Final scientific report

(2022 - 2024)

Competition:	**Experimental demonstration project – PED 2021**
Contract no.:	733PED / 27.06.2022
Project code:	PN-III-P2-2.1-PED-2021-0151
Research field:	3. Energy, environment and climate change
Title :	Simultaneous elemental microanalytical method for environmental and food monitoring using passive sampling and miniaturized instrumentation based on microplasma optical emission spectrometry
Acronym:	MULTIPASS
Project starting date:	27.06.2022
Project completion date:	26.06.2024
Duration (months):	24
Total budget:	600.000 RON
Source 1 State funding	600.000 RON
Source 2 Other fundings (co-funding):	0 RON
Project website:	https://icia.ro/multipass/
Coordinating institution:	INCDO-INOE 2000, Research Institute for Analytical Instrumentation Branch, Cluj-Napoca
Project director:	Marin Senila
Project partner 1 (P1):	Babes-Bolyai University of Cluj-Napoca
Project partner 2 (P2):	Tehnical University of Cluj-Napoca

1. General presentation of the project objectives, highlighting the results and the degree of achievement of the objectives. The presentation should include explanations justifying the differences (if any) between the planned and the achieved activities.

1.1 Short presentation of the project

The MULTIPASS project is in line with current international scientific concerns: to integrate analytical chemistry with the principles of green chemistry by reducing the harmful effects of the use of analytical methods on the environment and on the health and safety of operators. The principles of green analytical chemistry include: reducing the number of steps in sample processing; using the smallest possible quantities of chemical reagents with low toxicity to minimise waste; using equipment with low construction and maintenance costs. On the other hand, the performance parameters of the analytical methods must not be compromised by the features that make them green.

Within the MULTIPASS project it was proposed and achieved to increase the technological maturity level from TRL3 to TRL4 of an analytical system based on the determination of some elements (Hg, Pb, Cd, As, Sb, Se, Cu and Zn) by a fully miniaturized laboratory model based on optical emission spectrometry using a capacitively coupled plasma micro-torch and vaporization by a small-size electrothermal vaporizer (DGT-SSETV-µCCP-OES) after passive sampling by the thin film diffusion gradient technique (DGT). Highly sensitive microanalytical methods, free from matrix effects, for the simultaneous multi-element determination of potentially toxic elements have also been developed, validated and applied to the analysis of real environmental and food samples.

