Validation of the (μ-SPE)-SSETV-μCCP-OES methods by comparison with ICP-OES and GFAAS (finalization)

(Activity 2.2, CO-UBB)

In the first stage, the SSETV-μCCP-OES method was validated by comparison with ICP-OES for the analysis of food samples, and for the analysis of surface waters by the μ-SPE procedure optimized in the laboratory and implemented *on-site*. In this stage, this activity was finalized through the comparative validation of the detection limits for Cd, Pb, Cu and Zn, in comparison with ICP-OES and GFAAS in surface waters (river waters) processed *on-site* by μ-SPE preconcentration on a C18 cartridge functionalized with 1 mg of dithizone. The detection limits obtained by (μ-SPE)-SSETV-μCCP-OES compared to the other two methods are presented in Table 1. The detection limits by (μ-SPE)-SSETV-μCCP-OES were obtained for a sample volume of 10 μL introduced through electrothermal vaporization from a Rh filament heated to 1500 ± 20 °C in the capacitively coupled microplasma operated at 15 W and 150 mL min^{-1} Ar with spectroscopic observation at 0.8 mm above the Mo support electrode. The instrumental detection limits of (μ-SPE)-SSETV-μCCP-OES were evaluated on the basis of the signal-to-background ratio – relative standard deviation of the background (SBR-RSDB) (P.W.J.M. Boumans, *Spectrochim. Acta B*, 1991, 46, 431-445), and, respectively, by the method of the calibration curve signal residuals. In both methods the analytical signal was obtained by the 2D integration of the transient signal as a function of time and as a function of wavelength over the spectral line profile for 5 pixels. In the first stage, the variation of the signal, the SBR and the LODs as a function of the number of pixels used for signal integration over the spectral line profile was studied, and improvements of more than 4-fold for the signal and of 2–3-fold for the LODs were obtained for 5 pixels (Mot *et al. Journal of Analytical Atomic Spectrometry*, 2026, https://doi.org/10.1039/d5ja00297d). The RSDB value was calculated on the basis of the signals generated in 11 episodic spectra recorded before the appearance of the analytical signal, considering the same number of pixels used for the integration of the analytical signal, while the SBR was the signal-to-background ratio for a calibration solution. The calibration residuals were calculated on the basis of the calibration curves over the 0–20 μg L^{-1} concentration range (n = 6). The method detection limits in the water samples were calculated taking into account the instrumental LODs, the μ-SPE preconcentration factor and the recovery for each metal in the CRMs, presented in Table 1 of Activity 2.1. The detection limits were compared with (μ-SPE)-GFAAS and (μ-SPE)-ICP-OES, as reference in our laboratory, and with the SPE methods based on ICP-OES/MS from the literature, commonly used in the quality control laboratories of natural waters. The detection limits obtained are presented in Table 1 (Covaci *et al.*, *Talanta*, 2026, https://doi.org/10.1016/j.talanta.2026.130082).

The SSETV-μCCP-OES method without preconcentration provides instrumental LODs evaluated by the SBR-RSDB approach (ng L^{-1}) of 50 (Cd), 40 (Zn), 140 (Cu) and 350 (Pb). The instrumental LODs of SSETV-μCCP-OES evaluated on the basis of the calibration curve residuals were (ng L^{-1}) 66 (Cd), 100 (Zn), 290 (Cu) and 470 (Pb), being 1.3–2.5 times poorer than those evaluated by SBR-RSDB owing to the deviation of the calibration points from the calibration curve, even though the linearity was excellent (R^2 = 0.9998–0.9999) up to 20 μg L^{-1}.

Table 2. Limits of detection obtained by SSETV-μCCP-OES, ICP-OES and GFAAS with and without μ-SPE preconcentration on the dithizone-functionalized C18 cartridge (Covaci *et al.*, *Talanta*, 2026, https://doi.org/10.1016/j.talanta.2026.130082)

Element	Without preconcentration						With preconcentration			
	SSETV-μCCP-OES				ICP-OES [a]	GFAAS [b]	(μ-SPE)-SSETV-μCCP-OES [c]		(μ-SPE)-ICP-OES [d]	(μ-SPE)-GFAAS [c]
	SBR-RSDB	Calibration residual					SBR-RSDB	Calibration residual		
	LOD (ng L^{-1}) [e]	Residuals (a.u.)	Slope (a.u. L μg^{-1})	LOD (ng L^{-1}) [f]	LOD (ng L^{-1})	LOD (ng L^{-1})	LOD (ng L^{-1})	LOD (ng L^{-1})	LOD (ng L^{-1})	LOD (ng L^{-1})
Cd(II)	50	311	14190	66	1000	120	0.51 ± 0.06	0.66 ± 0.05	10.1 ± 0.80	1.20 ± 0.10
Cu(II)	140	117	1200	290	12000	600	1.41 ± 0.11	2.92 ± 0.22	121 ± 9.3	5.82 ± 0.47
Pb(II)	350	100	640	470	45000	600	3.53 ± 0.25	4.77 ± 0.34	457 ± 33	6.14 ± 0.46
Zn(II)	40	370	11350	100	1000	360	0.40 ± 0.03	1.01 ± 0.08	10.1 ± 0.8	3.65 ± 0.28

