

**Traces of Cu, Mn and Zn in Aquatic Animals and Sediments from the Cris River Basin – West Romania.
Part I: Statistical Evaluation of Data Obtained by Atomic Emission Spectrometry with Radiofrequency Capacitively Coupled Plasma Source and Flame Atomic Absorption Spectrometry**

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The paper presents the evaluation of a radiofrequency capacitively coupled plasma atomic emission spectrometry with two ring electrodes (TRT r.f.CCP-AES) operated at 275 W and 0.4 L min⁻¹ Ar in comparison with flame atomic absorption spectrometry (FAAS) in determination of Cu, Mn and Zn in sediments and aquatic animals. The limits of detection in r.f.CCP-AES were 2 (Cu), 6 (Mn) and 3 (Zn) µg g⁻¹. Statistic evaluation of the results was based on 31 samples collected in the basin of the Cris rivers, Romania. After removing the samples with a metal concentration lower than the limit of determination in TRT r.f.CCP-AES, the F-test (95% confidence level) showed similar precision in the two methods, with one exception in the case of Mn and one in the case of Zn. From 21, 28 and 31 determinations of Cu, Mn and Zn, statistical correlation and regression as well as the analysis of Bland and Altman (95% confidence level) showed systematic errors in TRT r.f.CCP-AES *versus* FAAS only in one case for Cu, two cases for Mn and one case for Zn. The metal content amounted to: 10–400 µg g⁻¹ (Cu), 20–16000 µg g⁻¹ (Mn) and 20–1200 µg g⁻¹ (Zn).

Key words: environment monitoring; biological samples; sediments; copper, manganese and zinc determination; capacitively coupled plasma.

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INTRODUCTION

Copper, manganese and zinc are essential elements for both plants and animals. Their insufficiency in animal food or, in turn, their excess can cause severe dysfunction in such organisms. Aquatic animal species do not show the same degree of individual sensitivity to a certain toxic agent. Attention should be paid to the interference of various toxic components that may cause attenuation in their toxicity or synergistic effects. Thus, Mn deficiency in food results in severe reproductive abnormalities while its excess brings about neurological dysfunction.¹⁻³ It has been shown that freshwater molluscs are very susceptible to pollution factors and can be used as bio-indicators since they concentrate high amounts of heavy metals. Manganese accumulates in comestible mollusc tissues (concentration factors from over 12000) and to a lesser extent in fish fillet.⁴ The Zn influence on aquatic animals is associated with the spawn growth, which is favored or inhibited by the Zn concentration. Aquatic animals accumulate Zn in variable concentrations depending on their age, weight and water salinity.⁴ The admitted levels of Cu, Mn and Zn in surface waters make the life of aquatic organisms safe and are related to salinity. Although the »without effect« level of Cu for many aquatic species is lower than the admitted level in surface water, many aquatic species could tolerate relatively high Cu levels in water with high alkalinity and many organic materials. Copper acts as activator or inhibitor in several redox and enzymatic vital processes.⁴

The traditional techniques used to determine Cu, Mn and Zn in a large variety of samples are flame atomic absorption spectrometry (FAAS) and electrothermal atomic absorption spectrometry (ETAAS), but also multielemental techniques such as inductively coupled plasma atomic emission spectrometry (ICP-AES) or inductively coupled plasma mass spectrometry (ICP-MS).⁵⁻¹⁰ Over the last ten years, radiofrequency capacitively coupled plasma (r.f.CCP) of low power and small gas consumption has begun to be reused as an alternative source for ICP because it provides several advantages.^{11,12}