1.2 Planned and accomplished objectives

Major objective		
Crt. No.	**Proposed objectives**	**Achieved objectives**
1.	Development of new microanalytical methods for the simultaneous determination of priority hazardous and other toxic elements (Hg, Pb, Cd, As, Sb, Se, Cu and Zn) using a fully miniaturised experimental laboratory model based on optical emission spectrometry using a small-size electrothermal vaporization device and a capacitively coupled plasma micro-torch (SSETV-µCCP-OES) in tandem with passive sampling based on the diffusion gradient in thin films (DGT) technique	**Yes:** The DGT- SSETV-µCCP-OES system was developed at TRL4 level and 6 new microanalytical methods (TRL4) were developed for the simultaneous determination of priority hazardous elements and other toxic elements (Hg, Pb, Cd, As, Sb, Se, Cu and Zn) using a fully miniaturized experimental laboratory model based on optical emission spectrometry in a capacitively coupled plasma micro-torch and small-scale electrothermal vaporization (SSETV-µCCP-OES) in tandem with a passive sampling device based on the diffusion gradient in thin films (DGT) technique
Obiective specifice		
Crt. No.	**Proposed objectives**	**Achieved objectives**
1.	Testing and optimization of working conditions for *in-situ* and *ex-situ* preconcentration of Hg, Pb, Cd, As, Sb, Se, Cu and Zn using the DGT device, prior to sample introduction by electrothermal vaporization in the plasma micro-torch	**Yes:** ►A testing and optimization report on the working conditions for *in-situ* and *ex-situ* preconcentration of Hg, Pb, Cd, As, Sb, Se, Cu and Zn using the DGT device, prior to the introduction of the sample by electrothermal vaporization in the plasma microtower, was carried out
2.	Optimization of working conditions for SSETV as a direct microsampling device after DGT preconcentration	**Yes:** ► A DGT-SSETV-µCCP-OES equipment optimization report for the working conditions for SSETV as a direct microsampling device after DGT preconcentration was carried out
3.	Development of a specialized software to control the thermal program of the Rh filament	**Yes:** ► A specialized software has been developed to control the thermal program of the Rh filament for Hg, Cd, Cu, Pb, Zn, As, Sb and Se evaporation
4.	Improvement of the analytical performance of the SSETV-µCCP-OES detection system by coupling with the DGT technique	**Yes:** ► An experimental report on the improvement of the analytical performance of SSETV-µCCP-OES methods with and without DGT was carried out
5.	Comparison of analytical performance with traditional methods and European requirements	**Yes:** ► An experimentation report was made - a comparative study of the analytical performance for DGT-SSETV-µCCP-OES with traditional methods GFAAS, TDAAS, ICP-OES and the European legislation requirements
6.	Validation of the DGT-SSETV-µCCP-OES method by analysis of certified standard materials in environmental and food samples	**Yes:** ►Two validation reports were carried out: Validation report on methods based on DGT-SSETV-µCCP-OES for simultaneous multi-element determination in environmental samples; Validation report on methods based on DGT-SSETV-µCCP-OES for simultaneous

		multi-element determination in food samples
7.	Development of DGT-SSETV-µCCP-OES microanalytical methods for real environmental samples and comparison of analytical performance with traditional methods and with the European legislative requirements	**Yes:** ▶ Three microanalytical methods for real environmental samples (DGT-SSETV-µCCP-OES) TRL4 were developed and the analytical performance was compared with traditional methods and with the European legislative requirements
8.	Development of DGT-SSETV-µCCP-OES microanalytical methods for real food samples and comparison of analytical performance with traditional methods and with the European legislative requirements	**Yes:** ▶ Three microanalytical methods for real food samples (DGT-SSETV-µCCP-OES) TRL4 were developed and the analytical performance was compared with traditional methods and witht the European legislative requirements
9.	Demonstration of the usefulness and functionality of the new microanalytical methods DGT-SSETV-µCCP-OES	**Yes:** ▶ A demonstration session was carried out and a report was written to demonstrate the usefulness and functionality of the new DGT-SSETV-µCCP-OES microanalytical methods
10.	Development of two standard operating procedures for laboratory implementation of the DGT-SSETV-µCCP-OES technique	**Yes:** ▶ Two standard operating procedures have been developed for laboratory implementation of the DGT-SSETV-µCCP-OES technique
11.	Drafting a National Patent Application	**Yes:** ▶ A national patent application has been drafted
12.	Dissemination of results through participation in international conferences	**Yes:** ▶ Results were disseminated by participation with 13 presentations at national and international conferences
13.	Dissemination of results by publishing 4 scientific articles in WoS indexed journals with IF>3.	**Yes:** ▶ Results were disseminated through 8 published ISI articles (IF>3), sum of impact factors = 41.5

2. Presentation and justification of the technological maturity level (TRL) at the end of the project.

Initial ⇒ TRL3 / Justification	**Final ⇒ TRL4 / Justification**
The MULTIPASS project started at the TRL3 technology maturity level, and there is experimental proof of concept functionality, i.e. the existence of the SSETV-µCCP-OES miniaturized spectrometric system developed in a previous research project (MICROCCP), code PN-II-PT-PCCA-2011-3.2-0219, contract no. 176/2012.	• The increasing maturity of the technology is demonstrated by the integration of passive sampling using the DGT technique for *in-situ* or *ex-situ* preconcentration of the elements prior to their instrumental determination, resulting in the new DGT-SSETV-µCCP-OES system. This new approach has led to the avoidance of spectral and non-spectral matrix effects and to a substantial improvement in analytical performance (detection and quantification limits, precision, accuracy). TRL4 is demonstrated by: • DGT-SSETV-µCCP-OES system implemented (product), equipped with the new thermal evaporation temperature control software (software product) • Test report and optimization of working conditions for *in-situ* and *ex-situ* preconcentration of Hg, Pb, Cd, As, Sb, Se, Cu and Zn using the DGT device, prior to sample introduction by electrothermal vaporization into the plasma micro-torch

