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Scientific paper

Validation of High-Resolution Continuum Source Flame Atomic Absorption Spectrometry for Determination of Selected Toxic Metals in the Decontamination Process of Wastewater Discharged in Natural Receivers

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Abstract

A new method based on high-resolution continuum source flame atomic absorption spectrometry (HR-CS FAAS) was validated for the determination of selected toxic metals in wastewater resulting from mining activity, compared to inductively coupled plasma optical emission spectrometry (ICP-OES) and line-source flame atomic absorption spectrometry (LS FAAS). The HR-CS FAAS method was characterized by detection limits (LODs) in the range (μg L^{-1}) 1(Mn)–30(Pb), better than ICP-OES for Cu, Fe, Ni, Co, Pb and Mn, and poorer for Cd, Zn and Cr. Dunnett's test showed that both methods were not affected by significant bias against certified values. The recovery in the HR-CS FAAS method was in the range of 98–103% with relative extended uncertainty of 9–18% and precision of 2–11%. Compared to LS FAAS, the HR-CS FAAS presented better LODs for Pb and Cr. The HR-CS FAAS method is suitable for determining selected toxic elements in filtered water samples without any chemical treatment.

Keywords: High-resolution continuum source flame atomic absorption spectrometry, inductively coupled plasma optical emission spectrometry, toxic metal, water analysis, method validation

1. Introduction

Over the years, chemical analysis, particularly in the determination and monitoring of environmentally significant elements, such as toxic metals (e.g., Pb, Cr and Cu, among many others) has necessitated the need for continued development of new and improved methods.[1,2] Classically, line-source flame atomic absorption spectrometry (LS FAAS) has been one of the methods of choice for determining such elements, even after introducing the high-resolution continuum source flame atomic absorption spectrometry (HR-CS FAAS) method.[2,3] In order to make the AAS competitive, HR-CS FAAS was developed by Becker-Ross's team from Institut für Spektrochemie und Angewandte Spektroskopie (ISAS) (Berlin, Germany).[2] Several advantages are associated with HR-CS FAAS *versus* LS FAAS, which include: (i) improvement of detection in the far UV region (below 250 nm) through the use

of a xenon short-arc lamp; (ii) simultaneous elemental and background signal measurements that contribute to high signal-to-noise ratio; (iii) fast sequential multielemental determination and reduction of sample consumption and residue; (iv) determination of all elements by the use of the xenon short-arc lamp, including the simultaneous determination of a few elements, which have analytical lines that can be measured in the same spectral window that can be up to ± 1 nm, according to the wavelengths of the elements; (v) determination of trace elements using molecular absorption spectrometry at bands of some molecular radicals of elements; (vi) determination of anions, such as phosphate and nitrate, and non-metals, like halogens.[1,3,4] The decision to use the xenon short-arc lamp and a high-resolution spectrometer instead of a typical xenon lamp was determined by the need for intense primary radiation and to obtain a high sensitivity for determination by HR-CS FAAS.[3,5] Therefore, the HR-CS FAAS instrument has individual components specifically tailored to contribute to a highly effective and competitive method that can be on par with current analysis methods, usually based on inductively coupled plasma optical emission spectrometry (ICP-OES).[2] Some studies have presented the comparison between HR-CS FAAS and ICP-OES in determining hazardous metals in soil samples and report the new method as successful and comparable to the ICP-OES.[5,6–10] Determination of toxic elements, such as Cd, Pb and Cr, in water samples requires highly sensitive methods, such as ICP-OES with or without preconcentration,[11–13] inductively coupled plasma mass spectrometry (ICP-MS),[14–16] or electrochemical methods based on potentiometry and voltammetry.[17–19] Although methods based on ICP-OES and ICP-MS are highly sensitive and simultaneous with high speed of analysis, the instrumentation is costly and often difficult to access in routine (mostly under resourced) laboratories, despite the fact that both ICP-OES and ICP-MS are standardized for the determination of elements in water samples.[20,21] Electrochemical methods are simpler than the spectrometric ones, but they are single elemental and affected by matrix, which require the use of standard addition calibration method for their compensation.[17]

