New approach for determination of Cd, Cu, Cr, Ni, Pb, and Zn in sewage sludges, fired brick, and sediments using two analytical methods by microwave-induced plasma optical spectrometry and induced coupled plasma optical spectrometry

Fabienne Baraud¹ · Ali Zaiter^{1,2} · Sandra Porée¹ · Lydia Leleyter¹

Received: 11 March 2020 / Accepted: 16 July 2020 / Published online: 19 August 2020
© Springer Nature Switzerland AG 2020

Abstract

Microwave-induced plasma optical spectrometry (MIP OES) and induced coupled plasma optical spectrometry (ICP OES) were implemented in parallel for the determination of Cd, Cu, Cr, Ni, Pb, and Zn in sediments, as well as in unexplored matrices such as sewage sludge and fired brick. Initially, a microwave-assisted digestion procedure was applied to solubilize the samples. A selective approach has recommended for the detection of elements with low and high concentration ranges in different environments to improve sensitivity. Limit of detection (LOD) and limit of quantification (LOQ) were found between 0.026–0.039 mg L⁻¹ and 0.08–0.11 mg L⁻¹, respectively. Precision and trueness were controlled using certified reference materials with the same matrices for all analysts. MIP OES showed results in accordance with ICP OES and LOD in the same range (or better, i.e., Pb) than ICP OES. MIP OES found a potential alternative with comparable performance and reduced costs for the analysis of trace metals.

Keywords Sewage sludge · Brick · Trace metals · MIP OES · ICP OES

1 Introduction

The elemental analysis makes it possible to determine the contents of a given chemical element in a matrix, independently of its chemical speciation. Many analytical tools exist, depending on the nature and range of concentrations sought. In this field, the spectrometric methods have particularly developed. Increasingly sensitive techniques made it possible to accurately detect elements at trace or ultra-trace levels. The metallic trace elements are naturally occurring in soils, sediments, and rocks at levels < 0.1%. Some of them are essential to life, but all are potentially toxic from a certain dose,

the toxicity also depending on their chemical speciation [1]. The massive use of these elements by humans led to an increase in their levels in the various environmental compartments (air, soil, water, sediment, biota, etc.). The health and environmental impacts related to these pollutants and their transfers are the subject of numerous studies, to get a better knowledge of the contents in different environments, or of the mechanisms that link chemical speciation, mobility, toxicity, etc. In the literature, the frequently used analytical tools are techniques such as AAS (atomic absorption spectrometry), ICP-MS (inductively coupled plasma mass spectrometry), and ICP-OES: inductively coupled plasma optical emission

Fabienne Baraud and Ali Zaiter are the first authors of this article and have contributed equally.

✉ Fabienne Baraud, fabienne.baraud@unicaen.fr; ✉ Ali Zaiter, ali.zaiter@univ-lorraine.fr; Lydia Leleyter, lydia.reinert@unicaen.fr |

¹Normandie Univ, UNICAEN, ABTE EA 4651, Boulevard du maréchal Juin, Bât Sciences 2, 14032 Caen Cedex, France. ²Université de Lorraine, Laboratoire de Chimie et Physique – Approche Multi-échelles des Milieux Complexes (LCP-A2MC), 57000 Metz, France.

SN Applied Sciences (2020) 2:1536 | <https://doi.org/10.1007/s42452-020-03220-0>

spectrometry also known as ICP AES inductively coupled plasma atomic emission spectrometry. Many standardized procedures for elementary analysis also refer to them; thus, reference ICP OES is widely used in the routine analysis in different fields such as geochemical, environmental, food, and fuel [2]. The interest of the ICP OES or ICP-MS techniques is related to their multi-element processing, unlike the AAS. On the other hand, analyses by ICP-MS or ICP OES are more expensive due to higher costs of the devices and operating conditions (i.e., consumption of argon for the formation and maintenance of plasma for ICP OES and ICP-MS). Since 2011, the appearance of the MP-AES (microwave plasma atomic emission spectrometry also named microwave-induced plasma optical spectrometry) has complemented this range of tools. This instrument, with an affordable acquisition cost, enables a multi-element analysis of major element and trace elements. It avoids the costs/hazards associated with the use of gases (flammable and/or expensive gases, handling of gas cylinders) since the plasma is obtained from N₂, which can be produced from compressed air by a nitrogen generator connected to the device. The use of an auto sampler also makes it possible to optimize the analytical costs. The acquisition of data in ICP OES is simultaneous: it is, therefore, rare to use this tool for the analysis of only one or a few elements. Similarly, it is rare to start the apparatus for a small number of samples concerning the cost related to the formation and maintenance of the plasma. Conversely, the MIP OES operates in sequential mode and has almost no cost in terms of gas. Its use for the analysis of one or a few elements and/or few samples is more common. However, the sequential measurements can constitute one drawback as that the time and solution volume spent in processing them is separate for each metal, as noticed by Vural et al. [3].

Since 2012, several studies have investigated the performance of this new tool with various applications in terms of elements and matrices [4]. Table 1 reports the nature of matrices and elements for some studies in which at least one of the following elements Cd, Cr, Cu, Ni, Pb, and Zn was analyzed by MIP OES. The use of MIP OES is increasingly noted in the literature, for extremely diverse applications (Table 1). The technique was applied for the analysis of foodstuff, textiles, plants, fuels, soils, sediments, ores, etc. However, some of these studies do not indicate the operating conditions and do not provide any evidence as to the quality of the results obtained. Thus, detailed comparative studies in terms of procedures and performances have been carried out on various matrices, but often on a limited number of analytes. Studies comparing the results obtained by MIP OES and other techniques are, however, rather few, particularly when focusing on the elements Cd,

Cr, Cu, Cd, Ni, Pb, and Zn. A few studies offer comparisons with the results obtained by ICP OES [5, 6], but again, the number of analytes and/or matrices and is often restricted.

