



Cite this: *J. Anal. At. Spectrom.*, 2024, 39, 141

Simultaneous determination of Cd, Pb, Cu and Zn as total and labile fractions in soil using a small-sized electrothermal vaporization capacitively coupled plasma microtorch optical emission spectrometer after diffusive gradients in thin-film passive accumulation†

Simion Bogdan Angyus,^{abc} Marin Senila,^a Eniko Covaci,^{id bc} Michaela Ponta,^{id bc} Maria Frentiu^a and Tiberiu Frentiu^{id *bc}

The study presents for the first time the figures of merit of a completely miniaturized instrumentation based on a capacitively coupled plasma microtorch as the core element interfaced with a small-sized electrothermal vaporization device and a low-resolution microspectrometer for the simultaneous determination of Cd, Pb, Cu and Zn by optical emission spectrometry in soil as total and labile fractions after diffusive gradients in thin-film (DGT) accumulation. The coupling of the low-power and low-argon consumption plasma (15 W; 150 mL min⁻¹) with the DGT passive accumulation technique, although requiring a too-long time for sample preparation, allowed a considerable improvement of the detection limits and avoidance of the non-spectral matrix effects, otherwise a recognized process in low power microplasmas, when a complex matrix is analysed, like environmental samples. The detection limits for the total content in soil were (mg kg⁻¹), 0.10(Cd), 0.40(Pb), 0.15(Cu), and 0.03(Zn), one order of magnitude better than in the procedure without DGT accumulation and 10–3300-times lower than the guide values in soil. In the DGT-based labile fraction exhibiting the highest bioavailability the detection limits were (μg kg⁻¹) 0.01(Cd, Cu, and Zn) and 0.03(Pb), which allowed the determination of Cd, Pb, Cu and Zn in the concentration range (μg kg⁻¹) of 0.3–2.0, 0.8–18.4, 2.4–56.3 and 9.4–60.6, respectively. Validation through the analysis of certified reference materials (CRMs) showed a recovery of 85–123% with a relative expanded uncertainty of 19–35% (*k* = 2) for the total content of analytes. The analysis of the certified reference materials highlighted that the DGT accumulation was not affected by the multielemental matrix, since the experimental diffusion coefficients of the analytes were similar in the four analyzed CRMs and to those provided by the manufacturer, respectively. Precision for the measurements of the total content and DGT-labile fraction in real samples evaluated from the combined uncertainty was 10–19% and 10–15%, respectively. The Bland–Altman plot applied to the results of real samples indicated the lack of statistical differences *versus* line-source graphite furnace atomic absorption spectrometry for both the total content and DGT-based labile fraction.

Received 31st July 2023
Accepted 3rd November 2023

DOI: 10.1039/d3ja00258f

rsc.li/jaas

Introduction

Because of the exposure risk of the population and environment to toxic elements (Cd, Pb, Hg, As, *etc.*) and potentially toxic, such

as Cu, Zn and Cr, the development of sample preparation procedures and advanced analytical techniques based on atomic and mass spectrometry for the determination and monitoring of these elements in the environment, food, beverages and biological materials continues to be a challenge for academic and routine analysis laboratories.^{1,2} High-sensitivity multielement analytical techniques, such as high-resolution continuum source atomic absorption spectrometry (HR-CS-AAS), inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES), laser-induced breakdown spectrometry (LIBS), total-reflection X-ray fluorescence spectrometry (TXRF) and energy dispersive X-ray fluorescence spectrometry (EDXRF) are still the

^aNational Institute for Research and Development of Optoelectronics INOE 2000 INCĐ Bucharest, Research Institute for Analytical Instrumentation, Donath 67, 400293 Cluj-Napoca, Romania

^bBabes-Bolyai University, Faculty of Chemistry and Chemical Engineering, Arany Janos 11, 400028 Cluj-Napoca, Romania. E-mail: tiberiu.frentiu@ubbcluj.ro

^cBabes-Bolyai University, Research Center for Advanced Analysis, Instrumentation and Chemometrics, Arany Janos 11, 400028 Cluj-Napoca, Romania

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d3ja00258f>



In two inter-laboratory studies, the DGT procedure using the standard DGT Chelex-100 devices (DGT Research Ltd., Lancaster, UK) coupled exclusively with simultaneous multielement analysis techniques such as ICP-MS and ICP-OES was validated as *in situ* sampling for surface water monitoring.^{45,46} Until now, there have been no studies on the validation of the passive DGT sampling for the determination of the total and labile fraction in soil using miniaturized instrumentation with microplasma sources equipped with low-resolution microspectrometers. The first study published by us highlights that the coupling between the DGT passive sampling with SSETV- μ CCP-OES (DGT-SSETV- μ CCP-OES) instrumentation is suitable for surface water monitoring related to the determination of elements with excitation energy below 7 eV.⁴⁷ Consequently, a highly sensitive method providing improved LODs was developed meeting the principles of GAC (AGREEprep) and WAC (Red/Green/Blue-RGB-12 concept) and providing high both green and white scores as a result of cost-effective SSETV- μ CCP-OES instrumentation and *in situ* DGT passive sampling.⁴⁷ Increasing the technological

In line with the state of the art, the present study is focused for the first time on the development and validation of an analytical method free of non-spectral interference for the determination of the total metal content and labile fraction in soil, after DGT passive accumulation coupled with SSETV- μ CCP-OES equipped with a low-resolution microspectrometer. The study was carried out for the simultaneous determination of Cd, Pb, Cu and Zn, four elements of interest for the environmental assessment. The working hypothesis in avoiding the non-spectral effects in the determination of these elements is sustained by the high selectivity of the Chelex-100 commercial resin towards transition elements, above that for alkaline and alkaline-earth elements, which would allow separation of analytes from the multielemental matrix of soil.⁴⁸ The simultaneous determination by SSETV- μ CCP-OES coupled with DGT is ensured by the fact that a certain binding resin (*e.g.*, Chelex-100) can be used for the sampling/accumulation of several transition metals. The DGT passive accumulation was conducted in *ex situ* batch experiments. The characteristics of the emission spectrum recorded by SSETV- μ CCP-OES in the eluate after the accumulation by DGT samplers and a study about the analytical performance are presented. The DGT-SSETV- μ CCP-OES method was validated in terms of LODs in comparison with those without DGT accumulation, accuracy for the total content in certified reference materials (CRMs) of soil and precision from measurements of total content and DGT-based labile fractions in several real soil samples. The validation of the DGT-SSETV- μ CCP-OES method was also conducted against the line-source graphite furnace atomic absorption spectrometry (GFAAS). The results were compared using the statistical Tukey's and Dunnett's tests and Bland–Altman plot ($p > 0.05$).^{49–51}

SSETV- μ CCP-OES instrumentation and DGT passive accumulation

programmable DC Power Supply Tenma, model 72-13360 (Premier Farnel, Leeds, UK) with adjustable heating ramp up to 60 V CC, output current up to 15 A, 1 mV/1 mA resolution and an USB interface, was used to heat the Rh filament. A Maya2000 Pro microspectrometer equipped with a charge-coupled detector (CCD), 165–309 nm spectral range, 0.35 nm FWHM, Ar purged CCD chamber (Ocean Optics, Dunedin USA) was used for recording the episodic emission spectra. A two-way valve SMCEVT307-5 DZ-01 F-Q supplied by the DC power source DC HY3003 (Mastech, Premier Farnell, Leeds, UK) was used to direct the Ar flow into the vaporization chamber or bypass it. The basic assembly is presented in ref. 47 The capacitively coupled plasma operated at 15 W appears as a diffuse bluish discharge with a length of 8–10 mm and a width of 2–3 mm developed at the tip of the Mo microelectrode.³¹ In the superficial luminescence zone, over the 0–1 mm viewing heights, appears the element excitation that allows the simultaneous multielemental emission spectra recording at 0.8 mm observation height through a lens, without fiber optics.⁵³ Although its operating power is low, the plasma energy is efficiently used only for atomization and excitation processes, because the sample is introduced into the plasma as dry vapor. It has been shown that the μ CCP operated at 15 W power has an excitation capability similar to other microplasma sources so that the emission spectrum consists of few resonant and non-resonant spectral lines with excitation energies (E_{ex}) below 7 eV.⁴⁷ Due to the simple spectrum, a low-resolution microspectrometer such as Maya2000 Pro (FWHM 0.35 nm) could be used for episodic spectra recording. As a reference, the argon-hydrogen microplasma, studied by Karanassios' group and developed on a hybrid chip for elemental analysis of microsamples, operated at a lower power (4 W) compared to our plasma, has a length/width of 20/0.75 mm and allows the excitation of elements with E_{ex} below 7 eV.³⁰

