

## **STUDY ON PROCEDURE FOR DETERMINATION OF Cr, As, Se, Cd, Hg, Pb IN SOME KINDS OF HERB PRODUCTS SUCH AS: KIND OF FUNGUS, PHILAMIN... BY ICP-MS”**

*Pham Ngoc Khai, Do Van Thuan, Nguyen Thi Kim Dung and Nguyen Hong Minh*

Institute for Technology of Radioactive and Rare Elements, VAEC, Vietnam.

**ABSTRACT:** The determination of Cr, As, Se, Cd, Hg, Pb in herb products such as: kind of fungus, philamin, etc by ICP-MS has been studied. The effects of the parameters of ICP-MS instrument, concentration of nitric acid and high concentration of some elements on the determination of Cr, As, Se, Cd, Hg, Pb by ICP-MS has been concerned. The study and choice the suitable internal standard for the accurate determination of Hg has been sold. The suitable parameters of the microwave, composition and content of the acid mixture for the complete decomposition of the sample have been studied. The recommended procedure has been applied to the determination of Cr, As, Se, Cd, Hg, Pb in the standard samples and real samples. The error of the results is acceptable.

**Key words:** Herb products, heavy metal, ICP-MS, digression, Microwave.

### **Introduction**

The determination of heavy metals in herb products is interested in many countries over the world such as: China, India, Turkey, Poland, Germany, Australia, etc. All medical products for human and animal must meet regulatory guidelines for quality, safety and efficacy. For example, the European Union (EU) recently established a Traditional Herbal Medicinal Products Directive. As a result, manufacturers who export herbal medicines to the EU must ensure that product quality complies with requirements of the European Pharmacopoeia. In Vietnam this is problem being not much interested in, there are only some basic studies.

This work focused on finding technical parameters for procedure of the simultaneous determination of trace level of heavy metals in herb products by ICP-MS such as: the parameters of ICP-MS instrument, nitric acid concentration, time and microwave parameters for complete digression of sample, the use of internal standard for accurate determination of mercury. The results of the studies are the base to choose the suitable parameters for accurate determination of the elements above.

### **Result and discussion**

An analytical procedure for determination of Cr, As, Se, Cd, Hg, Pb in some kinds of herb products has been established. In this report the following isotopes have been chosen for the measurement of the elements:

<b>Elements</b>	<b>Isotopes</b>	<b>Elements</b>	<b>Isotopes</b>
Cr	53	Cd	111
As	75	Hg	202
Se	82	Pb	208

This procedure is based on the result of the following studies:

1. Study to find the suitable parameters of the ICP-MS instrument for simultaneous determination of the elements in the real samples. The results are following:

Element	Concentration (ppb)	RF Power				
		1300W	1350W	1490W	<b>1550W</b>	1600W
Cr	4.0	9,669.60	9,391.61	8,687.75	<b>8,084.01</b>	7,660.40
As	0.35	1,403.47	1,467.92	1,532.38	<b>1,550.16</b>	1,611.30
Se	0.4	630.0403	667.8226	642.2621	<b>571.1463</b>	602.2588
Cd	0.4	1,211.22	1,310.13	1,524.61	<b>1,684.63</b>	1,666.85
Hg	0.35	1,402.36	1,741.32	2,498.16	<b>2,844.92</b>	<b>3,100.56</b>
Pb	20	304,482.80	357,521.40	466,023.10	<b>539,785</b>	566,751
		<b>Sample depth</b>				
		4.50mm	<b>5.00 mm</b>	<b>5.50 mm</b>	6.00mm	6.50mm
Cr	4.0	9,791.91	<b>10,212.33</b>	<b>10,184.49</b>	9,024.66	8,413.13
As	0.35	1,796.87	<b>1,799.10</b>	<b>1,731.30</b>	1,575.72	1,483.48
Se	0.4	860.0642	<b>776.725</b>	<b>754.4989</b>	686.7131	544.477
Cd	0.4	1,730.20	<b>1,772.43</b>	<b>1,837.99</b>	1,696.86	1,466.82
Hg	0.35	2,394.81	<b>2,500.39</b>	<b>2,612.63</b>	2,393.69	2,100.29
Pb	20	486,467.70	<b>526,974.00</b>	<b>542,696.90</b>	523,211	450,424.30
		<b>Carrier gas</b>				
		1.10l/ph	1.15 l/ph	<b>1.20 l/ph</b>	<b>1.22 l/ph</b>	1.25 l/ph
Cr	4.0	3,001.61	5,491.41	<b>7,992.83</b>	<b>9,436.09</b>	10,517.00
As	0.35	1,324.57	1,401.25	<b>1,539.04</b>	<b>1,567.97</b>	1,599.06
Se	0.4	261.1251	465.5826	<b>621.1489</b>	<b>673.3764</b>	697.8251
Cd	0.4	1,027.86	1,416.80	<b>1,616.84</b>	<b>1,790.20</b>	1,653.51
Hg	0.35	1,497.94	2,409.25	<b>2,334.78</b>	<b>2,246.99</b>	2,033.61
Pb	20	290,568.20	473,614.50	<b>529,559.50</b>	<b>530,956.90</b>	457,075
		<b>Prepump</b>				
		0.02v/s	<b>0.05 v/s</b>	<b>0.10 v/s</b>	0.15 v/s	0.20 v/s
Cr	4.0	2,056.92	<b>5,459.19</b>	<b>9,436.09</b>	11,595.73	12,950.41
As	0.35	605.5958	<b>1,131.22</b>	<b>1,567.97</b>	1,785.82	1,873.55
Se	0.4	265.5692	<b>470.0272</b>	<b>673.3764</b>	771.1654	801.171
Cd	0.4	645.6024	<b>1,199.00</b>	<b>1,790.20</b>	1,793.54	1,759.09
Hg	0.35	1,870.23	<b>2,214.76</b>	<b>2,246.99</b>	2,106.95	1,873.57
Pb	20	219,537.60	<b>449,797.60</b>	<b>530,956.90</b>	534,944	477,966.00

