Study for the determination of Cd, Pb and Zn in biological fluids by Inductively Coupled Plasma Mass Spectrometry

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OJECTIVES

•Developing high sensitivity analysis method for Cd, Cu, Pb and Zn determination from clinical samples (urine and whole blood)

•Study of polyatomic interferences removal using dynamic reaction cell method (with methane as a reaction gas)

•Determination of analytical performance of the method used, by analysis of certified reference materials

^{110}Cd	12.5	$^{39}K_2{}^{16}O^+$
^{111}Cd	12.8	$^{95}Mo^{16}O^+$, $^{94}Zr^{16}O^1H^+$, $^{39}K_2{}^{16}O_2{}^1H^+$
^{112}Cd	24.1	$^{48}Ca_2{}^{16}O_2{}^+$, $^{40}Ar_2{}^{16}O_2{}^+$, $^{96}Ru^{16}O^+$
^{113}Cd	12.22	$^{96}Ru^{16}O^1H^+$, $^{49}Ca_2{}^{16}O_2{}^1H^+$, $^{40}Ar_2{}^{16}O_2{}^1H^+$, $^{96}Ru^{16}O^1H^+$, $^{96}Ru^{17}O^+$
^{114}Cd	28.7	$^{98}Mo^{16}O^+$, $^{98}Ru^{16}O^+$
^{116}Cd	7.49	$^{100}Ru^{16}O^+$
^{63}Cu	69.1	$^{31}P^{16}O_2{}^+$, $^{40}Ar^{23}Na^+$, $^{47}Ti^{16}O^+$, $^{23}Na^{40}Ca^+$, $^{46}Ca^{16}O^1H^+$, $^{36}Ar^{12}C^{14}N^1H^+$, $^{14}N^{12}C^{37}Cl^+$, $^{16}O^{12}C^{35}Cl^+$
^{65}Cu	30.9	$^{49}Ti^{16}O^+$, $^{32}S^{16}O_2{}^1H^+$, $^{40}Ar^{25}Mg^+$, $^{46}Ca^{18}O^1H^+$, $^{36}Ar^{14}N_2{}^1H^+$, $^{32}S^{33}S^+$, $^{32}S^{16}O^{17}O^+$, $^{33}S^{16}O_2{}^+$, $^{12}C^{16}O^{37}Cl^+$, $^{12}C^{18}O^{35}Cl^+$
^{206}Pb	24.1	$^{190}Pt^{16}O^+$
^{207}Pb	22.1	$^{191}Ir^{16}O^+$
^{208}Pb	52.4	$^{192}Pt^{16}O^+$
^{64}Zn	48.89	$^{32}S^{16}O_2{}^+$, $^{48}Ti^{16}O^+$, $^{31}P^{16}O_2{}^1H^+$, $^{48}Ca_2{}^{16}O^+$, $^{31}P^{17}O^{16}O^+$, $^{34}S^{16}O_2{}^+$, $^{36}Ar^{14}N_2{}^+$
^{66}Zn	27.81	$^{50}Ti^{16}O^+$, $^{34}S^{16}O_2{}^+$, $^{33}S^{16}O_2{}^1H^+$, $^{32}S^{16}O^{18}O^+$, $^{32}S^{17}O_2{}^+$, $^{33}S^{16}O^{17}O^+$, $^{32}S^{34}S^+$, $^{33}S_2{}^+$
^{68}Zn	18.57	$^{36}S^{16}O_2{}^+$, $^{34}S^{16}O^{18}O^+$, $^{40}Ar^{14}N_2{}^+$, $^{35}Cl^{16}O^{18}O^+$, $^{34}S_2{}^+$, $^{36}Ar^{32}S^+$, $^{34}S^{17}O_2{}^+$, $^{33}S^{17}O^{18}O^+$, $^{32}S^{18}O_2{}^+$, , $^{32}S^{36}S^+$

Fig 1. Quadrupole chamber (foreground) and DRC (background)

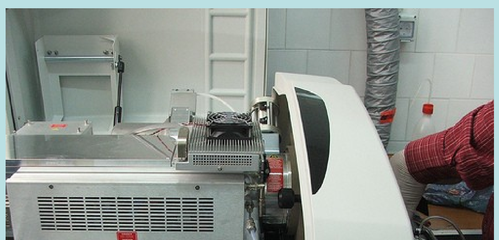

Fig. 2. Perkin-Elmer Elan DRC II with qudrupole region in foreground.

INSTRUMENTATION

The instrument used for determination was a ICP-MS Perkin-Elmer Elan DRC II with methane as a reaction gas for DRC determination.