	• Experimentation report on the improvement of the analytical performance of the DGT-SSETV-µCCP-OES methods • Comparative analytical performance study for DGT-SSETV-µCCP-OES with traditional methods GFAAS, TDAAS, ICP-OES and European legislation requirements, demonstrating that the analytical performance of DGT-SSETV-µCCP-OES is fit for purpose • DGT-SSETV-µCCP-OES TRL4 microanalytical methods developed and applied to real environmental (3 methods) and food (3 methods) samples, whose analytical performance was compared with traditional methods and European legislative requirements

Most significant result: DGT-SSETV-µCCP-OES model technology level TRL4

DGT-SSETV-µCCP-OES model technology level TRL4 developed is the central element of the research carried out in the MULTIPASS project. Its development was based on the inclusion of passive DGT sampling devices in the SSETV-µCCP-OES system developed at TRL3 in a previous research project. Using this system, tests and optimizations of the working conditions were performed, including the development of a new software for the control of thermal evaporation of the elements for introduction into the microplasma. The system then formed the basis for the development and validation of microanalytical methods and was used for the analysis of real environmental and food samples. The schematic diagram of the DGT-SSETV-µCCP-OES experimental model at the TRL4 technology level has been shown bellow in Figure 1.

Overall, the DGT-SSETV-µCCP-OES system is integrated into the current trend of green analytical chemistry, due to the following advantages:

- ✓ Miniaturized system with reduced dimensions, which does not require a lot of space in the laboratory
- ✓ Low cost instrument due to the use of miniaturized components
- ✓ Low operating costs: low energy consumption (10-15 W) and Ar consumption (100-150 mL min^{-1})
- ✓ Uses very small sample quantities using electrothermal evaporation (10 µL)
- ✓ By using passive DGT sampling, the analyte is separated from the matrix in a simple solution: ● matrix effects are eliminated; ● it is no longer necessary to use the standard addition method for quantification; ● spectral interferences are eliminated
- ✓ Sampling via DGT allows: ● continuous monitoring during the immersion period devices; ● determination of time-averaged concentrations; ● analyte separation from the complex matrix; ● *in-situ* preconcentration; ● obtaining specificity for analytes; ● determination of bioavailable concentration; ● chemical speciation at the sampling stage; ● reduction of total cost and time for sampling

3. Presentation of the deliverables/indicators obtained at the end of the project compared to those proposed

Crt. No.	Planned deliverables/indicators	No.	Obtained deliverables/indicators	No.
1.	ISI articles published in journals with FI>3	**4**	**8** ISI articles published in journals with FI>3: **1**▶S.B. Angyus, M. Senila, T. Frentiu, M. Ponta, M. Frentiu, E. Covaci, *Talanta*, 2023, 259, 124551 (*FI 6.1*); **2**▶S.B. Angyus, M. Senila, E. Covaci, M. Ponta, M. Frentiu, T. Frentiu, *Journal of Analytical Atomic Spectrometry*,	**8**

