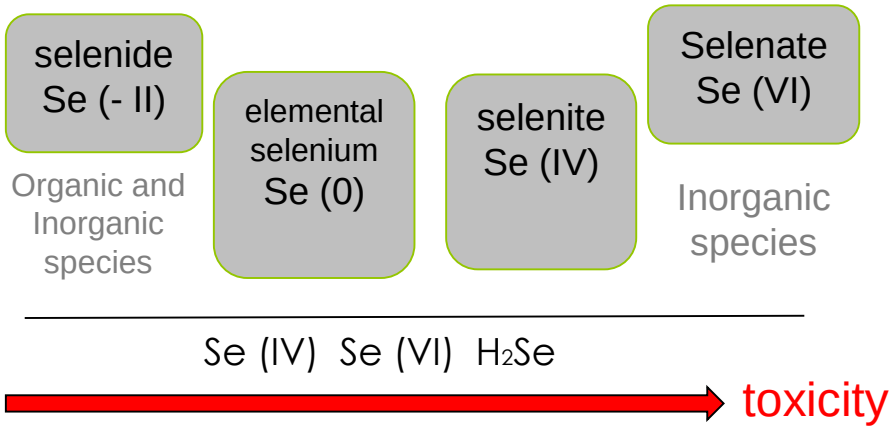
# Selenium properties

- 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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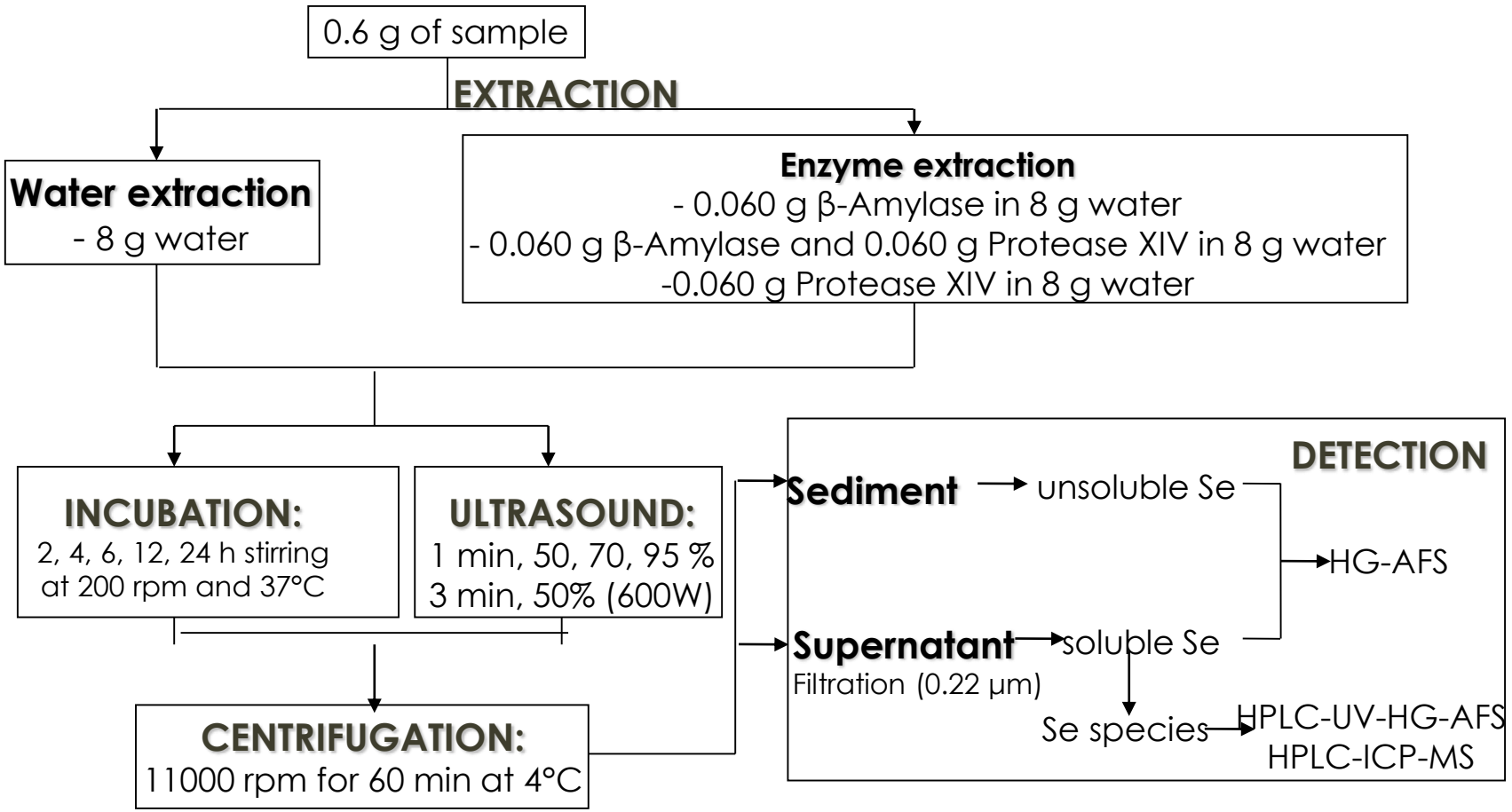
# Selenium in plants