The suitable parameters of the ICP-MS instrument for simultaneous determination of these elements in the real samples are following:

- RF Power: 1550W.
- Sample depth: 5,0-5,5 mm.
- Carrier gas: 1,15-1,22 l/ ph.
- Prepump: 0.05-0.1 v/s.

The influence of the concentration of nitric acid on the ICP-MS signals of Cr, As, Se, Cd, Hg, Pb

Element	Concentration (ppb)	Acid Concentration (%)						
		0.36	1.82	2	2.18	3.64	7.28	10.92
Cr	4.0	9126.977	8030.644	8009.481	8335.293	8197.411	6427.423	8308.608
As	0.35	2467.633	1949.12	1967.175	1980.238	1869.106	1449.033	1601.275
Se	0.40	524.4758	504.4763	438.9147	477.8076	401.1339	306.6829	323.3504
Cd	0.40	1567.94	1227.89	1244.554	1293.457	1106.76	803.3917	877.8457
Hg	0.35	1746.87	1480.159	1113.442	1164.556	1178.997	777.839	770.0664
Pb	20	411021.6	341242.4	342757.8	349646.5	317561.5	239616.1	288683

2. Study to use Tl, Bi, Pt, Au as an internal standard for accurate determination of mercury. The Results are following:

Acid concentration (%)	2	0.364	1.82	2.184	3.64	7.28	10.92
No internal Standard	0.353	0.911	0.644	0.412	0.519	0.105	0.065
Internal standard is Tl	0.418	0.731	0.621	0.669	0.651	0.110	0.073
Internal standard is Bi	0.291	2.651	0.328	0.512	0.507	0.043	0.019
Internal standard is Pt	0.35	0.348	0.342	0.382	0.347	0.224	0.206
Internal standard is Au	0.352	0.345	0.290	0.368	0.386	0.315	0.294

RF Power (W)	1300	1350	1490	1550	1600
No internal Standard	0.029	0.085	0.229	0.313	<b>0.350</b>
Internal standard is Tl	0.240	0.247	0.309	0.316	0.312
Internal standard is Bi	0.218	0.232	0.346	0.292	0.291
Internal standard is Pt	0.362	0.356	0.305	0.322	0.311
Internal standard is Au	0.346	0.314	0.355	0.307	0.305

Carrier gas (l/min)	1.1	1.15	1.2	1.22	1.25	1.3
No internal Standard	0.023	0.228	0.203	0.157	0.144	<0.000
Internal standard is Tl	0.268	0.295	0.196	0.141	0.194	0.115
Internal standard is Bi	0.239	0.263	0.171	0.117	0.166	0.084
Internal standard is Pt	0.246	0.303	0.305	0.362	0.326	0.33
Internal standard is Au	0.339	0.353	0.336	0.351	0.301	0.283