To our knowledge, fired brick has never been analyzed by MIP OES and the analysis of sewage sludge was only reported in an application note from the manufacturer (but Cd, Ni, and Pb were not measured) [7]. In this paper, our interest focuses on the analysis of Cd, Cr, Cu, Ni, Pb, and Zn in acid digests of various matrices: marine/estuarine sediments, sewage sludge, and fired brick. Ketheesan et al. [8] mentioned the analysis of the residual sewage sludge obtained after a sequential extraction procedure prepared, but only Fe was analyzed and not the other elements analyzed in our study. We conducted the analyses in parallel using MIP OES and ICP OES, to compare the methods and performances of both techniques. Tables 1 and 2 show that the different studies were performed with various instruments with different wavelengths. However, the purpose of our investigation was to close gaps that were revealed in the literature.

2 Materials and methods

2.1 Samples

Three different materials were analyzed to obtain the total content in Cd, Cr, Cu, Ni, Pb, and Zn. A sewage sludge was collected from a sewage treatment plant in Normandy, France. The sludge was sampled in the greenhouse and disposed after centrifugation for further and final drying. Back to the laboratory, the sludge dried at 40 °C until constant weight. The dried sludge then grinded for 15 min using an IKA crusher (IKA® Tube Mill Control) and finally stored in polyethylene vessels at 4 °C.

River sediment collected from the Seine River (France), near the harbor of Rouen. The sediment was homogenized, air-dried for 4 days, and grinded manually using an agate pestle and mortar, due to the particle solidity. The final sample materials stored at 4 °C for the further analysis of fired bricks (third material). Two samples were analyzed: BC (commercial fired brick) manufactured in France while BL (brick prepared in the laboratory). Both bricks were grinded and stored at 4 °C.

Certified reference materials were also used to ascertain the accuracy and precision of the methods. The HR-1 CRM is harbor sediment from the mouth of the Humber River (Ontario) and was obtained from Environment Canada (but Cd is non-certified for this one). The TH-2 CRM (purchased from Environmental and Climate Change Canada) is harbor sediment collected in Lake Ontario. The CRM031 is domestic sewage sludge purchased from Sigma-Aldrich.

Table 1 Nature of the samples and elements analyzed (including at least one of the following elements: Cd, Cr, Cu, Ni, Pb, and Zn) with MIP OES based on the literature study

Ref.	Sample	Element(s)	Comparison with:
[2]	Gasoline, ethanol fuel	Cr, Ni, Pb, V	–
[5]	Animal feed, fertilizers	Cu, Fe, Mn, Zn	ICP OES and AAS
[9]	Sunflower acid digests	Ca, K, Mg, Na, Al, Fe, Mn, As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, V, Zn	ICP-MS
[10]	Geological samples	Ag, Al, B, Ba, Bi, Ca, Cd, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sr, Ti, Zn	XRF and AAS
[11]	Textile fibers	Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Ti, Zn	–
[6]	Leather and fur, acid digestion	Cd, Co, Cr, Cu, Hg, Ni, Pb	ICP OES
[12]	Dragonfly larvae	Al, Ba, Cr, Fe, Mn, Pb, Sr, Zn	–
[3]	Soil	Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn	–
[13]	Fruit liquors	Cu, Ca, Mg, Na, K, Fe, Zn, Mn, P, Cd, Pb	–
[14]	Fish tissue	Ca, K, Mg, Na, Cd, Cr, Cu, Fe, Mn, Pb, Sr, Zn	–
[15]	Rice	Al, B, Ca, Cu, Co, Cr, Fe, K, Mg, Mn, Mo, Na, Ni, Zn	–
[16]	Environmental samples	Al, As, B, Ba, Ca, Cr, Cu, Fe, K, Mn, Na, Ni, Pb, Zn	ICP-MS
[17]	Synthetic solutions	Cd, Cu, Zn, Pb	–
[18]	Catalyst	Ni	–
[19]	Bioglass microcomposite scaffolds	Si, Ca, Zn, Ga	–
[20]	Soil and plants	Na, Cu	–
[21]	Surface sediment	Al, Cr, Cu, Fe, Mn, Pb, Zn	–
[22]	Acid and basic solution	Cu	–
[23]	Stock solutions	Cd, Cr, Cu, Pb, Zn	–
[24]	River water and sediment	Al, Cu, Mn, Fe, Ni, Zn, Cr, Pb, As, Se	–
[25]	Ground beetles	Al, Ba, Cd, Cu, Fe, Mn, Ni, Pb, Sr, Zn	–
[26]	Dust and leaves	Al, Ba, Cd, Cr, Fe, Na, Pb, Si, Sr, Zn	–
[27]	Leachates of pond ash samples	Cr, Mn, Pb, Zn, Cu, Ni, Co	–
[28]	Solution from the ion release of composite scaffolds	Si, Ca, Zn, Ga	–
[29]	Roasted V slag and slime	V, Cr, Mn, Fe	–
[30]	Synthetic solutions and wastewater	Cd, Pb, Cu, Zn	–
[31]	Aquaculture water-solids in wastewater	Fe, Zn, Mo, Na, Ni, Mg K	–
[32]	Fish sample	Fe, Zn	–
[33]	Aqueous solution	Pb	–
[34]	Glass polyalkenoate cement loaded with bone morphogenic proteins	Sr, Si, Ca, Zn	–
[35]	Solution	As, Cd, Cr, Cu, Mg, Ni, Pb, Zn	–
[36]	Aqueous solution	Ca, Zn, Cd, Cu, Ni, Pb, Cr	–
[37]	Mix of food waste and sewage sludge	Al, Cu, Mn, Zn, Mo, K, Cd, Co, Cr, Pb, Ni, Hg, As	–
[38]	Ores	Al, As, Ca, Co, Cr, Fe, K, Mg, Mn, Na, Ni, Ti V, Zn	–
[39]	Wastewater	Cu, Co, Fe, Mo, Mn, K, Mg, Zn, Na	–
[40]	River water and soil	Al, Cd, Cu, Ni, Pb, Zn	–
[41]	Soil	Zn, Al, Fe, Mn	–
[42]	Solution, biosolid	Zn	–
[43]	Plankton	Zn, Cd, Pb, Cu, Fe, Cr	–
[44]	Sediment	Cd, Cr, Cu, Ni, Pb, Zn	–
[45]	Fungi	Cd, Cu, Cr, Ni, Pb, Zn	–
[46]	Cotton plant and soil	As, Cr, Cu, Mn, Sr	–
[47]	Water samples	Zn, Cd, Fe, Cu, Ni, As, Hg, Co, Pb, Cr	–
[48]	Water	Cu, Pb, Zn	–
[49]	MCM-41 surface material	Cd, Cr, Cu, Pb, Zn	–
[50]	River water	Ba, Cr, Fe, Pb, Zn	–

