Total mercury (THg) concentrations in water, sediment and biota:

General principles, sampling, preparation and methods of analysis

Zorana Kljaković-Gašpić

Institute for Medical Research and Occupational Health (IMROH)

KICK-OFF MEETING

Integrated evaluation of aquatic organism responses to metal exposure: gene expression, bioavailability, toxicity and biomarker responses (BIOTOXMET)

Zagreb, 11th October 2021

Outline

- General aspects of total mercury analysis
- Sampling and storage
- Sample preparation: pre-processing, digestion
- Analytical methods
- Future prospects

General aspects

Determination of THg in environmental samples involves the following steps:
(a) sample collection;
(b) sample pretreatment/preservation/storage;
(c) liberation of mercury from its matrix;
(d) extraction/clean-up/pre-concentration;
(e) quantification

Each of these 5 steps requires that we adhere to the **general requirements**:

- High purity reagents (Suprapur or 'low in mercury')
- Deionized water (for rinsing, preparation of standards, dilution of samples, etc..)
- Inert plastic (PTFE) or glass cookware and laboratory ware
- Rigorous cleaning procedures of laboratory ware and other equipment!!!

  → necessary to minimize contamination; common to all matrices:

  (1) aqua regia treatment followed by soaking in diluted (~5-10%) HNO_3 for a week;
  (2) soaking in a hot oxidizing mixture of $KMn0_4$ and $K_2S_20_8$; NH_4OCl rinsing; soaking for a week in 5M HNO_3
  (3) soaking in a 1:1 mixture of concentrated chromic and nitric acids for a few days;
  (4) soaking in BrCl (mixture of HCl and $KBr0_3$);
  (5) Teflon usually cleaned in hot concentrated HNO_3 for 48 hours, followed by soaking in dilute HNO_3 (5%) etc…

- Storing in a mercury-free place, preferably sealed in mercury-free plastic bags

Total mercury analysis at IMROH

Primary tasks:
measurement of total mercury (THg) in **5 different media**:

- ➢ water samples (total and dissolved)
- ➢ sediments
- ➢ fish muscle
- ➢ fish intestine
- ➢ intestinal parasites (acanthocephalans)

Water is **the most demanding** of these media → Hg concentrations in natural waters are very low (nanogram-per-liter levels)

→ difficult to get accurate and reliable results!!!

Natural waters are susceptible to contamination from many sources:

- improperly cleaned equipment,
- improper sample-collection techniques,
- contaminated reagents
- atmospheric inputs (dust, dirt, rain)

Clean procedures → necessary to minimize contamination!!!

Sampling: natural waters

MethodsX 5 (2018) 1017–1026

Contents lists available at ScienceDirect

MethodsX

journal homepage: www.elsevier.com/locate/mex

Method Article

Cleaning and sampling protocol for analysis of mercury and dissolved organic matter in freshwater systems

Andrea G. Bravo[a,*,1], Dolly N. Kothawala[b,1], Katrin Attermeyer[b], Emmanuel Tessier[c], Pascal Bodmer[d,e], David Amouroux[c]

[a] Department of Environmental Chemistry, Institute of Environmental Assessment and Water Research (IDAEA), Spanish National Research Council (CSIC), Barcelona, Spain
[b] Limnology/Department of Ecology and Genetics, Uppsala University, Uppsala, Sweden
[c] CNRS/ UNIV PAU & PAYS ADOUR, Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les Materiaux, UMR5254, MIRA, Pau, France
[d] Institute for Environmental Sciences, University of Koblenz-Landau, Landau, Germany
[e] Chemical Analytics and Biogeochemistry, Leibniz-Institute of Freshwater Ecology and Inland Fisheries, Berlin, Germany

Bravo, A. G., Kothawala, D. N., Attermeyer, K., Tessier, E., Bodmer, P., & Amouroux, D. (2018). Cleaning and sampling protocol for analysis of mercury and dissolved organic matter in freshwater systems. MethodsX, 5, 1017–1026. doi:https://doi.org/10.1016/j.mex.2018.08.002

Sampling: cleaning procedures

<u>The cleaning procedure</u> for the amber borosilicate bottles and other plastic and glass utensils used to store water and analyze mercury species should be carried out in a **series of three baths** :

- Soaking in mild solution of **detergent** (Kemex; Kemika) for 1 h in ultra-sonic bath or 48 h without sonification
- Rinsing with Milli-Q water
- Soaking in a **10%** (v:v) **HNO_3** (Merck, p.a., distilled at sub-boiling temperature) bath for 2 h in ultra-sonic bath or 48 h without sonification
- Rinsing with Milli-Q water
- Soaking in a **10%** (v:v) **HCl** (Merck, p.a., distilled at sub-boiling temperature) bath for 2 h in ultra-sonic bath or 48 h without sonification
- rinsing with Milli-Q water

<u>How to **minimize** potential sources of **contamination** during sampling:</u>

- Wear clean, no-talc gloves during all operations
- Use metal free apparatus and materials (PTFE or glass bottles)
- All sampling equipment should be double bagged to reduce risk of contamination
- Avoid airborne particulate matter (dirt, dust, nearby bridges, wires and poles)
- Avoid cigarette smoke
- Avoid vapors from automobile exhaust
- Avoid breathing directly into the sample (dental mercury amalgam fillings)




Water sampling

Material required for 1 location:

2x250 mL Amber glass bottles

UNFILTERED **FILTERED**

1x50 mL Syringe

1xSyringe filter 0.45 µm

Summary of the samples collected:

SAMPLES

Unfiltered water (Total fraction)

Filtered water (Dissolved fraction)

FIELD BLANKS

Field blank for unfiltered water (Total fraction)

Field blank for filtered water (Dissolved fraction)

Field blanks → to evaluate the potential for contamination associated with the field methods, materials used, and sampling environment.