The LS FAAS is the most accessible standardized method for metal determination used in laboratories that do not require highly skilled analytical chemists. The relatively new HR-CS FAAS instrumental concept still needs to be validated for multielement analyses because the current standards do not refer to determining elements based on this concept.[22] Because HR-CS FAAS is rarely used in control laboratories versus HR GFAAS, it is interesting to check whether it can be used as an alternative to LS FAAS and ICP-OES to determine toxic metals in water/wastewater. The development and validation of analytical methods for multielemental determination in water samples based on relatively novel instrumental concepts are of broad scientific and social interest according to the water quality framework directive of the European Union.[23] Generally, the metals have been outlined as environmentally hazardous by the World Health Organization even at trace concentrations, and this is exacerbated by their ubiquitousness, non-biodegradability, and tendency to biomagnify in the food chain.[24–26] Some of these elements, such as Cd and Pb, are priority hazardous with high toxicity even at trace levels on humans, aquatic animals and plants, causing, among others, even cancer. On the other hand, Zn, Fe, Cu, Mn and Ni have been widely reported as micronutrients with biological importance to plant and animal life at trace levels. However, these metals could also become toxic if a certain concentration is exceeded.[27–33] Therefore, this work aimed to validate a multielemental method based on HR-CS FAAS for the determination of Cu, Fe, Ni, Cd, Co, Zn, Mn, Pb and Cr in waters sampled from wastewater treatment plants following Au, Ag, Cu, Zn and Pb non-ferrous ores mining and processing by extraction and roasting for metals. The figures of merit, namely the limits of detection (LODs), linearity of calibration curves, combined uncertainty in the laboratory ($u_{c\ lab}$), extended uncertainty in the laboratory (U_{lab}), and accuracy (recovery and precision), obtained in a performance study, were compared with those of ICP-OES method, in accordance with international regulations.[34–38] Also, the characteristic concentrations experimentally determined were compared with the data from the ContrAA 300 software and with those for conventional LS FAAS. The direct determination of the mentioned elements in the original filtered water, without any chemical pretreatment, such as acid digestion, was investigated. This study presents analytical relevance because the method developed on HR-CS FAAS should be evaluated in accordance with international legislation in order to be used later in official quality control laboratories.

2. Experimental

2. 1. Instrumentation

The ContrAA 300 high-resolution continuum source flame atomic absorption spectrometer manufactured by Analytik Jena AG (Jena, Germany) equipped with an air-acetylene flame was used for the multielemental determination in water. It is equipped with a compact high-resolution double monochromator (pre-prism monochromator and echelle monochromator), a linear charge-coupled device (CCD) as the detector and a xenon short-arc lamp that emits continuum radiation over a wide range of wavelength (185–900 nm) compared to specific hollow cathode lamps (HCLs). Thus, the fast-sequential determination of all elements is achievable using the Xe short-arc lamp, compared to the LS FAAS, which is a slow-sequential determination by selecting the corresponding single element HCL. The working conditions recommended by the manufacturer in order to obtain the best figures of merit for HR-CS FAAS ContrAA 300 spectrometer are outlined in Table 1.

Table 1. Optimum working conditions for the HR-CS FAAS ContrAA 300 spectrometer

Element	Wavelength (nm)	Wavelength range (nm)	Air (L h^{-1})	Acetylene (L h^{-1})	Burner Height (mm)
Cu	324.754	0.39	470	50	6
Fe	248.327	0.27	470	60	6
Ni	232.003	0.27	470	55	6
Cd	228.802	0.25	470	50	6
Co	240.725	0.28	470	50	6
Zn	213.857	0.23	470	50	6
Pb	217.001	0.25	470	65	6
Mn	279.482	0.33	470	80	6
Cr	357.869	0.40	400	100	8

Determinations by HR-CS FAAS were carried out at the principal analytical lines recommended by the instrument software, which ensures the best figures of merit. A LS FAAS spectrometer (PinAAcle 900T Perkin Elmer, Norwalk, USA), equipped with HCLs (Cu, Fe, Ni, Cd, Co, Zn, Mn and Cr) and electrodeless discharge lamps – EDLs (Cd, Pb), air-acetylene flame, high sensitivity nebulizer was used for comparison of LODs and characteristic concentration. The working conditions were the following: air flow rate 600 L h^{-1}, acetylene flow rate 150 L h^{-1}, slit 0.7 nm for Cd, Cr, Cu, Pb, Zn, and 0.2 nm for Co, Mn, Ni, HCLs current (mA) of (30)Co, (35)Cr, (15)Cu, (20)Mn, (25)Ni, (15)Zn, EDLs current (mA) of (230)Cd and (440) Pb. Measurements were carried out at the same wavelength as in the case of HR-CS FAAS, except for Pb, in which case 283.305 nm was used. Compared to the classical instrumentation with HCLs, in the case of HR-CS FAAS, the absorption spectrum is displayed over a range of between 0.23–0.40 nm (200 pixels), which increases with the element wavelength (Table 1). A number of 5 pixels (central pixel ± 2) in the middle of the spectral window were attributed to the analytical line, while the rest, on both sides of the analytical line, were used for the continuum background signal correction. The net signal was obtained through the difference between the total signal at the analytical line and the background signal. Thus, in the case of the HR-CS FAAS method, the simultaneous correction of the background with the measurement of the analytical signal is possible, which contributes to a better repeatability of the measurements. The fine background absorption spectrum and interference of NO on Zn 213.856 nm was avoided using the least square background correction offered by the instrument software, using as reference spectrum a solution of 2% (v/v) HNO_3 as blank. An example of the absorption spectrum of Cu 324.754 nm recorded in the optimum operating conditions (Table 1) is presented in Supplementary Material, Fig. S1.