Table 1 (continued)

Ref.	Sample	Element(s)	Comparison with:
[51]	Fruits, fruit juices	K, Ca, Mg, B, Fe, Cu, Zn , Mn	–
[52]	Plant samples	P, K, Ca, Mg, Na, Fe, Cu , Co, B, Mn, Mo, Zn , Al	–
[53]	Dust samples	Fe, Ca, Zn, Cu , Al, Pb , Co, Ni , Mn, Cr , Ba, Na	–
[54]	Aqueous samples	Cd, Cr, Cu, Pb, Zn	–
[55]	Ground nut seed-soil	Ca, Mg, Mn, Zn	–
[56]	Chinese hamster ovary cells	Mn, Zn	–
[57]	Soil and plant	Zn, Cd , Co, Cu, Ni, Pb , Mn, Cr , Fe, Ca, Mg	–
[58]	Soil	Ca, Mg, Fe, Al, Cu , Co, Ni	–
[59]	Soil	Cd, Pb, Cu	–

Table 2 Wavelengths selected for the elements (Cd, Cr, Cu, Ni, Pb, and Zn) analyzed with MIP OES based

Ref.	Wavelengths (nm)					
	Cd	Cr	Cu	Ni	Pb	Zn
[2]		42.433		352.456		405.781
[5]			324.754			213.857
[9]	226.502	357.858	324.754	352.454	368.346	213.857
	228.802	425.433	327.395	341.476	405.781	481.853
[10]	228.802	425.433	324.754	352.454	405.781	213.857
[11]	228.802	425.433	324.754	352.454	405.781	213.857
[6]	228.802	425.433	324.754	352.454	405.781	
[12]		4,25,433	3,24,754		405.781	213.857
[3]	228.802	425.433	324.754	352.454	405.781	213.857
[13]	226.502		324.754		368.346	213.857
[14]	228.802	425.433	324.754		405.781	481.053
[15]			324.754	352.454		213.857

2.1.1 Samples preparation

All the materials were digested before the analysis, microwave-assisted acid digestions performed in Teflon® reactors using a Berghof Speedwave MWS-2 microwave oven, and all the reagents were in analytical grade. The deionized water with a resistivity of 18.2 MΩ was produced by a Milli-Q water system (MAXIMA). A standard stock solution of 1000 mg L⁻¹ (Agilent) was used for all the elements calibration. Glassware and plastic materials (including the 50 mL polyethylene vessels used for storage) were pre-soaked for 24 h in 10% v/v HNO₃ and rinsed with deionized water.

Digestion procedure applied to the samples and certified materials: 0.2 g (sediment) or 0.5 g (sludge, brick) of dried sample was digested with 10 mL of HNO₃ (sludge) or of aqua regia (HCl/HNO₃ v/v = 3:1) (sediment and brick). The heating program consisted of 3 (sludge) or 4 (sediment, brick) steps with maximum temperature up to 175 °C for 10 to 15 min. The obtained digests were then transferred and completed to 50 mL in a volumetric flask with deionized water. After filtration at 0.45 μm, the digest

solutions were stored in polyethylene vessels at 4 °C before chemical analysis. Each digestion was performed in triplicate, and blank prepared with the same medium. Each replicate of each acid digest obtained from the various samples (sediment or brick or sludge or CRM) was furtherly analyzed by MIP OES and by ICP OES.

2.2 Instrumental apparatus

Determinations of the Cd, Cr, Cu, Ni, Pb, and Zn in the digests previously prepared were performed using a microwave-plasma atomic emission spectrometer (MIP OES) and an inductively coupled plasma atomic emission spectrometer (ICP OES). An Agilent 5100 ICP OES was used for the determination of the elemental concentrations. The operating conditions are reported in Table 3.

