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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.

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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

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most commonly used for the determination of element traces.³ To achieve the required sensitivity, these spectrometric techniques are often coupled with preconcentration/accumulation procedures by solid phase extraction, liquid–liquid extraction, direct liquid or solid micro-sampling by electrothermal vaporization (ETV) and laser ablation (LA), or derivatization by generating chemical vapor using the classical method or the UV photoinduced procedure.^{4–15} Although the ICP-OES and ICP-MS techniques are high-performing and provide excellent sensitivity, the laboratory-scale equipment involves high operating costs related to energy consumption and Ar as a support gas for plasma generation and is still not easily accessible for many laboratories. On the other hand, line-source atomic absorption is by its very nature a sequential, slow method with high sample consumption and less competitive with the simultaneous methods in the current state of the art. The methods based on derivatization, providing a highly sensitive and selective determination of several elements through the avoidance of the non-spectral interferences, although easily accessible in laboratories, remain complicated by the large number of parameters that need to be optimized, and the use of expensive and sometimes unstable reagents. The alternative is the unconventional technology using completely miniaturized instrumentation, in which the core element is a microplasma-based excitation/ionization source interfaced with a low-resolution microspectrometer or mass spectrometer.^{16,17} This led to the development of very attractive analytical applications obeying the principles of green analytical chemistry (GAC) in spectrometry and, more recently, of white analytical chemistry (WAC).^{18–22} Since introducing a gaseous sample into a microplasma was found to be a relatively simple task, the microplasma technology was mainly developed as a specific high-sensitivity detector by optical emission spectrometry (OES) and mass spectrometry (MS) in gas chromatography (GC) or as a device for introducing derivatized species of elements generated under UV irradiation by plasma, known as plasma-induced vapor generation technology.^{23–28} However, there are several limitations in the development of microplasma analytical technologies, the most important of which are the lack of stability and poor excitation capability in the case of samples with a complex matrix, because of the low operating power.¹⁶ Thus, the discharge stability is disturbed in the case of direct introduction of liquid samples because of low tolerance for water-loaded aerosols. It was shown that this shortcoming could be overcome by introducing liquid microsamples by ETV using the ideal miniaturized electrothermal vaporized-microplasma coupling, which provided the simultaneous determination of several elements with limits of detection (LODs) at the ng mL^{−1} or pg level, similar to ICP-OES.^{29,30} In our laboratory it was demonstrated that a fully miniaturized analytical system consisting of a small-sized electrothermal vaporization device (SSETV), a low-power (15 W) and low argon consumption (150 mL min^{−1}) capacitively coupled plasma microtorch (μCCP) interfaced with a low-resolution microspectrometer with a full width at half maximum (FWHM) of 0.35 nm accomplished instantaneous and efficient vaporization of a liquid microsample and high flow of analytes into plasma.

Under these conditions the simultaneous determination of several elements was achieved, including the priority hazardous ones (Hg, Cd and Pb) in environmental samples and foods with LODs similar to those of ICP-OES.^{31–34} Unfortunately, elemental determination using a small-sized electrothermal vaporization capacitively coupled plasma microtorch optical emission spectrometer (SSETV-μCCP-OES) proved to be affected by non-spectral interferences when the Rh filament was heated around 1500 °C, a temperature necessary for the vaporization of less volatile elements (such as Cu), so it was necessary to use standard addition instead of external calibration for measurements. However, the non-spectral effects could be overcome by the selective vaporization of analytes at 1300 °C and was successfully applied to the speciation of Hg as Hg²⁺ and CH₃Hg⁺ in food, and determination of As, Sb, Bi, Se, Te, Hg and Sn in environmental samples.^{35,36}

The diffusive gradients in thin-film (DGT) technique proposed by Davison and Zhang^{37,38} has been extensively used in the analysis of surface water, soil, water sediment, food, *etc.* as a passive sampling technique.^{39,40} The DGT technique is based on the diffusion of labile species through a diffusive gel and passive accumulation in a suitable binding gel over a deployment period of the order of hours or days followed by the elution of analytes in solution, *e.g.* 1 mol L^{−1} HNO₃ for metals. Next, it follows their quantification in the eluent and calculation of the time-averaged mean concentration in the uptake solution (*c*_{DGT}) based on an equation derived from Fick's first law, which takes into account the characteristics of the DGT gel.⁴⁰

The DGT passive accumulation technique mimics the retention of metal ions in soil solution by plant roots at the root–soil interface, which involves first the transfer of ions from the solid phase of soil into solution, and then absorption by the roots. Studies regarding the bioavailability of toxic metals have demonstrated that the labile fraction in the soil solution (*c*_{DGT}) obtained after the DGT passive sampling was a very good indicator to measure the bioavailability of metals through roots, given the good correlation coefficients between metal concentrations in plants and *c*_{DGT}.^{41–44}