- processed in the same manner and under the same environmental conditions as environmental samples

- Water samples were acidified (HCl, Suprapur) and stored at +4°C in clean plastic bags with zipper
- Analyzed as soon as possible, but can be stable for 30 days

Sample preparation: pre-processing

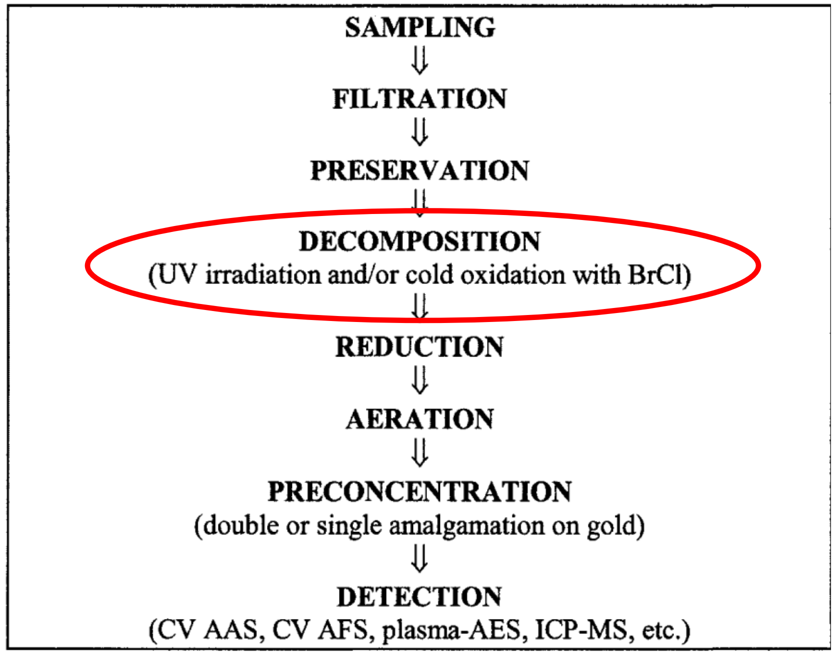
1. **Natural waters**:
   Preservation: acidified in the field (HCl, Suprapur)
2. **Biological material:**
   dissection conducted during the field trip; stored at -18°C or -80°C (IRB team);
   no freeze-drying
3. **Sediments:**
   collected in to clean zip bags, labeled and stored at -18°C
   in laboratory: freeze-drying and sieving

Freeze-drying
HETOSIC (Heto Ltd., Denmark)

Sieved (Ø=2 mm) to remove gravel and branches

Sample preparation: digestion of samples

Principal steps for the determination of THg in water samples



Decomposition of samples for the THg analysis:

1. **Natural waters:**

- depends on the instrument used

  AMA 254: no decomposition required → decomposition occurs in the instrument itself, as part of the analysis

  ICP-MS: decomposition with concentrated HNO_3 (Ultraclave IV, IMROH)

Sample preparation: digestion of samples (2)

2. **Biological material** (fish muscle, intestine, acanthocephalans)

   wet decomposition with acids:

- ✓ intestine, acanthocephalans: digestion at IRB facilities due to **small amount** of biological samples (agreement VFM and ZKG)
- ✓ muscle tissue of fish: IMROH (Ultraclave IV System)

3. **Sediments:**

   Hg in sediments associated with humic matter and/or sulphides (HgS)

   → **strong oxidizing agents** required!! ($HN0_3$, HCl, BrCl, H_2S0_4, $HCl0_4$, H_2O_2, V_20_5, $KMn0_4$, $K_2Cr_20_7$)

   wet decomposition with Aqua regia (HNO_3:HCl =1:3) in Al-block on 70-90°C (IMROH)

Sample preparation: digestion of biological material

High pressure microwave destruction of samples (fresh or freeze-dried) in a high-pressure microwave device using method for biological samples

UltraCLAVE IV (Milestone, Italy)

- Samples of fresh biological material (0.250-0.500 g) are weighed in quartz tubes
- 4 ml of concentrated HNO_3 (65%; S.p.) is added and left to react for 10 to 15 minutes; then 2 ml of deionized water is added
- Tubes are closed with a Teflon stoppers and placed on a stand which is immersed in a stock solution (water, H_2O_2, H_2SO_4) which serves to conduct the microwaves more evenly
- **Quality Control**: Blanks and Certified Reference Materials digested in the same manner with every batch of samples!

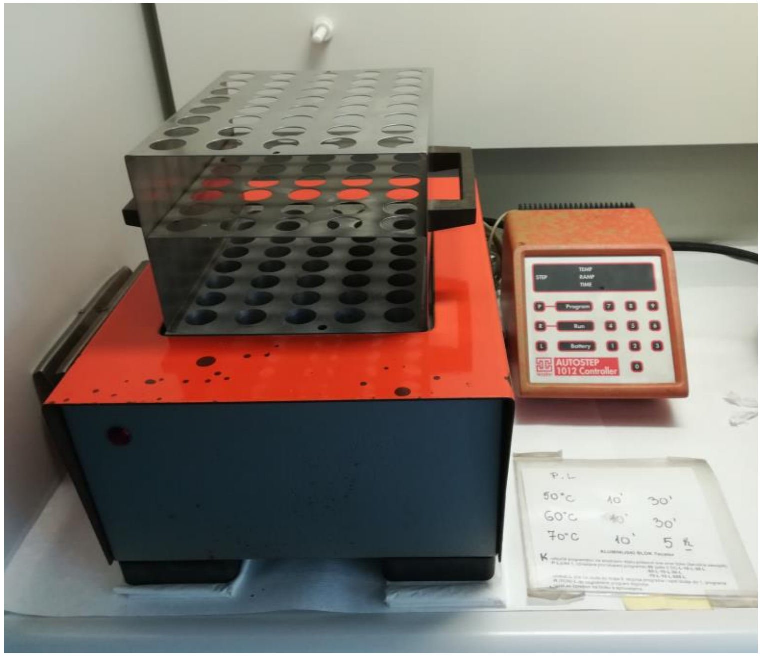
Temperature program for destruction of biological samples in high-pressure microwave device UltraCLAVE IV (Milestone, Italy)

	t (min:s)	E (W)	T_1 (°C)	T_2 (°C)	p (bar)
1.	3:30	700	70	60	100
2.	15:00	1000	180	60	100
3.	10:00	1000	220	60	120
4.	30:00	1000	220	60	120
5.	40:00	0	30	25	20