Cordos *et al.* have developed an Ar r.f.CCP torch in coaxial configuration with tip-ring electrode geometry that is used in the analysis of pneumatically nebulized liquid samples or conductible and nonconductible solid samples by AES.¹³⁻¹⁸ They tested it in the speciation of Pb, Cu and Zn in soil samples and airborne particulate matter or sedimented dust.¹⁴ Cordos and co-workers have also built an r.f.CCP plasma torch (275 W, 27.12 MHz, Ar 0.4 L min⁻¹) with a Mo tubular central electrode and one (SRT) or two ring electrodes (TRT) in coaxial and coaxial-annular configuration, respectively. The limits of detection obtained with this torch and a sequential atomic emission spectrometer equipped with photomultiplier for a group of 20 elements

in pneumatically nebulized solutions are in the range: 3–2000 ng mL⁻¹.^{19,20} Determination of Cd in a monitoring study of dust samples was achieved with a true detection limit of 3 µg g⁻¹.²¹ This torch has also been interfaced with a simultaneous spectrometer equipped with a photodiodes array (PDA) and has been used to study the chemical processes of Ca in plasma.²²

The aim of this paper is to establish a methodology for determining Cu, Mn and Zn in aquatic beings and sediments by r.f.CCP-AES in TRT geometry. Another paper will present an environmental study concerning the distribution of Cu, Mn and Zn in aquatic animals, sediments and water samples from the basin of the Cris rivers in West Romania, in relation to the existing mining and processing centers for Fe, Mn, Cu and Zn ores.

Determinations carried out in sediments and aquatic organisms by r.f. CCP-AES in TRT configuration were compared with the FAAS results. The equivalence of the data was analyzed using the F-test, correlation and regression statistics.²³ The statistical analysis advocated by Bland and Altman was also used.²⁴ This approach allowed evaluation of the r.f.CCP in the analysis of real samples. All samples were analyzed using the standard addition method.

EXPERIMENTAL

Reagents

Single element stock solutions of 1000 µg mL⁻¹ were prepared by dissolution of high-purity metal (Merck, Darmstadt, Germany) in a minimum volume of HNO₃ (Cu, Mn) or HCl (Zn) and diluting to 1 L. From these, solutions for the standard addition method were prepared. Reagents for the digestion of sediment and aquatic animal samples were HNO₃, 65%, *puriss* and H₂O₂, 30%, *puriss* (Merck, Darmstadt, Germany). The blank sample contained only reagents used for the digestion. All solutions were stored in plastic vials cleaned with acid solution and rinsed with distilled water.

Sample Collection and Digestion Procedure

Samples of sediment and aquatic animals were collected at seven sites on each river, marked as localities on the map in Figure 1. Freshwater molluscs were collected only at five points, starting from about 50 km from the spring. White Cris and Black Cris rivers collect the rivulets from the southwest of the Apuseni Mountains in West Romania. Together with two other rivers with similar geographical characteristics they form the Körös river in Hungary, an affluent of Tisa. In the Cris basin area there are several mining centers for Fe and Mn ores (black rectangles on the map) and Cu, Zn complex ores (black triangle on the map) that might have a polluting effect on the rivers. Concentrates of these ores are obtained at Brad (black circle on the map).

(i) Sediment samples were collected at a depth between 0 and 5 cm using a grab sampler. Several kilograms of samples were collected, mixed and subdivided by quartering them into subsamples that were stored in plastic bags. The wet sediment was

