Validation of monoelement and multielement SSETV-μCCP-OES methods for food and environmental samples, with or without *ex-situ/on-site* μ-SPE

(Activity 1.6, CO-UBB, P1-FI)

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

(Activity 1.7, CO–UBB)

The SSETV-μCCP-OES method, both without preconcentration and with *ex-situ/on-site* μ-SPE preconcentration, was validated for food and water samples based on the LODs, which were discussed in Activity 1.5. The (OFC)-SSETV-μCCP-OES method was also validated in food samples without μ-SPE preconcentration through the analysis of CRM samples, presented in Table 1. In addition, the impact of non-spectral matrix interferences in food samples was evaluated using the (OFC)-SSETV-μCCP-OES method without μ-SPE preconcentration, based on the results obtained for several CRM samples analyzed by both external calibration and the standard addition method.

According to the results presented in Table 1, there is good agreement between the values obtained by the (OFC)-SSETV-μCCP-OES method using both external calibration and the standard addition method. Recoveries ranged from 90–113%, with an expanded uncertainty of 9–25% (k = 2) for external calibration, and from 91–110% with an expanded uncertainty of 9–27% for the standard addition method. These results demonstrate that the (OFC)-SSETV-μCCP-OES method is accurate and not affected by non-spectral matrix interferences. The z-scores, calculated according to the recommendations of the Eurachem Guide for analytical method validation (*Eurachem Guide: Selection, Use and Interpretation of Proficiency Testing (PT) Schemes*, ed. B. Brookman and I. Mann, 3rd ed., 2021, EPT_2021_P1_EN.pdf, accessed July 17, 2025), indicated that the (OFC)-SSETV-μCCP-OES method performs adequately, as the calculated z-score values were in the range of 0.1–1.8, well below the recommended limit of 2 from the European guide. Additional discussion on the validation of the (OFC)-SSETV-μCCP-OES method for food analysis has been published in *J. Anal. At. Spectrom.*, 2025, Advance Article, DOI: 10.1039/D5JA00297D.

The SSETV-μCCP-OES method was validated by comparison with ICP-OES for the analysis of food samples, and with GFAAS for the analysis of surface water samples using the μ-SPE procedure optimized in the laboratory and implemented *on-site*. In Stage II of the project, validation by comparison with ICP-OES and GFAAS for environmental samples (soil and water) will be completed. Thus, the SSETV-μCCP-OES method was validated against ICP-OES for the determination of Cu, Zn, Cd, Pb, Hg, Se, and As in food samples by comparing detection limits and recoveries obtained from CRM analyses. For ICP-OES analysis, classical sample preparation was applied using high-pressure microwave-assisted digestion (HP-MAWD) in a HNO_3–H_2O_2 mixture, whereas for SSETV-μCCP-OES, the OFC procedure without μ-SPE preconcentration was used. The results obtained by (HP-MAWD)-ICP-OES for CRM food samples (vegetables and meat) are presented in Table 2. Recoveries (k = 2) ranged from 91–111%, with expanded uncertainties of 12–27% (k = 2). These values were similar to those obtained by SSETV-μCCP-OES with OFC sample preparation presented in Table 1. The Tukey statistical test (J.M. Tukey, *Biometrics*, 1949, 5, 99–114) indicated no significant differences ($p < 0.05$) between the results obtained by the (OFC)-SSETV-μCCP-OES method and those obtained by the reference (HP-MAWD)-ICP-OES method in food samples.

Table 1. Concentrations obtained by the (OFC)-SSETV-µCCP-OES method for Cu, Zn, Cd, Pb, Hg, Se, and As in certified reference materials of vegetables and meat. (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)