- T_{max} = 220°C
- P_{max} = 120 bar
- Number of $samples_{max}$ = 40
- Required time: ~2.5 h

t - time, T_1 - set temperature, T_2 - temperature in the outer vessel,
E - microwave radiation power, p - pressure in the reaction vessels

Sample preparation: digestion of sediments



TECATOR:
Aluminium block with 40 slots
Autostep 1012 Controller

Wet digestion in Al-block:

- Sediment samples (0.100–0.150 g) are weighed into quartz tubes;
- 3 ml of Aqua-regia (HNO_3:HCl = 1:3) is added and mixture is allowed to react overnight.
- After addition of 1 ml of deionized water, the tubes are closed with a Teflon-coated stoppers, placed in the Aluminum block and heated for 5 hours at 90°C.
- After cooling, the samples are made up with Ultrapure water to a total volume of 20 mL and stored at room temperature.
- **Quality Control**: Blanks and Certified Reference Materials digested in the same manner with every batch of samples!

Sample analysis: Instrumentation

Common analytical techniques for the analysis of Total mercury:

- Atomic Absorption Spectrometry (AAS): GF-AAS, CV-AAS

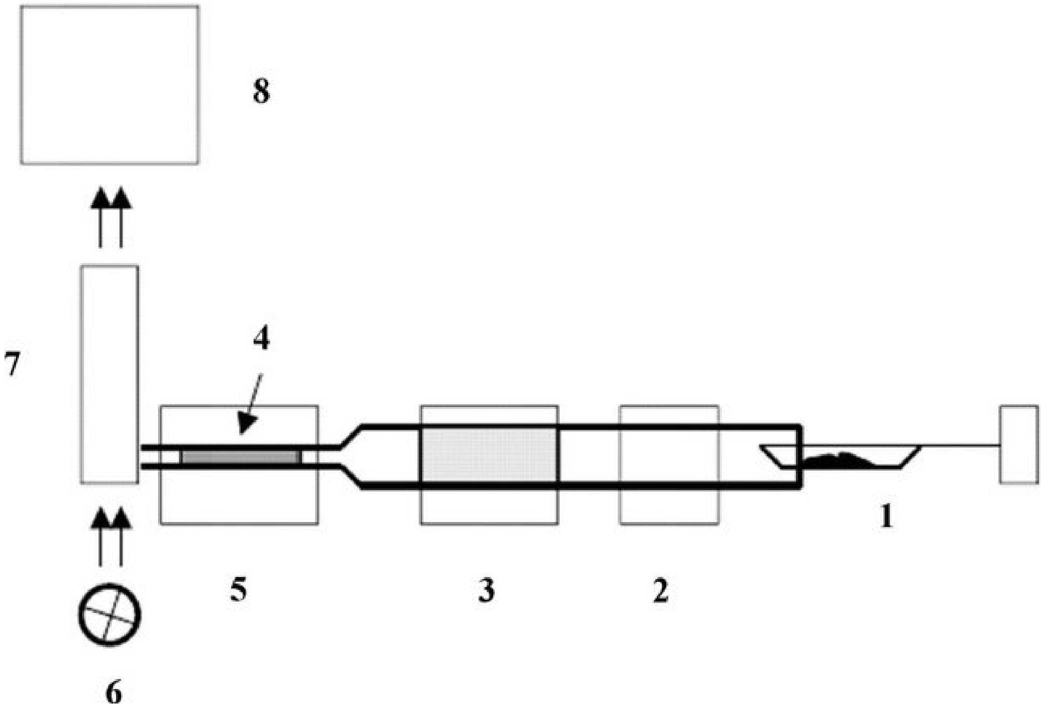
  Cold Vapor Atomic Absorption Spectrometry (CV-AAS)

  - **Total mercury analyzer** (Direct thermal decomposition – Gold Amalgamation – Cold Vapor Atomic Absorption Spectrometry)
- Atomic Fluorescence Spectrometry (AFS): CV-AFS
- Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)
- Neutron Activation Analysis (NAA)
- Gas Chromatography (GC): GC-ECD (GC with Electron Capture Detector)
- …………………………..

Sample analysis: AMA 254 Total Mercury Analyzer

- Principle: Direct thermal decomposition – Gold Amalgamation – CVAAS

AMA 254 Mercury Analyzer (LECO, Korea)
- **Application**: mercury content analysis in solid, liquid and gaseous samples (direct measurements are possible)
- LOD = **0.003 ng** Hg



Scheme of the AMA 254 spectrometer:
(1) Sampling boat, (2) decomposition furnace, (3) catalytic column, (4) gold amalgamator, (5) releasing furnace, (6) mercury cathode lamp, (7) optical cell system, and (8) detector

(**Source**: Spěváčková et al. (2004). *Analytical and Bioanalytical Chemistry*, *380*(2), 346–350. doi:10.1007/s00216-004-2739-2)

AMA254 Total Mercury Analyzer: Results

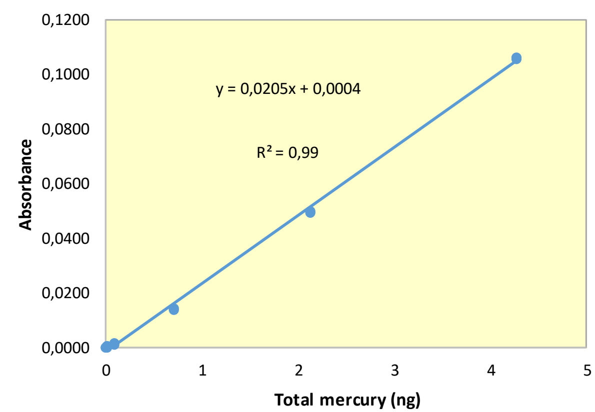
Datum: 17.08.2021. **Napomena:** vrijednosti THg u svim uzorcima (filtriranim i nefiltriranim) su na granici detekcije metode

Uzorci: Filtrirane i nefiltrirane prirodne i otpadne vode s Krke oko Knina

Analitičar: Zorana Kljaković-Gašpić

Instrument: AMA-254 Mercury analyser (Leco Inc.)