The used microwave-plasma atomic emission spectrometer was an Agilent 4200 MIP OES. The N₂-based plasma was operated from the compressed air supply and a nitrogen generator (Agilent 4107). An autosampler (Agilent SP4), an OneNeb concentric nebulizer, and a double pass spray chamber were used. The instrument software

Table 3 Operating conditions of the analytical instruments

Equipments		
Agilent 4200 MP-AES		Agilent 5100 ICP-AES
Autosampler SP4 Agilent		Autosampler SP4 Agilent
MP Expert software (Agilent) Agilent 4107 N ₂ generator		ICP Expert Software (Agilent) with Argon gas
Acquisition parameters		
	ICP OES	MIP OES
Sample uptake delay	50 s	20 s
Stabilization time	15 s	15 s
Read time	3/5 s	20 s
Number of replicates	3	3
Analytes wavelengths (nm)		
	ICP OES	MIP OES
Cd	228.802	228.802
Cr	425.433	267.716
Cu	324.754	324.754
Ni	352.454	216.555
Pb	283.305 // 405.781	220.353
Zn	213.857	213.857

(MP Expert) was allowed to optimize automatically some instrumental parameters (i.e., torch alignment and wavelength calibration by using a wavelength calibration solution (Agilent) as well as nebulizer gas pressure and was also used for automatic background correction or FLIC (Fast Linear Interference Correction) correction, when it was necessary. The MIP OES conditions are summarized in Table 3.

For both devices, each elemental concentration was estimated from its respective calibration curve. A multi-elemental standard solution (Agilent) was used to prepare the calibration solutions (concentration range 0–5 or 10 mg L⁻¹ depending on elements and instruments, in 5% v/v HNO₃).

3 Results and discussion

In Table 3, the wavelengths are selected for each element and technique, to get the best sensitivity for the minimum interferences. The same wavelengths were selected for MIP OES and ICP OES (except for Cr and Pb, optimized routinely with different sensitivity and possible interferences); the sensitivity of the elements depends on many instrument parameters and matrices. The wavelengths selected for MIP OES are the most frequently reported in the literature (Table 2). Some other lines are sometimes chosen, i.e., 226.502 nm for Cd and 368.346 nm for Pb [13], 405.781 nm [2], or 481.053 nm [14] for Zn. Two lines per element can be

selected for the measurements, particularly when interferences were suspected. Similarly, Karlsson et al. [9] selected two lines for each element they analyzed. They discarded the Pb line at 283.305 nm that presented interferences with Cr and Fe, which then required a FLIC correction. The analytical lines were chosen for optimal sensitivity using certified reference materials matrices (sediment, sludge, and brick).

The calibration curve range was 0–5 mg L⁻¹ for each element analyzed with MIP OES with ICP OES. A linear or rational calibration curve could be selected for each instrument, according to the R² values. The linear curves were chosen without any exception for both instruments. The R² values obtained for the linear calibration range are reported in Table 4 and were greater than 0.9984 for all analyses, as described also by Niedzielsky et al. [10].

3.1 Limits of detection and limits of quantification

For the ICP OES and MIP OES, the instrumental limits of detection (LOD) and limits of quantification (LOQ), for the different elements of interest, were estimated via the calibration curves approach, as well as were obtained using certified standard materials with the same medium. The LOD and LOQ were calculated as $3\sigma/a$ and $10\sigma/a$ of calibration graph, respectively, with σ being the standard deviation of the regression line/intercept and a is the slope of the calibration curve [13, 60]. The LODs and LOQs values are reported in Table 4.

Table 4 Limits of detection and quantification calculated by calibration curves (R^2 , LOD, and LOQ in mg L^{-1})

	MIP OES			ICP OES		
	LOD	LOQ	R^2	LOD	LOQ	R^2
Cd	0.0329	0.1098	0.999	0.0046	0.0154	0.9991
Cr	0.0388	0.1294	0.9984	0.0634	0.2114	0.9994
Cu	0.0327	0.1091	0.9994	0.0282	0.0939	0.9999
Ni	0.0335	0.1116	0.9989	0.0523	0.1743	0.9991
Pb	0.0288	0.0959	0.9992	0.3451	1.1503	0.9989
Zn	0.026	0.0865	0.9997	0.0709	0.2362	0.9993

As reported by Li et al. [5], the LOD and LOQ values estimated by both techniques were comparable, suggesting comparable performances for both devices. Moreover, it can be noticed that, except for Cd, the estimated LOD and LOQ for MIP OES are lower (or very close to for Cu) than for ICP OES. Such observations, for various elements, have been reported by several authors: Li et al. [5] for Mn, Zhao et al. [6] for Ni and Pb, or Donati et al. [2] for Cr, Ni, and Pb. Donati et al. [2] proposed several hypotheses to support such observations. They mentioned the influence of the integration time and sample introduction/nebulization system. They also referred to the fact that contrary to ICP OES, that collects emission signals simultaneously, with a radial and axial view, then at one plasma position for all the lines and elements, the MIP OES allows collecting emission signals at different (then optimized) position in the plasma for each emission line (atomic and ionic lines realized to obtain the concentrations). As already reported by previous authors, the MIP OES is not superior performance than ICP OES. The nitrogen plasma temperature is lower (5000 K) compared with argon plasma (6000–10,000 K), and the resulting lower sensitivities. Also, the MIP OES detection system is more straightforward than ICP OES. The commercial MIP OES instrument is based on a Czerny–Turner monochromator (600 mm focal length) and a back-thinned Peltier-cooled charge-coupled device (CCD) detector. The MIP OES instrument has been optimized for many analyses in large material matrices and routine applications.