[a] LODs calculated as ($3s_b/m$); [b] LODs calculated as ($3s_b/m$); [c] LODs calculated for a preconcentration factor of 100 and recovery in the water CRM samples; [d] LODs calculated as $3s_b/m$ for a preconcentration factor of 40 and recovery in water CRM samples; [e] LODs calculated as ($3s_b/m$); [f] LODs calculated on the basis of the calibration residuals (0 – 20 μg L^{-1}, n = 6 calibration standards)

The detection limits obtained by the SSETV-μCCP-OES method without preconcentration, evaluated by the SBR-RSDB approach and the calibration curve residuals, are 20–130 and, respectively, 15–100 times better than those obtained by ICP-OES with pneumatic nebulization, highlighting the superiority of sample introduction through the electrothermal vaporization of a microsample, even when coupled to a microplasma. The detection limits obtained by the SSETV-μCCP-OES method are 2–9 times better compared to GFAAS, which could be explained by the signal enhancement through integration over the spectral line profile in SSETV-μCCP-OES, versus the measurement of the signal at the line maximum in GFAAS. An improvement of the LODs (ng L^{-1}) to 0.51 ± 0.06 (Cd), 1.41 ± 0.11 (Cu), 3.53 ± 0.25 (Pb) and 0.40 ± 0.03 (Zn) (SBR-RSDB) and 0.66 ± 0.05 (Cd), 2.92 ± 0.22 (Cu), 4.77 ± 0.34 (Pb) and 1.01 ± 0.08 (Zn) was obtained by (μ-SPE)-SSETV-μCCP-OES, considering a preconcentration factor of 100 in the river water analysis and the recovery for the CRMs. The detection limits are better than those obtained by (μ-SPE)-GFAAS and in particular by (μ-SPE)-ICP-OES, for which only a preconcentration factor of 40 was applied, owing to the larger sample volumes required for pneumatic nebulization into the plasma.

A comparison was also made between the LODs obtained by the (μ-SPE)-SSETV-μCCP-OES method and those for the commonly used spectral techniques reported in the literature (FAAS, GFAAS, ICP-OES and ICP-MS) and different microplasmas coupled with various preconcentration procedures, such as liquid-liquid extraction (LLE) or SPE/SPME-based methods applied to natural water analysis (Covaci *et al.*, *Talanta*, 2026, https://doi.org/10.1016/j.talanta.2026.130082). The detection limits obtained by the (μ-SPE)-SSETV-μCCP-OES method are significantly better than those reported for ICP-OES, FAAS and GFAAS, irrespective of the preconcentration strategy used. However, the preconcentration factors applied in the reference methods (from 3 to 300) should also be taken into account, since the analytical performances depend on the sample preparation procedure. On the other hand, the LODs obtained by (μ-SPE)-SSETV-μCCP-OES are poorer than those reported for ICP-MS, in particular for Pb and Cd, for example when SPE preconcentration on a C18 cartridge functionalized with 2-mercaptoethanol and elution with cysteine was applied. The superior sensitivity of ICP-MS and the enrichment factors one order of magnitude higher than those applied in our procedure could explain the better LODs. The detection limits obtained by the (μ-SPE)-SSETV-μCCP-OES method are substantially better than those reported for the *on-site* DGT-SSETV-μCCP-OES approach in river waters and elution with 1 mol L^{-1} HNO_3 (ng L^{-1}): 10 (Cd), 20 (Cu), 70 (Pb) and 10 (Zn) (Angyus *et al.*, *Talanta*, 2023, https://doi.org/10.1016/j.talanta.2023.124551). This improvement is due to the higher preconcentration factors obtained on the dithizone-functionalized μ-SPE cartridge *on-site*, compared to the *in-situ* DGT passive preconcentration on Chelex-100 resin, which usually provided a preconcentration factor of approximately 10 for a DGT device immersion period of 24 hours.

A comparison of the accuracy (recovery and precision) of the (μ-SPE)-SSETV-μCCP-OES method with μ-SPE-GFAAS is presented in Table 1. The method based on the capacitively coupled microplasma provided recoveries and precisions similar to those obtained by the reference method. Details can be found in the reference (Covaci *et al.*, *Talanta*, 2026, https://doi.org/10.1016/j.talanta.2026.130082).

Degree of achievement of the objective. The objective concerning the *Validation of the (μ-SPE)-SSETV-μCCP-OES methods by comparison with ICP-OES and GFAAS* was finalized in accordance with the project implementation plan. The LODs and the recoveries were compared for the analysis of the certified reference materials of water for the determination of Cu, Zn, Cd and Pb, versus μ-SPE-ICP-OES and μ-SPE-GFAAS.

Results:

- Report on the validation of the (μ-SPE)-SSETV-μCCP-OES method in water CRM samples with respect to the detection limits compared to μ-SPE-ICP-OES and μ-SPE-GFAAS
- One ISI article published (Covaci *et al.*, *Talanta*, 2026, https://doi.org/10.1016/j.talanta.2026.130082) with impact factor 6.7
- 2 participations with 2 posters at the 52nd International Conference of the Slovak Society of Chemical Engineering – SSCHE 2026, Strbske Pleso, Slovakia, 26–29 May 2026 https://www.sschi.sk/en/event/ssche2026/