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-μCCP-OES (DGT-SSETV-μCCP-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-μCCP-OES instrumentation and *in situ* DGT passive sampling.⁴⁷ Increasing the technological



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be used for sequential multielemental analysis of any type of sample, including soil analysis. Compared to this common sequential atomic absorption technique of high sensitivity, the (DGT)-SSETV- μ CCP-OES technique is simultaneous. It requires validation to check if it is an appropriate alternative for the determination of Cd, Pb, Cu and Zn in total and DGT-based labile fraction in soil.

The ICP-OES 5300 Optima DV spectrometer from PerkinElmer (Waltham, Massachusetts, USA) was used for the determination of Na, K, Ca, Mg, Sr, Fe, Ni, Cr, Co and Mn in a multielemental matrix. The 761 Compact IC Metrohm ion chromatograph, Metrohm (Herisau, Switzerland) was used for the determination of anions (F^- , Cl^- , NO_3^- and SO_4^{2-}) in soil solution in which the DGT-based labile fraction of Cd, Pb, Cu and Zn was determined. The concentration of dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) fractions was quantified in soil solution using the 2100S Multi N/C analyzer, Analytik Jena (Jena, Germany). The Multi 350i, Geotech (Denver, USA) was used for pH measurement of soil solution and for pH adjustment of solutions in which the DGT devices were immersed for the determination of total content of Cd, Pb, Cu and Zn in soil. All these procedures were previously described.⁴⁷

The Milli-Q water purification system Millipore (Bedford, USA) and the microwave digester Berghof MWS3+ (Berghof, Germany) were employed for the preparation of ultrapure water and microwave-assisted digestion of the samples, respectively.

Reagents, solutions and certified reference materials (CRMs)

Hydrochloric acid ultrapure (30%), nitric acid ultrapure (60%), ammonia solution (25%) suprapur, and ICP multielement standard solution IV 1000 mg L⁻¹ were purchased from Merck (Darmstadt, Germany). Multielement ($n = 7$ point calibration curves for Cd, Pb, Cu and Zn) solutions containing 0–100 μ g L⁻¹ Cd and 0–1000 μ g L⁻¹ Pb, Cu and Zn in 2% (v/v) HNO₃ were prepared to be used for the calibration of the SSETV- μ CCP-OES equipment. Multielement solutions of Cd, Pb, Cu and Zn in the range of 0–10 μ g L⁻¹ in 2% (v/v) HNO₃ were used for the calibration of the GFAAS instrument. Arsenic calibration standards in the range of 0–100 μ g L⁻¹ in 2% (v/v) HNO₃ were also used for the determination of As by GFAAS and 0–1000 μ g L⁻¹ by SSETV- μ CCP-OES at 189.042 nm, respectively. The appropriate chemical modifiers (PerkinElmer Pure, Shelton, USA) were used to compensate for the matrix effects in GFAAS (Cd and Pb: 1% NH₄H₂PO₄ + 0.06% Mg(NO₃)₂, Cu: 0.1% Pd(NO₃)₂ + 0.06% Mg(NO₃)₂, and Zn: 0.1% Mg(NO₃)₂). A solution of 0.1 mol L⁻¹ NH₃ was used to adjust the pH in the uptake solution to 4.0 $\pm$ 0.1 prior to immersion of the DGT devices for the passive accumulation of analytes for the determination of their total concentration in soil. A solution of 1 mol L⁻¹ HNO₃ was used for the elution of the target elements from the binding gel.

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

in soil from Resource Technology Corporation (Laramie, USA), after *ex situ* DGT passive accumulation at pH 4.0 $\pm$ 0.1 in 100 mL solution obtained by 10 and 20-fold dilution of aliquot volumes of digest. The CRMs were used also to study the uptake kinetics of the target elements and determination of the diffusion coefficients and elution factors.

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

Determination of the total content of analytes. The main stages in the sample processing for the determination of the total and DGT-based labile fraction of target elements in soil are depicted in Fig. 1.

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 waste-water 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 $^{\circ}$ C, ground in a ball mill and sieved to <100 μ m. 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 μ m).