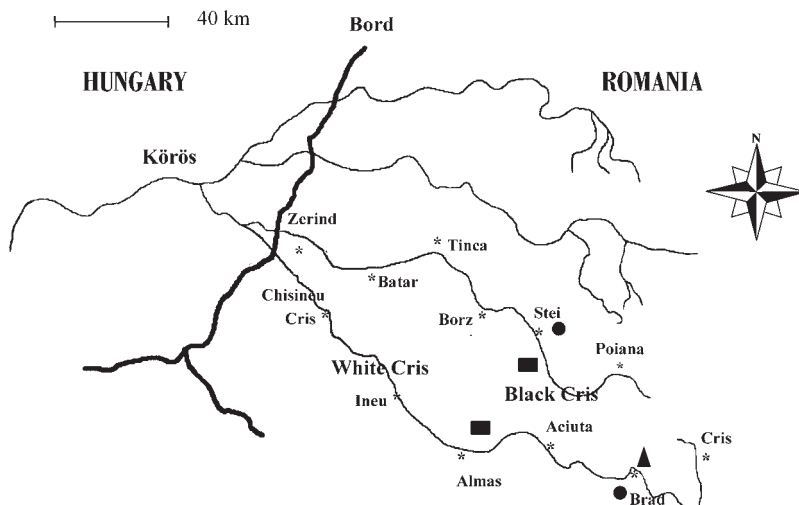


Figure 1. Sampling sites for sediments and aquatic organisms on the White Cris and Black Cris rivers: ■ mining centers for Fe and Mn ores, ▲ mining center for Cu and Zn complex ores, ● ore processing centers.

sieved at 2 mm and air-dried at room temperature. For the digestion procedure, the samples were ground in an agate mortar, sieved at 90 μm , homogenized and dried at 105 $^{\circ}\text{C}$. Approximately 5 g of sample was refluxed with 20 ml concentrated (65%) HNO_3 , then with 30% H_2O_2 . The resulting solution was filtered and diluted to 250 mL. No further analysis was carried out to study the undissolved fraction.

(ii) Soft bodies (muscles and gills) of freshwater molluscs (*Unio crassus*, *Anodonta woodiana*, *Pseudanodonta complanata*) and fish fillet (*Alburnus alburnus*, *Gobio albipinatus*, *Stizostedion lucioperca*), representative of the White Cris and Black Cris, were collected. The samples were separated, dried at 105 $^{\circ}\text{C}$ to constant weight, ground and sieved. Approximately 0.5 g of the 90 μm fraction sample was weighed directly into the digestion vessel to which 3 mL of HNO_3 65% and 1 mL of H_2O_2 30% was added. Biological samples were digested using a high-pressure microwave system in order to minimize contamination and losses through volatility.^{25,26} Five samples and 1 blank were digested following the digestion procedure shown in Table I. The resulting clear solutions were quantitatively transferred without filtration, made up to volume with distilled water and stored in polyethylene vials till analysis. Blanks prepared by the digestion procedure gave a negligible response and no correction was made to the results.

TABLE I
Profile of the sample digestion program

<i>P</i> / <i>W</i>	250	0	250	400	650
Time / min	1	1	5	5	5

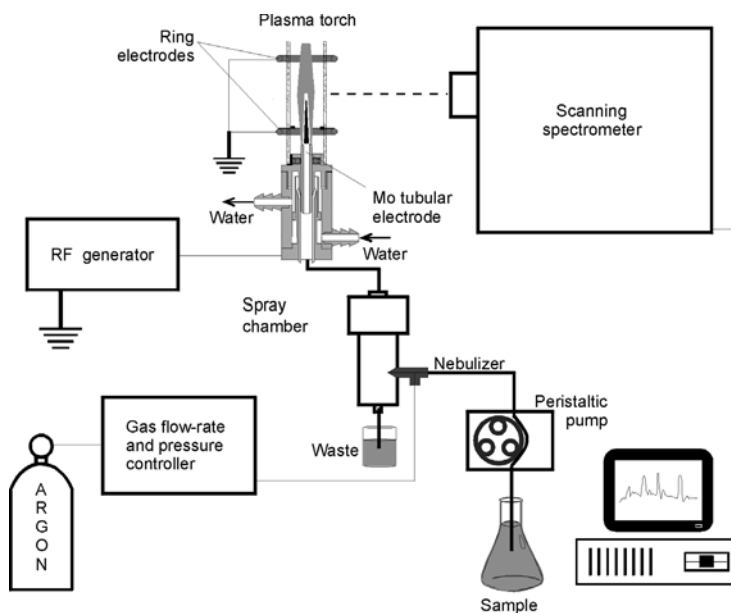


Figure 2. Experimental set-up for TRT r.f.CCP and scanning monochromator.