3.2 Samples analysis

3.2.1 Analysis of certified reference materials

The analysis of the three certified reference materials was performed to test the accuracy of the methods. The results determined were satisfying for both instruments. The detected values were generally within the uncertainty limits of the certified values at 95% confidence level (Fig. 1). Mainly, such results validate the various digestion procedures applied; they also confirm the analytical techniques. Indeed, even if all measured values were of

Fig. 1 Tests using certified reference materials **a** sludge; **b** TH2 sediment; **c** HR1 sediment (the found values by ICP OES or MIP OES are the mean $\pm$ SD of three parallel determinations; variations between instruments were statistically significant ($p < 0.05$))

the same order of magnitude than the certified values, it could be observed that MIP OES slightly overestimated Cr levels in the sludge and TH2 CRM, overestimated Pb. Meanwhile, it underestimated Zn in the sludge, whereas ICP OES overestimated Cu and Zn in the sludge. Such differences could be attributed to the analytical instrument, related to the ionization mode, parameters, etc. However, the recoveries are satisfying for all the tested elements and CRM. Finally, the results demonstrated the ability of the MIP OES to accurately determine Cd, Cr, Cu, Ni, Pb, and Zn in estuarine or marine sediments and sewage sludges; the *t* test ($p < 0.05$) was performed for all the simple analysis.

3.2.2 Analysis of samples of sediments, bricks, and sewage sludge

The various samples (domestic sludge, estuarine sediment, and fired brick) were analyzed, after acid digestion, by both MIP OES and ICP OES. The results are reported in Table 5.

The data obtained by both instruments and for all the tested samples (CRM included) were statistically analyzed. One-way ANOVA statistical analysis was performed to evaluate the statistical difference between the two sets of data obtained by MIP OES and ICP OES. Table 5 reports the probability of *p* values. The acquired results from MIP OES and ICP OES are considered different with $p < 0.05$.

The obtained results from MIP OES were very close to those obtained by ICP OES, which suggested that the analysis performance of MIP OES and ICP OES was comparable for the elements analyzed and the various matrix tested, as it was already reported. Donati et al. [2] concluded that the performance of MIP OES for determining Cr, Ni, Pb (and V) in gasoline was comparable if not better than ICP OES. Li et al. [5] also concluded to comparable performance of the two techniques, with respect to the tested matrices (animal feed and fertilizers digested or extracted in acids) for Zn and Cu, even if some individual *p* values were found < 0.05 (for one sample for Cu and one sample for Zn). Zhao et al. [6] compared the performance of MIP OES and ICP OES for the analysis of fur and leather acid digests, for the same trace elements Cd, Cr, Cu, Ni, and Pb (Zn excluded). They concluded to comparable performances even if, again, they noticed individual statistically significant differences for the two techniques for Pb (in two samples) Cu (in one sample) and Cr (in four samples), that they attributed to the inhomogeneity of their samples. Jung et al. [60], also compared the performance of the two instruments, but only for one element (Mn in wine) and also concluded that the sensitivity of MIP OES and ICP OES was comparable. We demonstrated that MIP OES elemental analyses are realizable in different matrices such as sludge, sediment, and bricks, with high efficacy. Although the plasma is less robust than an ICP OES,

Table 5 Comparison of analyses for different samples by MIP OES and ICP OES

	ICP OES		MIP OES		<i>p</i>
	mg kg ⁻¹	SD	mg kg ⁻¹	SD	
Cd					
Sludge	5.99	0.44	<	<	–
Brick 1	0.05	0.05	<	<	–
Brick 2	23.02	0.89	24.42	0.76	0,064
Sediment	6.53	1.4	<	<	–
Cr					
Sludge	76.67	0.61	87.66	2.38	0.005
Brick 1	66.02	1.57	74.27	1.35	0.073
Brick 2	116.18	5.98	189.5	17.08	0
Sediment	17.81	1.67	24.67	2.25	0.013
Cu					
Sludge	130.16	2.68	132.7	1.66	0.347
Brick 1	3.04	0.1	3.79	0.02	0.017
Brick 2	89.42	2.65	92.59	5.05	0.138
Sediment	15.35	1.58	16.33	1.23	0.444
Ni					
Sludge	54.79	0.66	32.72	0.5	<0.001
Brick 1	23.19	0.76	23.98	0.93	0.607
Brick 2	40.9	2.19	37.39	0.99	0.001
Sediment	8.41	0.39	<	<	–
Pb					
Sludge	20.98	0.31	28.32	0.01	0.012
Brick 1	2.33	0.33	2.84	0.01	0.268
Brick 2	60.28	2.68	94.25	3.45	<0.001
Sediment	19.93	1.07	39.2	1.89	<0.001
Zn					
Sludge	417.08	12.47	402.66	2.97	0.244
Brick 1	10.22	1	7.56	5.67	0.277
Brick 2	322.8	5.01	272.54	26.3	0.001
Sediment	102.26	2.1	54.72	1.47	0.001

<: concentration in the analyzed solution under the instrumental detection limit

(Variations between ICP OES and MIP OES were statistically significant ($p < 0.05$))

which requires matrix-matching calibration methods (e.g., standard additions) to ensure adequate accuracy when analyzing complex matrix samples [61, 62], MIP OES may be considered an attractive alternative to ICP OES for tailored applications when both proper operational conditions and calibrations strategies are adopted [63].

4 Conclusion

This study compared the concentrations of Cd, Cu, Cr, Ni, Pb, and Zn which were performed by ICP OES and MIP OES, in which acids (HNO₃ or *aqua regia*) digested the

samples of various nature (bricks, sediments, and sewage sludges). Similar performances of both devices were established for the studied trace elements, with better-observed LOD for MIP OES regarding all the tested elements, except for Cd. The results obtained by MIP OES and ICP OES were very comparable, and the differences somehow observed were acceptable. MIP OES appeared as ultimately suitable to analyze the trace elements (Cd, Cu, Cr, Ni, Pb, and Zn) in acid digests of sewage sludge and fired bricks. The cost reduction that is partly related to the absence of argon consumption is an added advantage, confirmed MIP OES as a good alternative instrument to ICP OES.