	Standard concentration (µg/L)	**ng Hg**	**Absorban**	Average blank absorbance
Blank	0	0,0029	0,0002	
	0	0,0099	0,0002	**0,0002**
STD 1	0,2134	0,02134	0,0006	
	0,2134	0,02134	0,0005	
STD 2	0,8536	0,08536	0,0014	
	0,8536	0,08536	0,0016	
STD 3	7,1133	0,7113	0,0142	
	7,1133	0,7113	0,0144	
STD 4	21,34	2,134	0,0497	
	21,34	2,134	0,0500	
STD 5	21,34*200µL	4,268	0,1060	
	21,34*200µL	4,268	0,1062	



Sample			**Aliquot (mL)**	**Absorbance**	**Absorbance (Sample-Blank)**	**Total Hg (ng)**	**Blank substituted concentration (ug/L)**	**AVERAGE concentration (ug/L)**		
NIST 1641e		r=10	0,10	0,0214	0,02120	1,0291	102,9		Certified val	Range
			0,10	0,0213	0,02110	1,0293	102,9	102,9	**101,6 µg/L**	**99,9-103,3**
BLF_KRS	Krka river source	Filtrirano	0,5	0,0004	0,0002	0,0098	0,020			
BLF-KRK	Krka River Knin	Filtrirano	0,5	0,0006	0,00040	0,0195	0,039			
KRS_F	Krka river source	Filtrirano	0,5	0,0005	0,00030	0,0146	0,029			
KRK_F	Krka River Knin	Filtrirano	0,5	0,0004	0,00020	0,0098	0,020			
KBL_F	Krka Brljan Lake	Filtrirano	0,1	0,0004	0,00020	0,0098	0,098			
TOR_F	tributary Orašnica	Filtrirano	0,1	0,0005	0,00030	0,0146	0,146			
TBU_F	tributary Butišnica	Filtrirano	0,1	0,0003	0,00010	0,0049	0,049			
TKO_F	tributary Kosovčica	Filtrirano	0,1	0,0002	0,00000	0,0000	0,000			
IWW_F	industrial wastewaters	Filtrirano	0,1	0,0004	0,00020	0,0098	0,098			
BL-KRS	Krka river source	Nefiltrirano	0,5	0,0003	0,00010	0,0049	0,010			
BL-KRK	Krka River Knin	Nefiltrirano	0,5	0,0004	0,00020	0,0098	0,020			
KRS	Krka river source	Nefiltrirano	0,5	0,0005	0,00030	0,0146	0,029			
KRK	Krka River Knin	Nefiltrirano	0,5	0,0005	0,00030	0,0146	0,029			
KBL	Krka Brljan Lake	Nefiltrirano	0,1	0,0003	0,00010	0,0049	0,049			
TOR	tributary Orašnica	Nefiltrirano	0,5	0,0002	0,00000	0,0000	0,000			
TBU	tributary Butišnica	Nefiltrirano	0,5	0,0003	0,00010	0,0049	0,010			
TKO	tributary Kosovčica	Nefiltrirano	0,5	0,0002	0,00000	0,0000	0,000			
IWW	industrial wastewaters	Nefiltrirano	0,1	0,0002	0,00000	0,0000	0,000			