The optimum working conditions for the determination of total and DGT-based labile fraction of Cd, Pb, Cu and Zn in soil using SSETV- μ CCP-OES equipment are summarized in the ESI (ESI, Section 1 and Table S1).[†]

Commercial DGT devices (DGT Research Ltd., Lancaster, UK) equipped with agarose cross-linked polyacrylamide (APA) diffusive gel, membrane filters (polyethersulphone) and Chelex-100 binding resin of iminodiacetate with high selectivity for transition metals were used for the accumulation of the target ions.⁴⁸ All assembly/disassembly operations of the DGT devices, handling and sample processing were performed in a clean room.

For the determination of Cd, Pb, Cu and Zn in eluates by atomic absorption spectrometry, the PerkinElmer PinAAcle 900T GFAAS spectrometer (Norwalk, USA) was used under the operating conditions previously presented.⁵⁴ The spectrometer is equipped with electrodeless discharge lamps (EDLs) for Cd and Pb, and hollow cathode lamps (HCLs) for Cu and Zn, a transversally heated graphite furnace atomizer and allows the background correction by the longitudinal Zeeman effect. Chemical modifiers were used according to the recommendation of the manufacturer, using 5 μ L of chemical modifier for a sample aliquot of 20 μ L. The PinAAcle 900T spectrometer can

Glassware, the DGT supports, storage boxes, elution tubes and digestion vessels were cleaned by soaking in 10% (v/v) HNO₃ for 12 h and rinsing with ultrapure water, dried and stored in clean plastic bags.⁴⁶

Sample preparation

Amounts of 2.5 kg agricultural soil of luvisol type with clay texture were collected from the topsoil layer (20 cm depth), from three locations, north-western Romania (city of Baia Mare), in the vicinity of former tailing ponds, where the tailings and wastewater resulted from Pb and Cu mining and ores processing, were stored. The samples were air-dried at room temperature, then crushed, homogenized and sieved to <2 mm to remove stones and roots. Next, 1 kg sample was oven-dried at $105 \pm 5^\circ\text{C}$, ground in a ball mill and sieved to <100 μm . Amounts of 0.1 g soil sample were subjected to microwave-assisted digestion with 12 mL *aqua regia* using a 4-step protocol previously presented.³¹ The digest was diluted to 100 mL with ultrapure water and filtered (0.45 μm).

Reagents, solutions and certified reference materials (CRMs)

The flowchart illustrates the DGT-ICP-MS method for soil analysis, starting with **Microwave digestion** of 0.1 g soil + 12 mL aqua regia to produce a 100 mL solution. This is followed by **Dilution and pH adjustment** to pH 4.00 ± 0.01. The solution is then used for **DGT passive accumulation** (24 h, 400 rpm) to measure **TOTAL METAL CONTENT IN SOIL**. Alternatively, **Soil paste** (100 g dry soil + 80 mL water) is equilibrated for 48 h and then undergoes **DGT passive accumulation** (24 h, 3000 rpm) to measure **TOTAL DISSOLVED ELEMENTS IN SOIL SOLUTION**. Both methods involve **Analytes elution** in 1 mL of 1 mol L⁻¹ HNO₃ for 24 h, followed by **Chelex-100 resin binding** and **Rh coiled filament (SSET device)** for **Excitation in μCCP torch**. The resulting **Signal measurement** is performed using a **Maya2000 Pro microspectrometer**, yielding concentrations for **Cd 228.802 nm**, **Pb 261.418 nm**, **Cu 249.215 nm**, and **Zn 213.856 nm**. A 3D surface plot shows the **Intensity (Counts)** versus **Wavelength (nm)** and **Wavelength (nm)**.

The accuracy of the (DGT)-SSETV- μ CCP-OES and (DGT)-GFAAS methods for total concentration of Cd, Pb, Cu and Zn was checked by analyzing four CRMs: SQC001 Metals in soil and CRM048 Trace metals – Sand 1 from Sigma Aldrich Chemie GmbH (Taufkirchen, Germany), Metranal-34 Loam from Analytika Spol (Vysocany, Czech Republic) and CRM025-050 Metals

Determination of the DGT-based labile fraction of elements in soil. The procedure for preparing the soil samples to determine the DGT-based labile fraction of Cd, Pb, Cu and Zn was similar to that used by Babalola and Zhang, but also considering the DGT manufacturer recommendations (<https://www.dgtresearch.com/general-guides/DGT-soil-deployment-guide-A2-20.pdf>), namely wetting the soil to 100% maximum water holding capacity (MWHC).⁵⁵ Amounts of 100 g dried soil in triplicate with grain size <2 mm were mixed by stirring with 80 mL ultrapure water (100% MWHC) in two steps, at the beginning and after 24 h. The smooth paste-looking mixture was left to equilibrate for 48 h at 21 ± 1 °C in vessels covered with a polypropylene film. Then, the DGT devices were immersed in the paste for 24 h at 21 ± 1 °C, after smearing the filter surface with soil paste, and the vessels were covered with polypropylene film to avoid water evaporation. After the deployment period, the DGT devices were retrieved and rinsed by spraying water jets to remove soil particles. The devices were disassembled and the resin binding gel was transferred into tubes for elution in 1 mL of 1 mol L⁻¹ HNO₃ (24 h, 21 ± 1 °C). The eluate was analyzed to determine the retained amount of Cd, Pb, Cu and Zn used further to calculate the concentration of the DGT-based labile fraction in soil solution (c_{DGT}) and dry soil. In parallel the soil solution was separated by centrifugation at 3000 ($\times g$) for 15 min and subjected to analysis to determine pH, multielemental matrix by ICP-OES, anions by ion chromatography, DOC, DIC, As by GFAAS and the content of total dissolved Cd, Pb, Cu and Zn (c_{sol}) by SSETV- μ CCP-OES and GFAAS. This concentration was used as a reference to evaluate the capacity of soil to release metals in the soil solution.⁵⁵

The precision of the DGT-SSETV- μ CCP-OES method for the determination of the total content and DGT-based labile fraction of analytes was evaluated from the percentage relative standard deviation (RSD%) resulting from u_{lab} for DGT accumulation in triplicate for each real sample. For the validation of the method, a threshold of maximum 30% RSD was considered.^{45,46} The precision of the DGT-SSETV- μ CCP-OES method was compared to that of DGT-GFAAS.