Funding This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interests.

References

- Koller M, Saleh HM (2018) Introductory chapter: introducing heavy metals. In: Saleh H, Aglan R (eds), Heavy metals. <https://doi.org/10.5772/intechopen.74783> (ISBN 978-1-78923-360-5)
- Donati GL, Amais RS, Schiavo D, Nobrega JA (2013) Determination of Cr, Ni, Pb and V in gasoline and ethanol fuel by microwave plasma optical emission spectrometry. *J Anal At Spectrom* 28:755–759
- Vural A, Gundogdu A, Akpinar I, Baltaci C (2017) Environmental impact of Gümüşhane City, Turkey, waste area in terms of heavy metal pollution. *Nat Hazards* 88:867–890
- Williams CB, Amais RS, Fontoura BM, Jones BT, Nobrega JA, Donati JL (2019) Recent developments in microwave-induced plasma optical spectrometry and applications of a commercial Hammer-cavity instrument. *Trends Anal Chem* 116:151–157
- Li W, Simmons P, Shrader D, Herrman TJ, Dai SY (2013) Microwave plasma-atomic emission spectroscopy as a tool for the determination of copper, iron, manganese and zinc in animal feed and fertilizer. *Talanta* 112:43–48
- Zhao Y, Li Z, Ross A, Huang Z, Chang W, Ou-yang K, Chen Y, Wu C (2015) Determination of heavy metals in leather and fur by microwave plasma atomic emission spectrometry. *Spectrochimica Acta Part B* 112:6–9
- Drvodelic N (2015) Analysis of domestic sludge using the Agilent 4200 MP AES—application note—environmental, Publication Number :5991-6239EN, Agilent Technologies, Inc, 2015.
- Ketheesan B, Thanh PM, Stuckey DC (2016) Iron deficiency and bioavailability in anaerobic batch and submerged membrane bioreactors (SAMBR) during organic shock loads. *Biores Technol* 211:136–145
- Karlsson S, Sjöberg V, Ogar A (2015) Comparison of MIP OES and ICP-MS for analysis of principal and selected trace elements in nitric acid digests. *Talanta* 135:124–132
- Niedzielski P, Kozak L, Wachelka M, Jakubowski K, Wybieralska J (2015) The microwave induced plasma with optical emission spectrometry (MIP-OES) in 23 elements determination in geological samples. *Talanta* 132:591–599
- Sungur F, Gülmez F (2015) Determination of metal contents of various fibers used in textile industry by MP AES. *J Spectrosc.* <https://doi.org/10.1155/2015/640271>
- Simon E, Kis O, Jakab T, Kolozsvári I, Málnás K, Harangi S, Baranyai E, Miskolczi M, Tóthmérész B, Dévai G (2017) Assessment of contamination based on trace element concentrations in *Gomphus flavipes* (Odonata: Insect) larvae of the Upper Tisza Region. *Ecotoxicol Environ Saf* 136:55–61
- Rodríguez-Solana R, Carlier JD, Costa MC, Romano A (2018) Multi-element characterisation of carob, fig and almond liqueurs by MIP OES. *J Inst Brew* 124:300–309. <https://doi.org/10.1002/jib.495>
- Nyeste K, Dobrocsi P, Czeglédi I, Czédli H, Harangi S, Baranyai E, Simon E, Nagy SA, Antal L (2019) Age and diet-specific trace element accumulation patterns in different tissues of chub (*Squalius cephalus*): Juveniles are useful bioindicators of recent pollution. *Ecol Ind* 101:1–10
- Ozbek N, Tinas H, Atespare AE (2019) A procedure for the determination of trace metals in rice varieties using microwave induced plasma atomic emission spectrometry. *Microchem J* 144:474–478
- Kamala CT, Balaram V, Dharmendra V, Satyanarayanan M, Subramanyam KSV, Krishnaiah A (2014) Application of microwave plasma atomic emission spectrometry (MP AES) for environmental monitoring of industrially contaminated sites in Hyderabad City. *Environ Monit Assess* 186:7097–7113
- Abdolali A, Hao Ngo H, Guo W, Zhou JL, Du B, Wei Q, Wang XC, Dan Nguyen P (2015) Characterization of a multi-metal binding biosorbent: chemical modification and desorption studies. *Biores Tech* 193:477–487
- Karthikeyan J, Song H, Olsbye U, Fjellvag H, Olafsen Sjøstad A (2015) Supported nickel based catalysts, Ni/Mg(Al)O, for natural gas conversion, prepared via delamination and restacking of MgAl- and NiAl-nanosheets. *Top Catal* 58:877–886
- Zeimaran E, Pourshahrestani S, Pingguan-Murphy B, Kadri NA, Rothan HA, Yusof R, Towler MR, Djordjevic I (2015) Fabrication and characterization of poly(octanediol citrate)/gallium-containing bioglass microcomposite scaffolds. *J Mater Sci* 50:2189–2201
- Sacristán D, Recatalá L, Viscarra Rossel RA (2015) Toxicity and bioaccumulation of Cu in an accumulator crop (*Lactuca sativa* L.) in different Australian agricultural soils. *Sci Horticul* 193:346–352
- Balogh Z, Harangi S, Kundrát JT, Gyulai I, Tóthmérész B, Simon E (2016) Effects of anthropogenic activities on the elemental concentration in surface sediment of oxbows. *Water Air Soil Pollut* 227:13. <https://doi.org/10.1007/s11270-015-2714-x>
- Garifzyanov AR, Chibirev EO, Cherkasov MR, Cherkasov RA (2016) Liquid-liquid extraction of copper(II) ions with a novel aminophosphoryl extractant, 2-ethylhexyl hydrogen {[Bis(2-ethylhexyl)amino]methyl}phosphonate. *Russ J Gen Chem* 86(12):2723–2724
- Olah V, Hepp A, Mészáros I (2016) Assessment of giant duckweed (*Spirodela polyrrhiza* L. Schleiden) turions as model objects in ecotoxicological applications. *Bull Environ Contam Toxicol* 96:596–601
- Sim SF, Chai HP, Nyanti L, Ling TY, Grinang J (2016) Baseline trace metals in water and sediment of the Baleh River—a tropical river in Sarawak, Malaysia. *Environ Monit Assess* 188:537
- Simon E, Harangi S, Baranyai E, Braun M, Fábrián I, Mizser S, Nagy L, Tóthmérész B (2016) Distribution of toxic elements between biotic and abiotic components of terrestrial ecosystem along an