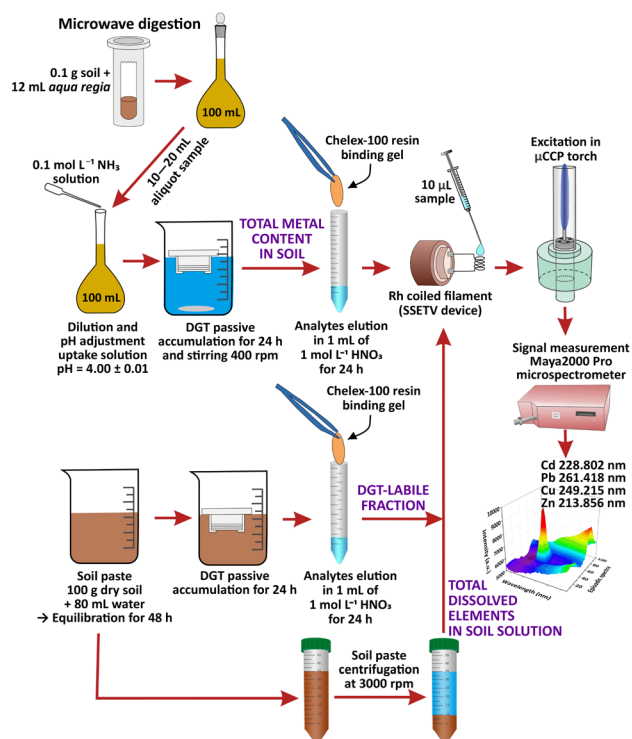


Fig. 1 Schematic diagram of soil sample preparation for the determination of total content and labile fraction of Cd, Pb, Cu and Zn in soil by SSETV- μ CCP-OES after DGT passive accumulation on Chelex-100 resin.



The uptake solutions for DGT accumulation were prepared from aliquot volumes of 10 to 20 mL diluted with water and the pH adjustment to 4.0 ± 0.1 by potentiometric titration with $0.1 \text{ mol L}^{-1} \text{ NH}_3$ and finally made up to 100 mL. The working pH value of 4.0 ± 0.1 was selected based on a previous study showing that in the 4–7 pH range the accuracy of the ratio of the concentration determined using the DGT sampling to the analytical concentration of the uptake solution ($c_{\text{DGT}}/c_{\text{sol}}$) was in the range of 0.83–1.13 with a relative extended uncertainty of $\pm 20\%$ ($k = 2$).⁴⁷ After assembling the DGT devices (filter membrane of polyethersulphone, the APA diffusive gel and the Chelex-100 binding gel) were immersed for 24 h in the uptake solution in triplicate ($3 \times 100 \text{ mL}$ solution) avoiding touching the diffusion surface with the vessel walls. The solutions were gently stirred at $400 (\times \text{g})$. The solution temperature measured at least 3 times during accumulation was $21 \pm 1^\circ \text{C}$. After exposure, the DGT devices were extracted from the uptake solutions, rinsed with ultrapure water jets and disassembled. The Chelex-100 gel was separated with tweezers, washed with ultrapure water and subjected to elution of analytes by immersion in 1 mL of $1 \text{ mol L}^{-1} \text{ HNO}_3$ for 24 h at $21 \pm 1^\circ \text{C}$ in a clean tube. The eluate was analyzed for the determination of the total content of Cd, Pb, Cu and Zn in soil by SSETV- $\mu\text{CCP-OES}$ and GFAAS using external calibration.

The CRM soils analyzed for the assessment of the accuracy of the DGT-SSETV- $\mu\text{CCP-OES}$ method were processed using the same protocol and 24 h accumulation time.

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 $< 2 \text{ mm}$ 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 $21 \pm 1^\circ \text{C}$ in vessels covered with a polypropylene film. Then, the DGT devices were immersed in the paste for 24 h at $21 \pm 1^\circ \text{C}$, 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 $1 \text{ mol L}^{-1} \text{ HNO}_3$ (24 h, $21 \pm 1^\circ \text{C}$). 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 $3000 (\times \text{g})$ 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- $\mu\text{CCP-OES}$ and GFAAS. This concentration was used as a reference to evaluate the capacity of soil to release metals in the soil solution.⁵⁵

Calculation of the total concentration of metals and DGT-based labile fractions is presented in the ESI (Section 2).†