			2024, 39, 141 (*FI* 3.4); **3**▶M. Senila, *Reviews in Analytical Chemistry*, 2023, 42, 20230065 (IF 4.3); **4**▶*M. Senila, M.A. Resz, L. Senila, I. Torok*, *Science of The Total Environment*, 2024, 909, 168591 (*FI = 9.8*); **5**▶*M. Senila, E. Kovacs, Environmental Science and Pollution Research*, 2024 (*FI* 5.8); **6**▶*M. Senila, E.A. Levei, T. Frentiu, C. Mihali, S.B. Angyus, Environmental Monitoring and Assessment*, 2023, 195, 1554 (*FI 3.0*); **7**▶*M. Senila, M.A. Resz, I. Torok, L. Senila*, *Journal of Food Composition and Analysis*, 2024, 128, 106061 (*FI 4.3*); **8**▶*M. Senila, O. Cadar, T. Frentiu, L. Senila, S.B. Angyus*, *Microchemical Journal*, 2024, 198, 2024, 110195 (*FI 4.8*)	
2.	International and national scientific conferences	**8**	13 participations at international and national scientific conferences: **1**▶E. Covaci, Z. Sandor, B.S. Angyus, M. Senila, T. Frentiu. National Chemistry Conference, XXXVI edition, **2022 (Oral presentation); 2**▶Z. Sandor, E. Covaci, B.S. Angyus, M. Senila, T. Frentiu National Chemistry Conference, XXXVI edition, **2022 (Oral presentation); 3**▶E. Covaci, S.B. Angyus, M. Senila, M. Frentiu, T. Frentiu, 49th International Conference of Slovak Society of Chemical Engineering (SSCHE), Tatranske Matliare, Slovakia, **2023 (Poster)**; **4**▶E. Covaci, S.B. Angyus, M. Senila, M. Frentiu, T. Frentiu 49th International Conference of Slovak Society of Chemical Engineering (SSCHE), Tatranske Matliare, Slovakia, **2023 (Poster)**; **5**▶S.B. Angyus, M. Senila, E. Covaci, T. Frentiu, M. Frentiu, 49th International Conference of Slovak Society of Chemical Engineering (SSCHE), Tatranske Matliare, Slovakia, **2023 (Poster)**; **6**▶**S**.B. Angyus, M. Senila, E. Covaci, T. Frentiu, 4th Young Researchers' International Conference on Chemistry and Chemical Engineering (YRICCCE IV), Debrecen, Hungary, **2023 (Oral presentation)**; **7**▶E. Covaci, S.B. Angyus, M. Senila, M. Frentiu, T. Frentiu, 4th Young Researchers' International Conference on Chemistry and Chemical Engineering (YRICCCE IV), Debrecen, Hungary, **2023 (Oral presentation); 8**▶S. Cadar, D. Petreus, T. Patarau, E. Szilagyi, B. Angyus, F. Tiberiu, 14th International Conference Processes in Isotopes and Molecules, Romania, **2023 (Poster); 9**▶S. Cadar, D. Petreus, T. Patarau, E. Szilagyi, IEEE 29th International Symposium for Design and Technology in Electronic Packaging (SIITME), Romania, **2023 (Poster); 10**▶M. Senila, M. Roman, B. Angyus Agriculture and Food - current and future challenges, AGRIFA, Cluj-Napoca, Romania, **2023 (Poster); 11**▶S. Cadar, D. Petreus, T. Patarau, E. Szilagyi, International Spring Seminar on Electronics Technology, Prague, Czech Republic, **2024 (Poster); 12**▶S. Angyus, T. Frentiu, M. Frentiu, E. Covaci, M. Senila 50th International Conference of	**13**

