Validation of the single-element and multielement SSETV-μCCP-OES methods for food and environmental samples with or without *ex-situ/on-site* μ-SPE (finalization) (A2)

(Activity 2.1, CO-UBB, P-FI)

The SSETV-μCCP-OES method was validated for the determination of Cd(II), Pb(II), Cu(II) and Zn(II) ions with *on-site* preconcentration from river water samples or water CRM samples processed in the field by micro-solid phase extraction (μ-SPE) on a C18 microcartridge functionalized with 1 mg of dithizone at pH 8.6, the description of which was the subject of the first stage of the project. The *ex-situ* miniaturized SSETV-μCCP-OES configuration used for the simultaneous determination was powered from a photovoltaic panel-charged battery, since it is not a bulky laboratory instrument with a high energy consumption. The miniaturized SSETV-μCCP-OES experimental configuration consists of a low-power (15 W), low-Ar consumption (150 mL min^{-1}) capacitively coupled plasma microtorch (Babeș-Bolyai University, Cluj-Napoca, Romania), a miniaturized 13.56 MHz radiofrequency generator (Technical University of Cluj-Napoca, Romania), a Maya2000 Pro microspectrometer with a spectral range of 165–309 nm and a spectral bandwidth of 0.35 nm (Ocean Optics, Dunedin, USA), purged with high-purity N_2 6.0. The miniaturized electrothermal vaporizer (SSETV) used for the introduction of the microsample of 10 μL volume consists of a Rh microfilament with 99.9% purity and a diameter of 250 μm (Goodfellow, Cambridge, United Kingdom) heated using a Tenma 72-13360 programmable power supply (TENMA Inc., China). A two-way SMCEVT307–5 DZ–01 F–Q valve, powered by an HY3003 Mastech supply (Premier Farnell, Leeds, United Kingdom), was used to control the Ar flow pathway for the operation of the microplasma (Covaci *et al.*, *Talanta*, 2026, https://doi.org/10.1016/j.talanta.2026.130082).

For the development and validation of the μ-SPE-SSETV-μCCP-OES method, the following were used: dithizone for analysis ≥98.0% from Sigma Aldrich (Massachusetts, USA), thiourea GR for analysis, glacial acetic acid 100% Suprapur, ammonia solution 25% Suprapur, HCl 36% Suprapur, HNO_3 65% Suprapur, ethanol 99.9% for chromatography, single-element standard solutions of 1000 mg L^{-1} Cd, Cu, Pb, Zn, Co, Ni and Hg, acetone for HPLC ≥99.9%, anhydrous dichloromethane ≥99.8% and KCl 99.999% trace metals basis from Merck (Darmstadt, Germany), and humic acid ≥95% from Thermo Fisher Scientific (Waltham, Massachusetts, USA). HyperSep C18 SPE cartridges (40–60 μm) with a column capacity of 1 mL and a bed weight of 100 mg from Thermo Scientific (Massachusetts, USA) were used in laboratory studies and for the *on-site* implementation of a battery-operated μ-SPE system with a dithizone-functionalized C18 cartridge for the preconcentration of metals from river water. A solution of 0.5 g L^{-1} dithizone in 1 mol L^{-1} ammonium acetate buffer (pH 8.6) was used for the functionalization of the C18 cartridges. The pH of the water CRM samples was adjusted to 6.5 with a 0.05 mol L^{-1} ammonium acetate solution, on the basis of the optimization studies of the preconcentration on the dithizone-functionalized C18 cartridge from the first stage, in which an optimal pH range between 4 and 7 was shown. The following water CRM samples were used for validation: Environmental Matrix Reference Materials of water TM – 40.1, TMDA – 70.3, TM – 9.3 and TMDA – 64.4 from Environment and Climate Change (Quebec, Canada), BCR – 505 Estuarine water, ERM-CA713 Wastewater and ERM-CA615 Groundwater from the Institute for Reference Materials and Measurements – IRMM (Geel, Belgium), Trace Metals 1-WP QC1132-20 ML from Sigma Aldrich (Laramie, USA) and the ICP Multi element standard solution X from Merck (Darmstadt, Germany). A solution with pH 6.5 was used as field blank in the analysis of the water samples. The calibration blank was the 2% (v/v) HNO_3 solution. Ultrapure water was produced in the laboratory using a Milli-Q system (Millipore, Bedford, USA).