The simultaneous Spectro Ciros^{CCD} (Spectro, Kleve, Germany) ICP-OES with axial plasma viewing was used for comparison. This simultaneous multielemental analysis equipment features 22 CCD detectors and was designed to ensure the best sensitivity without spectral interference. The best signal-to-noise (SNR) strategy was selected for measurements for an integration time of 48 s for the lines with the highest sensitivity. The background correction was achieved by the two-point model background strategy. The optimum operating conditions of the Spectro Ciros^{CCD} spectrometer are presented in Table 2.

Table 2. Operating conditions of the Spectro Ciros^{CCD} spectrometer

Parameter	Value
Plasma power (W)	1400
Radio frequency (MHz)	27.12
Outer Ar flow rate (L min^{-1})	12
Auxiliary Ar flow rate (L min^{-1})	0.6
Nebulizer Ar flow rate (L min^{-1})	1
3D torch position for axial viewing (mm)	x = –3.9, y = +3.6, z = +2.6 (for all elements)
Sample introduction (cross-flow nebulizer) (mL min^{-1})	2
Flushing time (s)	40
Delay time (s)	20
Elements wavelength (nm)	Cu 324.754; Fe 259.940; Ni 341.476; Cd 228.802; Co 237.862; Zn 213.857; Pb 220.351; Mn 260.569; Cr 267.716; Ca 422.673; Mg 285.213.

In the case of all three methods, the quantification of elements was achieved by external calibration using multielemental standards solution without appropriate sample matrix preparation. The concentrations of Na and K in the water samples as concomitants were determined by flame atomic emission spectrometry using the Sherwood Model 360 instrument (Cambridge, UK). Also, Ca and Mg determined by ICP-OES were considered as concomitant elements.

2. 2. Solutions, Reagents and Certified Reference Materials (CRMs)

Multielemental standard solution IV 1000 mg L^{-1} from Merck (Darmstadt, Germany) was used to prepare

the standard solutions up to 5000 μg L^{-1} for HR-CS FAAS/LS FAAS and 25000 μg L^{-1} for ICP-OES by serial dilution with 2% (v/v) HNO_3 starting from the smallest concentration presented in Table 3, near the limit of quantification (LOQ = 3.3 x LOD). These standards were used to establish the range of linearity of the calibration curves, and in which concentration range the proposed method could be used for the determination of selected elements in wastewaters. A 2% (v/v) HNO_3 solution was used as blank for background correction in the case of all three methods. Nitric acid 63% (m/m) for analysis was purchased from Merck (Darmstadt, Germany). Three water CRMs, namely TMDA-64.4 Lake Ontario water from Environment and Climate Change Canada (Burlington, ON, Canada), ERM® - CA713 wastewater and ERM® - CA615 groundwater from Institute for Reference Materials and Measurements (Geel, Belgium) were used to check the accuracy of the methods.

2. 3. Description of real test samples

Three real test water samples of 2 L each were collected using polyethylene bottles rinsed with ultrapure water. These were collected before and after decontamination of a plant treatment station of wastewater resulting from Au, Ag, Cu, Zn and Pb non-ferrous ores mining and processing by extraction and roasting for metals in the vicinity of Baia-Mare town, North-Western Romania, together with one sample from a natural receiver (river). This area is of particular interest because of the metal pollution that has previously been reported.[39,40] The samples were homogenized, filtered (0.45 μm), acidified with 2% (v/v) HNO_3 and the concentrations of Cu, Fe, Ni, Cd, Co, Pb, Zn, Mn and Cr were determined by HR-CS FAAS and ICP-OES using external calibration, without any chemical preliminary pretreatment.

2. 4. Strategy for Validation of HR-CS FAAS Method

The HR-CS FAAS method was validated by evaluating the LODs, accuracy (recovery and precision), and linearity of calibration curves compared with ICP-OES. The sensitivities of the HR-CS FAAS and LS FAAS methods were compared by the characteristic concentration (0.0044 (1% Abs)/slope of the calibration curve ratio), an essential parameter for methods based on AAS. The values of the experimental characteristic concentrations, determined from the calibration curves for HR-CS FAAS, were compared with the data from the ContrAA 300 software. This comparison is useful, because the operator can check if the instrument operates under optimum conditions. Additionally, the LODs were evaluated, because the values of this figure of merit depend both on the sensitivity and stability of analytical signal. The LODs in water samples were evaluated based on instrumental LODs according to the 3σ criterion (LOD = $3s_b/m$, where (s_b) is the standard deviation of the blank signal (n = 11) and (m) is the slope of the calibration curve).[41] Methods accuracy was checked by analyzing three CRMs by evaluating the mean recovery (n = 3 parallel measurements) and laboratory extended uncertainty ($U_{lab} = 2u_{c\,lab}$) of the found results and comparison with the certified values. The laboratory combined uncertainty ($u_{c\,lab} = \sqrt{\sum u_i^2}$) for each method was calculated based on individual uncertainties (u_i), namely uncertainty for the certified value ($u_{CRM} = U_{CRM}/2$), uncertainty of standards and sample preparation, calibration curve fitting and aliquots analysis. A relative value ($u_{rel\,lab}$(%)) was calculated for both methods using equation (1).