Instrumentation

The microwave system used for biological samples preparation was Milestone (MLS-1200 MEGA, Sorisole, Italy) with a Teflon vessel (MRD 1000/6/100/110), designed for pressures of up to 11×10^6 Pa.

Determinations by AAS were performed with a PHILIPS Atomic Absorption Spectrometer PU9180 equipped with an air-acetylene flame unit. In FAAS, the optimum acetylene-to-oxidant ratio and instrumental parameters were chosen for the maximum signal of the solution being analyzed.

Determinations in AES were performed using a low powered Ar TRT r.f.CCP source (Research Institute for Analytical Instrumentation, Cluj-Napoca, Romania). A schematic diagram of the scanning monochromator and TRT r.f.CCP source is presented in Figure 2 while the main characteristics are given in Table II.

RESULTS AND DISCUSSION

Optimization of Analytical Performance in TRT r.f.CCP-AES

The experimental set-up of the r.f. CCP source with a central tube electrode and two ring electrodes has been analytically characterized in several recent papers.^{19–22} The optimum operation conditions of the plasma source are: TRT geometry, power level of 275 W and 0.4 L min^{-1} Ar flow rate. In such conditions, the instrumental limits of detection were calculated (3σ

TABLE II
Instrumentation and operating conditions

Equipment	Characteristics
Plasma power supply	Plasma r.f. generator, free-running oscillator, 27.12 MHz, 275 W (Research Institute for Analytical Instrumentation, Cluj-Napoca, Romania).
Plasma torch	Capacitively coupled in coaxial-annular configuration with central Mo tubular electrode (i.d. = 3.5 mm; o.d. = 5 mm) and two outer ring electrodes – TRT. The tubular electrode is connected to the r.f. generator and the ring electrodes of 25 mm diameter are connected to the ground. The distance between the tubular electrode and the lower ring electrode is 5 mm and the distance between ring electrodes is in the range 40–150 mm (Research Institute for Analytical Instrumentation, Cluj-Napoca, Romania). Plasma support gas: high purity Ar, flow rate 0.4 L min ⁻¹ .
Sample introduction system	Concentric pneumatic nebulizer, equipped with a 4-roller peristaltic pump (Research Institute for Analytical Instrumentation, Cluj-Napoca, Romania). Desolvation: 120 cm ³ spray chamber. Intake of aerosol into the plasma core through the tubular electrode (1 mL min ⁻¹ , 5% nebulization efficiency).
Optics	Scanning monochromator and photocurrent measurements system: Model SMS Czerny-Turner mount, spectral range 190–800 nm, internal wavelength calibration with a Si hollow cathode lamp, 1 m focal length, 2400 grooves mm ⁻¹ grating blazed at 340 nm, bandpass 25 pm, entrance and exit slits 20 μm, 32 (±1) °C thermostated, photomultiplier detector EMI 9781R (Research Institute for Analytical Instrumentation, Cluj-Napoca, Romania). Analytical wavelengths: Cu 324.75 nm, Mn 403.07 nm and Zn 213.81 nm.
Data acquisition and processing	Computer model PC486 DX-4, laboratory constructed interface, 64 μs data acquisition in-house software (with automatic background correction).

criteria) for different distances between ring electrodes in the TRT geometry. Results in Figure 3 show that the lowest limits of detection – 16 (Cu), 75 (Mn) and 40 (Zn) ng mL⁻¹ – correspond to ring electrodes spaced 60 mm in the case of Cu and Mn and 70 mm in the case of Zn. The corresponding optimum observation heights are 14 mm for Cu, 12 mm for Mn and 6 mm for

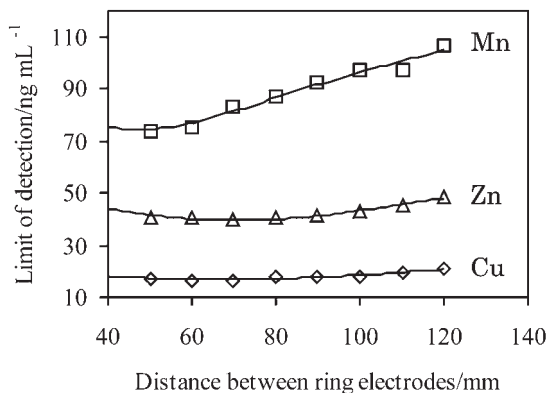


Figure 3. Instrumental limit of detection for Cu, Mn and Zn in TRT r.f.CCP-AES at different distances between ring electrodes.

