Improvement of analytical performance (detection limits, non-spectral matrix effects) for SSETV-μCCP-OES for multielement determination in food and environmental samples after *ex-situ/on-site* μ-SPE

(Activity 1.5, CO-UBB, P1-FI)

Since the Maya2000 Pro microspectrometer is equipped with a multichannel CCD detector in which each pixel functions as an individual microdetector generating a signal, it is possible to integrate the signal over several pixels along the spectral line profile, rather than measuring only the signal at the pixel corresponding to the peak maximum. Therefore, this approach was evaluated as a means to improve sensitivity and detection limits by integrating the signal over 1, 3, 5, and 7 pixels of the spectral line profile. Detection limits were calculated using the SBR–RSDB procedure (P.W.J.M. Boumans, Spectrochim. Acta B, 1991, 46, 431–445), where SBR is the signal-to-background ratio for a given concentration within a calibration range, and RSDB is the percentage standard deviation of the background, obtained from 11 measurements of episodic spectra recorded before the appearance of the elemental signal, using the same number of pixels as applied for signal integration on the analytical line. Using this approach, the sensitivity of the SSETV-μCCP-OES method was improved by a factor of 4.2–4.7 when increasing the number of integrating pixels to 7, without applying μ-SPE preconcentration. The signal-to-background ratio increased with the number of pixels following a second-degree polynomial relationship. One would expect the detection limits to improve proportionally; however, in practice, the best LODs were obtained using a 5-pixel integration, where an improvement of 3.7–4 times was observed. The best LODs for 5 pixels, improved only by 2–3 times compared to single pixel measurement, are attributed to changes in the background signal when increasing the number of background measurement pixels, especially for certain spectral lines, the clearest case being Zn. Details regarding LOD improvement using up to 5 pixels have been published in *Journal of Analytical Atomic Spectrometry*, 2025, Advance Article, DOI: 10.1039/D5JA00297D, in the context of an (OFC)-SSETV-μCCP-OES method applied to food samples without μ-SPE preconcentration. Instrumental LODs based on the SBR–RSDB procedure, along with LODs obtained in food samples combusted under the optimized conditions described earlier, were evaluated. The instrumental LODs and those obtained in food samples using (OFC)-SSETV-μCCP-OES with 5 pixel integration at the analytical line, by combusting 50 mg of sample in a 500 mL flask, are presented in Table 1. Also the improved LODs obtained after μ-SPE preconcentration on a dithizone-functionalized C18 silica column for preconcentration from the 10 mL absorbing solution resulting from combustion, followed by elution in 1 mL of 0.2 mol L^{-1} thiourea in 1 mol L^{-1} HNO_3 are presented. As a comparison, LODs achieved by pneumatic-nebulization ICP-OES, as well as those obtained for Hg, Se, and As using cold vapor or hydride generation, were also evaluated.

Table 1. Detection limits for the (OFC)-SSETV-μCCP-OES method obtained using the SBR–RSDB approach with 5 pixel signal integration of the analytical line, and detection limits obtained by (μ-SPE)-SSETV-μCCP-OES after μ-SPE preconcentration on a dithizone-functionalized C18 column. (AC. Mot, A.-I. Dudu, T. Frentiu, D. Petreus, E.-A. Levei, Z. Stupar, M. Frentiu, E. Covaci. *J. Anal. At. Spectrom.*, 2025, Advance article, DOI:10.1039/D5JA00297D)

Element	SSETV-μCCP-OES[a]	(OFC)-SSETV-μCCP-OES in food[b]	(μ-SPE)-SSETV- μCCP-OES in food[c]	ICP-OES[d]
	μg L^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Hg	0.05	0.010	0.001	0.04[a]
Cu	0.14	0.030	0.003	0.62
Zn	0.04	0.010	0.001	0.04
Pb	0.35	0.070	0.007	0.85
Cd	0.05	0.010	0.001	0.06
Se	6.0	1.20	-	0.05[a]
As	5.0	1.00	-	0.06[a]

[a] Instrumental LODs obtained by 5 pixel signal integration; [b] LODs in food samples for 50 mg sample combusted and absorbed in 10 mL of 0.1 mol L^{-1} HNO_3; [c] μ-SPE preconcentration on a dithizone-functionalized C18 cartridge; [d] LODs obtained by pneumatic-nebulization ICP-OES or by cold vapor generation (Hg) and hydride generation (Se, As) from microwave-digested pressurized samples.

The SSETV-μCCP-OES method provided instrumental LODs ranging from 0.04 μg L^{-1} (Zn) to 6.0 μg L^{-1} (Se). In food samples, the OFC approach yielded the following LOD values without μ-SPE preconcentration: 0.01 mg kg^{-1} (Hg, Cd, Zn); 0.030 mg kg^{-1} (Cu); 0.070 mg kg^{-1} (Pb); 1.00 mg kg^{-1} (As); and 1.20 mg kg^{-1} (Se), considering 50 mg of sample combusted in an oxygen flask and dissolved in 10 mL of 0.1 mol L^{-1} HNO_3. After μ-SPE microextraction, the LODs were improved by one order of magnitude, as shown in Table 1. For surface water samples, applying μ-SPE preconcentration leads to LOD improvements of at least two orders of magnitude, yielding values (in μg L^{-1}) of: 0.002 for Cu, 0.0004 for Zn, 0.004 for Pb, and 0.0005 for Cd.

Results: Improved analytical performance of the SSETV-μCCP-OES method with and without *ex-situ/on-site* multielement preconcentration using dithizone-functionalized μ-SPE cartridges