$$u_{rel\,lab} = \sqrt{u_{CRM}^2 + u_{ss}^2 + u_{sp}^2 + u_{cs}^2 + u_{meth}^2} \times 100 = \sqrt{u_{c\,lab}^2} \times 100 = u_{c\,lab} \times 100 \quad (1)$$

Where, u_{CRM} is the uncertainty from the certificate, u_{ss} is the uncertainty of stock solution concentration, u_{sp} is the uncertainty of sample preparation, u_{cs} is the uncertainty of calibration standards preparation, u_{meth} is the uncertainty of the method measurement, and $u_{c\,lab}$ is the laboratory combined uncertainty.

The precision was assessed through the relative standard deviation (RSD, %), based on n = 3 replicate measurements of real water test samples and $u_{c\,lab}$. In the case of real wastewater samples, the u_{CRM} (equation 1) was not considered in the calculation of $u_{rel\,lab}$ *(%)* for RSD(%). The bias (Δm) between the found and certified values was discussed in accordance with the fulfillment of relationships ($\Delta m < U_{CRM}$ and $\Delta m < U_{lab}$) and Dunnett's statistical test ($p > 0.05$).[42] The bias between HR-CS FAAS and ICP-OES methods was checked using Tukey's statistical test ($p > 0.05$), considering the mean concentration determined in CRMs and real test samples and $u_{c\,lab}$ for each method.[43]

Calibration curve linearity was checked using Mandel's fitting test[44,45], which compares the residual standard deviation of the linear model ($S_{y/x,lin}$) with that of the nonlinear quadratic model ($S_{y/x,non}$). The experimental Fischer-Snedecor (F_{exp}) was calculated with equation (2).

$$F_{exp,Mandel} = \frac{(n-2)S_{y/x,lin}^2 - (n-3)S_{y/x,non}^2}{S_{y/x,non}^2} \quad (2)$$

where, n is the number of calibration points between the lowest concentration used for the calibration curve, and the highest concentration over the linear range.

If $F_{exp,Mandel} < F_{tab(95\%,1,\,n-3)}$, the null hypothesis is retained for a 95% confidence level, and the tested concentration range is considered linear.

Also, the variation coefficients on the linear range of the HR-CS FAAS, LS FAAS and ICP-OES (V_{ox}) were calculated[38]:

$$V_{ox} = \frac{\sqrt{\frac{\sum_{i=1}^{n}(y_i - \hat{y}_i)^2}{n-2}}}{m\ x\ \bar{c}}\ x\ 100 \quad (3)$$

where (y_i) are the measured signals for elements in calibration standards, ($\hat{y}_i$) are the calculated signals for elements from the calibration curve equation, n is the number of calibration standards for HR-CS FAAS, LS FAAS and ICP-OES on the linear range, (m) is the slope of the calibration curve and ($\bar{c}$) is the mean concentration of elements in the calibration standards.

The fishbone diagram illustrating the individual uncertainties on $u_{rel\ lab}$ *(%)* for the determination of the metals in water CRMs by HR-CS FAAS and ICP-OES methods is presented in Supplementary Material, Fig. S2.

