Green and white method for the determination of selected essential and toxic elements in vegetable and meat-based samples by small-sized electrothermal vaporization capacitively coupled microplasma optical emission spectrometry and combustion-assisted digestion

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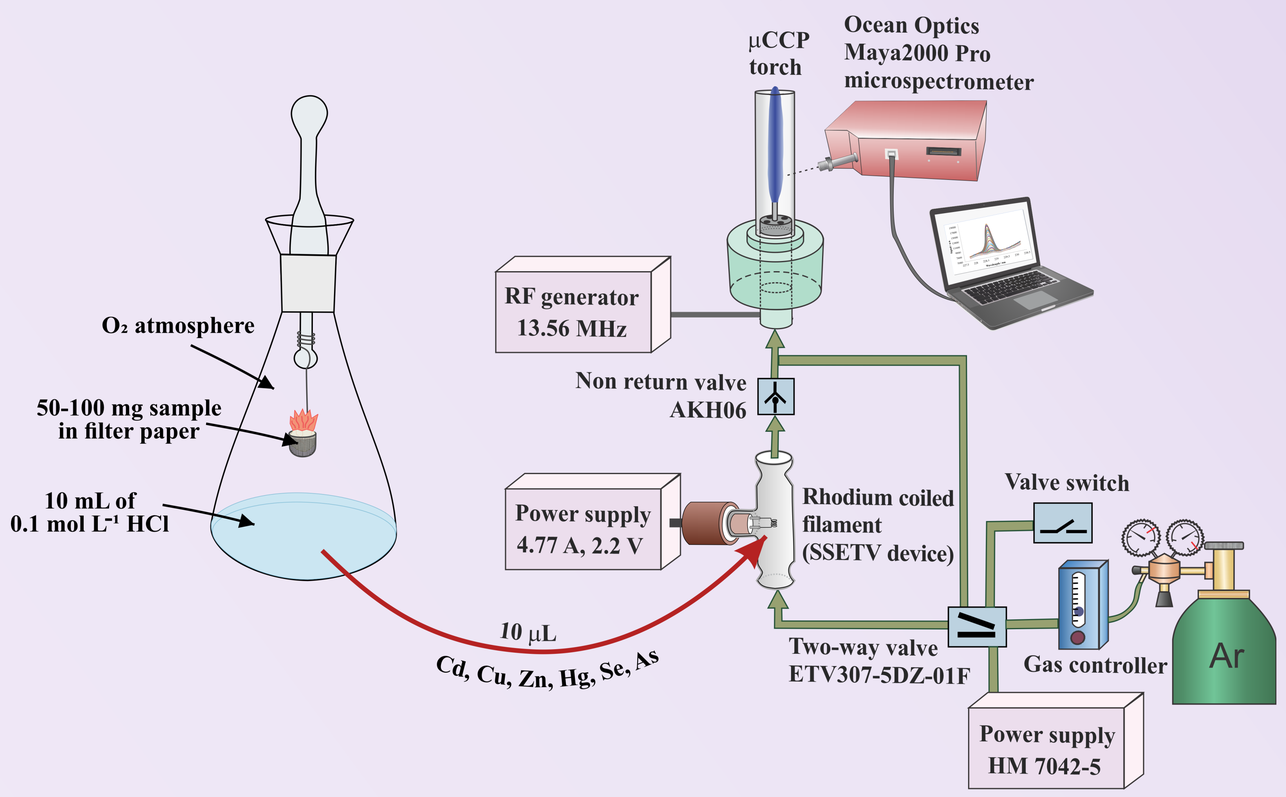
Introduction

The determination of essential and toxic elements, such as Se, Zn, Cu, Cd, Hg and As, using green sample preparation techniques coupled with miniaturized instrumentation, is a critical research focus in the field of analytical methods development. The aim of this study was the development of a green and white method based on oxygen flask combustion of the sample, and detection by small-sized electrothermal vaporization capacitively coupled microplasma optical emission spectrometry (SSETV-μCCP-OES). A microsample (10 μL) was vaporized from a small-sized Rh-coiled filament, while the low power (15 W) and low Ar consumption (150 mL min^{-1}) microplasma was used as excitation source and a low-resolution microspectrometer for recording the multielemental spectrum. The combustion method, as a greener alternative to wet acid digestion, involved weighing 50–100 mg sample, wrapping in a small ashless filter paper, and placing in a platinum basket. The sample was then combusted in an oxygen-filled Erlenmeyer flask, and the resulted gas was absorbed in a volume of 10 mL 0.1 mol L^{-1} HCl solution.