CRM	Calibration type	Cu		Zn		Cd		Pb		Hg		Se		As	
		Certified value ± U_{CRM}[a] (mg kg^{-1})	Found value ± U_{lab}[b] (mg kg^{-1})	Certified value ± U_{CRM}[a] (mg kg^{-1})	Found value ± U_{lab}[b] (mg kg^{-1})	Certified value ± U_{CRM}[a] (mg kg^{-1})	Found value ± U_{lab}[b] (mg kg^{-1})	Certified value ± U_{CRM}[a] (mg kg^{-1})	Found value ± U_{lab}[b] (mg kg^{-1})	Certified value ± U_{CRM}[a] (mg kg^{-1})	Found value ± U_{lab}[b] (mg kg^{-1})	Certified value ± U_{CRM}[a] (mg kg^{-1})	Found value ± U_{lab}[b] (mg kg^{-1})	Certified value ± U_{CRM}[a] (mg kg^{-1})	Found value ± U_{lab}[b] (mg kg^{-1})
Tort-3 (Lobster hepatopancreas)	Ext. calib.	497 ± 22	515 ± 63	136 ± 6	146 ± 16	42.3 ± 1.8	39.6 ± 5.5	0.225 ± 0.018	0.249 ± 0.044	0.292 ± 0.022	0.328 ± 0.046	10.9 ± 1.0	11.9 ± 2.4	59.5 ± 3.8	53.7 ± 8.4
	Std. add.		524 ± 66		147 ± 17		41.5 ± 3.8		0.238 ± 0.047		0.319 ± 0.052		12.0 ± 3.2		63.5 ± 12.1
CE278k (Mussel tissue)	Ext. calib.	5.98 ± 0.27	6.35 ± 0.98	71 ± 4	66 ± 6	0.336 ± 0.025	0.357 ± 0.064	2.18 ± 0.18	2.09 ± 0.46	0.071 ± 0.007	0.072 ± 0.018	1.62 ± 0.12	< 3.96 (LOQ)	6.7 ± 0.4	6.5 ± 1.2
	Std. add.		5.77 ± 1.36		73 ± 11		0.371 ± 0.048		2.10 ± 0.50		0.079 ± 0.020		< 3.96 (LOQ)		6.9 ± 1.6
CS-M-3 (Dried mushroom powder)	Ext. calib.	18.73 ± 0.70	18.72 ± 2.81	113.30 ± 3.28	106.05 ± 16.23	1.229 ± 0.110	1.195 ± 0.291	1.863 ± 0.108	1.943 ± 0.330	2.849 ± 0.104	3.137 ± 0.445	17.43 ± 1.36	18.69 ± 3.74	0.651 ± 0.026	< 3.30 (LOQ)
	Std. add.		20.83 ± 4.15		105.63 ± 18.21		1.285 ± 0.325		1.691 ± 0.343		2.796 ± 0.448		17.56 ± 4.25		< 3.30 (LOQ)
GBW 10011 (Wheat)	Ext. calib.	2.7 ± 0.2	2.5 ± 0.4	11.6 ± 0.7	12.1 ± 2.3	18 ± 4	19 ± 5	0.065 ± 0.024	< 0.23 (LOQ)	1.6	1.7 ± 0.2	0.053 ± 0.007	< 1.20 (LOD)	0.031 ± 0.005	< 3.30 (LOQ)
	Std. add.		2.7 ± 0.6		12.2 ± 2.6		17 ± 4		< 0.23 (LOQ)		1.5 ± 0.4		< 1.20 (LOD)		< 3.30 (LOQ)
SRM 3280 (Multivitamin tablets)	Ext. calib.	1400 ± 170	1309 ± 215	10150 ± 810	10170 ± 1179	0.08015 ± 0.00086	0.09067 ± 0.02295	0.2727 ± 0.0024	0.2963 ± 0.0718	-	-	17.42 ± 0.45	17.67 ± 3.77	0.132 ± 0.044	< 1.00 (LOD)
	Std. add.		1374 ± 249		10140 ± 1300		0.08519 ± 0.01952		0.2894 ± 0.0679		-		17.58 ± 3.64		< 1.00 (LOD)
Recovery degree (%)	Ext. calib.		99 ± 15		100 ± 14		103 ± 22		105 ± 18		108 ± 17		106 ± 18		94 ± 17
	Std. add.		102 ± 20		102 ± 16		103 ± 20		100 ± 20		103 ± 22		104 ± 21		105 ± 21
Precision (%)	Ext. calib.		6.1–8.2		4.6–9.5		4.9–13.2		6.8–12.1		5.9–12.5		10.0–10.7		7.8–9.2
	Std. add.		6.1–12.0		5.8–10.7		4.6–12.6		8.5–11.9		8.0–13.3		10.3–13.3		9.5–11.6
Scor $\|z\|$[c]	Ext. calib.		0.1–1.7		0.1–1.8		0.3–1.3		0.4–1.4		0.1–1.8		0.1–1.0		0.4–1.8