The agricultural Luvisols analyzed in this study contained 25–33% sand, 40–43% silt and 27–32% clay (ESI, Section 3 and Table S2†). The concentration of the multielemental matrix in the

This journal is © The Royal Society of Chemistry 2024

Table 1 Diffusion coefficients from uptake kinetics and elution factors determined in the analysis of soil CRMs compared to the values recommended by the manufacturer of the DGT devices used in the study

Parameter	Experimental value (mean $\pm$ U_{lab}) ^{a,b}				Values recommended by the manufacturer (mean $\pm$ U_{lab}) ^{a,b}			
	Cd	Pb	Cu	Zn	Cd	Pb	Cu	Zn
D (cm ² s ⁻¹)10 ⁻⁶	5.00 $\pm$ 0.38	7.60 $\pm$ 0.50	5.50 $\pm$ 0.40	5.82 $\pm$ 0.38	5.46 $\pm$ 0.32	7.19 $\pm$ 0.40	5.58 $\pm$ 0.32	5.44 $\pm$ 0.30
f_e	0.89 $\pm$ 0.06	0.91 $\pm$ 0.08	0.76 $\pm$ 0.10	0.81 $\pm$ 0.08	0.80 $\pm$ 0.06	0.80 $\pm$ 0.06	0.80 $\pm$ 0.06	0.80 $\pm$ 0.06

^a Diffusion coefficient determined for accumulation by Chelex-100 resin at pH 4.0 $\pm$ 0.1 and 21 $\pm$ 1 °C; U_{lab} is the absolute expanded uncertainty ($k = 2$) assessed using the uncertainty of the uptake kinetics slope and influence of the temperature for a variation of ± 1 °C. ^b Elution factor in 1 mL of 1 mol L⁻¹ HNO₃ solution for 24 h; U_{lab} is the expanded uncertainty ($k = 2$) for 3 parallel measurements for each CRM.

The f_{exp} was calculated as the ratio between the analyte mass in the eluate and the mass difference of the analyte in the uptake solution before and after removing the DGT device. The expanded uncertainty of f_{exp} was evaluated from a study on the elution repeatability ($n = 3$) and uncertainty in the mass balance in the analysis of CRMs ($f_{exp} \pm U_{lab}$, $k = 2$). The found values for f_{exp} and D_{exp} were compared with those provided by the manufacturer and reported in the literature (Table 1).

The data in Table 1 show a good agreement between the experimental values (D_{exp} and f_{exp}), and the standard values recommended by the manufacturer of the DGT devices. Therefore, the values found (D_{exp} and f_{exp}) and those recommended by the manufacturer were used to calculate the total content and DGT-based labile fraction of Cd, Cu, Pb and Zn in soil CRMs and all test samples. The results were statistically compared according to the validation section of the DGT-SSETV- μ CCP-OES method.

Limits of detection

In a previous study, the instrumental LODs for the SSETV- μ CCP-OES method without DGT passive accumulation (3σ criterion) were (μ g L⁻¹): 0.12(Cd), 0.20(Cu), 0.80(Pb) and 0.05(Zn).⁴⁷ By comparison, the corresponding values in GFAAS were (μ g L⁻¹): 0.12(Cd), 0.60(Cu), 0.60(Pb) and 0.36(Zn).⁴⁷ Accumulation of analytes by Chelex-100 DGT for 24 h led to one order of magnitude improvement in LODs expressed in μ g L⁻¹, namely

0.01(Cd and Zn), 0.02(Cu), and 0.07(Pb), and allowed quantification of elements in river water by DGT-SSETV- μ CCP-OES at concentrations below the mentioned instrumental LODs.⁴⁷ In comparison, the LODs reported in the literature for ICP-MS, one of the most sensitive methods, coupled with DGT passive accumulation were (μ g L⁻¹): 0.006 and 0.0032(Cd), 0.005 and 0.019(Pb), 0.051 and 0.047(Cu), and 0.58(Zn).^{56,57} Poorer LODs in DGT-SSETV- μ CCP-OES, compared to DGT-ICP-MS should be judged in terms of lower power for plasma generation (15 W) versus (1000 W), and lower sensitivity of the detection system based on a low-resolution microspectrometer equipped with a CCD. However, the SSETV- μ CCP-OES instrumentation is cost-effective and easy-to-run, compared to lab-scale ICP-MS instrumentation.

Table 2 presents the LODs for the total content and DGT-based labile fraction of target analytes by SSETV- μ CCP-OES and GFAAS methods, for 24 h under the optimal working conditions. According to data in Table 2, the LODs of the SSETV- μ CCP-OES method for the determination of total content of analytes after the DGT passive accumulation for 24 h were in the range (mg kg⁻¹) 0.03(Zn)–0.40(Pb), while the LOD range was 0.10(Cd)–0.40(Cu) for GFAAS. One can observe the improvement of the LODs by one order of magnitude as a result of the pre-concentration using the DGT technique, similar to the results obtained in the monitoring of Cd, Cu, Pb and Zn in river water.⁴⁷ The LODs for total content determination were 10 to 3300-times

Table 2 Limits of detection for total content and DGT-based labile fraction of Cd, Pb, Cu and Zn in soil by SSETV- μ CCP-OES and GFAAS after passive accumulation for 24 h at 21 $\pm$ 1 °C

Method	LODs for total content ^a (mg kg ⁻¹)				LODs for the DGT-based labile fraction ^b (μ g kg ⁻¹)			
	Cd	Pb	Cu	Zn	Cd	Pb	Cu	Zn
SSETV- μ CCP-OES without DGT accumulation	1.2	8.0	2.0	0.5	—	—	—	—
SSETV- μ CCP-OES with DGT accumulation	0.10	0.40	0.15	0.03	0.01	0.03	0.01	0.01
GFAAS without DGT accumulation	1.2	6.0	6.0	3.6	—	—	—	—
GFAAS with DGT accumulation	0.10	0.30	0.40	0.25	0.01	0.03	0.03	0.02
Guide values ^c	1	20	20	100	—	—	—	—

^a LOD for 0.1 g sample made up to 100 mL followed by 10-times dilution. ^b LOD for 100 g sample and 80 mL ultrapure water. ^c Guide values in soil according to Romanian legislation (order no. 756/1997 for the approval of the regulation regarding the assessment of environmental pollution, published in Official Monitor of Romania, no. 303 bis from 6 November 1997, in Romanian). <https://legislatie.just.ro/Public/DetaliuDocument/13572> (accessed 14 June 2022).



lower than the guide values in soil showing that Cd, Pb, Cu, and Zn could be quantified below these concentrations. In contrast, SSETV- μ CCP-OES without DGT preconcentration provided quantification for contents above (mg kg^{-1}) 3.6(Cd), 24(Pb), 6(Cu), and 1.5(Zn), which would be useful only for Cu and Zn determination. The LODs of the SSETV- μ CCP-OES method for the DGT-based labile fraction of analytes were ($\mu\text{g L}^{-1}$): 0.008(Cd, Cu and Zn) and 0.024(Pb), corresponding to ($\mu\text{g kg}^{-1}$) in dry soil: 0.01(Cd, Cu and Zn) and 0.03(Pb). Compared to GFAAS, the LODs obtained by SSETV- μ CCP-OES coupled with DGT passive sampling were similar for Cd and Pb, and better for Cu and Zn.

Accuracy of the DGT-SSETV- μ CCP-OES method for the determination of the total content of analytes

The found values by SSETV- μ CCP-OES and external calibration without DGT passive accumulation indicated negative systematic errors compared to the certified values with recovery in the range of 58–83% and relative expanded uncertainty of 12–37% ($k = 2$) (ESI, Section 4 and Table S6†). Dunnett's test revealed a statistical difference ($p > 0.05$) between found and certified results. The negative bias was caused by the presence of

depressive non-spectral effects coming from the multielemental matrix on the emission signal of Cd, Cu, Pb and Zn in SSETV- μ CCP-OES, generating significant systematic errors compared to certified values. Previous results indicated that in the case of soil analysis by SSETV- μ CCP-OES the depressive effects of the multielemental matrix could be compensated by using the standard addition method, which is tedious compared to external calibration.^{31–34}

Table 3 presents the results for the analysis of soil CRMs after DGT passive accumulation in an uptake solution with 4.0 ± 0.1 pH for 24 h at 21 ± 1 °C using experimental and recommended diffusion coefficients and elution factors. All quantifications were based on external calibration.