3. Results and Discussion

3. 1. Linearity of Calibration Curves, Characteristic Concentrations and LODs

Table 3 presents the figures of merit of HR-CS FAAS compared to ICP-OES, while Table 4 a comparison *versus* LS FAAS. According to Table 3, the HR-CS FAAS method ensured better LODs (μg L^{-1}) for Cu (2), Fe (4), Ni (3), Co (3) and Pb (30) compared to ICP-OES, in which case the LODs (μg L^{-1}) were Cu (12), Fe (29), Ni (15), Co (7) and Pb (45), due to the lower and less background noise in the method based on AAS compared to ICP-OES. In the case of three elements, poorer LODs were obtained by HR-CS FAAS (μg L^{-1}): Cd (3), Zn (11) and Cr (7), in comparison with Cd (1), Zn (1) and Cr (4) in ICP-OES. The poorer detection limits for Cd and Zn in HR-CS FAAS could be due to the lower energy of the Xe short-arc lamp in the UV region. Also, in the case of Zn, this was attributed to the background noise around the 213.856 nm analytical line due to the molecular absorption bands of NO, despite the background correction by the least square method being applied. A poorer LOD for Cr in HR-CS FAAS can be explained by lower atomization degree of Cr in an air-acetylene flame, in which case an acetylene-N_2O flame would be more appropriate. However, in the case of all elements, the LODs for HR-CS FAAS are lower than the pollutant loading limits of industrial and urban wastewater discharged into natural receivers, presented in Table 3.[46] The LODs in HR-CS FAAS are better for Pb and Cr, similar for Cu, Ni, Co and Mn, and poorer for Cd, Zn and Fe, compared to the LS FAAS method (Table 4). The characteristic concentration values, presented in Table 4, for the HR-CS FAAS method were in the range of 17–120 μg L^{-1}, while those for LS FAAS were 7–206 μg L^{-1}, which indicates that the sensitivity in HR-CS FAAS method is better for Pb and Cr, similar for Cu, Ni, Co and Mn, and poorer for Cd, Zn and Fe, compared to the LS FAAS method. The experimental values of the characteristic concentrations obtained for HR-CS FAAS method are similar with the values from the ContrAA software, except for Cr. This demonstrates that indeed, the HR-CS FAAS spectrometer was operated in optimum conditions. The highest characteristic concentration for Cr of 80 μg L^{-1} compared to that from the software (47 μg L^{-1}) could be explained by the use of air-acetylene flame, and not that of N_2O-acetylene, recommended for Cr. Mandel's fitting test, which compares the residual standard deviation of the linear model ($S_{y/x,lin}$) with that of the nonlinear quadratic model ($S_{y/x,non}$), indicated a linear range for HR-CS FAAS method between 10–1000 μg L^{-1} for Cu and Cd, 50–1000 μg L^{-1} for Zn, 10–2000 μg L^{-1} for Ni, 10–4000 μg L^{-1} for Fe and Co, and 100–4000 μg L^{-1} for Pb, for 95% confidence level, with determination coefficients in the range 0.9980–0.9999. These were similar to those obtained for LS FAAS method, but narrower than those for ICP-OES with up to 15000 μg L^{-1} (Cu and Pb) and 20000 μg L^{-1} for the rest of the elements, known for larger dynamic range compared to AAS based methods. Anyway, according to data presented in Table 3, the HR-CS FAAS method could be applied on the determination of lower concentration values for Cu, Fe and Co,

Table 3. Figures of merit of the HR-CS FAAS and ICP-OES methods for multielemental determination in wastewater

Element	Linear range (μg L^{-1}) and no. of standards in brackets		Determination coefficient (R^2)		$F_{exp,Mandel} < F_{tab(95\%,1,n-3)}$[a]		Variation coefficient V_{ox} (%)		Limit of detection LOD (μg L^{-1})		Pollutant loading limits (μg L^{-1})[46]
	HR-CS FAAS	ICP-OES	HR-CS FAAS	ICP-OES	HR-CS FAAS	ICP-OES	HR-CS FAAS	ICP-OES	HR-CS FAAS	ICP-OES	
Cu	10–1000(7)	50–15000(10)	0.9999	0.9990	0.29<7.71	3.08<5.59	1	4	2	12	200
Fe	10–4000(10)	100–20000(10)	0.9998	0.9999	3.29<5.59	0.12<5.59	2	1	4	29	5000
Cd	10–1000(7)	5–20000(11)	0.9993	0.9999	3.61<7.71	0.03<5.32	2	2	3	1	200
Ni	10–2000(8)	50–20000(11)	0.9998	0.9990	1.75<6.61	0.63<5.32	2	4	3	15	500
Co	10–4000(10)	25–20000(11)	0.9994	0.9998	1.47<5.59	1.17<5.32	3	2	3	7	1000
Zn	50–1000(7)	5–20000(11)	0.9995	0.9998	4.89<7.71	0.04<5.32	2	2	11	1	500
Pb	100–4000(9)	150–15000(9)	0.9996	0.9992	2.64<5.99	0.02<5.99	2	2	30	45	200
Mn	5–1000(7)	5–20000(11)	0.9996	0.9999	0.32<7.71	3.14<5.32	2	3	1	1	1000
Cr	20–1000(7)	10–20000(11)	0.9980	0.9999	0.82<7.71	0.18<5.32	4	2	7	4	1000

[a] The null hypothesis was retained when $F_{exp,Mandel} < F_{tab(95\%,,1,n-3)}$.

Table 4. Figures of merit of LS FAAS and characteristic concentrations for HR-CS FAAS and LS FAAS methods for multielemental determination in wastewater