Instrumental parameters	
RF power	1168 W
Nebulizer gas flow	0.931 min^{-1}
Lens Voltage	5.50 V
Sample flow	0.80 ml min^{-1}
Analog Voltage	- 1800 V
Data aquisition parameters	
Mode	Peak hopping
Peak points	1
Read / point	20
Aquisition time (ms)	50
Integration time (ms)	1000
Replicates	3

CRMs

For the method developing, we've used certified reference
materials for biological fluids, from the next suppliers:

- Urine CRM (SERO AS Norway):
- SERONOM 201205 level 2 lot no. 02525
- SERONOM 201305 blank lot OK4636
- LGC Prochem Germany
- Control level 2-05404
- Control level 1-05403 (Medichem)
- Blood CRM:
- SERONOM 201605 Trace Elements Whole Blood L2 Lot. No. 0503109

Used reagents:

- Deionized water Milli-Q, Millipore
- Ultrapure nitric acid 60%, Merck

Monoelement standard solutions 1000ppm containing Cd, Cu, Pb, Zn (Merck)

- Triton X-100 1% v/v (Merck – K Ga A)
- Methane (99.9995%) for reaction gas

Urine sample was diluted 1+9 in 100ul HNO3 60%. Following concentration were added: Cd 0.5 (1) Cu 5 (10) Pb 5 (10) Zn 50 (100). For blood, we used 1+19 dilution with Triton X-100 1% and the same concentrations.

ANALITICAL PERFORMANCE

	LOD/ppt	RPq
Cd110	9	0.3
Cd111	6	0.45
Cd112	5	0.35
Cd113	4	0.25
Cd114	4	0.35
Cu63	12	0.45
Cu65	20	0.6
Pb206	29	0.35
Pb207	25	0.55
Pb208	16	0.60
Zn64	12	0.45
Zn66	20	0.45
Zn68	17	0.45

RESULTS

The signal and also the concentration in stadard mode is higher than in standard mode because of the interference. When still using internal standards, this difference in signal strength can be seen.

For background evaluation determination we used Millipore deionized water with 1% nitric acid. Also, the parameters of the Elan DRC II were is the specification: the vacuum value and the signal intesities for etalons.

CRM Urine 05404 level 2				
Element	Isotope	ppb measurred concentration		CRM conc. (ppb)
		without DRC	with DRC	
Cd	^{110}Cd	11.77 ± 0.30	10.33 ± 0.40	8.00 ± 1.86
	^{111}Cd	11.39 ± 0.20	9.30 ± 0.10	
	^{112}Cd	9.62 ± 0.30	8.83 ± 0.10	
	^{113}Cd	11.34 ± 0.10	8.75 ± 0.30	
	^{114}Cd	9.21 ± 0.10	8.85 ± 0.20	
Cu	^{63}Cu	256 ± 24	303 ± 18	250 ± 60
	^{65}Cu	256 ± 29	286 ± 17	
Pb	^{206}Pb	124 ± 35	103 ± 25	80 ± 18
	^{207}Pb	121 ± 20	105 ± 27	
	^{208}Pb	122 ± 18	106 ± 22	
Zn	^{64}Zn	856 ± 59	805 ± 47	800 ± 200
	^{66}Zn	840 ± 70	805 ± 52	
	^{68}Zn	836 ± 34	812 ± 34	

CRM Urine	Cd		Cu		Pb		Zn	
	M	CRM	M	CRM	M	CRM	M	CRM
SERONORM 201205	5.05 ± 0.10	5.06 ± 0.22	18.6 ± 0.3	16.1 ± 1.4	85.9 ± 4.2	91.1± 7.0	259 ± 17	261 ± 13
05403	13.02 ± 0.25	13.00 ± 3.00	49.5 ± 5.6	50.0 ± 14.8	98±10	130 ± 32	1445 ± 74	1300 ± 400
05404	9.21 ± 0.30	8.00 ± 1.86	256 ± 29	250 ± 60	103 ± 25	80 ± 18	807 ± 40	800 ± 200
OK4636			19.0 ± 1.4	18.6 ± 2.1			384 ± 25	393 ± 28

Urine CRM sample

Whole Blood CRM 201605 level 2 lot no. 0503109							
Cd		Cu		Pb		Zn	
M	CRM	M	CRM	M	CRM	M	CRM
5.8 ± 0.1	6.0 ± 0.4	684± 36	666 ± 29	402 ± 33	393 ± 21	5304 ± 174	5038 ± 369

Whole blood determination results

CONCLUSIONS

- The method developed for urine analysis based on 1+9 dilution with HNO_3 1% and blood 1+19 diluted with Triton-X 0.5% is suitable for direct determination oh heavy metals in clinical samples using ICP-MS method.
- Polyatomical interferences on Pb and Zn cand be elemininating by using Dynamica Reaction Chamber with methane as reaction gas.
- DRC with methane gas is not suitable for interference removal of Cu compounds because of the carbon ions that results in the chamber. This should be further investigated using amonia instead of methane as a reaction gas.
- The method we developed stands for high sensitivity and allows determination of concentration in the range of ppt (parts per trillion) from chemical samples with low salts content (Cd – 20 ppt, Cu – 60 ppt, Pb – 90 ppt, Zn – 60 ppt)

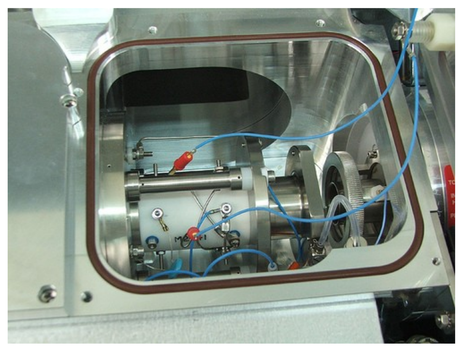

Fig. 3: DRC opened (detail).

Pentru informații suplimentare:

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