The weight of the individual sources in the relative combined uncertainty of the mean concentration of analytes in the CRM soil samples found by DGT-SSETV- μ CCP-OES and DGT-GFAAS is presented in the ESI (Section 5, Fig. S3 and S4).†

In the case of analysis performed after DGT accumulation, the differences (Δm) for all four elements were lower than U_{lab} ($k = 2$) of found results, evaluated based on the combined uncertainty of sample preparation and analysis steps in the laboratory and certified uncertainty. In addition, Dunnett's test

Table 3 Results for the total content of Cd, Pb, Cu and Zn in soil CRMs after determination by external calibration by SSETV- μ CCP-OES and GFAAS with DGT passive accumulation for 24 h at pH 4.0 ± 0.1 and 21 ± 1 °C using experimental and recommended values for diffusion coefficients and elution factors

		Experimental diffusion coefficients and elution factors				Recommended diffusion coefficients and elution factors			
		Found concentration mean $\pm U_{\text{lab}}^b$ (mg kg^{-1})		Accuracy recovery $\pm U_{\text{lab}}^c$ (%)		Found concentration mean $\pm U_{\text{lab}}^b$ (mg kg^{-1})		Accuracy recovery $\pm U_{\text{lab}}^c$ (%)	
CRM/ analyte	Certified concentration mean $\pm U_{\text{CRM}}^a$ (mg kg^{-1})	DGT-SSETV- μ CCP-OES	DGT-GFAAS	DGT-SSETV- μ CCP-OES	DGT- GFAAS	DGT-SSETV- μ CCP-OES	DGT-GFAAS	DGT-SSETV- μ CCP-OES	DGT-GFAAS
SQC001 metals in soil									
Cd	118 $\pm$ 2	123 $\pm$ 28	113 $\pm$ 28	105 $\pm$ 23	95 $\pm$ 25	126 $\pm$ 25	115 $\pm$ 25	107 $\pm$ 19	98 $\pm$ 22
Pb	144 $\pm$ 2	147 $\pm$ 49	145 $\pm$ 38	102 $\pm$ 33	101 $\pm$ 26	176 $\pm$ 56	175 $\pm$ 40	123 $\pm$ 32	121 $\pm$ 23
Cu	330 $\pm$ 4	363 $\pm$ 94	359 $\pm$ 102	110 $\pm$ 26	109 $\pm$ 28	341 $\pm$ 69	337 $\pm$ 79	103 $\pm$ 20	102 $\pm$ 23
Zn	874 $\pm$ 11	827 $\pm$ 278	921 $\pm$ 260	95 $\pm$ 34	105 $\pm$ 28	902 $\pm$ 280	1004 $\pm$ 252	103 $\pm$ 31	115 $\pm$ 25
CRM048 trace metals – sand 1									
Cd	92.8 $\pm$ 1.55	93.7 $\pm$ 32.00	102.8 $\pm$ 27.18	101 $\pm$ 34	111 $\pm$ 26	96.0 $\pm$ 30.81	105.2 $\pm$ 25.17	103 $\pm$ 32	113 $\pm$ 24
Pb	320 $\pm$ 6.27	327 $\pm$ 103.38	324 $\pm$ 87.04	102 $\pm$ 32	101 $\pm$ 27	394 $\pm$ 113.62	390 $\pm$ 89.40	123 $\pm$ 29	122 $\pm$ 23
Cu	84.3 $\pm$ 1.45	78.4 $\pm$ 19.33	80.5 $\pm$ 19.61	93 $\pm$ 25	95 $\pm$ 24	73.7 $\pm$ 13.92	75.6 $\pm$ 14.00	87 $\pm$ 19	90 $\pm$ 19
Zn	425 $\pm$ 9.14	428 $\pm$ 148.41	414 $\pm$ 103.64	101 $\pm$ 35	97 $\pm$ 25	466 $\pm$ 147.94	451 $\pm$ 93.54	110 $\pm$ 32	106 $\pm$ 21
Metranal-34 loam									
Cd	1.44 $\pm$ 0.07	1.33 $\pm$ 0.38	1.38 $\pm$ 0.36	93 $\pm$ 28	96 $\pm$ 26	1.37 $\pm$ 0.34	1.41 $\pm$ 0.32	95 $\pm$ 25	98 $\pm$ 22
Pb	83.1 $\pm$ 2.3	75.9 $\pm$ 24.4	71.9 $\pm$ 17.6	91 $\pm$ 32	87 $\pm$ 24	91.3 $\pm$ 27.4	86.5 $\pm$ 17.9	110 $\pm$ 30	104 $\pm$ 21
Cu	167 $\pm$ 1	151 $\pm$ 49	153 $\pm$ 41	91 $\pm$ 33	92 $\pm$ 27	142 $\pm$ 40	144 $\pm$ 31	85 $\pm$ 28	86 $\pm$ 22
Zn	198 $\pm$ 6	168 $\pm$ 56	170 $\pm$ 38	85 $\pm$ 33	86 $\pm$ 22	180 $\pm$ 55	182 $\pm$ 32	91 $\pm$ 31	92 $\pm$ 18
CRM025–050 metals in soil									
Cd	369 $\pm$ 19.0	372 $\pm$ 107.1	375 $\pm$ 94.0	101 $\pm$ 29	101 $\pm$ 25	381 $\pm$ 100.4	383 $\pm$ 85.5	103 $\pm$ 26	104 $\pm$ 22
Pb	1447 $\pm$ 88	1234 $\pm$ 372	1216 $\pm$ 315	85 $\pm$ 30	84 $\pm$ 26	1487 $\pm$ 415	1465 $\pm$ 319	103 $\pm$ 28	101 $\pm$ 22
Cu	7.76 $\pm$ 0.73	7.99 $\pm$ 2.32	8.38 $\pm$ 2.01	103 $\pm$ 29	108 $\pm$ 24	7.53 $\pm$ 1.96	7.92 $\pm$ 1.82	97 $\pm$ 26	102 $\pm$ 23
Zn	51.8 $\pm$ 3.35	50.1 $\pm$ 13.41	46.1 $\pm$ 13.00	97 $\pm$ 27	89 $\pm$ 28	54.6 $\pm$ 12.63	50.3 $\pm$ 12.45	105 $\pm$ 23	97 $\pm$ 25

^a – U_{CRM} is the absolute expanded uncertainty for certified concentration ($k = 2$; 95% confidence level). ^b – U_{lab} is the absolute expanded uncertainty in the laboratory for found concentration ($k = 2$, $n = 3$ parallel measurements and 95% confidence level). ^c – $U_{\text{lab}}\%$ is the relative expanded uncertainty in the laboratory for found concentration ($k = 2$, $n = 3$ parallel measurements and 95% confidence level).



($p > 0.05$) indicated no significant difference between the found results in both methods and reference values, when DGT accumulation was used (p -values 0.052–0.999). Tukey's test ($p > 0.05$) performed using the average results and combined uncertainty values found by DGT-SSETV- μ CCP-OES and DGT-GFAAS, using both experimental and recommended values for diffusion coefficient and elution factor indicated the absence of significant differences (p values 0.202–0.985). The negative bias between the results caused by the differences between the experimental diffusion coefficients and elution factors and those recommended by the manufacturer was only 2%(Cd), 4%(Cu), 7%(Zn) and 17%(Pb), which fit in any case in the analysis errors expressed as combined uncertainty. Therefore, in the case of coupling the analysis method with DGT accumulation, the recovery of the certified concentrations was in the range of 85–123% with a relative expanded uncertainty of 19–35% ($k = 2$) for SSETV- μ CCP-OES and 84–122% with a relative expanded uncertainty of 18–28% ($k = 2$) for GFAAS, respectively. The good agreement between found results and certified values indicated the lack of non-spectral interference from the multi-elemental matrix, including As, in the analysis of CRMs for the total content of analytes by SSETV- μ CCP-OES when DGT passive accumulation was used. Arsenic was determined by GFAAS, with a LOD of 0.001 mg L^{-1} , and not by SSETV- μ CCP-OES or ICP-OES, as its concentration in the uptake solution or soil solution was usually below the LOD of 0.014 mg L^{-1} of these methods.³⁶ The lack of matrix effects can be observed even in the case of Cd, which demonstrates its separation from As in the uptake solution using the DGT devices with Chelex-100 at concentration levels of As in the range of 0.004 – 0.036 mg L^{-1} , presented in the ESI (Section 3 and Table S3).[†] The coupling of the DGT selective, passive accumulation with detection by optical emission in a low-power microplasma, prone to non-spectral effects caused by the multi-elemental matrix, is a suitable approach. Besides, analyte accumulation in the DGT sampling led to substantial improvement of sensitivity and LODs.