Zn. As compared to the limits of detection in FAAS – 2 (Cu), 3 (Mn) and 1 (Zn) ng mL⁻¹ – the instrumental limits of detection in TRT r.f.CCP-AES are higher up to one order of magnitude.

The matrix effect of Na and Ca as chlorides on Cu, Mn and Zn emission in the TRT r.f.CCP-AES has been investigated under the optimum conditions regarding the observation height and distance between ring electrodes. The choice of the matrix was determined on the basis of Na and Ca content in the analyzed samples. The experimental results, in comparison with those obtained by FAAS, are presented in Figure 4.

Unlike FAAS (A_2 and B_2 curves), where Na and Ca have a slight depressive effect on the signal, the depressive effect is more evident, in the case of TRT r.f.CCP-AES (A_1 and B_1 curves), which is characteristic of the low power plasma sources. The depressive effect of Ca (B_1 curves) is lower than that of Na (A_1 curves), since the higher is the ionization potential of the interferent, the lower is the matrix effect. Up to 400 $\mu\text{g mL}^{-1}$, the matrix effect of Ca is almost similar in FAAS and TRT r.f.CCP-AES, especially in the case of Cu and Zn. A preliminary determination of Na and Ca levels in the samples showed a concentration of 70 and 800 $\mu\text{g mL}^{-1}$ Na and Ca, respectively. To minimize the matrix effect, the samples were appropriately diluted and analyzed using the standard addition method. Taking into account the sampling of biological matter (0.5 g diluted to 25 mL) and the matrix effects, the real limits of detection in TRT r.f.CCP-AES for solid samples, expressed as dry mass (dm), are 2 (Cu), 6 (Mn) and 3 (Zn) $\mu\text{g g}^{-1}$. Although the real limits of detection are higher than those in FAAS, determination of Cu, Mn and Zn in aquatic samples and sediments by TRT r.f.CCP-AES was possible in most samples because their concentrations were at least 5 times higher than the detection limit, which assured a satisfactory reproducibility.