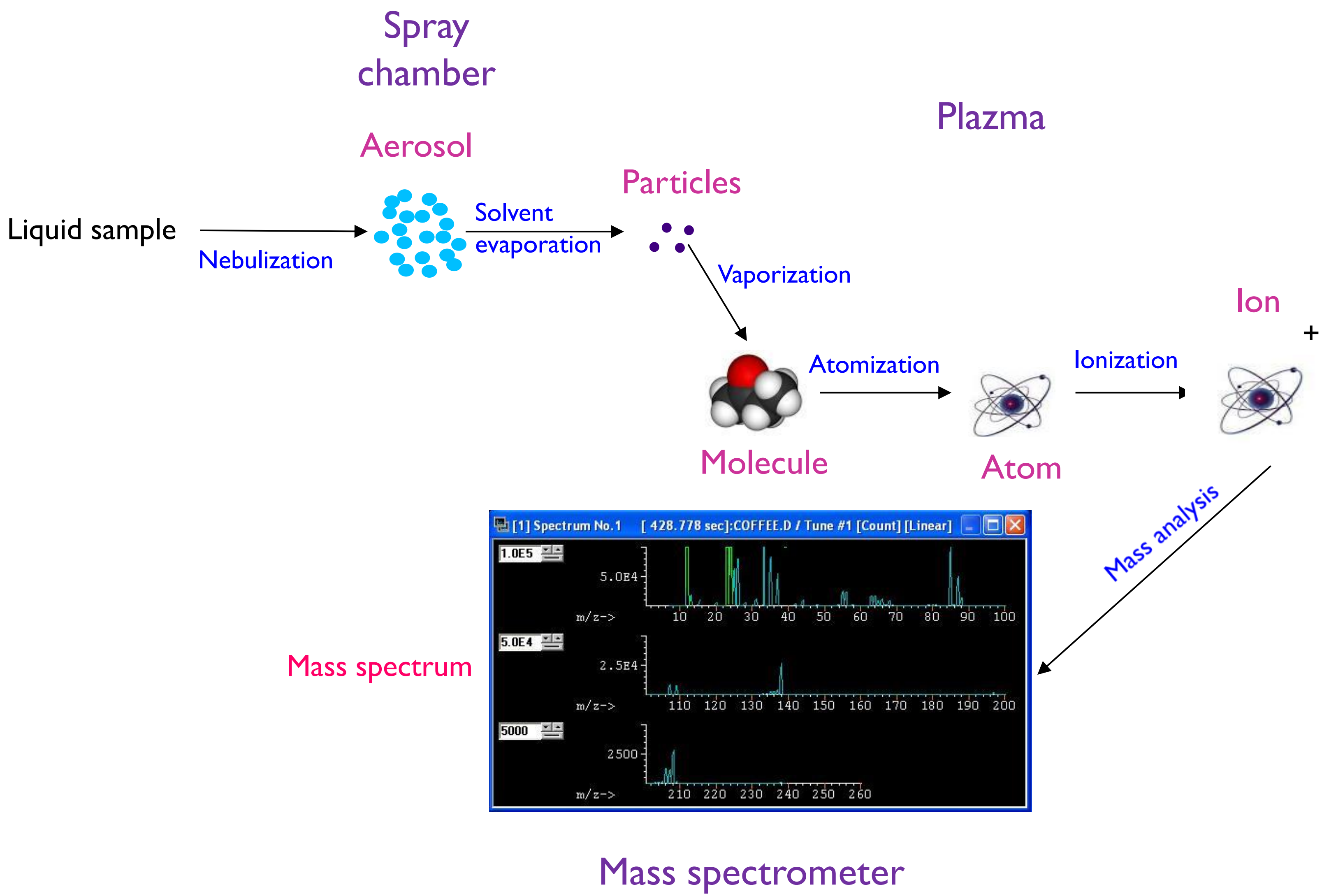
Sample analysis: ICP-MS

- **Water samples:** an internal standard (IS) solution is added to a given sample volume and the samples are measured directly, <u>without dilution</u>
- **Biological samples** are diluted with 1% (v/v) HNO_3 5-20 times, depending on the matrix
- **Sediment samples** are diluted with 1% (v/v) HNO_3 ~ 20 times
- Internal standard of 2 µg/L is added to all samples

Agilent 7500cx, Agilent Technologies

- High sensitivity
- Low detection limits → **LOD** for Hg ≈ **0.005 µg/L** or lower
- Can analyze many other metals at the same time (about fifty elements in one run)
- Allows for verification by analysis of multiple isotopes
- Linearity of detector response in a large concentration range (through nine orders of magnitude)
- Internal standardization improves accuracy of results
- Requires small sample volume for analysis (~ 2-3 mL of sample solution)

Sample analysis: Processes in ICP-MS



Schematic representation of the process in ICP-MS from sample input to mass analysis

ICP-MS: Results (1)