As shown in Fig. S3 and S4 (Section 5),[†] the combined uncertainty in the laboratory (u_{lab}) for the found concentration by DGT-SSETV- μ CCP-OES and DGT-GFAAS was higher than the uncertainty provided for certified concentration (u_{CRM}), because the main contribution came from aliquot analysis, followed by the DGT accumulation, including the uncertainty of diffusion coefficient dependent on temperature and pH. However, the uncertainty of recovery in the analysis of CRMs was generally below $\pm 30\%$ recommended in interlaboratory studies conducted for the validation of analysis methods involving the DGT passive sampling or accumulation.^{45,46}

Determination of total and labile fractions of Cd, Pb, Cu, and Zn found in the soil samples using DGT-SSETV- μ CCP-OES

Tables 4 and 5 present the results for the total content and labile fraction of the analytes in soil obtained by DGT-SSETV- μ CCP-OES and DGT-GFAAS calculated using the experimental parameters related to accumulation and elution. Quantification was made using external calibration with multielement synthetic standards. The total contents (Table 4) referred to the DGT passive accumulation for 24 h in 100 mL of 1 : 10 diluted digest ($n = 3$) at 4.0 ± 0.1 pH. The pH values for soil and soil solution were 6.5–7.3 and 6.3–7.4, respectively, also suitable for DGT accumulation.⁴⁷ The DGT-based labile fraction (Table 5) was determined using DGT accumulation from soil paste prepared according to the procedure presented earlier. Comparatively, the total dissolved concentration of analytes found in soil solution after separation by centrifugation without acid digestion is also presented.

The results indicated the lack of multi-elemental matrix effects, including As at concentrations in the range of 0.004 – 0.075 mg L^{-1} , for the determination of the total concentration and DGT-based labile fraction of Cd, Pb, Cu and Zn in soil, attributed to the selective retention of analytes against the dominant metals and separation of Cd from As found by GFAAS in the matrix.

Table 4 Results for total Cd, Pb, Cu and Zn in soil by DGT-SSETV- μ CCP-OES and DGT-GFAAS after passive accumulation

Sample	Total Cd content mean $\pm U_{\text{lab}}^a$ (mg kg ⁻¹)		Total Pb content mean $\pm U_{\text{lab}}^a$ (mg kg ⁻¹)		Total Cu content mean $\pm U_{\text{lab}}^a$ (mg kg ⁻¹)		Total Zn content mean $\pm U_{\text{lab}}^a$ (mg kg ⁻¹)	
	DGT-SSETV- μ CCP-OES	DGT-GFAAS	DGT-SSETV- μ CCP-OES	DGT-GFAAS	DGT-SSETV- μ CCP-OES	DGT-GFAAS	DGT-SSETV- μ CCP-OES	DGT-GFAAS
S1	4.1 $\pm$ 1.2	4.8 $\pm$ 1.2	95.2 $\pm$ 29.4	104 $\pm$ 33	142 $\pm$ 33	131 $\pm$ 33	321 $\pm$ 95	306 $\pm$ 93
S2	4.8 $\pm$ 1.5	6.0 $\pm$ 1.5	71.0 $\pm$ 21.6	69.5 $\pm$ 14.8	59.0 $\pm$ 15.7	63.4 $\pm$ 18.9	135 $\pm$ 34	111 $\pm$ 31
S3	14.5 $\pm$ 3.3	14.1 $\pm$ 3.9	171 $\pm$ 37	160 $\pm$ 37	432 $\pm$ 137	420 $\pm$ 128	359 $\pm$ 90	372 $\pm$ 89
S4	4.4 $\pm$ 0.9	5.6 $\pm$ 1.5	35.6 $\pm$ 9.3	37.0 $\pm$ 8.0	75.2 $\pm$ 28.0	83.6 $\pm$ 23.4	86.4 $\pm$ 32.2	64.5 $\pm$ 20.2
S5	7.3 $\pm$ 1.8	7.2 $\pm$ 2.2	74.2 $\pm$ 20.3	71.3 $\pm$ 15.0	78.2 $\pm$ 22.3	79.4 $\pm$ 19.8	246 $\pm$ 68	255 $\pm$ 52
S6	8.9 $\pm$ 2.3	8.6 $\pm$ 2.3	71.0 $\pm$ 17.0	77.1 $\pm$ 18.2	85.8 $\pm$ 29.1	78.0 $\pm$ 22.9	202 $\pm$ 62	179 $\pm$ 44
S7	11.1 $\pm$ 2.8	11.9 $\pm$ 3.7	91.4 $\pm$ 28.5	92.4 $\pm$ 23.4	49.7 $\pm$ 13.1	50.6 $\pm$ 18.4	114 $\pm$ 32	125 $\pm$ 35
S8	4.9 $\pm$ 1.5	5.6 $\pm$ 1.4	228 $\pm$ 57	215 $\pm$ 69	74.8 $\pm$ 18.7	70.6 $\pm$ 20.0	152 $\pm$ 46	162 $\pm$ 50
S9	13.5 $\pm$ 3.7	13.2 $\pm$ 4.7	146 $\pm$ 31	146 $\pm$ 31	79.3 $\pm$ 25.1	79.8 $\pm$ 22.2	227 $\pm$ 57	207 $\pm$ 64
S10	8.1 $\pm$ 1.9	9.5 $\pm$ 2.3	128 $\pm$ 30	135 $\pm$ 38	135 $\pm$ 40	145 $\pm$ 36	223 $\pm$ 54	204 $\pm$ 55
RSD ^b (%)	12–19	12–18	10–16	12–18	11–16	11–16	12–19	10–16

^a – U_{lab} is the absolute expanded uncertainty in the laboratory for found concentration ($k = 2$, $n = 3$ parallel measurements and 95% confidence level). ^b – RSD is the relative standard deviation evaluated from the combined uncertainty ($n = 3$ parallel measurements and 95% confidence level).