The effectiveness of the combustion-based digestion was verified compared to microwave-assisted digested samples in concentrated HNO_3 - H_2O_2 mixture. The accuracy (recovery and precision) of the method was evaluated by analyzing several certified reference materials (CRMs), using both external calibration and standard addition method.



Found values for Hg, Cu, Zn, Cd, Se and As in vegetables and meat-based CRMs obtained by SSETV-μCCP-OES method after combustion in O_2 atmosphere

Element	Calibration	Tort-3 (Lobster hepatopancreas)			CE278k (Mussel tissue)			CS-M-3 (Dried mushroom powder)			GBW 10011 (Rice)			RSD[b] (%)
		Certified value ± U_{CRM}[a] (mg kg^{-1})	Found value ± U_{lab}[a] (mg kg^{-1})	R ± U (%)	Certified value ± U_{CRM}[a] (mg kg^{-1})	Found value ± U_{lab}[a] (mg kg^{-1})	R ± U (%)	Certified value ± U_{CRM}[a] (mg kg^{-1})	Found value ± U_{lab}[a] (mg kg^{-1})	R ± U (%)	Certified value ± U_{CRM}[a] (mg kg^{-1})	Found value ± U_{lab}[a] (mg kg^{-1})	R ± U (%)	
Hg	External calibration	0.292 ± 0.022	0.328 ± 0.041	112 ± 13	0.071 ± 0.007	0.072 ± 0.018	102 ± 25	2.849 ± 0.104	3.137 ± 0.445	110 ± 14	1.6*	1.7 ± 0.2	106 ± 13	6.3-12.5
	Standard addition		0.319 ± 0.052	109 ± 16		0.079 ± 0.020	112 ± 26		2.796 ± 0.448	98 ± 16		1.5 ± 0.4	94 ± 27	8.0-13.3
Cu	External calibration	497 ± 22	515 ± 63	104 ± 12	5.98 ± 0.27	6.35 ± 0.98	106 ± 15	18.73 ± 0.70	18.72 ± 2.81	100 ± 15	2.7 ± 0.2	2.47 ± 0.39	92 ± 16	6.1-7.9
	Standard addition		544 ± 66	109 ± 12		5.77 ± 1.36	97 ± 24		20.83 ± 4.15	111 ± 20		2.71 ± 0.65	100 ± 24	5.1-12.0
Zn	External calibration	136 ± 6	146 ± 16	107 ± 11	71 ± 4	66 ± 6	92 ± 10	113.30 ± 3.28	106.0 ± 16.2	94 ± 16	11.6 ± 0.7	12.1 ± 2.3	104 ± 19	4.8-9.3
	Standard addition		147 ± 17	108 ± 11		73 ± 11	103 ± 15		105.6 ± 12.2	93 ± 12		13.2 ± 1.9	113 ± 14	5.7-7.5
Cd	External calibration	42.3 ± 1.8	39.6 ± 3.9	94 ± 10	0.336 ± 0.025	0.357 ± 0.064	106 ± 18	1.229 ± 0.110	1.195 ± 0.291	97 ± 24	18 ± 4	19 ± 3	106 ± 15	4.9-12.2
	Standard addition		41.5 ± 3.8	98 ± 9		0.371 ± 0.048	110 ± 13		1.285 ± 0.325	105 ± 25		17 ± 3	94 ± 18	4.6-12.6
Se	External calibration	10.9 ± 1.0	11.9 ± 2.4	109 ± 20	1.62 ± 0.12	1.50 ± 0.44	93 ± 29	17.43 ± 1.36	18.69 ± 3.74	107 ± 20	0.053 ± 0.007	< LOD		9.9-14.5
	Standard addition		12.0 ± 3.2	110 ± 27		1.54 ± 0.33	95 ± 22		17.56 ± 4.25	101 ± 24		< LOD		10.8-13.3
As	External calibration	59.5 ± 3.8	53.7 ± 6.4	90 ± 12	6.7 ± 0.4	6.5 ± 1.2	97 ± 19	0.651 ± 0.026	< LOQ		0.031 ± 0.005	< LOD		5.9-9.6
	Standard addition		63.5 ± 12.1	107 ± 19		6.9 ± 1.6	103 ± 23		< LOQ			< LOD		9.5-12

[a] U_{CRM} and U_{lab} is the expanded uncertainty for the certified concentration and found concentration, respectively (k = 2, n = 3, 95% confidence level); [b] RSD (%) is the relative standard deviation from combined uncertainty

Found values for Hg, Cu, Zn, Cd, Se and As in vegetables and meat-based CRMs obtained by SSETV-μCCP-OES method after microwave-assisted digestion