			Slovak Society of Chemical Engineering (SSCHE), Slovakia, **2024 (Poster); 13▶** E. Covaci, S. Angyus, M. Senila, M. Frentiu, T. Frentiu 50th International Conference of Slovak Society of Chemical Engineering (SSCHE), Slovakia, **2024 (poster)**	
3.	National patent applications	**1**	Patent application registered at OSIM with no. A00226 dated 29/04/2024	**1**
4.	Product	**1**	DGT-SSETV-µCCP-OES model technology level TRL4	**1**
5.	Software product	**1**	Software product developed in two stages: **1▶** Specialized software, Rh microfilament temperature control for Cd, Pb, Cu, Hg evaporation; **2▶** Specialized software, Rh microfilament temperature control for As, Sb, Se evaporation	**2**
6.	Other			
	● Experimental data: experimental report		**1▶** Report on testing and optimisation of working conditions with DGT; **2▶** SSETV working conditions optimisation report; **3▶** SSETV working conditions optimisation report; **4▶** Report on working conditions optimization for plasma microtorch for simultaneous multi-element determination by DGT-SSETV-µCCP-OES; **5▶** Experimental report on the improvement of the analytical performance of the SSETV-µCCP-OES method with and without DGT; **6▶** Comparative study of analytical performance for DGT-SSETV-µCCP-OES with traditional methods GFAAS, TDAAS, ICP-OES and with European legislation requirements; **7▶** Validation report on DGT-SSETV-µCCP-OES based methods for simultaneous multi-element determination in environmental samples; **8▶** Validation report on DGT-SSETV-µCCP-OES based methods for simultaneous multi-element determination in food sample	**8**
	● Analytical methods		**1▶** Microanalytical methods developed for environmental samples (DGT-SSETV-µCCP-OES) TRL4; **2▶** Microanalytical methods developed for food samples (DGT-SSETV-µCCP-OES) TRL4; **3▶** Analytical method developed for environmental and food samples based on DGT-ICP-OES TRL4; **4▶** Analytical method developed for environmental and food samples based on DGT-GFAAS TRL4	**4**
	● Documentation		**1▶** DGT-SSETV-µCCP-OES based standard operating procedure for water sample analysis; **2▶** DGT-SSETV-µCCP-OES based standard operating procedure for soil sample analysis; **3▶** Report demonstrating the usefulness and functionality of the new microanalytical methods DGT-SSETV-µCCP-OES; **4▶** VP intellectual property rights for industrial research	**4**
7.	Project website	**1**	https://icia.ro/multipass/	**1**

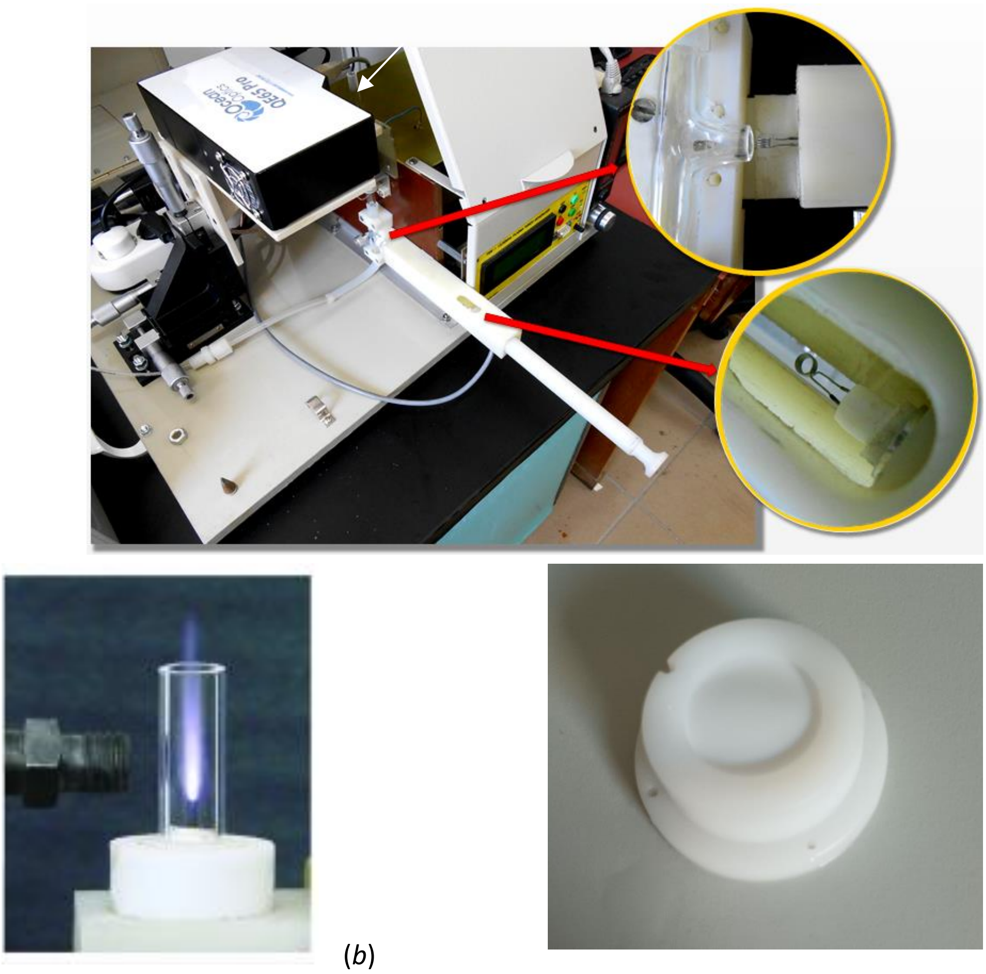
<u>Note</u>: *In addition to the above, the final report must also contain a brief presentation (2-3 paragraphs) of the results obtained in the project, which will be disseminated by the Contracting Authority in materials promoting the results obtained under the funding programmes. Please note that this text must be understandable to the public. The presentation must be accompanied by 2-4 representative pictures of the project (JPG format), which must also be available on the project web page* https://icia.ro/multipass/