Validation of the SSETV- $\mu\text{CCP-OES}$ method for the determination of the total content and DGT-based labile fraction of analytes in soil. In the case of real samples the validation of the (DGT)-SSETV- $\mu\text{CCP-OES}$ method was carried out on the basis of the average results and absolute extended uncertainty (U_{lab}) obtained through external calibration and comparison with the GFAAS reference method, using the Bland-Altman statistical test.⁵¹ This test may be applied even when data are not normally distributed and are not affected by extreme values, which are not rejected from evaluation. The (DGT)-SSETV- $\mu\text{CCP-OES}$ method was also validated in terms of LODs, accuracy and precision. The method LODs were assessed using the instrumental LODs ($\text{LODs} = 3s_b/m$) calculated according to the 3σ criterion from the standard deviation of the blank (s_b) and calibration slope (m) and considering the sample preparation protocol and accumulation by the DGT technique (24 h). Accuracy for the determination of the total concentration of analytes was checked by analyzing soil CRMs, evaluation of recovery against the certified value (R , %) and relative expanded uncertainty ($U_{\text{lab}}\%$) ($R \pm U_{\text{lab}}\%$, $k = 2$) after the DGT passive accumulation. The $U_{\text{lab}}\%$ was calculated with the relation ($U_{\text{lab}}\% = U_{\text{lab}} \times 100/\text{found concentration}$). The absolute U_{lab} in the case of CRM analysis was calculated from extended combined uncertainty ($U_c = 2 \times u_c$) including the individual uncertainties associated with the main steps in sample preparation and analysis, and U_{CRM} provided in the certificate ($U_{\text{lab}} = \sqrt{U_c^2 + U_{\text{CRM}}^2}$). The average concentrations were calculated using both the experimental diffusion coefficients and elution factors ($D_{\text{exp}}, f_{\text{exp}}$), and those provided by the manufacturer. The existence of significant differences ($p > 0.05$) between the found mean and certified value was investigated by verifying the fulfillment of relation $\Delta m < U_{\text{lab}}$, where Δm is the difference between the found mean and certified value. The bias between the results obtained by (DGT)-SSETV- $\mu\text{CCP-OES}$ and (DGT)-GFAAS methods was statistically checked using Tukey's test, while the bias of the two methods against the certified values by Dunnett's test ($p > 0.05$).^{49,50}

The acceptance criterion for accuracy was that the interval ($R \pm U_{\text{lab}}\%$) contained the 100% theoretical recovery value with a confidence limit of $\pm 30\%$, considered for the coupling of a spectrometric method with DGT passive accumulation.^{45,46}

The precision of the DGT-SSETV- $\mu\text{CCP-OES}$ 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- $\mu\text{CCP-OES}$ method was compared to that of DGT-GFAAS.

Results and discussion

Matrix characterization of CRMs and soil samples

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



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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).



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}

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

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

		Experimental diffusion coefficients and elution factors				Recommended diffusion coefficients and elution factors			
		Found concentration mean $\pm U_{lab}^b$ (mg kg ⁻¹)		Accuracy recovery $\pm U_{lab}^c$ (%)		Found concentration mean $\pm U_{lab}^b$ (mg kg ⁻¹)		Accuracy recovery $\pm U_{lab}^c$ (%)	
CRM/ analyte	Certified concentration mean $\pm U_{CRM}^a$ (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

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($p > 0.05$) 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 multielemental 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 ± 1.2	4.8 ± 1.2	95.2 ± 29.4	104 ± 33	142 ± 33	131 ± 33	321 ± 95	306 ± 93
S2	4.8 ± 1.5	6.0 ± 1.5	71.0 ± 21.6	69.5 ± 14.8	59.0 ± 15.7	63.4 ± 18.9	135 ± 34	111 ± 31
S3	14.5 ± 3.3	14.1 ± 3.9	171 ± 37	160 ± 37	432 ± 137	420 ± 128	359 ± 90	372 ± 89
S4	4.4 ± 0.9	5.6 ± 1.5	35.6 ± 9.3	37.0 ± 8.0	75.2 ± 28.0	83.6 ± 23.4	86.4 ± 32.2	64.5 ± 20.2
S5	7.3 ± 1.8	7.2 ± 2.2	74.2 ± 20.3	71.3 ± 15.0	78.2 ± 22.3	79.4 ± 19.8	246 ± 68	255 ± 52
S6	8.9 ± 2.3	8.6 ± 2.3	71.0 ± 17.0	77.1 ± 18.2	85.8 ± 29.1	78.0 ± 22.9	202 ± 62	179 ± 44
S7	11.1 ± 2.8	11.9 ± 3.7	91.4 ± 28.5	92.4 ± 23.4	49.7 ± 13.1	50.6 ± 18.4	114 ± 32	125 ± 35
S8	4.9 ± 1.5	5.6 ± 1.4	228 ± 57	215 ± 69	74.8 ± 18.7	70.6 ± 20.0	152 ± 46	162 ± 50
S9	13.5 ± 3.7	13.2 ± 4.7	146 ± 31	146 ± 31	79.3 ± 25.1	79.8 ± 22.2	227 ± 57	207 ± 64
S10	8.1 ± 1.9	9.5 ± 2.3	128 ± 30	135 ± 38	135 ± 40	145 ± 36	223 ± 54	204 ± 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).



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

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