Limit of detection for Se, Zn, Cu, Cd, Pb, Hg and As determination by white small-sized electrothermal vaporization capacitively coupled microplasma optical emission spectrometry and sample combustion compared to inductively coupled plasma optical emission spectrometry

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Introduction

The aim of the current study was the evaluation of the limits of detection (LODs) of a green and white analytical method based on sample combustion (50 mg sample combustion in O_2 atmosphere followed by uptake in 0.1 mol L^{-1} HCl) and detection by small-sized electrothermal vaporization capacitively coupled microplasma optical emission spectrometry (SSETV-μCCP-OES). The analytical signal was obtained by 2D signal integration (time-wavelength) for different pixel numbers around the Central Pixel (CP) of the analytical line (CP, CP ± 1, CP ± 2 and CP ± 3).

The LODs were compared to inductively coupled plasma optical emission spectrometry (ICP-OES). Arsenic, Hg and Se were determined by ICP-OES after hydride generation with $NaBH_4$ solution.

Working conditions for SSETV-μCCP-OES determination

Component	Specifications	Operating conditions
Plasma microtorch	Home-made, INCDO-INOE 2000 Bucharest, Research Institute for Analytical Instrumentation (Cluj-Napoca, Romania)	Plasma power: 15 W; Ar flow rate: 150 mL min^{-1}; Observation height: 0.8 mm
Microspectrometer	Maya2000 Pro Ocean Optics (Dunedin, USA), 0.35 nm FHWM equipped with CCD, 165-309 nm spectral range	Detector chamber purged with Ar
Small-sized electrothermal vaporizer	Rh filament (99.9% purity, 250 μm diameter, 4 turns with 1.5 mm diameter) mounted in a T-shaped quartz chamber (Babes-Bolyai University, Cluj-Napoca, Romania)	10 μL sample; drying temperature: 80 °C for 180 s; vaporization temperature: 1500 °C for 10 s
Power source for the Rh filament heating	Tenma 72-13360 power supply, Farnell (Leeds, UK)	Drying: 0.25 V, 1.93 A; vaporization: 1.62 V, 4.32 A
Data acquisition and signal processing	Spectra Suite software; High speed acquisition mode	100 spectra with 100 ms/episode integration time; peak height measurements;
Calibration	External	0-100 μg L^{-1} Zn, Cd and Hg 0-1000 μg L^{-1} Cu, Se and As

Figures of merit

Element	Wavelength (nm)	SSETV-μCCP-OES method								ICP-OES method	Maximum admitted concentration in foodstuffs and food supplements (mg kg^{-1})[1]
		CP		CP ± 1		CP ± 2		CP ± 3			
		LOD (mg kg^{-1})	RSDB[a] (%)	LOD (mg kg^{-1})	RSDB[a] (%)	LOD (mg kg^{-1})	RSDB[a] (%)	LOD (mg kg^{-1})	RSDB[a] (%)	LOD (mg kg^{-1})	
Hg	253.652	0.028	0.66	0.052	3.45	0.063	5.91	0.078	8.39	2.17[b]	0.1-1
Cu	249.215	0.058	0.49	0.051	1.18	0.052	1.69	0.067	2.42	0.53	-
Zn	213.857	0.040	0.69	0.148	6.74	0.176	11.10	0.215	15.08	0.30	-
Pb	261.417	0.608	1.73	0.242	1.87	0.222	2.47	0.268	3.44	1.68	0.05-3
Cd	228.802	0.0073	0.54	0.0042	0.86	0.0048	1.42	0.0064	2.24	0.22	0.020-3
Se	196.026	0.644	1.27	0.322	1.73	0.329	2.55	0.425	3.83	2.83[b]	-
As	189.042	0.281	0.77	0.173	1.15	0.041	2.08	0.037	2.68	4.17[b]	0.02-0.3

[a] RSDB (%) is the relative standard deviation of the background signal
[b] Hg, Se and As determination by ICP-OES were carried out after hydride generation with $NaBH_4$

[1]Commission Regulation (EU) 2023/915 of 25 April 2023 on maximum levels for certain contaminants in food and repealing Regulation (EC) No 1881/2006, *Off. J. Eur. Union*, 2023, **L119**, 103-157