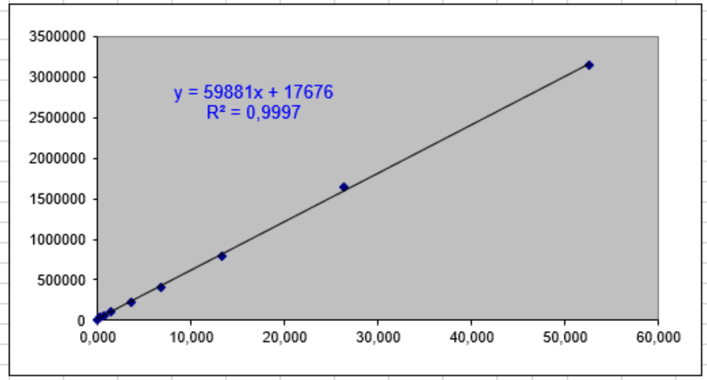
K21 | 53071888

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1			7 Li	7 Li	7 Li	7 Li	23 Na	23 Na	23 Na	23 Na	24 Mg	24 Mg	24 Mg	24 Mg
2	Date Acquired	Sample Name	(T3,#7)Raw Co	(T3,#7)Raw Co	(T3,#7)Raw Co	(T3,#7)Raw Co	(T2,#23)Raw C	(T2,#23)Raw C	(T2,#23)Raw C	(T2,#23)Raw C	(T2,#24)Raw C	(T2,#24)Raw C	(T2,#24)Raw C	(T2,#24)Raw C
3	10:00 am	Dummy (1%HNO3)	906,72552	913,39221	886,72125	920,06287	41767,789	41972,703	41675,313	41655,355	3531,646	3590,5371	3627,2329	3377,1692
4	10:07 am	Bl 1_P	856,7196	870,05145	850,05206	850,05524	41909,289	42403,965	41621,707	41702,18	3776,155	3907,3103	3677,2268	3743,9265
5	10:13 am	Bl 2_P	878,94641	913,39191	886,72729	836,71997	41952,73	41484,508	41849,246	42524,434	3752,8369	3797,2939	3630,5688	3830,6489
6	10:19 am	Bl 3_P	835,60571	826,71405	796,71448	883,38867	42077,559	43212,965	41665,293	41354,434	3642,7939	3553,8867	3530,5371	3843,9587
7	10:24 am	Bl 1_MQH2O	756,71271	726,711	716,70929	826,71771	41108,109	41214,23	40926,336	41183,77	298,90289	306,6806	283,34738	306,6806
8	10:30 am	Bl 2_MQH2O	774,49011	770,04779	786,71326	766,70935	41205,219	41304,563	41234,102	41076,996	362,24219	400,0275	330,01563	356,68359
9	10:36 am	Bl 3_MQH2O	738,93268	776,71301	690,04181	750,04352	41285,281	41036,809	40929,926	41889,129	404,46411	400,01962	410,02042	403,35223
10	10:42 am	Kal 1_trav	5257,7432	5314,4326	5404,4546	5054,3418	3553137	3556873,3	3540223,8	3562314,5	51722480	51840232	51759460	51567756
11	10:48 am	Kal stap_trav	5395,583	5421,1436	5377,7871	5387,8184	3685064	3700050,8	3681519	3673622	53237632	52882464	53288040	53542368
12	10:53 am	Kor_1_trav	4978,7559	5034,3486	5024,332	4877,5864	3592082	3597811,5	3577918,3	3600516,5	53517928	53296660	53525492	53731644
13	10:59 am	Kor_stap_trav	4952,083	5131,0537	4800,9189	4924,2759	3600899	3594089	3603485,3	3605122,5	53854088	53969904	53880988	53711396
14	11:05 am	Rij_1_trav	5818,0269	5701,2407	5737,9312	6014,9102	2663144	2661338,5	2663683	2664410,3	87633200	88143000	87319072	87437520
15	11:11 am	Rij_stap_trav	5635,668	5597,8647	5644,5415	5664,5977	2670779	2660369,3	2683729,5	2668238	88152896	87840568	88582960	88035184
16	11:16 am	Pro_1_trav	5696,8042	5511,167	5988,0493	5591,1968	3952933	3931574	3937714,5	3989510,8	54735088	54989868	54514472	54700924
17	11:22 am	Pro_stap_trav	5757,9561	5614,5708	5684,5977	5974,6997	4001827	3989430,8	3993398,3	4022653,8	55264660	55064780	55578424	55150772
18	11:28 am	Mat_1_trav	5836,876	5801,3369	5874,667	5834,6245	4554514	4574011	4557572	4531959,5	48884208	49035080	48862560	48754996
19	11:34 am	Mat_stap_trav	5827,96	5921,3379	5544,5122	6018,0317	4527951	4504576,5	4553712	4525564	48580368	48676200	48452612	48612308
20	11:39 am	Plit_1_trav	2979,3201	2983,7178	2857,1499	3097,093	2626607	2638715	2630935,5	2610171,3	53013000	52954604	52861664	53222732
21	11:45 am	Plit_stap_trav	2807,0259	2783,6816	2867,0308	2770,3645	2602903	2614375,3	2609115	2585219,3	53071888	53273184	52908432	53034064
22	11:51 am	Koz_1_trav	4949,8442	4964,2954	4817,5718	5067,666	3775731	3794670,8	3769313,3	3763208,3	54590240	54512884	54952144	54305700
23	11:57 am	Koz_stap_trav	4904,3032	5077,6787	4817,6104	4817,6216	3796326	3762308,8	3805113,3	3821555,3	55067328	54835976	55266744	55099272
24	12:02 pm	sum_a_1_trav	13779,79	13828,75	14377,1	13133,521	47773640	48333344	47639972	47347600	31472970	31516766	31561462	31340682
25	12:08 pm	sum_a_2_trav	15033,47	14123,138	16561,988	14415,294	47478088	47508028	47148164	47778072	31054690	31064780	31121366	30977912
26	12:14 pm	sum_b_1_trav	17729,18	16754,498	17838,059	18594,99	45019300	44974244	45403324	44680320	29293570	29159840	29397670	29323196
27	12:20 pm	sum_b_2_trav	14102,24	14352,947	13929,119	14024,654	44549168	44035252	44933304	44678956	29077280	29014412	28997490	29219932
28	12:25 pm	Dummy (1%HNO3)	265,56741	273,34497	233,34518	290,01196	59314,129	58872,348	59983,656	59086,371	4756,4678	4777,6035	4730,9019	4760,8975
29	12:31 pm	SLRS-5_l	23420,891	23415,215	23328,648	23518,818	22961390	22986340	22972526	22925292	6488265	6496964	6482746,5	6485085,5
30	12:37 pm	Nist_l	88897,109	89217,664	88674,711	88798,938	8990115	8953847	9090391	8926106	2118304	2155568,3	2099024,5	2100318
31	12:43 pm	seronorm urin	9335,416	9426,6074	9393,25	9186,3936	206243600	205290850	206356580	207083380	3797464	3800844,5	3777481,5	3814064,5
32	12:48 pm	Dummy (1%HNO3)	375,5733	386,68533	366,68448	373,3501	76824,289	77553,766	76515,016	76404,086	5222,1782	5221,0776	5271,0903	5174,3652
33	12:54 pm	Rstd 1 Hg	416,68701	413,35281	453,35474	383,35342	72235,727	72350,844	71914,859	72441,5	5515,6699	5791,3555	5321,1533	5434,502
34	01:00 pm	Rstd 2 Hg	426,68781	440,02075	376,68503	463,3577	69994,32	69905,805	69199,68	70877,445	5374,4722	5444,5068	5361,1343	5317,7744
35	01:06 pm	Rstd 3 Hg	443,3555	453,35605	440,02213	436,68842	69711,977	71235,688	68087,953	69812,281	5888,0288	5961,4097	5931,3467	5771,3306
36	01:12 pm	Rstd 4 Hg	524,47083	543,36041	453,35406	576,69781	69132,406	68918,008	69688,305	68790,938	5370,0322	5447,8291	5304,4492	5357,8164
37	01:17 pm	Rstd 5 Hg	587,8125	540,02625	586,69745	636,71393	68814,477	68630,234	68881,281	68931,953	5613,4492	5584,5342	5657,9478	5597,8662
38	01:23 pm	Dummy (1%HNO3)	321,12561	286,67981	350,01495	326,68213	65948,289	65375,734	66587,867	65881,266	5163,269	4897,6084	5067,6914	5524,5078
39	01:29 pm	Rstd 1 Na,Ca,K,Mg	431,13199	430,01962	390,01724	473,35907	1355636	1354725	1352618,5	1359563,8	1527952	1521102,3	1532138,6	1530615
40	01:35 pm	Rstd 2 Na,Ca,K,Mg	443,3544	443,3551	400,01846	486,68976	3234997	3238477,8	3245693	3220820,3	3733847	3713945,8	3752016,5	3735580,3
41	01:40 pm	Rstd 3 Na,Ca,K,Mg	417,7977	446,68832	406,68558	400,01932	6341661	6356398	6389490	6279095	7321407	7288761,5	7363556,5	7311905
42	01:46 pm	Rstd 4 Na,Ca,K,Mg	467,80042	490,02536	440,0206	473,35541	12689120	12758236	12711131	12598001	14820050	14834093	14870343	14755713
43	01:52 pm	Rstd 5 Na,Ca,K,Mg	436,689	403,35574	453,35495	453,35626	24191300	24108658	24187806	24277434	28448530	28440706	28306696	28598202
44	01:58 pm	Dummy (1%HNO3)	294,45831	323,34937	296,67947	263,34595	67874,703	67819,789	68084,383	67719,938	5341,1289	5347,7856	5421,1685	5254,4326