	LS FAAS method					HR-CS FAAS method		
Element	**Linear range (μg L^{-1}) and no. of standards in brackets**	**Determination coefficient (R^2)**	**$F_{exp,Mandel} < F_{tab(95\%,1,n-3)}$[a]**	**Variation coefficient V_{ox} (%)**	**Limit of detection LOD (μg L^{-1})**	**Characteristic concentration (μg L^{-1})[b]**	**Characteristic concentration (μg L^{-1})[b]**	
						Experimental value	**Experimental value**	**ContrAA software**
Cu	10–1000(7)	0.9999	0.69<7.71	1	2	29	29	24
Fe	10–4000(6)	0.9992	0.49<10.13	3	2	39	65	63
Cd	10–1000(7)	0.9996	7.23<7.71	2	2	11	17	14
Ni	10–4000(6)	0.9998	8.22<10.13	1	3	57	67	57
Co	10–1000(7)	0.9996	0.01<7.71	2	3	47	56	40
Zn	20–1000(7)	0.9989	7.65<7.71	3	6	7	13	10
Pb	200–4000(6)	0.9999	9.92<10.13	1	58	206	120	117
Mn	5–1000(7)	0.9993	4.82<7.71	2	1	21	19	18
Cr	50–4000(6)	0.9963	4.15<10.13	6	17	194	80	47

[a] The null hypothesis was retained when $F_{exp,Mandel} < F_{tab(95\%,1,\,n-3)}$.
[b] Experimental characteristic concentration = 0.0044 (1% absorbance)/slope of the calibration curve

compared to ICP-OES. Variation coefficients (V_{ox}) for the linear range were 1–4% for HR-CS FAAS, 1–6% for LS FAAS, and 1–4% for ICP-OES. The HR-CS FAAS method could be applied on elements concentration determination in wastewaters and in the monitoring of decontamination process on the linear ranges presented in Table 3. Therefore, the HR-CS FAAS method is suitable for monitoring wastewater from mining activities of non-ferrous metals at concentration levels below the pollutant loading limits of industrial wastewater discharged into natural receivers (values for pollutant loading limits in Table 3).

3. 2. Accuracy of HR-CS FAAS Method

The results obtained for the determination of selected metals in the CRMs are shown in Table 5. Data in Table 5 shows that there are no significant differences between found and certified values for all CRMs in the HR-CS FAAS and ICP-OES methods, as the bias (Δm) between the found and certified values is lower than the extended uncertainty found in the laboratory and that given in certificate for k = 2 and 95% confidence level. Dunnet's test indicated no significant differences between found and certified values for $p > 0.05$, with experimental values p = 0.122–0.999 for both methods. The statistical Tukey's test indicated no significant differences between the concentrations found by HR-CS FAAS and ICP-OES for $p > 0.05$ (experimental p-values = 0.064–0.891). For the HR-CS FAAS, the pooled recovery was in the range of 98–103% with relative extended uncertainty of 9–18%, compared to 96–109% and 9–18% for ICP-OES, respectively. The combined uncertainties presented in Supplementary Material, Fig. S3, indicate that the values obtained in the laboratory are higher than those of certified values, as a result of significant contribution from aliquots analysis (weight 41%), followed by CRM uncertainty (weight 24%) and calibration curve fitting (weight 16%), from the $u_{c\,lab}$.

3. 3. Analysis of Real Water Samples

The results obtained for the determination of selected metals in several water samples by HR-CS FAAS and ICP-OES are presented in Table 6. The $u_{rel\,lab}$ (%), calculated based on combined uncertainty and the contribution of each analytical step are presented in Supplementary Material, Fig. S4. The concentration of Na and K in water samples determined by FAES and Ca and Mg by ICP-OES as multielement matrix are presented in Supplementary Material, Table S1. The HR-CS FAAS method precision used for water analysis without any chemical treatment was in the range of 2–11%, while for ICP-OES 3–11%. The main contribution of uncertainty was from aliquot analysis (weight of 37%). Tukey's test indicated the lack of bias between HR-CS FAAS and ICP-OES methods for $p > 0.05$ (experimental values 0.070–0.999), which also demonstrates the lack of non-spectral effects of Na, K, Mg and Ca on the signal of analytes in FAAS and ICP-OES at concentration levels in wastewater presented in Table S1. According to data presented in Table 6, the wastewater is treated efficiently in terms of Cu, Fe, Ni, Cd, Co and Pb, for which the concentrations in the decontaminated water were much below the pollutant loading limits. In the case of two elements (Cu and Cd), the concentrations in decontaminated water were below the LODs of HR-CS FAAS and ICP-OES. Unfortunately, the wastewater is not treated efficiently regarding Zn and Mn, as their concentrations are higher than the pollutant loading limits (500 μg L^{-1} Zn and 1000 μg L^{-1} Mn). This also affected the river water, that had

Table 5. Concentration of selected metals and recovery obtained in water CRMs by HR-CS FAAS and ICP-OES