Element	Tort-3 (Lobster hepatopancreas)			CE278k (Mussel tissue)			CS-M-3 (Dried mushroom powder)			RSD (%)
	Certified value ± U_{CRM}[a] (mg kg^{-1})	Found value ± U_{lab}[a] (mg kg^{-1})	R ± U (%)	Certified value ± U_{CRM}[a] (mg kg^{-1})	Found value ± U_{lab}[a] (mg kg^{-1})	R ± U (%)	Certified value ± U_{CRM}[a] (mg kg^{-1})	Found value ± U_{lab}[a] (mg kg^{-1})	R ± U (%)	
Hg	0.292 ± 0.022	0.296 ± 0.043	101 ± 14	0.071 ± 0.007	0.079 ± 0.021	111 ± 27	2.849 ± 0.104	2.662 ± 0.474	93 ± 18	7.2-13.5
Cu	497 ± 22	460 ± 61	93 ± 13	5.98 ± 0.27	5.77 ± 1.36	97 ± 24	18.73 ± 0.70	20.83 ± 4.15	111 ± 20	6.7-11.8
Zn	136 ± 6	128 ± 23	94 ± 18	71 ± 4	75 ± 11	106 ± 15	113.30 ± 3.28	110.3 ± 21.5	97 ± 19	7.3-9.7
Cd	42.3 ± 1.8	42.6±14.8	101±15	0.336 ± 0.025	0.306±0.084	91±27	1.229 ± 0.110	1.232±0.306	100±25	7.4-13.7
Se	10.9 ± 1.0	10.5±1.6	96±15	1.62 ± 0.12	1.80±0.47	111±26	17.43 ± 1.36	16.91±2.35	97±14	7.0-13.0
As	59.5 ± 3.8	53.7±6.4	90±12	6.7 ± 0.4	6.5±1.2	97±19	0.651 ± 0.026	< LOD		7.1-11.5

Limits of detection for Se, Zn, Cu, Cd, Hg and As determination by SSETV-μCCP-OES (mg kg^{-1})

Se	Zn	Cu	Cd	Hg	As
0.322	0.148	0.051	0.0042	0.052	0.173

The instrumental LODs for the SSETV-μCCP-OES method were calculated using the SBR-RSDB approach

$$LOD = 3 \times 0.01 \times RSDB \times \frac{c_0}{SBR}$$

Where: RSDB – is the relative standard deviation of the background signal (%);
c_0 – is the analyte concentration (μg L^{-1});
SBR – is the signal to background ratio.

Conclusions

- The study demonstrated for the first time that the low power and low Ar consumption SSETV-μCCP-OES set-up and sample preparation by combustion in an O_2 filled flask is a viable green and white method for Hg, Cu, Zn, Cd, Se and As determination.
- The method accuracy, checked by four vegetable and meat-based certified reference materials analysis, showed good results, with recovery in the range 90-112%.
- Non-spectral matrix effects in the SSETV-μCCP-OES method, evaluated using the standard addition method using the same CRMs, produced results very similar to those obtained through external calibration, with recoveries between 98% and 113%.
- Furthermore, parallel microwave-assisted digested samples did not show significant differences compared to the combusted ones, confirming that the combustion-based preparation is an effective alternative method.
- The precision, expressed as relative standard deviation (RSD,%) values ranged from 4.8% to 14.5% for external calibration, and 4,6-13,3% for the standard addition method.

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Working conditions for Se, Zn, Cu, Cd, Hg and As determination by SSETV-μCCP-OES

Component	Operating conditions
Plasma microtorch (Home-made, INCDO-INOE 2000, Cluj-Napoca, Romania)	Plasma power: 15 W; Ar flow rate: 150 mL min^{-1}; Observation height: 0.8 mm
Maya2000 Pro Microspectrometer, Ocean Optics (Dunedin, USA)	Detector chamber purged with Ar, 165-309 nm spectral range
Electrothermal vaporizer of Rh filament (Babes-Bolyai University, Cluj-Napoca, Romania)	10 μL sample; drying temperature: 80 °C for 180 s; vaporization temperature: 1500 °C for 10 s
Tenma 72-13360 power supply, Farnell (Leeds, UK)	Drying: 0.25 V, 1.93 A; Vaporization: 1.62 V, 4.32 A
Spectra Suite software for High-speed acquisition mode and signal processing	100 spectra with 100 ms/episode integration time; time-integrated (area signal);
External calibration	0-100 μg L^{-1} Zn, Cd and Hg 0-1000 μg L^{-1} Cu, Se and As