- 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



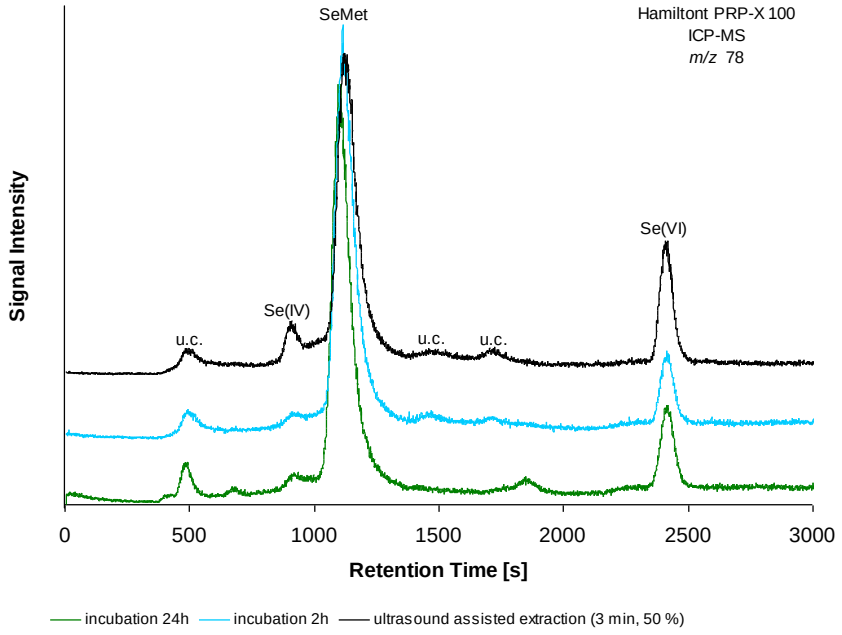
# Verification of the method

| 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

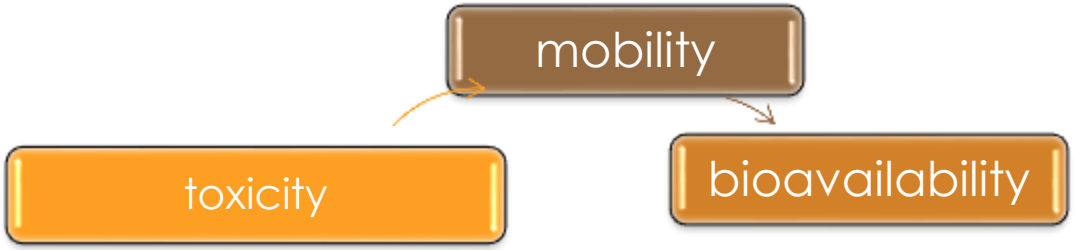
| EXTRACTION | | anion exchange column | | | | |
|---|---|---|---|---|---|---|
| | | Se(VI) [ng/g] | | SeMet* [ng/g] | | % SeMet* acording total Se |
| | | ICP-MS | HG-AFS | ICP-MS | HG-AFS | |
| Water | W- | 89 | 64 | <LOD | <LOD | - |
| | W+ | 321 | 338 | <LOD | <LOD | - |
| Protease XIV | W- | 80 | 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