Table 5 Results for the labile fraction of Cd, Pb, Cu and Zn in dry soil by DGT-SSETV- μ CCP-OES and DGT-GFAAS after passive accumulation for 24 h in the paste obtained by mixing soil sample with water in a ratio of 10 : 8 compared to the total dissolved concentration in soil solution separated by centrifugation

Sample	Labile Cd content mean $\pm U_{lab}^a$ ($\mu\text{g kg}^{-1}$)		Dissolved Cd content mean $\pm U_{lab}^a$ ($\mu\text{g kg}^{-1}$)		Labile Pb content mean $\pm U_{lab}^a$ ($\mu\text{g kg}^{-1}$)		Dissolved Pb content mean $\pm U_{lab}^a$ ($\mu\text{g kg}^{-1}$)	
	DGT-SSETV- μ CCP-OES	DGT-GFAAS	SSETV- μ CCP-OES ^b	GFAAS	DGT-SSETV- μ CCP-OES	DGT-GFAAS	SSETV- μ CCP-OES ^b	GFAAS
S1	0.3 $\pm$ 0.1	0.3 $\pm$ 0.1	1.0 $\pm$ 0.1	0.9 $\pm$ 0.1	2.7 $\pm$ 0.6	2.3 $\pm$ 0.6	75.6 $\pm$ 9.8	88.0 $\pm$ 12.2
S2	0.7 $\pm$ 0.2	0.8 $\pm$ 0.1	1.4 $\pm$ 0.2	1.0 $\pm$ 0.2	2.8 $\pm$ 0.8	3.2 $\pm$ 0.7	17.9 $\pm$ 3.9	14.2 $\pm$ 3.8
S3	1.5 $\pm$ 0.4	1.9 $\pm$ 0.4	3.4 $\pm$ 0.5	2.9 $\pm$ 0.6	9.5 $\pm$ 2.4	7.9 $\pm$ 1.7	43.3 $\pm$ 8.1	45.1 $\pm$ 8.5
S4	0.5 $\pm$ 0.1	0.5 $\pm$ 0.1	1.0 $\pm$ 0.2	0.8 $\pm$ 0.1	1.8 $\pm$ 0.5	1.7 $\pm$ 0.4	8.5 $\pm$ 1.6	6.3 $\pm$ 0.9
S5	0.8 $\pm$ 0.2	1.0 $\pm$ 0.2	4.9 $\pm$ 0.7	1.5 $\pm$ 0.2	1.0 $\pm$ 0.2	0.9 $\pm$ 0.2	20.2 $\pm$ 2.6	21.0 $\pm$ 6.1
S6	0.8 $\pm$ 0.2	0.8 $\pm$ 0.2	4.6 $\pm$ 0.8	4.1 $\pm$ 0.5	2.5 $\pm$ 0.6	2.7 $\pm$ 0.9	39.2 $\pm$ 6.6	31.0 $\pm$ 4.1
S7	0.7 $\pm$ 0.1	0.7 $\pm$ 0.1	4.4 $\pm$ 0.8	4.0 $\pm$ 0.7	0.8 $\pm$ 0.2	0.9 $\pm$ 0.2	28.3 $\pm$ 3.8	21.2 $\pm$ 3.0
S8	1.3 $\pm$ 0.4	1.6 $\pm$ 0.3	10.4 $\pm$ 2.1	7.2 $\pm$ 1.0	18.4 $\pm$ 4.4	18.1 $\pm$ 4.0	157 $\pm$ 26	150 $\pm$ 36
S9	2.0 $\pm$ 0.4	1.7 $\pm$ 0.3	6.8 $\pm$ 1.0	5.4 $\pm$ 0.8	15.0 $\pm$ 3.5	15.4 $\pm$ 4.6	114 $\pm$ 16	128 $\pm$ 25
S10	1.6 $\pm$ 0.4	1.6 $\pm$ 0.3	5.2 $\pm$ 0.9	6.4 $\pm$ 1.5	3.5 $\pm$ 0.7	4.1 $\pm$ 1.0	42.7 $\pm$ 6.5	46.9 $\pm$ 6.9
RSD ^c (%)	10–14	8–12	7–10	7–12	10–15	11–16	6–11	7–14

Sample	Labile Cu content mean $\pm U_{lab}^a$ ($\mu\text{g kg}^{-1}$)		Dissolved Cu content mean $\pm U_{lab}^a$ ($\mu\text{g kg}^{-1}$)		Labile Zn content mean $\pm U_{lab}^a$ ($\mu\text{g kg}^{-1}$)		Dissolved Zn content mean $\pm U_{lab}^a$ ($\mu\text{g kg}^{-1}$)	
	DGT-SSETV- μ CCP-OES	DGT-GFAAS	SSETV- μ CCP-OES ^b	GFAAS	DGT-SSETV- μ CCP-OES	DGT-GFAAS	SSETV- μ CCP-OES ^b	GFAAS
S1	2.4 $\pm$ 0.6	1.9 $\pm$ 0.4	70.0 $\pm$ 14	51.4 $\pm$ 10.8	12.0 $\pm$ 2.6	14.9 $\pm$ 3.1	81.7 $\pm$ 10.5	51.4 $\pm$ 15.2
S2	5.4 $\pm$ 1.5	5.0 $\pm$ 1.2	75.3 $\pm$ 16.2	78.2 $\pm$ 16.9	24.3 $\pm$ 5.7	21.3 $\pm$ 4.9	25.2 $\pm$ 5.2	28.2 $\pm$ 9.2
S3	56.3 $\pm$ 13.5	81.7 $\pm$ 18.3	295 $\pm$ 49	345 $\pm$ 63	15.9 $\pm$ 4.5	19.5 $\pm$ 4.5	116 $\pm$ 18	120 $\pm$ 25
S4	7.4 $\pm$ 1.6	8.6 $\pm$ 2.1	76.4 $\pm$ 10.1	78.2 $\pm$ 15.8	21.9 $\pm$ 5.5	21.8 $\pm$ 4.1	27.3 $\pm$ 5.4	28.2 $\pm$ 5.3
S5	8.7 $\pm$ 2.4	7.9 $\pm$ 2.0	100 $\pm$ 22	67.2 $\pm$ 13.0	60.6 $\pm$ 12.2	70.2 $\pm$ 11.9	70.8 $\pm$ 10.1	67.2 $\pm$ 8.6
S6	15.5 $\pm$ 4.3	12.2 $\pm$ 2.7	85.8 $\pm$ 12.6	120 $\pm$ 23	31.1 $\pm$ 7.9	24.3 $\pm$ 5.4	38.2 $\pm$ 4.6	40.3 $\pm$ 4.1
S7	7.5 $\pm$ 2.1	6.4 $\pm$ 1.4	60.7 $\pm$ 10.7	67.6 $\pm$ 13.3	26.7 $\pm$ 6.9	30.4 $\pm$ 5.1	33.6 $\pm$ 4.1	37.6 $\pm$ 4.5
S8	20.1 $\pm$ 4.9	23.6 $\pm$ 6.2	166 $\pm$ 22	175 $\pm$ 25	9.4 $\pm$ 2.5	11.9 $\pm$ 2.8	282 $\pm$ 64	282 $\pm$ 57
S9	13.8 $\pm$ 3.1	12.1 $\pm$ 3.7	105 $\pm$ 23	107 $\pm$ 25	10.0 $\pm$ 2.6	13.2 $\pm$ 2.5	198 $\pm$ 24	197 $\pm$ 54
S10	22.3 $\pm$ 5.2	26.1 $\pm$ 6.8	84.6 $\pm$ 17.7	90.6 $\pm$ 21	19.7 $\pm$ 4.8	15.9 $\pm$ 4.0	92.6 $\pm$ 12.1	90.6 $\pm$ 11.5
RSD ^c (%)	11–14	11–15	7–11	7–12	10–15	11–16	6–11	5–16

^a – U_{lab} is the absolute expanded uncertainty in the laboratory for found concentration ($k = 2$, $n = 3$ parallel measurements and 95% confidence level). ^b – Concentration determined by the standard addition method for matrix effect compensation. ^c – RSD is the relative standard deviation evaluated from the combined uncertainty ($n = 3$ parallel measurements and 95% confidence level).

The total contents (mg kg^{-1}) of 4.1–13.5(Cd), 35.6–228(Pb), 49.7–432(Cu) and 86.4–359(Zn) in soil were determined with precision in the range of 10–19% calculated from combined uncertainty. Precision in the DGT-SSETV- μ CCP-OES measurement was found to be similar to that in DGT-GFAAS. The concentrations of the DGT-based labile fractions ($\mu\text{g kg}^{-1}$) were 0.3–2.0(Cd), 0.8–18.4(Pb), 2.4–56.3(Cu) and 9.4–60.6(Zn) and measurement precision derived from combined uncertainty was in the range of 10–15%, similar to that in DGT-GFAAS.