- urbanization gradient: soil, leaf litter and ground beetles. *Ecol Indic* 60:258–264
26. Simon E, Harangi S, Baranyai E, Fábián I, Tóthmérész B (2016) Influence of past industry and urbanization on elemental concentrations in deposited dust and tree leaf tissue. *Urban For Urban Green* 20:12–19
 27. Suthar M, Aggarwal P (2016) Environmental impact and physicochemical assessment of pond ash for its potential application as a fill material. *Int J of Geosynth Ground Eng* 2:20
 28. Zeimaran E, Pourshahrestani S, Djordjevic I, Pingguan-Murphy B, Kadri NA, Wren AW, Towler MR (2016) Antibacterial properties of poly (octanediol citrate)/gallium containing bioglass composite scaffolds. *J Mater Sci Mater Med* 27:18
 29. Zhdanov PA, Seregina IF, Bol'shov MA, Volkov AI, Seregin AN (2016) Determination of forms of element occurrence in samples of vanadium slag and slime. *Inorgan Mater* 52(14):1431–1439
 30. Abdolali A, Hao Ngo H, Guo W, Zhou JL, Zhang J, Liang S, Chang SW, Duc Nguyen D, Liu Y (2017) Application of a breakthrough biosorbent for removing heavy metals from synthetic and real wastewaters in a lab-scale continuous fixed-bed column. *Biore-sour Technol* 229:78–87
 31. Guldhe A, Ansari FA, Singh P, Bux F (2017) Heterotrophic cultivation of microalgae using aquaculture wastewater: a biorefinery concept for biomass production and nutrient remediation. *Ecol Eng* 99:47–53
 32. Hermenean A, Gheorghiu G, Stan MS, Herman H, Onita B, Ardelean DP, Ardelean A, Braun M, Zsuga M, Kéki S, Costache M, Dinischiotu A (2017) Biochemical, histopathological and molecular responses in gills of *Leuciscus cephalus* exposed to metals. *Arch Environ Contam Toxicol* 73:607–618
 33. Ifthikar J, Wang J, Wang Q, Wang T, Wang H, Khan A, Jawad A, Sun T, Jiao X, Chen Z (2017) Highly efficient lead distribution by magnetic sewage sludge biochar: sorption mechanisms and bench applications. *Biores Technol* 238:399–406
 34. Jiráťová K, Balabánová J, Kovanda F, Klegová A, Obalová L, Fajgar R (2017) Cobalt oxides supported over ceria-zirconia coated cordierite monoliths as catalysts for deep oxidation of ethanol and N₂O decomposition. *Catal Lett* 147:1379–1391
 35. Lizama AC, Figueiras CC, Herrera RR, Pedreguera AZ, Ruiz Espinoza JE (2017) Effects of ultrasonic pretreatment on the solubilization and kinetic study of biogas production from anaerobic digestion of waste activated sludge. *Int Biodeteriorat Biodegrad* 123:1–9
 36. López-Maldonado EA, Zavala García OG, Cruz Escobedo K, Oropeza-Guzman MT (2017) Evaluation of the chelating performance of biopolyelectrolyte green complexes (NIBPEGCs) for wastewater treatment from the metal finishing industry. *J Hazard Mater* 335:18–27
 37. Ma Y, Yin Y, Liu Y (2017) New insights into co-digestion of activated sludge and food waste: biogas versus biofertilizer. *Biores Technol* 241:448–453
 38. Molnár Z, Polgári M, Hein JR, Józsa SR, Fekete J, Gyollai I, Fintor K, Bíró L, Szabó M, Rapi S, Forgó P, Vigh T (2017) Fe-Mn oxide indications in the feeder and mound zone of the Jurassic Mn-carbonate ore deposit, Úrkút, Hungary. *Ore Geol Rev* 86(2017):839–855
 39. Ramsundar P, Guldhe A, Singh P, Bux F (2017) Assessment of municipal wastewaters at various stages of treatment, process as potential growth media for *Chlorella sorokiniana* under, different modes of cultivation. *Biores Technol* 227:82–92
 40. Rennert T, Rinklebe J (2017) Modelling the potential mobility of Cd, Cu, Ni, Pb and Zn in Mollic Fluvisols. *Environ Geochem Health* 39:1291–1304
 41. Wisawapipat W, Janlaksana Y, Christl I (2017) Zinc solubility in tropical paddy soils: a multi-chemical extraction technique Study. *Geoderma* 301:1–10
 42. Zhang DQ, Eng CY, Stuckey DC, Zhou Y (2017) Effects of ZnO nanoparticle exposure on wastewater treatment and soluble microbial products (SMPs) in an anoxic-aerobic membrane bioreactor. *Chemosphere* 171:446–459
 43. Eken MD, Akman B (2018) Assessment of heavy metal pollution of seston from freshwater, resources poured into the Northeast Mediterranean region. *Environ Monit Assess* 190:308
 44. Eketi SI, Fred-Ahmadu OH, Adedapo AE, Benson NU (2018) Trace and major elements distribution in coastal sediment cores from Lagos Lagoon, Nigeria. *Data Brief* 19:93–100
 45. Gola D, Malik A, Namburath M, Ahammad SZ (2018) Removal of industrial dyes and heavy metals by *Beauveria bassiana*: FTIR, SEM, TEM and AFM investigations with Pb(II). *Environ Sci Pollut Res* 25:20486–20496
 46. Kaur R, Bhatti SS, Singh S, Singh J, Singh S (2018) Phytoremediation of heavy metals using cotton plant: a field analysis. *Bull Environ Contam Toxicol* 101:637–643
 47. Kumar A, Sharma S, Mehra R, Kanwar P, Mishra R, Kaur I (2018) Assessment of radon concentration and heavy metal contamination in groundwater of Udhampur district, Jammu & Kashmir, India. *Environ Geochem Health* 40:815–831
 48. Loganathan P, Shim WG, Sounthararajah DP, Kalaruban M, Saravanamuthu Vigneswaran TN (2018) Modelling equilibrium adsorption of single, binary, and ternary combinations of Cu, Pb, and Zn onto granular activated carbon. *Environ Sci Pollut Res* 25:16664–16675
 49. Machado Pereira Montenegro L, Vohlbrecht de Souza L, Lima KO, de Oliveira HPM, Fernandes AU, de Mattosmorawski F, Benvenutti EV, Arenas LT, Bianchini D (2018) Copper porphyrin immobilized on MCM-41 surface by using aminopropyl as coupling agent and its use in electrochemical oxygen determination. *J Inorganic Organometal Polym Mater* 28:2518–2524
 50. Marzola EL, Tavares Rosa LM, Hartung Toppa R, Martines MR, Machado Pitombo L, Cavagis ADM, Braga do Carmo J, Botero WG, de Oliveira LC (2019) Spatial modeling applied to environmental monitoring: identifying sources of potentially toxic metals in aquatic system. *Environ Geochem Health* 41(3):1339–1350. <https://doi.org/10.1007/s10653-018-0218-5>
 51. Meena NK, Asrey R (2018) Tree age affects postharvest attributes and mineral content in amrapali mango (*Mangifera indica*) fruits. *Horticult Plant J* 4(2):55–61
 52. Mia S, Dijkstra FA, Singh B (2018) Enhanced biological nitrogen fixation and competitive advantage of legumes in mixed pastures diminish with biochar aging. *Plant Soil* 424:639–651
 53. Mohsen M, Ahmed MB, Zhou JL (2018) Particulate matter concentrations and heavy metal contamination, levels in the railway transport system of Sydney, Australia. *Transport Res Part D* 62:112–124
 54. Nguyen TC, Loganathan P, Nguyen TV, Kandasamy J, Naidu R, Vigneswaran S (2018) Adsorptive removal of five heavy metals from water using blast furnace slag and fly ash. *Environ Sci Pollut Res* 25:20430–20438
 55. Pawar PB, Khadilkar JP, Kulkarni MV, Melo JS (2018) An approach to enhance nutritive quality of groundnut (*Arachis hypogaea* L.) seed oil through endo mycorrhizal fertigation. *Biocatal Agricult Biotechnol* 14:18–22
 56. Prabhu A, Gadre R, Gadgil M (2018) Zinc supplementation decreases galactosylation of recombinant IgG in CHO cells. *Appl Microbiol Biotechnol* 102:5989–5999
 57. Salihaj M, Bani A, Shahu E, Benizri E, Echevarria G (2018) Metal accumulation by the ultramafic flora of Kosovo. *Ecol Res* 33:687–703
 58. Baysal A, Saygin H, Ustabasi GS (2019) Influence of Al₂O₃ nanoparticles on the soil elements. *Bull Environ Contam Toxicol* 102:98–104