[a] U_{CRM} – extended uncertainty from the certificate (k=2, 95% confidence level); [b] U_{lab} – extended uncertainty in the laboratory (k=2, 95% confidence level, n=3 repeated measurements); [c] $|z|$ score calculated according to the EURACHEM guide (Eurachem Guide: Selection, Use and Interpretation of Proficiency Testing (PT) Schemes, ed. B. Brookman and I. Mann, 3rd edn., 2021, EPT_2021_P1_EN.pdf, accessed 17 July 2025).

Table 2. Values determined in certified reference materials of vegetables and meat, obtained by the (HP-MAWD)-ICP-OES method for Cu, Zn, Cd, and Pb, and by chemical vapor generation for Hg, Se, and As. (AC. Mot, A.-I. Dudu, T. Frentiu, D. Petreus, E.-A. Levei, Z. Stupar, M. Frentiu, E. Covaci. *J. Anal. Atom. Spectrom.*, 2025, Advance article, DOI:10.1039/D5JA00297D)

CRM	Cu		Zn		Cd		Pb	
	Certified value ± U_{CRM}[a] (mg kg^{-1})	Found value ± U_{lab}[b] (mg kg^{-1})	Certified value ± U_{CRM}[a] (mg kg^{-1})	Found value ± U_{lab}[b] (mg kg^{-1})	Certified value ± U_{CRM}[a] (mg kg^{-1})	Found value ± U_{lab}[b] (mg kg^{-1})	Certified value ± U_{CRM}[a] (mg kg^{-1})	Found value ± U_{lab}[b] (mg kg^{-1})
Tort-3 (Lobster hepatopancreas)	497 ± 22	460 ± 61	136 ± 6	128 ± 23	42.3 ± 1.8	42.6 ± 4.9	0.225 ± 0.018	< 0.85 (LOD)
CE278k (Mussel tissue)	5.98 ± 0.27	5.77 ± 1.36	71 ± 4	75 ± 11	0.336 ± 0.025	0.306 ± 0.084	2.18 ± 0.18	< 2.81 (LOQ)
CS-M-3 (Dried mushroom powder)	18.73 ± 0.70	20.83 ± 4.15	113.30 ± 3.28	110.30 ± 21.5	1.229 ± 0.110	1.232 ± 0.306	1.863 ± 0.108	< 2.81 (LOQ)
GBW 10011 (Wheat)	2.7 ± 0.2	2.5 ± 0.4	11.6 ± 0.7	12.1 ± 1.8	18 ± 4	19 ± 5	0.065 ± 0.024	< 0.85 (LOD)
SRM 3280 Multivitamin Tablets	1400 ± 170	1470 ± 260	10150 ± 810	9870 ± 1460	0.08015 ± 0.00086	< 0.20 (LOQ)	0.2727 ± 0.0024	< 0.85 (LOD)
Recovery degree (%)		100 ± 18		100 ± 16		99 ± 23		
Precision (%)		6.6–11.8		7.3–9.7		5.8–13.7		
|*z*| score[c]		0.3–1.8		0.3–1.0		0.1–0.8		

CRM	Hg		Se		As	
	Certified value ± U_{CRM}[a] (mg kg^{-1})	Found value ± U_{lab}[b] (mg kg^{-1})	Certified value ± U_{CRM}[a] (mg kg^{-1})	Found value ± U_{lab}[b] (mg kg^{-1})	Certified value ± U_{CRM}[a] (mg kg^{-1})	Found value ± U_{lab}[b] (mg kg^{-1})
Tort-3 (Lobster hepatopancreas)	0.292 ± 0.022	0.296 ± 0.043	10.9 ± 1.0	10.5 ± 1.6	59.5 ± 3.8	53.7 ± 7.8
CE278k (Mussel tissue)	0.071 ± 0.007	< 0.13 (LOQ)	1.62 ± 0.12	1.80 ± 0.47	6.7 ± 0.4	6.5 ± 1.2
CS-M-3 (Dried mushroom powder)	2.849 ± 0.104	2.662 ± 0.474	17.43 ± 1.36	16.91 ± 2.35	0.651 ± 0.026	0.662 ± 0.095
GBW 10011 (Wheat)	1.6	1.7 ± 0.3	0.053 ± 0.007	< 0.16 (LOQ)	0.031 ± 0.005	< 0.06 (LOD)
SRM 3280 Multivitamin Tablets	-		17.42 ± 0.45	17.73 ± 1.64	0.132 ± 0.044	< 0.20 (LOQ)
Recovery degree (%)		100 ± 17		102 ± 17		96 ± 16
Precision (%)		7.3–8.9		4.6–13.1		7.2–9.2
|*z*| score[c]		0.2–0.8		0.4–0.8		0.3–1.8