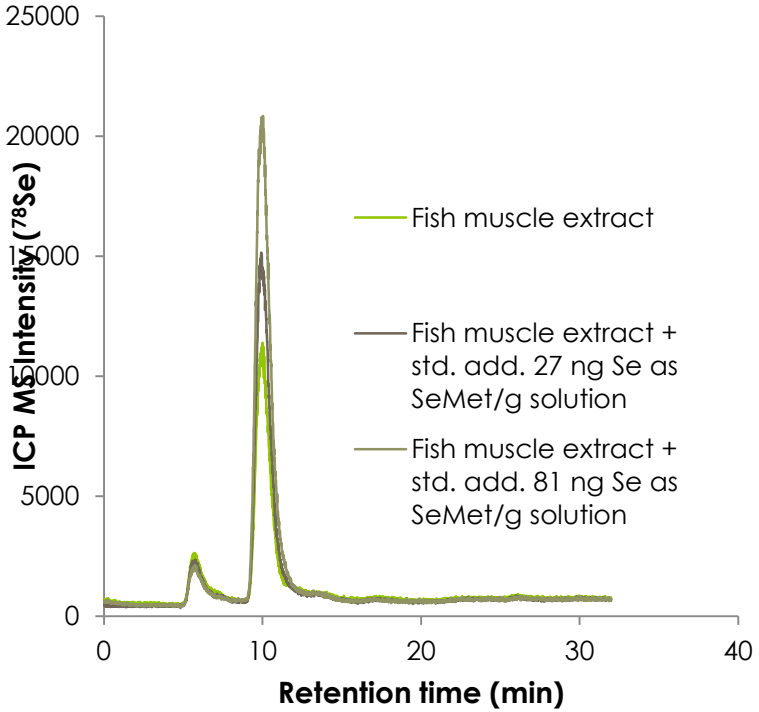


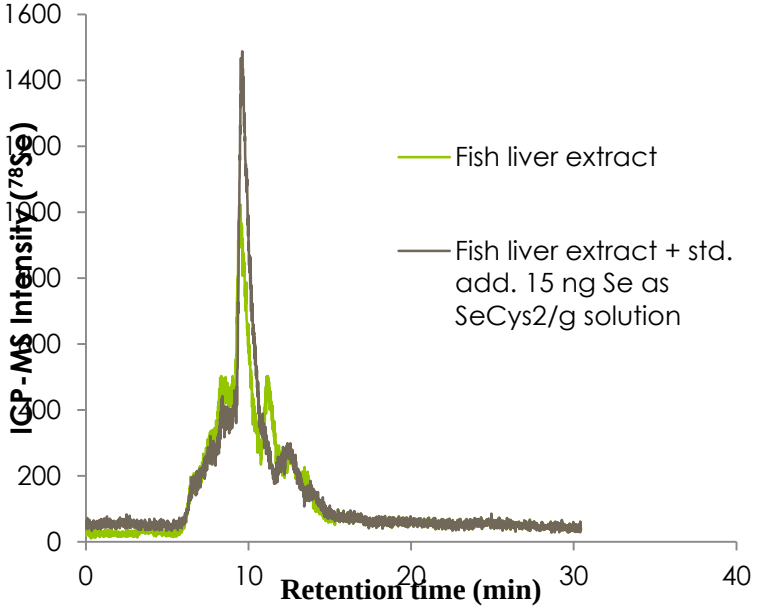

- understanding the absorption of Se from fish to humans
  - **little is known about the chemical forms of organoselenium compounds in seafood**

# 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

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

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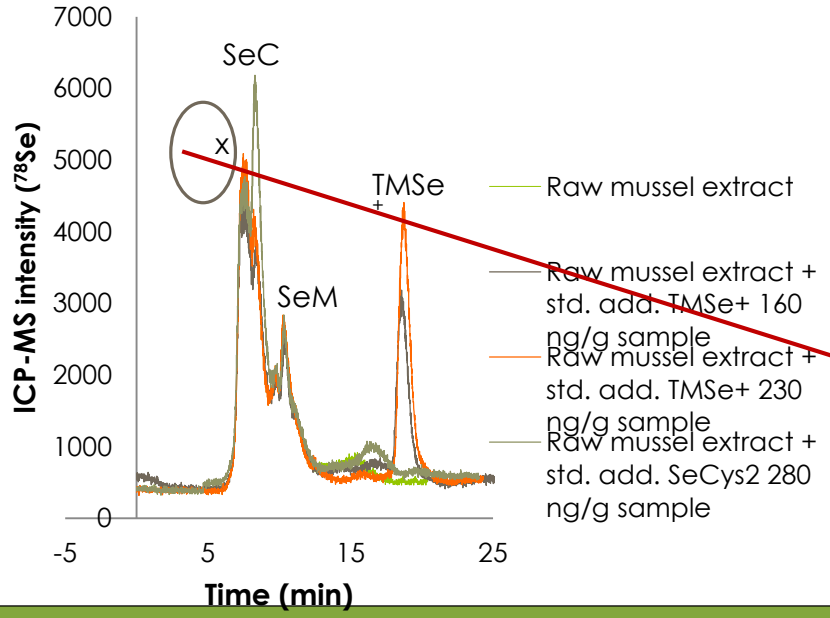
# Se species in wild and fish farm fish

| | 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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