The C18 cartridge was functionalized by the retention of 1 mg of dithizone by passing a volume of 2 mL of 0.5 g L^{-1} solution over the support at a flow rate of 0.5 mL min^{-1}. The functionalized microcartridges were kept in a refrigerator at 4 °C in the dark until use, when they were mounted in the portable μ-SPE preconcentration assembly. The CRM sample of 10–400 mL volume was passed over the dithizone-functionalized C18 microcartridge with a peristaltic pump at a flow rate of 10 mL min^{-1}, in the preconcentration step, when the divalent

metal ions are retained by complexation by the dithizone immobilized on the C18 support. In the next step, the elution step, the Cd(II), Pb(II), Cu(II) and Zn(II) metal ions were eluted in 2 mL of a 0.2 mol L^{-1} thiourea solution in 1 mol L^{-1} HNO_3 medium at a flow rate of 0.5 mL min^{-1}, a volume for which the complete elution of all ions was found. The metal concentration was determined from the eluate by SSETV-μCCP-OES, after calibration with multielement solutions. On the basis of the concentration in the eluent, the concentration in the CRM sample was calculated, which was compared with that in the certificate. The recovery and the expanded uncertainty were evaluated for a coverage factor k = 2 and a 95% confidence level for n = 3 parallel processing and measurements. The results are presented in Table 1 (Covaci *et al.*, *Talanta* 2026, https://doi.org/10.1016/j.talanta.2026.130082).

The recoveries obtained by the (μ-SPE)-SSETV-μCCP-OES method ranged between 91 and 111%, with an expanded uncertainty of 22–33% (k = 2), comparable to those obtained by the (μ-SPE)-GFAAS method (recovery of 90–110% and expanded uncertainty of 14–31%). The data presented in Table 1 show a good agreement between the found and certified values, since the differences between the determined concentrations and the certified values (Δm) are smaller than $(U^2_{lab} + U^2_{CRM})^{1/2}$ (95% confidence level, n = 3 complete processing and measurements of the CRM samples), where U_{lab} is the expanded laboratory uncertainty and U_{CRM} is the expanded uncertainty of the certified values. The (μ-SPE)-SSETV-μCCP-OES method provides reliable results for field applications, although the expanded uncertainty of the precision is broad. The recoveries and the expanded uncertainty of the results obtained for the analysis of the CRM samples meet the requirements of the AOAC Guidelines for Standard Method Performance regarding recoveries in the 60–120% range and precision between 15 and 30% for analytes at the μg L^{-1} level (AOAC Official Methods of Analysis, Guidelines for Standard Method Performance Requirements, Appendix F (2016) 1–18. https://www.aoac.org/wp-content/uploads/2019/08/app_f.pdf). The z' scores, calculated on the basis of the differences between the measured and certified concentrations, the standard deviation for proficiency assessment and the standard uncertainty of the certified values, are in the range 0.12–1.84 < 2, which indicates a satisfactory performance of the (μ-SPE)-SSETV-μCCP-OES method and the absence of a significant analytical error, according to the Eurachem Guide for the selection, use and interpretation of proficiency testing schemes (Selection, Use and Interpretation of Proficiency Testing (PT) Schemes, ed. B. Brookman and I. Mann, 3rd edn., 2021, EPT_2021_P1_EN.pdf). The expanded uncertainty of the recoveries was evaluated on the basis of the combined uncertainty, taking into account the individual uncertainties of all steps of the analytical process, namely the *on-site* sample processing (preconcentration and elution), the analysis of the aliquots by SSETV-μCCP-OES, the calibration standards and sample preparation, and the calibration curve fitting. The individual uncertainties associated with the analytical steps of the (μ-SPE)-SSETV-μCCP-OES method showed that the largest weight in the combined laboratory uncertainty (u_{lab}) is due to the *on-site* sample processing (10–12%), compared to the analysis of the aliquots (6–8%, n = 3 parallel sample measurements) by SSETV-μCCP-OES, similar to the modern comparison method ICP-OES (≤10%). The uncertainty of the stock solution concentrations, the calibration standards, the sample preparation and the calibration curve fitting was in the range 2–3%.

Degree of achievement of the objective. The objective concerning the *Validation of the multielement SSETV-μCCP-OES methods for food and environmental samples with and without μ-SPE preconcentration* was finalized and achieved, in accordance with the proposed project implementation plan.

Results:

- Report on the validation of the multielement (μ-SPE)-SSETV-μCCP-OES method for the determination of Cd, Pb, Cu and Zn in river waters
- One ISI article published in *Talanta* (Covaci *et al.* 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/

Table 1. Results of the analysis of the water CRM samples by the (μ-SPE)–SSETV–μCCP–OES method in comparison with (μ-SPE)-GFAAS for preconcentration factors of 5–200. (Covaci *et al. Talanta*, 2026, https://doi.org/10.1016/j.talanta.2026.130082)