[a] U_{CRM} – extended uncertainty from the certificate (k=2, 95% confidence level); [b] U_{lab} – extended uncertainty in the laboratory (k=2, 95% confidence level, n=3 repeated measurements); [c] |*z*| score calculated according to the EURACHEM guide (Eurachem Guide: Selection, Use and Interpretation of Proficiency Testing (PT) Schemes, ed. B. Brookman and I. Mann, 3rd edn., 2021, EPT_2021_P1_EN.pdf, accessed 17 July 2025

The results obtained by the (μ-SPE)-SSETV-μCCP-OES method after *on-site* preconcentration are presented in Table 3, compared with the concentrations initially determined in the water samples by graphite furnace atomic absorption spectrometry (GFAAS). The concentrations determined by SSETV-μCCP-OES in the water samples, calculated based on the concentrations measured in the eluate, ranged from 0.09 μg L^{-1} (Cd) to 14.3 μg L^{-1} (Zn). There is good agreement between the results obtained in the water samples by the (μ-SPE)-SSETV-μCCP-OES method and those obtained by GFAAS, demonstrating the viability and validity of the *on-site* μ-SPE sampling and processing method followed by microplasma optical emission analysis. In Stage II of the project, full validation of this method will be carried out for surface waters, as well as validation for soil and sediment samples, in comparison with ICP-OES and GFAAS.

Table 3. Metal concentrations obtained by (μ-SPE)–SSETV-μCCP-OES from water samples collected and preconcentrated *on-site* using dithizone-functionalized C18 μ-SPE cartridges and eluted in 2 mL of 0.2 mol L^{-1} thiourea in 1 mol L^{-1} HNO_3.

Surface water sample	Cu		Cd	
	Concentration in water determined by GFAAS ± U_{lab}[a] (μg L^{-1})	Concentration in water calculated from those obtained in eluate ± U_{lab}[a] (μg L^{-1})	Concentration in water determined by GFAAS ± U_{lab}[a] (μg L^{-1})	Concentration in water calculated from those obtained in eluate ± U_{lab}[a] (μg L^{-1})
P1	2.21 ± 0.33	2.10 ± 0.34	< LOD[b]	0.02 ± 0.005
P2	3.08 ± 0.40	3.00 ± 0.57	0.10 ± 0.013	0.09 ± 0.02
	Zn		Pb	
	Concentration in water determined by GFAAS ± U_{lab}[a] (μg L^{-1})	Concentration in water calculated from those obtained in eluate ± U_{lab}[a] (μg L^{-1})	Concentration in water determined by GFAAS ± U_{lab}[a] (μg L^{-1})	Concentration in water calculated from those obtained in eluate ± U_{lab}[a] (μg L^{-1})
P1	10.1 ± 1.4	10.6 ± 1.9	0.27 ± 0.05	0.27 ± 0.04
P2	13.0 ± 2.1	14.3 ± 2.9	0.15 ± 0.03	0.14 ± 0.03

[a]U_{lab} – extended uncertainty in the laboratory (k=2, 95% confidence level, n=3 repeated measurements); [b]LOD in GFAAS is 0.03 μg L^{-1}.

Results: Validated multielement (OFC)-SSETV-μCCP-OES method for the determination of Cu, Zn, Cd, Pb, Hg, Se, and As in food samples without μ-SPE preconcentration, in comparison with (HP-MAWD)-ICP-OES, and partial validation of the (μ-SPE)-SSETV-μCCP-OES method against GFAAS in surface water samples.