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On-site battery-operated micro-solid phase extraction of Cu(II), Cd(II), Pb(II) and Zn(II) from river water followed by *ex-situ* small-sized electrothermal vaporization capacitively coupled microplasma optical emission spectrometry determination

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The development of analytical methods aligned with the principles of Green and White Analytical Chemistry for the determination of priority hazardous metals, such as Cd and Pb, remains a significant challenge due to their ultra-trace concentration levels and the need for highly sensitive yet sustainable methodologies. Thus, the aim of this study was the development of a battery-operated *on-site* micro-solid phase extraction (μ-SPE) system based on dithizone-functionalized C18 cartridges coupled with *ex-situ* small-sized electrothermal vaporization capacitively coupled plasma optical emission spectrometry (SSETV–μCCP–OES) for the simultaneous determination of Cd(II), Cu(II), Pb(II), and Zn(II) in river water. The μ-SPE procedure was optimized in terms of immobilized dithizone quantity on the C18 cartridge, sample pH and flow rate during preconcentration and eluent composition and volume. The accuracy (recovery and precision) of the method was evaluated by analyzing several water certified reference materials (CRMs), obtaining recoveries in the range 93–108%, and precision of 11–15%, respectively. The *ex-situ* optimized method was then applied for *on-site* river water processing, powered by a photovoltaic panel-charged battery, followed by *ex-situ* simultaneous determination of Cd(II), Cu(II), Pb(II), and Zn(II) using the fully miniaturized SSETV–μCCP–OES system, characterized by low power (15 W) and low Ar consumption (150 mL min^{-1}). The proposed approach provides a portable, energy-autonomous, and cost-effective alternative for sustainable ultra-trace metal monitoring in surface waters, compared to classical benchtop laboratory instrumentation.

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