Brief presentation of the project results

The main goal of the MULTIPASS project was to develop new microanalytical methods for the simultaneous determination of priority hazardous elements and other toxic elements (Hg, Pb, Cd, As, Sb, Se, Cu and Zn) using a fully miniaturized experimental laboratory model based on optical emission spectrometry in a capacitively coupled plasma micro-torch and small-sized electrothermal vaporization (SSETV-µCCP-OES) in tandem with a passive sampling device based on the diffusion gradient in thin films technique (DGT).

The system consisting of passive samplers and miniaturised laboratory spectrometric equipment has been developed to a higher technological level (TRL4) and can be used for the determination of elements after passive sampling. Figure 1 shows photographs of: (a) the miniaturised spectrometric equipment; (b) the torch in which a low power, low Ar consumption, capacitively coupled microplasma is produced; (c) a passive sampler based on the diffusion gradient in thin films technique (DGT). The advantages of using miniaturised equipment are: ►reduced production and maintenance costs, ►reduced consumption of reagents, energy, special gases, and sample, ►the small space it occupies in the laboratory. The advantages of coupling passive sampling with this type of equipment are: ►elimination of spectral interference and matrix interference, ►pre-concentration over time of the elements to be analysed, ► obtaining of average concentrations over a period of days to weeks by immersing the devices in the medium to be analysed. The combination of the two techniques benefits from the advantages of each, all leading to improved analytical performance of the system as a whole.

High-performance and economically viable analytical methods based on the proposed analytical system have been developed and applied. These were tested, optimized and validated both by analysis of certified reference materials and by comparison of results with those obtained using commercial spectrometric equipment: inductively coupled plasma atomic emission spectrometry, atomic absorption spectrometry, and the results were comparable. The developed methods were applied to the analysis of real environmental and food samples, and it was shown that they are suitable and meet the requirements of European legislation in the field of environmental and food quality control. The results obtained were disseminated through participation with 13 participations at scientific conferences and publication of 8 articles in ISI listed journals. A national patent application has been filed to protect intellectual property rights.



(a) (*b*) (*c*)

Figura 1. Photographs of: (a) miniaturized spectrometric equipment (assembly of components); (b) torch in which capacitively coupled, low power, low Air consumption microplasma is produced; (c) a passive sampling device based on the diffusion gradient in thin films technique