Sample depth (mm)	4.50	5.00	6.00	6.50	7.00
No internal Standard	0.197	0.245	0.207	0.133	0.135
Internal standard is Tl	0.228	0.243	0.204	0.196	0.235
Internal standard is Bi	0.183	0.207	0.175	0.174	0.209
Internal standard is Pt	0.313	0.292	0.322	0.308	0.304
Internal standard is Au	0.317	0.337	0.319	0.294	0.312

Pripump (r/s)	0.02	0.05	0.1	0.15	0.2
No internal Standard	0.139	0.145	0.229	0.158	0.109
Internal standard is Tl	0.808	0.212	0.309	0.131	<b>0.127</b>
Internal standard is Bi	0.730	0.183	0.346	0.117	<b>0.114</b>
Internal standard is Pt	0.679	0.323	0.305	0.295	<b>0.253</b>
Internal standard is Au	0.900	0.385	0.355	0.320	<b>0.317</b>

3. Study to find the optimum parameters of the microwave for the complete digestion of the sample. The Results are following:

Element	Concentration ( $\times 10^{-3}$ mg/l)			
	2min.-2min.-2min.	3min.-2min.-2 min.	3min.-3min.-3 min.	3min.-4min.-4 min.
Cr	61.21	69.8	71.77	71.50
As	19.16	23.6	24.11	24.24
Se	0.638	0.809	0.817	0.820
Cd	1.736	2.148	2.217	2.207
Hg	0.4733	0.691	0.836	0.828
Pb	60.5	71.12	76.26	76.50

The Results of the sample digestion by different mix solutions are following:

Element	Concentration ( x10 <sup>-3</sup> mg/l)		
	5ml HNO <sub>3</sub> + 2ml H <sub>2</sub> O <sub>2</sub>	3ml HNO <sub>3</sub> + 2ml H <sub>2</sub> O <sub>2</sub>	2ml HNO <sub>3</sub> + 2ml H <sub>2</sub> O <sub>2</sub>
Cr	70.34	71.77	69.47
As	25.27	24.11	21.39
Se	0.815	0.817	0.823
Cd	2.248	2.217	2.103
Hg	0.752	0.836	0.799
Pb	73.7	76.26	82.96

Element	Concentration ( x10 <sup>-3</sup> mg/l)		
	1,5ml HNO <sub>3</sub> + 2ml H <sub>2</sub> O <sub>2</sub>	2ml HNO <sub>3</sub> + 1ml H <sub>2</sub> O <sub>2</sub>	2ml HNO <sub>3</sub> + 2ml H <sub>2</sub> O <sub>2</sub> + 0,25ml HF
Cr	49.77	56.8	101.77
As	14.92	18.62	29.11
Se	0.623	0.691	0.917
Cd	1.816	1.795	2.917
Hg	0.644	0.621	1.536
Pb	58.07	61.12	76.26

4. Analysis the Standard Reference, descriptive statistics, evaluation error.

Analyze the standard reference 6 times, descriptive statistics the data, we have the results as in the following table:

Element	found content (µg/g)	Certified content (µg/g)	Relative Error (%)	Absolute Error (µg/g)
Cr	1.219±0.082	1.30	6.75	-0.0810
As	0.102 ± 0.011	0.1	10.64	0.0020
Se	0.119 ± 0.020	0.12	16.50	-0.0010
Cd	0.118 ± 0.021	0.12	17.28	-0.0020
Hg	0.0125 ± 0.0014	0.013	11.50	-0.0005
Pb	0.684 ± 0.018		2.62	

*The recommended procedure has been applied to the determination of Cr, As, Se, Cd, Hg, Pb in some real samples.*

#### Conclusion

The proposed matters are well fulfilled by this project. They are following:

- The suitable parameters of ICP-MS instrument for simultaneous determination of Cr, As, Se, Cd, Hg and Pb in herb products by ICP-MS have been studied and chosen.

- The optimum parameters of microwave and suitable content of mix acids for complete digestion of the sample have been studied and chosen.

- The effects of nitric concentration and high content of some metals in real samples on the determination of Cr, As, Se, Cd, Hg and Pb in herb products by ICP-MS have been studied.

- The study on using some different metals as internal standard for accurate determination of mercury by ICP-MS has been carried out.

- Analysis the Standard Reference, descriptive statistics and evaluation the errors have been carried out. The calculations of relative Errors are from 3 to 20 percent.

- The recommended procedure has been applied for the determination of Cr, As, Se, Cd, Hg and Pb in some real Vietnamese herb products by ICP-MS.