Element	Method	Certified reference material (CRM) TMDA-64.4*			ERM CA-713*			ERM CA-615*			Pooled
		Certified value ± U_{CRM}[a] (µg L^{-1})	Found value ± U_{lab}[b] (µg L^{-1})	Recovery ± U_{rel}[c] (%)	Certified value ± U_{CRM} (µg L^{-1})	Found value ± U_{lab} (µg L^{-1})	Recovery ± U_{rel} (%)	Certified value ± U_{CRM} (µg L^{-1})	Found value ± U_{lab} (µg L^{-1})	Recovery ± U_{rel} (%)	Recovery ± U_{rel} (%)
Cu	HR-CS FAAS	251 ± 15	253 ± 28	101 ±11	101 ± 7	107 ± 9	106 ± 8	-	-	-	103 ± 10
	ICP-OES		237 ± 38	94 ± 16		99 ± 14	98 ± 14		-	-	96 ± 15
Fe	HR-CS FAAS	291 ± 23	291 ± 28	100 ± 10	445 ± 27	436 ± 33	98 ± 8	5110 ± 260	5360 ± 440	105 ± 8	101 ± 9
	ICP-OES		287 ± 28	99 ± 10		446 ± 41	100 ± 9		5260 ± 460	103 ± 9	101 ± 9
Ni	HR-CS FAAS	246 ± 14	251 ± 31	102 ± 12	50.3 ± 1.4	49.8 ± 7.8	99 ± 16	25.3 ± 1.1	24.7 ± 6.0	98 ± 24	100 ± 8
	ICP-OES		240 ± 18	98 ± 8		51.6 ± 7.3	103 ± 14		<50[e]		101 ± 11
Cd	HR-CS FAAS	256 ± 12	261 ± 36	102 ± 14	5.09 ± 0.20	<10[e]		0.106 ± 0.011	< 3[f]	-	102 ± 14
	ICP-OES		265 ± 26	104 ± 10		5.28 ± 1.17	104 ± 22		< 1[f]	-	104 ± 17
Co	HR-CS FAAS	252 ± 19	254 ± 29	101 ± 11	-	-	-	-	-	-	101 ± 11
	ICP-OES		269 ± 38	107 ± 14					-	-	107 ± 14
Zn	HR-CS FAAS	329 ± 25	348 ± 58	106 ± 17	78[d]	78 ± 12	100 ± 15	-	-	-	103 ± 16
	ICP-OES		352 ± 40	107 ± 11		86 ± 16	110 ± 19		-	-	109 ± 15
Pb	HR-CS FAAS	277 ± 20	269 ± 33	97 ± 12	49.7 ± 1.7	<100[e]		7.1 ± 0.6	<30[f]	-	98 ± 12
	ICP-OES		292 ± 37	105 ± 13		<150[e]			< 45[f]	-	104 ± 13
Mn	HR-CS FAAS	289 ± 21	279 ± 41	97 ± 15	95 ± 4	96 ± 12	101 ± 12	107 ± 5	107 ± 15	100 ± 14	99 ± 14
	ICP-OES		305 ± 56	106 ± 18		98 ± 13	103 ± 13		110 ± 18	103 ± 16	104 ± 16
Cr	HR-CS FAAS	274 ± 22	273 ± 41	100 ± 15	20.9 ± 1.3	22.0 ± 4.2	105 ± 19	-	-	-	102 ± 17
	ICP-OES		291 ± 39	106 ± 13		21.8 ± 4.7	104 ± 22			-	105 ± 18

[a] U_{CRM} is absolute expanded uncertainty for certified concentration (k = 2; 95% confidence level)
[b] U_{lab} is absolute expanded uncertainty in laboratory for found concentration (k = 2, n = 3 parallel measurements and 95% confidence level)
[c] U_{rel} is relative expanded uncertainty in laboratory for found concentration (k = 2, n = 3 parallel measurements and 95% confidence level)
[d] Indicative value; [e]Values corresponding to the lowest concentration of the linear range; [f]Values corresponding to LODs of the method

Table 6. Results for Cu, Fe, Ni, Cd, Co, Zn, Pb and Mn in real water samples determined by HR-CS FAAS and ICP-OES

