On-site implementation and testing of multilemental preconcentration from surface waters by µ-SPE using dithizone-functionalized C18 cartridges for the determination of metals by capacitively coupled microplasma optical emission spectrometry with electrothermal vaporization from a Rh filament (SSETV-µCCP-OES)

(Activity 1.3, CO-UBB, P1-FI)

In this activity, the goal was to implement the preconcentration procedure for Cu^{2+}, Cd^{2+}, Zn^{2+}, and Pb^{2+}, previously tested and optimized *ex-situ*, into an *on-site* preconcentration procedure for surface waters using µ-SPE on dithizone-functionalized C18 silica cartridges. Considering that the aim of the WHIGREEN project was the development of green and white methods, both in terms of sample preparation procedures and the analytical step itself, a portable experimental setup powered by a solar panel was selected, ensuring the energy independence of the method. The *on-site* working conditions were similar to those optimized during the *ex-situ* procedure. Thus, pH adjustment of the water samples, µ-SPE preconcentration, and elution steps were performed directly *on-site*. The eluates were subsequently analyzed in the laboratory using the SSETV-µCCP-OES instrument, which was also powered by a battery previously charged photovoltaically from the same solar panel.

The experimental setup for *in-situ* multielement preconcentration and elution of Cu^{2+}, Cd^{2+}, Zn^{2+}, and Pb^{2+}, shown in Figure 1, consists of a 12.8 V, 100 Ah $LiFePO_4$ battery (Volt, Romania) connected to a 200 W monocrystalline photovoltaic panel (Breckner, model 87TH449, Germany) through a Victron Energy SmartSolar MPPT 100/30 charge controller (Victron, Almere, Netherlands) and a Victron Energy Phoenix 12 V/1200 W, 230 V inverter (Victron, Almere, Netherlands). The Sartorius filtration system (Sartorius AG, Göttingen, Germany) and the Masterflex L/S four-channel peristaltic pump, model 7528-30 (Cole-Parmer, Massachusetts, USA), were powered according to the *on-site* setup (Figure 1). *On-site* testing and implementation of the preconcentration procedure were carried out on water samples collected from the Arieș River. Two liter surface water samples were collected from various locations and filtered using the Sartorius system. From the filtered samples, volumes of up to 250 mL were taken and adjusted to pH 6.5 using a Multi 350i portable pH meter (Weilheim, Germany), powered by its internal battery. The Cole Parmer pump was then used to pass the sample through the dithizone-functionalized C18 µ-SPE cartridge at a flow rate of 2.5 mL min^{-1}, and elution was performed with 2 mL of 0.2 mol L^{-1} thiourea in 1 mol L^{-1} HNO_3 at a flow rate of 0.5 mL min^{-1}. Since the peristaltic pump is equipped with four channels, four water samples were preconcentrated in parallel. The collected eluates were transported to the laboratory, where Cu, Cd, Zn, and Pb contents were determined by (µ-SPE)-SSETV-µCCP-OES, the system being likewise powered by the battery. The laptop used for operation was also powered by the same battery.

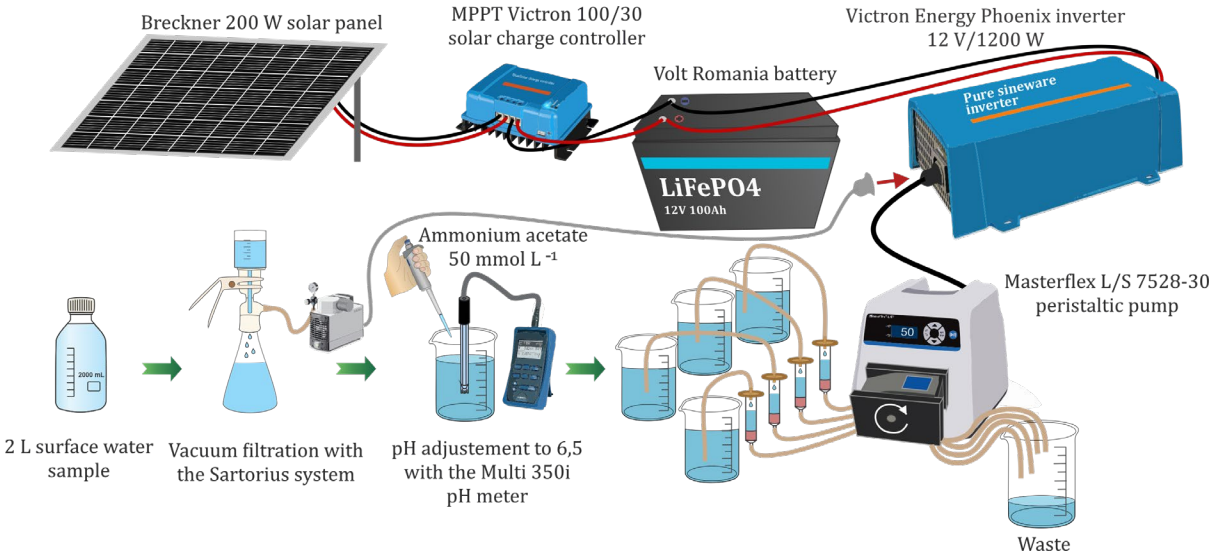

Figure 1. Experimental setup tested and implemented for *in-situ* multielement preconcentration of Cu^{2+}, Cd^{2+}, Zn^{2+}, and Pb^{2+} from surface water samples