... | 202 Hg no gas | 205 Tl no gas | 208 Pb nog 110714 | 209 Bi no gas | 238 U no gas | Sheet2 | rez_graficki | Svi rezultati | **Rezultati_ICPMS_110714** | STD u mjernim otopinama | Shee

ICP-MS: Results (2)

			Al									
2												
3			Al			vodeni						
4				vodeni		X/Sc	X/72Ge	X/74	X/Rh	X/Tb	X/Lu	X/Ir
5												
6			0,000	11984		0,3	1,2	0,9	0,2	0,1	0,1	0,3
7		STD1	0,304	39916		0,8	3,4	2,7	0,6	0,4	0,4	1,0
8		STD2	0,679	58788		1,2	5,0	3,9	0,9	0,6	0,6	1,4
9		STD3	1,384	103476		2,1	8,8	6,8	1,5	1,1	1,1	2,4
10		STD4	3,551	230953		4,8	20,2	15,3	3,4	2,4	2,5	5,5
11		STD5	6,723	409939		8,4	35,5	26,7	6,0	4,3	4,4	9,9
12		STD6	13,351	795802		16,2	68,1	52,1	11,7	8,2	8,4	18,8
13		STD7	26,349	1641027		33,8	139,2	104,1	24,2	17,1	17,3	39,0
14		STD8	52,520	3146388		65,2	259,8	192,3	45,6	32,0	32,6	73,4
15			bez std 7 i 8.	58549		1,19	4,98	3,80	0,85	0,60	0,62	1,38
16			Nagib=	59881		1,24	4,96	3,67	0,87	0,61	0,62	1,40
17			Odsječak=	17676		0,43	1,82	1,36	0,29	0,21	0,21	0,49
18			RSQ=	0,99967		1,000	0,999	0,999	0,999	0,999	0,999	0,999
19												
20	Blank 1%HNO3		11984,2	12766	12553	10634						
21	BlankMQH2O		12331,5		12721	11942						
22				5826								



23				COUNTS /CPS (Mean)				RSD	45Sc	72Ge	74Ge	103Rh	159Tb	175Lu	193Ir
27	Bl 3_P			10634	10022	11277	10603	5,9	43894	10059	13193	62101	91254	89327	39691
28	Bl 1_MQH2O			5826	5793	5753	5931	1,6	41769	10423	13815	61602	89997	88633	40236
29	Bl 2_MQH2O			12721	12837	12605	12721	0,9	42668	10284	13606	62272	90606	88983	39914
30	Bl 3_MQH2O			11942	11990	11900	11935	0,4	42671	10275	13478	62266	89933	88997	39793
31	Kal 1_trav			60520	61055		59985	1,3	70899	10799	13983	61142	93405	93083	40398
32	Kal stap_trav			52960	53612	51617	53653	2,2	72404	11140	14177	62370	94790	94612	41224
33	Kor_1_trav			81690	81249	87434	76387	6,8	72133	11330	14475	63507	96557	95201	41995
34	Kor_stap_trav			75125	78557	72583	74236	4,1	72816	11259	14580	63508	96092	94513	41857
35	Rij_1_trav			252244	255504	249461	251766	1,2	73641	11543	14797	63313	96043	95136	42051
36	Rij_stap_trav			255094	253285	252310	259688	1,6	74015	11548	14666	63716	96800	95917	41885
37	Pro_1_trav			182613	179489	184966	183383	1,5	71097	11641	15038	64760	97532	96577	41832
38	Pro_stap_trav			104492	102081	106902		3,3	71873	11644	15154	66226	98400	98009	42622
39	Mat_1_trav			439508	444929	434946	438648	1,1	87621	11796	15325	64991	97586	97138	42551
40	Mat_stap_trav			376278	382190	372558	374085	1,4	88020	11416	14725	64574	96903	96342	41830
41	Plit_1_trav			336152	327380	343733	337342	2,5	74554	11903	15099	65071	97508	96771	42639
42	Plit_stap_trav			352371	359434	346848	350829	1,8	73801	11675	14778	64660	97660	96527	41892
43	Koz_1_trav			70838	70103		71572	1,5	74404	11556	15065	64698	97044	96799	42123
44	Koz_stap_trav			74946	74315	75670	74853	0,9	75205	11651	15027	64980	96787	96240	42191
45	sum_a_1_trav			14312527	15734630	12438274	14764676	11,8	57481	11573	14953	64179	95959	95244	41332
46	sum_a_2_trav			12317054	12900168	12245353	11805641	4,5	55791	11631	14639	63684	94496	93827	41208
47	sum_b_1_trav			35064986	35899016	32001822	37294120	7,8	62175	12235	14544	62618	94584	91853	40605
48	sum_b_2_trav			29433147	29190760	28148236	30960446	4,8	59540	11650	14384	62111	94894	91701	40679
49	Dummy (1%HNO3)			27705	27298	28873	26944	3,7	4843	651	83	33	12	22	39
50	SLRS-5_l	49,5	(44.5-54.5)	2909327	2894185	2927770	2906028	0,6	#####	11434	14954	64609	96729	95004	41186
51	Nist_l	141,8	(133.2-150.4)	843130	840113	845207	844070	0,3	46492	10858	14590	65091	94749	93287	41303
52	seronorm urin	100	(91-106)	191677	196189	188370	190473	2,1	57674	11708	15054	65173	97585	96026	42088