Parameter	Methods	Wastewater before decontamination		Wastewater before decontamination		Decontaminated wastewater		River water	
		Mean concentration ± U_{lab}[a] (µg L^{-1})	*RSD*[b] (%)	Mean concentration ± U_{lab} (µg L^{-1})	*RSD*[b] (%)	Mean concentration ± U_{lab} (µg L^{-1})	*RSD*[b] (%)	Mean concentration ± U_{lab} (µg L^{-1})	*RSD*[b] (%)
Cu	HR-CS FAAS	980 ± 40	2	950 ± 140	7	< 2[d]	-	131 ± 24	9
	ICP-OES	1020 ± 97	5	1030 ± 160	8	< 12[d]	-	134 ± 13	5
Fe	HR-CS FAAS	32000 ± 4300	7	35100 ± 2900	4	1540 ± 120	4	58 ± 10	9
	ICP-OES	33600 ± 2500	4	36800 ± 2800	4	1580 ± 140	4	<100[c]	-
Ni	HR-CS FAAS	87 ± 12	7	87 ± 10	6	37 ± 6	8	< 3[d]	-
	ICP-OES	83 ± 16	10	78 ± 17	11	<50[c]	-	< 15[d]	-
Cd	HR-CS FAAS	153 ± 13	4	166 ± 20	6	< 3[d]	-	14 ± 3	11
	ICP-OES	161 ± 29	9	182 ± 29	8	< 1[d]	-	14 ± 3	11
Co	HR-CS FAAS	105 ± 19	9	145 ± 19	7	47 ± 9	10	22 ± 5	11
	ICP-OES	113 ± 21	9	155 ± 29	9	43 ± 9	10	25 ± 5	10
Zn	HR-CS FAAS	39500 ± 3900	5	39400 ± 4900	6	1390 ± 220	8	6920 ± 800	6
	ICP-OES	41500 ± 2800	3	41600 ± 3400	4	1490 ±150	5	7480 ± 890	6
Pb	HR-CS FAAS	141 ± 25	9	<100[c]	-	<100[c]	-	<100[c]	-
	ICP-OES	<150[d]	-	<150[c]	-	<150[c]	-	<150[c]	-
Mn	HR-CS FAAS	21900 ± 2000	5	22300 ± 1600	4	5090 ± 620	6	3530 ± 220	3
	ICP-OES	23100 ± 1900	4	22900 ± 2040	5	5140 ± 720	7	3550 ± 460	6
Cr	HR-CS FAAS	< 7[d]	-	< 7[d]	-	< 7[d]	-	< 7[d]	-
	ICP-OES	< 4[d]	-	< 4[d]	-	< 4[d]	-	< 4[d]	-

[a] U_{lab} is the absolute uncertainty in laboratory (k = 2, n = 3 parallel measurements and 95% confidence level)
[b] *RSD* is the relative standard deviation in (%) obtained from the combined uncertainty in laboratory ($u_{c\,lab}$)
[c] Values corresponding to the lowest concentration of the linear range
[d] Values corresponding to LODs of the method

in consequence, higher concentrations than the regulated values for metal pollutants. Chromium could not be determined, both in non-treated and decontaminated water, and river water, because the concentration values were below the LODs of both methods. The recovery and precision for Cr determinations in a spiked water sample with a concentration of 50 μg L^{-1} was 98 ± 12% (RSD 6%) for HR-CS FAAS and 103 ± 13% (RSD 6%) for ICP-OES.

4. Conclusions

The HR-CS FAAS method was validated for the determination of Cu, Fe, Ni, Cd, Co, Zn, Pb, Mn and Cr in wastewater resulting from mining activities of non-ferrous metals and those discharged into natural receivers in comparison with the ICP-OES method. It was demonstrated that like ICP-OES, the HR-CS FAAS method does not present systematic errors in the analysis of CRMs and real water samples. Furthermore, HR-CS FAAS ensured better LODs for Cu, Fe, Ni, Co, Pb and Mn, and poorer LODs for Cd, Zn and Cr compared to ICP-OES. The LODs for selected toxic elements obtained by HR-CS FAAS were much lower than the pollutant loading limits, and thus, they could be determined by the proposed method at concentrations below the regulated values. Compared to conventional LS FAAS, the HR-CS FAAS presented better LODs for Pb and Cr, similar for Cu, Cd, Ni, Co and Mn, and poorer for Fe and Zn, in agreement with their characteristic concentrations for the two instrumental concepts. The dynamic range was similar for FAAS methods equipped with line-sources and the continuum Xe short-arc lamp. Unfortunately, the HR-CS FAAS method presented a narrower dynamic range than ICP-OES. The major advantage of the HR-CS FAAS method *versus* the LS FAAS is the higher speed of analysis since it does not require lamp changing, while in comparison with ICP-OES, the better LODs for most elements.

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Povzetek

Nova metoda, ki temelji na plamenski atomski absorpcijski spektrometriji z visoko ločljivostjo (HR-CS FAAS), je bila validirana za določanje izbranih toksičnih kovin v odpadni vodi, ki je posledica rudarske dejavnosti. Zmogljivost metode smo primerjali z zmogljivostjo metod, ki temeljita na optični emisijski spektrometriji z induktivno sklopljeno plazmo (ICP-OES) in plamenski atomski absorpcijski spektrometriji z linijskim virom (LS FAAS). Za metodo HR-CS FAAS so bile meje zaznavnosti (LOD) v območju (μg L^{-1}) 1(Mn)–30(Pb) in boljše od ICP-OES za Cu, Fe, Ni, Co, Pb in Mn ter slabše za Cd, Zn in Cr. Dunnettov test je pokazal, da rezultati pridobljeni z eno ali drugo metodo ne odstopajo bistveno od certificiranih vrednosti. Izkoristek pri metodi HR-CS FAAS je bil v območju 98–103 % z relativno razširjeno negotovostjo 9–18 % in natančnostjo 2–11 %. V primerjavi z LS FAAS je imel HR-CS FAAS nižje LOD za Pb in Cr. Metoda HR-CS FAAS je primerna za določanje izbranih toksičnih elementov v vzorcih filtrirane vode brez kemične obdelave.