59. Pittarello M, Busato JG, Carletti P, Sodré FF, Dobbss LB (2019) Dissolved humic substances supplied as potential enhancers of Cu, Cd, and Pb adsorption by two different mangrove sediments. *J Soils Sediments* 19:1554–1565
 60. Jung MY, Kang JH, Choi YS, Lee DY, Lee JY, Park JS (2019) Analytical features of microwave plasma-atomic emission spectrometry (MP AES) for the quantitation of manganese (Mn) in wild grape (*Vitis coignetiae*) red wines: comparison with inductively coupled plasma-optical emission spectrometry (ICP-OES). *Food Chem* 274:20–25
 61. Gonçalves DA, McSweeney T, Donati GL (2016) Characteristics of a resonant iris microwave-induced nitrogen plasma. *J Anal At Spectrom* 31:1097–1104. <https://doi.org/10.1039/C6JA00066E>
 62. Chalyavi N, Doidge PS, Morrison RJS, Partridge GB (2017) Fundamental studies of an atmospheric-pressure microwave plasma sustained in nitrogen for atomic emission spectrometry. *J Anal At Spectrom* 32:1988–2002. <https://doi.org/10.1039/C7JA00159B>
 63. Williams CB, Jones BT, Donati GL, Amais RS, Fontoura BM, Nóbrega JA (2019) Recent developments in microwave-induced plasma optical emission spectrometry and applications of a commercial Hammer-cavity instrument. *Trends Anal Chem.* <https://doi.org/10.1016/j.trac.2019.05.007>
- Publisher's Note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.