Fig. S5 and S6† (ESI, Section 6) depict the Bland-Altman plots for the comparison of the results obtained by DGT-SSETV- μ CCP-OES and DGT-GFAAS for the total content and labile fraction in soil. Graphics show no significant difference ($p > 0.05$) for both sets of determination, since the bias between methods is much lower than the determined concentration, its confidence interval includes the zero value and the differences between the pair results fall within the limits of agreement. In short, the DGT-SSETV- μ CCP-OES method provides reliable

results both for total content and labile fraction of Cd, Pb, Cu and Zn in soil samples after DGT passive sampling used for preconcentration of analytes and separation from the matrix.

Unfortunately, several data presented in Table 5, show statistically significant differences between the SSETV- μ CCP-OES and GFAAS methods in the determination of total dissolved metals in soil solution, although quantification in microplasma was performed using the standard addition method. These differences most probably are due to the presence of organic matter in relatively high concentration in the range of 32–170 mg L^{-1} in soil solution, which affects the evaporation process of analytes from the Rh microfilament. Periodically, a carbon-like residue was observed on the filament, which required its periodic cleaning by evaporating a mixture of HNO_3 and H_2O_2 . These secondary phenomena, caused by the presence of organic matter, could have been avoided if the soil solution had been acid digested when organic matter is destroyed.



The time-integrated mean concentration of elements (c_{DGT}) reported to the total dissolved concentration determined in the bulk soil solution (c_{sol}) provides the ratio (R) as an indicator of the ability of the solid phase of soil to resupply elements into soil solution.^{58,59}

$$R = \frac{c_{\text{DGT}}}{c_{\text{sol}}} \quad (2)$$

$R > 0.8$ stands for a fast and sustained supply capacity from the solid phase; $R < 0.1$ means low resupply capacity in soil solution and limited mobilization of elements from the solid phase; $0.1 < R < 0.8$ resupply is intermediary.

The status of these indices for the target analytes in our study is presented in the ESI (Section 7 and Fig. S7).[†] In the case of Cd, the plot indicated an intermediary capacity of soil to resupply the soil solution, with R values in the range of 0.13–0.50. In the case of Pb and Cu, the resupply indices were rather weak, with intermediary values of 0.03–0.22 and 0.03–0.26, respectively. Only for Zn resupply was intermediary or fast and sustained, with R values in the range of 0.03–0.96. The results were in agreement with the low percentage of total dissolved in soil solution, below 0.2% for Cd, Cu and Zn and 0.08% for Pb, compared to the total content in soil.

Conclusions

The study highlighted for the first time the unique capability of cost-effective instrumentation based on optical emission spectrometry with a low-power and low-argon consumption plasma microtorch interfaced with a low-resolution microspectrometer compared to GFAAS analytical instrumentation to determine the total and the labile fraction of some elements of interest in soil solution after DGT passive sampling/accumulation. The proposed method allowed the quantification of priority hazardous elements, such as Cd and Pb. First of all, the selective accumulation of analytes provided by the DGT passive sampling led to overcoming the non-spectral interference in the low-power plasma caused by the dominant elements in soil and allowed the use of external calibration instead of the standard addition. Furthermore, it was possible to determine Cd by DGT-SSETV- μ CCP-OES at the most sensitive line, without spectral interference from As, as the Chelex-100 binding gel ensures the selective retention of Cd *versus* As. Another advantage when using DGT accumulation was the improvement of LODs, enabling the determination of the labile fraction of the elements with the highest toxicity. However, significant differences have been observed between SSETV- μ CCP-OES and GFAAS in the determination of total dissolved metals in soil solution caused by the presence of organic matter that affects the evaporation process of metals from the Rh filament. Although the use of the passive DGT accumulation as a time-integrated technique would be an impediment to developing fast methods, the present study exhibits a new idea by implementing DGT devices in a simultaneous multielement method on a completely miniaturized spectral instrumentation. However, the advantages of the new easy-to-run set-up that does

not require a skilled analyst, make it a viable alternative to the classic laboratory methods broadly used, such as ICP-MS and GFAAS, the latter considered as a reference for validation of the proposed method. Anyway, the versatility of the DGT technique is a challenge for the development of analytical technologies incorporating microtorch/microplasma with high green and white scores, and capable of widening the area of applicability. The study put in evidence the opportunity to convert the miniaturized spectrometric instrumentation used so far in academic laboratories into mature analytical systems, to be used for analytical applications where their figures of merit are suitable for fit-of-purpose.

Conflicts of interest

There are no conflicts of interest to declare

Acknowledgements

This work was supported by a grant from the Romanian Ministry of Research and Innovation, CNCS/CCCDI-UEFISCDI, contract nr. 733PED/2022, project number PN-III-P2-2.1-PED2021-0151, within PNCDI III.

References

- 1 J. R. Bacon, O. T. Butler, W. R. L. Cairns, O. Cavoura, J. M. Cook, C. M. Davidson and R. Mertz-Kraus, *J. Anal. At. Spectrom.*, 2023, **38**, 10–56.
- 2 M. Patriarca, N. Barlow, A. Cross, S. Hill, A. Robson and J. Tyson, *J. Anal. At. Spectrom.*, 2023, **38**, 496–577.
- 3 E. H. Evans, J. Pisonero, C. M. M. Smith and R. N. Taylor, *J. Anal. At. Spectrom.*, 2022, **37**, 942–965.
- 4 S. Cerutti, P. H. Pacheco, R. Gil and L. D. Martinez, *Curr. Opin. Green Sustainable Chem.*, 2019, **19**, 76–86.
- 5 I. Lavilla, V. Romero, I. Costas and C. Bendicho, *TrAC, Trends Anal. Chem.*, 2014, **61**, 1–10.
- 6 R. E. Sturgeon, *J. Anal. At. Spectrom.*, 2017, **32**, 2319–2340.
- 7 M. Slachcinski, *J. Anal. At. Spectrom.*, 2019, **34**, 257–273.
- 8 K. A. Romanovskiy, M. A. Bolshov, A. V. Munz, Z. A. Temerdashev, M. Y. Burylin and K. A. Sirota, *Talanta*, 2018, **187**, 370–378.
- 9 Z. H. Fernandez, L. A. V. Rojas, A. M. Alvarez, J. R. E. Alvarez, J. A. dos Santos Junior, I. P. Gonzalez, M. R. Gonzalez, N. A. Macias, D. I. Sanchez and D. H. Torres, *Food Control*, 2015, **48**, 37–42.
- 10 C. M. M. Santos, M. A. G. Nunes, A. B. Costa, D. Pozebon, F. A. Duarte and V. L. Dressler, *Anal. Methods*, 2017, **9**, 3497–3504.
- 11 R. A. Althobiti and D. Beauchemin, *J. Anal. At. Spectrom.*, 2021, **36**, 535–539.
- 12 A. S. Henn, E. M. M. Flores, V. L. Dressler, M. F. Mesko, J. Feldmann and P. A. Mello, *J. Anal. At. Spectrom.*, 2018, **33**, 1384–1393.
- 13 L. Chirita, E. Covaci, A. Mot, M. Ponta, A. Ganda and T. Frentiu, *J. Anal. At. Spectrom.*, 2021, **36**, 267–272.