The energy autonomy of the experimental power supply setup for operating the components (Sartorius filtration system and peristaltic pump) used in the *on-site* implementation of the preconcentration and elution steps, as well as the energy consumption of the SSETV-μCCP-OES instrument (powering the radiofrequency generator and the miniaturized electrothermal evaporator via the Tenma source), was evaluated. For this purpose, the output voltage of the battery was monitored, and the energy consumption was measured using an OR-WAT-419(OR) meter (Orno, Poland). Figure 2 shows the battery discharge rate during the *on-site* μ-SPE preconcentration and elution procedure, as well as during the *ex-situ* SSETV-μCCP-OES analysis.

The energy consumption of the *on-site* μ-SPE preconcentration (Figure 2a) was 110 W in total for one cycle of four samples, consisting of 69 W for the filtration step (40 min), 39 W for the preconcentration step (up to 100 min), and 2 W for the elution step (10 min). Thus, over an 8 hour period, three processing cycles can be completed (number of samples: 4 × 3 = 12, total energy consumption: 330 W). Consequently, the battery charged from the photovoltaic panel provides an autonomy of 24 hours, corresponding to three 8 hour days, and a total of 36 samples processed *on-site* for μ-SPE preconcentration. This autonomy can be further increased considering that the solar panel can deliver up to 200 W under sunny weather conditions, meaning the battery can be recharged by the solar panel during sample processing. Regarding *ex-situ* analyses performed using the SSETV-μCCP-OES instrument powered from the fully charged battery, the energy autonomy is at least 3 hours (Figure 2b), which allows the analysis of 60 samples at an energy consumption of 10 W per sample. Of this, 2 W corresponds to powering the source for sample drying and vaporization, 2 W to powering the radiofrequency generator for the microplasma, and 6 W to supplying the laptop and microspectrometer via the laptop's USB port, assuming the laptop battery is discharged and the power is supplied from the solar-charged battery. Naturally, the autonomy can be extended to more than 6 hours if the laptop and microspectrometer operate on the laptop's internal battery. The experimental results and the assessment of the power supply autonomy clearly demonstrate that the solar-powered experimental setup is feasible both for the *on-site* μ-SPE sample preconcentration step and for the *ex-situ* analytical measurements. Since the SSETV-μCCP-OES instrument is portable, both the μ-SPE preconcentration and *on-site* sample processing steps, as well as the actual analysis, can be performed *on-site* with a total autonomy of approximately 16 hours (two working days of 8 hours each).

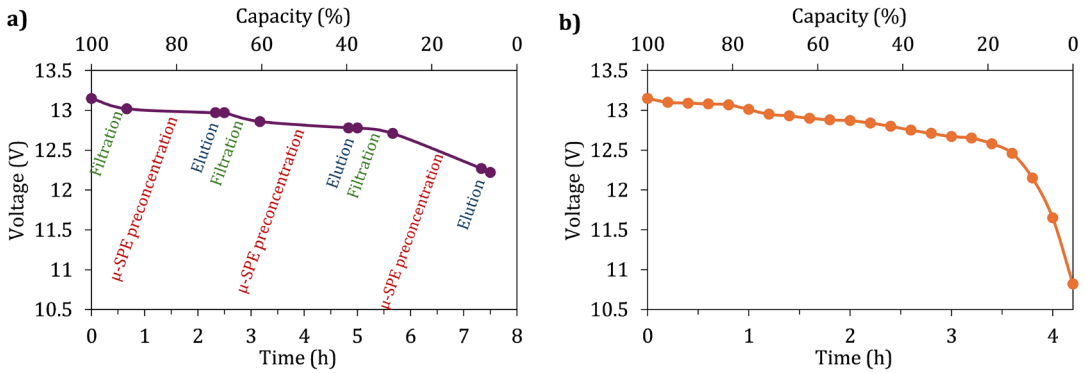

Figure 2. Energy consumption for *on-site* μ-SPE preconcentration (a) and for powering the SSETV-μCCP-OES instrument (b) from the battery charged by the photovoltaic panel

Results: *On-site* implementation of a portable, self-sustained system for multielement preconcentration of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} from surface water samples on dithizone-functionalized C18 μ-SPE cartridges.