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

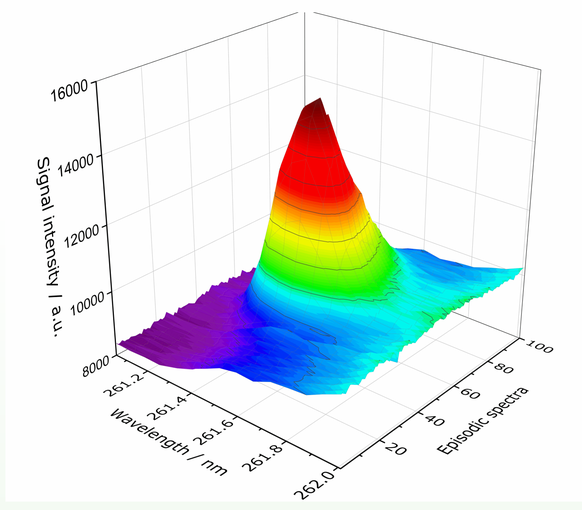
$$\mathrm{LOD} = 3 \times 0.01 \times \mathrm{RSDB} \times \frac{c_0}{\mathrm{SBR}}$$

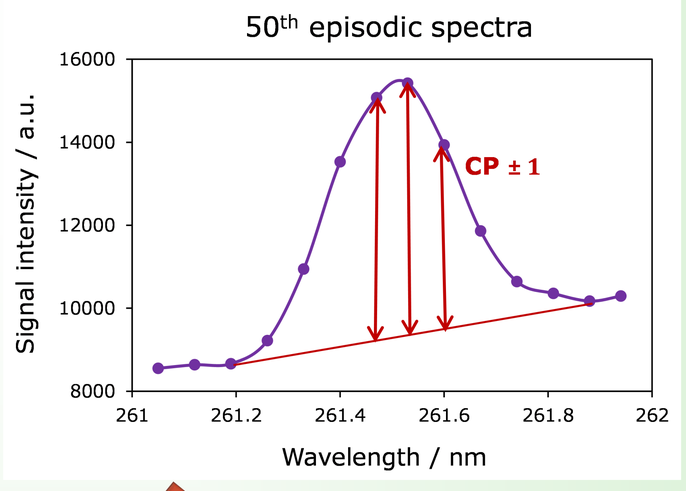
Where: RSDB – is the relative standard deviation of the background signal (%);
c_0 – is the analyte concentration (μg L^{-1});
SBR – is the signal to background ratio.

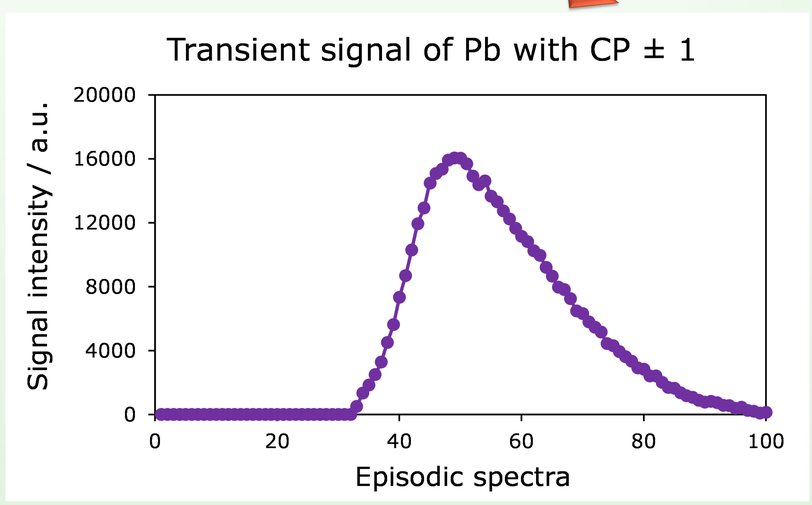
Conclusions

- The best limits of detection were obtained with CP±1 and CP±2 strategy, compared to only CP, resulting in values (mg kg^{-1}) of 0.052 (Hg); 0.051 (Cu); 0.148 (Zn); 0.242 (Pb); 0.0042 (Cd); 0.322 (Se) and 0.173 (As).
- The LODs obtained using the SSETV-μCCP-OES method were found to be better than those achieved with ICP-OES. However, for Hg, Pb, and Cd, the detection limits are still not low enough for determining these elements in certain foodstuffs, as the observed values exceed the maximum admitted concentrations[1]. Therefore, for these elements, coupling the method with a preconcentration technique, such as solid-phase extraction (SPE), would be necessary.
- In terms of calibration curve linearity, it was found that the number of pixels does not affect linearity, but it does impact the relative standard deviation of the blank (RSDB, %), which becomes poorer as the number of pixels increases.

3D spectra for Pb (261.417 nm) and signal calculation strategy







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