- 14 L. Chirita, E. Covaci, M. Ponta and T. Frentiu, *Anal. Methods*, 2023, **15**, 1734–1746.
- 15 I. S. Denmark, E. Begu, Z. Arslan, F. X. Han, J. M. Seiter-Moser and E. M. Pierce, *Anal. Chim. Acta*, 2018, **1041**, 68–77.
- 16 M. Wang, B. Qian, Q. X. Tian, J. L. Lin, J. Hao, Y. Zhang and B. J. Han, *Appl. Spectrosc. Rev.*, 2023, **58**, 443–488.
- 17 S. Liu, Y. L. Yu and J. H. Wang, *J. Anal. At. Spectrom.*, 2017, **32**, 2118–2126.
- 18 C. Bendicho, I. Lavilla, F. Pena-Pereira and V. Romero, *J. Anal. At. Spectrom.*, 2012, **27**, 1831–1857.
- 19 W. Wojnowski, S. Tobiszewski, F. Pena-Pereira and E. Psillakis, *TrAC, Trends Anal. Chem.*, 2022, **149**, 116553.
- 20 P. M. Nowak, R. Wietecha-Posluszny and J. Pawliszyn, *TrAC, Trends Anal. Chem.*, 2021, **138**, 116223.
- 21 C. M. Hussain, C. G. Hussain and R. Kecili, *TrAC, Trends Anal. Chem.*, 2023, **159**, 116905.
- 22 E. Covaci and T. Frentiu, *Stud. Univ. Babes-Bolyai, Chem.*, 2022, **67**, 7–25.
- 23 B. J. Han, X. M. Jiang, X. D. Hou and C. B. Zheng, *Anal. Chem.*, 2014, **86**, 936–942.
- 24 M. Li, Y. Deng, C. B. Zheng, X. M. Jiang and X. D. Hou, *J. Anal. At. Spectrom.*, 2016, **31**, 2427–2433.
- 25 M. F. Mirabelli, J. C. Wolf and R. Zenobi, *Analyst*, 2017, **142**, 1909–1915.
- 26 M. Zhang, Q. S. Tang, P. X. Li, L. He, X. D. Hou and X. M. Jiang, *Anal. Chem.*, 2023, **95**, 5151–5158.
- 27 E. Covaci, M. Senila, C. Tanaselia, S. B. Angyus, M. Ponta, E. Darvasi, M. Frentiu and T. Frentiu, *J. Anal. At. Spectrom.*, 2018, **33**, 799–808.
- 28 K. Greda, M. Welna, A. Szymczycha-Madeja and P. Pohl, *Talanta*, 2022, **249**, 123694.
- 29 X. M. Jiang, Y. Chen, C. B. Zheng and X. D. Hou, *Anal. Chem.*, 2014, **86**, 5220–5224.
- 30 S. Weagant, G. Dulai, L. Li and V. Karanassios, *Spectrochim. Acta, Part B*, 2015, **106**, 75–80.
- 31 T. Frentiu, E. Darvasi, S. Butaciu, M. Ponta, D. Petreus, A. I. Mihaltan and M. Frentiu, *Talanta*, 2014, **129**, 72–78.
- 32 T. Frentiu, E. Darvasi, S. Butaciu, M. Ponta, D. Petreus, R. Etz and M. Frentiu, *Microchem. J.*, 2015, **121**, 192–198.
- 33 S. Butaciu, T. Frentiu, M. Senila, E. Darvasi, S. Cadar, M. Ponta, D. Petreus, R. Etz and M. Frentiu, *Food Control*, 2016, **61**, 227–234.
- 34 T. Frentiu, S. Butaciu, E. Darvasi, M. Ponta, M. Frentiu and D. Petreus, *Chem. Pap.*, 2017, **71**, 91–102.
- 35 S. B. Angyus, E. Darvasi, M. Ponta, D. Petreus, R. Ratz, M. Senila, M. Frentiu and T. Frentiu, *Talanta*, 2020, **217**, 121067.
- 36 S. B. Angyus, E. Levei, D. Petreus, R. Etz, E. Covaci, O. T. Moldovan, M. Ponta, E. Darvasi and T. Frentiu, *Molecules*, 2021, **26**, 2642.
- 37 W. Davison and H. Zhang, *Nature*, 1994, **367**, 546–548.
- 38 W. Davison, *Diffusive Gradients in Thin-Films for Environmental Measurements*, Cambridge University Press, UK, 2016.
- 39 C. Li, S. M. Ding, I. Y. Yang, Y. Wang, M. Y. Ren, M. S. Chen, X. F. Fan and E. Lichtfouse, *Environ. Chem. Lett.*, 2019, **17**, 801–831.
- 40 M. Reichstadter, P. Divis, E. Abdulbur-Alfakhoury and Y. Gao, *Talanta*, 2020, **217**, 121059.
- 41 S. Wagner, J. Santer, J. Irrgeher, M. Puschenreiter, S. Happel and T. Prohaska, *Anal. Chem.*, 2022, **94**, 6338–6346.
- 42 S. Zarrouk, A. Bermond, N. K. Benzina, V. Sappin-Didier and L. Denaix, *Environ. Chem. Lett.*, 2014, **12**, 191–199.
- 43 S. Marrugo-Madrid, M. Turull, H. Zhang and S. Diez, *Environ. Chem. Lett.*, 2021, **19**, 3761–3788.
- 44 R. Chen, X. L. Mu, J. X. Liu, N. Cheng, R. G. Shi, M. M. Hu, Z. O. Chen and H. Wang, *Sci. Total Environ.*, 2023, **860**, 160523.
- 45 A. Dabrin, J. P. Ghestem, E. Uher, J. L. Gonzalez, I. J. Allan, M. Schintu, N. Montero, J. Balaam, E. Peinerud, C. Miegge and M. Coquery, *Environ. Pollut.*, 2016, **208**, 299–308.
- 46 J. L. Gonzalez, I. Amouroux, S. Guesdon, F. Menet-Nedelec, E. Ponzevera, N. Montero, B. Marras, M. Schintu, M. Caetano, M. C. Dos Santos, M. R. Sanz, V. M. Gabet, G. R. Jose, M. J. Belzunce-Segarra, J. Larreta, I. Menchaca, P. Bersuder, T. Bolam, F. Regan, B. White and H. Zhang, *Sci. Total Environ.*, 2022, **847**, 157499.
- 47 S. B. Angyus, M. Senila, T. Frentiu, M. Ponta, M. Frentiu and E. Covaci, *Talanta*, 2023, **259**, 124551.
- 48 H. Zhang and W. Davison, *Anal. Chem.*, 1995, **67**, 3391–3400.
- 49 J. M. Tukey, *Biometrics*, 1949, **5**, 99–114.
- 50 C. W. Dunnett, *J. Am. Stat. Assoc.*, 1955, **50**, 1096–1121.
- 51 J. M. Bland and D. G. Altman, *Stat. Methods Med. Res.*, 1999, **8**, 135–160.
- 52 T. Frentiu, M. Ponta, E. Darvasi, S. Butaciu, S. Cadar, M. Senila, A. Mathe, M. Frentiu, D. Petreus, R. Etz, F. Puskas and D. Sulea, RO Patent 131066 B1, 2020.
- 53 T. Frentiu, D. Petreus, M. Senila, A. I. Mihaltan, E. Darvasi, M. Ponta, E. Plaian and E. A. Cordos, *Microchem. J.*, 2011, **97**, 188–195.
- 54 V. Ivanova-Petropoulos, B. Balabanova, E. Bogeve, T. Frentiu, M. Ponta, M. Senila, R. Gulaboski and F. D. Irimie, *Food Anal. Methods*, 2017, **10**, 459–468.
- 55 B. Babalola and H. Zhang, *Groundw. Sustain. Dev.*, 2021, **12**, 100493.
- 56 O. A. Garmo, O. Royset, E. Steinnes and T. P. Flaten, *Anal. Chem.*, 2003, **75**, 3573–3580.
- 57 C. Gaulier, C. Zhou, Y. Gao, W. Guo, M. Reichstadter, T. Ma, W. Baeyens and G. Billon, *Sci. Total Environ.*, 2021, **757**, 143827.
- 58 M. P. Harper, W. Davison, H. Zhang and W. Tych, *Geochim. Cosmochim. Acta*, 1998, **62**, 2757–2770.
- 59 H. M. Conesa, R. Schulin and B. Nowack, *Environ. Sci. Pollut. Res.*, 2010, **17**, 657–664.