Analyte	CRM	Certified concentration Mean ± U_{CRM} (μg L^{-1})[a]	Found concentration Mean ±U_{lab} (μg L^{-1})[b]		Recovery Mean ± U_{lab} (%)[b]	
			(μ-SPE)-SSETV-μCCP-OES	(μ-SPE)-GFAAS	(μ-SPE)-SSETV-μCCP-OES	(μ-SPE)-GFAAS
Cu	TM – 40.1	45.9 ± 3.6	45.1 ± 10.9	44.7 ± 11.0	98 ± 24	97 ± 25
	TMDA - 70.3	389 ± 26	374 ± 90	369 ± 83	96 ± 24	95 ± 22
	TM – 9.3	32.6 ± 2.2	33.5 ± 9.1	32.0 ± 8.2	103 ± 27	98 ± 26
	TMDA – 64.4	251 ± 15	263 ± 65	260 ± 64	105 ± 25	104 ± 25
	ERM-CA713	101 ± 7	98 ± 28	104 ± 25	97 ± 29	103 ± 24
	Trace Metals 1-WP	843 ± 7	816 ± 192	784 ± 198	97 ± 24	93 ± 25
	ICP X	22 ± 10	23 ± 5	24.0 ± 5.7	104 ± 22	109 ± 24
	BCR – 505	0.85 ± 0.04	0.81 ± 0.21	0.86 ± 0.21	95 ± 26	101 ± 24
Cd	TM – 40.1	42.8 ± 3.3	40.0 ± 9.77	41.7 ± 10.0	93 ± 24	97 ± 24
	TMDA - 70.3	138 ± 8	132 ± 31	142 ± 33	96 ± 23	103 ± 23
	TM – 9.3	5.00 ± 0.36	5.30 ± 1.42	4.91 ± 1.21	106 ± 27	98 ± 25
	TMDA – 64.4	256 ± 12	262 ± 60	264 ± 62	102 ± 23	103 ± 23
	ERM-CA713	5.09 ± 0.20	4.90 ± 1.26	5.24 ± 1.35	96 ± 26	103 ± 26
	Trace Metals 1-WP	242 ± 3	226 ± 53	255 ± 62	93 ± 23	105 ± 24
	ICP X	20 ± 10	19 ± 5	22 ± 5	95 ± 26	110 ± 24
	BCR – 505	0.038 ± 0.002	0.039 ± 0.011	0.039 ± 0.010	103 ± 28	103 ± 26
	ERM-CA615	0.106 ± 0.011	0.116 ± 0.037	0.109 ± 0.027	111 ± 32	106 ± 26
Pb	TM – 40.1	35.6 ± 2.7	33.7 ± 9.2	33.3 ± 9.4	95 ± 27	94 ± 28
	TMDA - 70.3	440 ± 35	430 ± 114	412 ± 107	98 ± 27	94 ± 26
	TM – 9.3	8.40 ± 0.73	8.10 ± 2.44	8.21 ± 2.13	96 ± 30	98 ± 26
	TMDA – 64.4	277 ± 20	289 ± 75	266 ± 71	104 ± 26	96 ± 27
	ERM-CA713	49.7 ± 1.7	48.1 ± 13.4	48.6 ± 13.3	97 ± 28	98 ± 27
	Trace Metals 1-WP	224 ± 2	206 ± 53	235 ± 62	92 ± 26	105 ± 26
	ICP X	24 ± 10	22 ± 6	22 ± 6	92 ± 27	92 ± 27
	BCR – 505	0.020 ± 0.011	0.022 ± 0.007	0.021 ± 0.006	110 ± 32	105 ± 28
	ERM-CA615	7.1 ± 0.6	7.3 ± 2.0	6.9 ± 1.8	103 ± 27	97 ± 26
Zn	TM – 40.1	100 ± 10	108 ± 29	101 ± 25	108 ± 27	101 ± 25
	TMDA - 70.3	502 ± 40	521 ± 131	534 ± 131	104 ± 25	106 ± 25
	TM – 9.3	50.6 ± 5.0	53.7 ± 13.3	51.8 ± 12.6	106 ± 25	102 ± 24
	TMDA – 64.4	329 ± 25	318 ± 83	337 ± 83	97 ± 26	102 ± 25
	ERM-CA713	78[c]	74 ± 22	70 ± 20	95 ± 30	90 ± 31
	Trace Metals 1-WP	956 ± 8	890 ± 233	886 ± 222	93 ± 26	93 ± 25
	ICP X	55 ± 10	50 ± 13	55 ± 14	91 ± 26	100 ± 25
	BCR – 505	11.2 ± 0.7	10.7 ± 2.8	10.5 ± 2.9	96 ± 26	94 ± 28

[a] U_{CRM} – is the expanded uncertainty from the certificate (k = 2, 95%); [b] U_{lab} – is the expanded uncertainty in the laboratory (k = 2, 95% , n = 3 measurements); [c] Informative value