23	X/Sc	X/72Ge	X/74Ge	X/Rh	X/Tb	X/Lu	X/Ir	V1 uk/ ml	V2 uk/ ml	C1 (bazd 1)	vodeni C2 / Sc	C2 / 72Ge	C2 / 74Ge	C2 / Rh	C2 / Tb	C2 / Lu	C2 / 193Ir
27	0,2	1,1	0,8	0,2	0,1	0,1	0,3	1	1	-0,03	-0,04	-0,03	-0,03	-0,03	-0,03	-0,03	-0,03
28	0,1	0,6	0,4	0,1	0,1	0,1	0,1	1	1	-0,11	-0,12	-0,13	-0,13	-0,12	-0,12	-0,12	-0,12
29	0,3	1,2	0,9	0,2	0,1	0,1	0,3	1	1	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01
30	0,3	1,2	0,9	0,2	0,1	0,1	0,3	1	1	-0,01	-0,01	-0,01	-0,01	-0,01	-0,01	-0,01	-0,01
31	0,9	5,6	4,3	1,0	0,6	0,7	1,5	1	1	0,80	0,46	0,89	0,93	0,91	0,84	0,82	0,85
32	0,7	4,8	3,7	0,8	0,6	0,6	1,3	1	1	0,68	0,36	0,72	0,77	0,75	0,69	0,68	0,70
33	1,1	7,2	5,6	1,3	0,8	0,9	1,9	1	1	1,16	0,68	1,21	1,29	1,25	1,16	1,16	1,17
34	1,0	6,7	5,2	1,2	0,8	0,8	1,8	1	1	1,05	0,60	1,10	1,16	1,13	1,05	1,05	1,06
35	3,4	21,9	17,0	4,0	2,6	2,7	6,0	1	1	4,01	2,53	4,17	4,39	4,35	4,07	4,04	4,06
36	3,4	22,1	17,4	4,0	2,6	2,7	6,1	1	1	4,05	2,55	4,21	4,49	4,38	4,09	4,05	4,13
37	2,6	15,7	12,1	2,8	1,9	1,9	4,4	1	1	2,84	1,84	2,92	3,06	3,01	2,84	2,82	2,90
38	1,5	9,0	6,9	1,6	1,1	1,1	2,5	1	1	1,54	0,94	1,57	1,63	1,59	1,51	1,49	1,53
39	5,0	37,3	28,7	6,8	4,5	4,5	10,3	1	1	7,13	3,81	7,27	7,56	7,55	7,14	7,05	7,15
40	4,3	33,0	25,6	5,8	3,9	3,9	9,0	1	1	6,08	3,21	6,41	6,71	6,47	6,13	6,06	6,20
41	4,5	28,2	22,3	5,2	3,4	3,5	7,9	1	1	5,41	3,40	5,45	5,81	5,71	5,41	5,36	5,41
42	4,8	30,2	23,8	5,4	3,6	3,7	8,4	1	1	5,68	3,62	5,85	6,24	6,04	5,68	5,65	5,78
43	1,0	6,1	4,7	1,1	0,7	0,7	1,7	1	1	0,98	0,53	0,99	1,03	1,03	0,97	0,95	0,98
44	1,0	6,4	5,0	1,2	0,8	0,8	1,8	1	1	1,05	0,57	1,06	1,11	1,10	1,04	1,03	1,05
45	249,0	1236,7	957,2	223,0	149,2	150,3	346,3	1	1	238,8	200,6	249,2	260,4	256,2	243,6	241,3	247,0
46	220,8	1059,0	841,4	193,4	130,3	131,3	298,9	1	1	205,5	177,8	213,4	228,9	222,2	212,9	210,8	213,2
47	564,0	2866,1	2410,9	560,0	370,7	381,8	863,6	1	1	585,4	454,6	577,8	656,2	643,7	605,9	613,4	616,3
48	494,3	2526,6	2046,2	473,9	310,2	321,0	723,5	1	1	491,3	398,4	509,3	556,9	544,7	506,9	515,7	516,4
49	5,7	42,5	332,4	831,1	2266,7	1246,7	712,4	1	1	0,3	4,4	8,3	90,3	955,5	3705,7	2003,8	508,4
50	27,7	254,5	194,6	45,0	30,1	30,6	70,6	1	1	48,38	22,09	51,08	52,73	51,55	48,95	49,00	50,21
51	18,1	77,7	57,8	13,0	8,9	9,0	20,4	0,4	4	138,74	143,91	154,20	154,88	146,67	143,25	143,06	143,54
52	3,3	16,4	12,7	2,9	2,0	2,0	4,6	0,1	4	149,75	122,35	153,00	160,96	157,71	149,40	149,30	151,53

7 Li no gas | 23 Na He | 24 Mg He | 27 Al no gas | 39 K He | 43 Ca He | 52 Cr H2 | 54 Fe H2 | 55 Mn He | 56 Fe He | 59 Co He | 60 Ni He | 63 Cu He | 66 Zn He | 75 As He | 78 ...

What was already performed and future prospects

What we have done so far:

- Concentrations of THg in water samples (January, April and June of 2021)

To be achieved:

1st Project period:

- Analysis of THg in water samples (field trip in October 2021)
- Analysis of THg in sediments (will be finished by the end of the 1st Project period) → samples are already digested

2nd Project period

- Digestion and analysis of THg in biological material (fish muscle, intestine and acanthocephalans)

My wishes that are not included in the project tasks:

? Development of the quick method for the analysis of **MeHg** in biological samples (at least in muscle tissue) with AMA 254

? Application of this method for the analysis of **MeHg** content in biological samples

BIOTOXMET

HRZZ Hrvatska zaklada za znanost