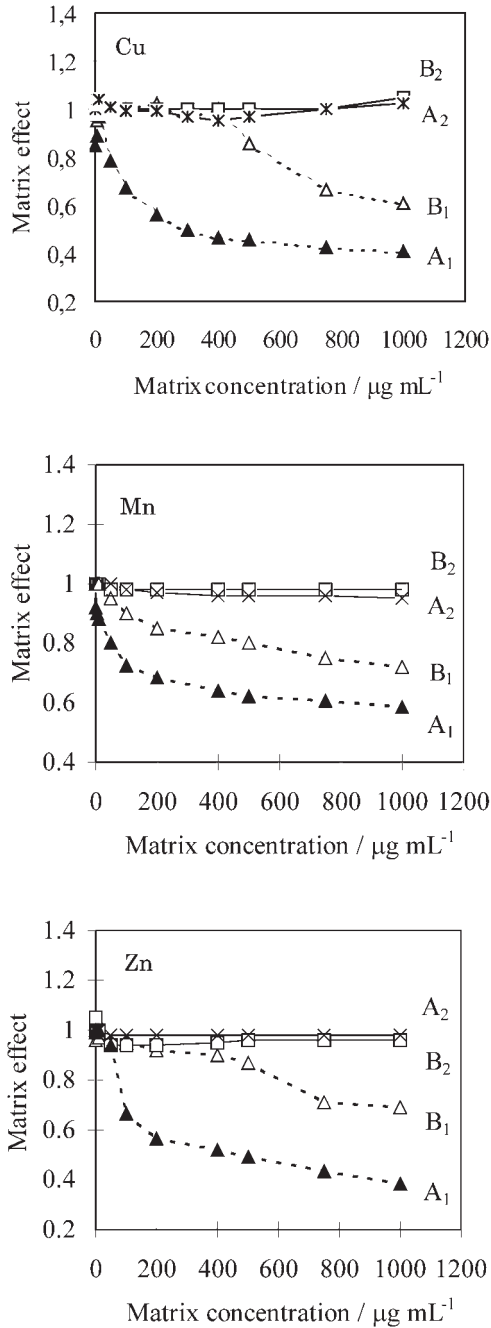


Figure 4. Matrix effect of NaCl (A) and CaCl₂ (B) on Cu, Mn and Zn analysis. Index significance: 1 – TRT r.f. CCP-AES, 2 – FAAS.

Given that, besides the low Ar consumption, the TRT r.f.CCP-AES does not necessitate hollow-cathode lamps, the plasma source under study could be a viable alternative in the multielemental analysis of some environmental samples.

Comparison of TRT r.f.CCP-AES and FAAS. Validation of Results

Table III displays comparatively the analytical results of several determinations of Cu, Mn and Zn in mollusc gills and muscles, in fish fillet and sediment by TRT r.f.CCP-AES and FAAS. The reported values are the average of 5 successive measurements. Standard deviations and the mean determinations by TRT r.f.CCP-AES were compared with those of the well-established FAAS using significance tests. Thus, the two-tailed F-test was used to compare standard deviations while the means were compared using the usual statistics of correlation and regression and statistical analysis advocated by Bland and Altman.^{23,24} The F-test (95% confidence level) showed that the standard deviations were not significantly different in the two techniques, with two exceptions, one for Mn and one for Zn, when TRT r.f.CCP-AES furnished less precise results. Decreased precision was attributed to the instability of the plasma source in the presence of a high NaCl matrix content. These exceptions are marked boldface and given as footnote (b) in Table III.

For comparison of the mean results, 31 samples (14 sediment samples and 17 biological samples) were analyzed. Metal contents were not quantitated by TRT r.f.CCP-AES in samples having concentrations below the limit of determination because of the low reproducibility at these concentration levels. Thus, in the statistical comparison of the techniques, 10 results were eliminated in the case of Cu and 3 in the case of Mn. Several such situations are marked as < LD in Table III. The content of Zn was in all samples above the limit of determination in TRT r.f.CCP-AES.

Figures 5, 6 and 7 show Cu, Mn and Zn regression plots as well as the corresponding Bland and Altman plots. The coefficient of correlation (r) and the equation of the regression line are also given. Uncertainties are quoted at a 95% probability level. Agreement between two methods is usually considered satisfactory if r and the slope of the regression equation (m) are both close to unity and the intercept of the regression equation is zero. However, it has been suggested that neither r nor the regression equation measure the agreement of methods. The Bland and Altman method has been specifically designed to assess agreement between measurement techniques. In this test, the difference (Δ) of the mean results in TRT r.f.CCP-AES and FAAS for each sample (5 successive measurements in each technique) was plotted against the mean value between the two methods. Ideally, the data should lie within a normal distribution about the horizontal line through the zero

TABLE III

Analytical results for Cu, Mn and Zn in several samples of freshwater mollusc gills and muscles, fish fillet and sediments as dry mass fraction ($w_{dm} \times 10^6$) obtained by TRT r.f.CCP-AES / AAS

Sampling site	Sample	Mass fraction ($w_{dm} \times 10^6$)		
		Cu	Mn	Zn
White Cris				
Freshwater gills				
Brad	-			
Almas	<i>Unio crassus</i>	43.1 ± 3.0 / 42.6 ± 2.1	12500 ± 625 / 13300 ± 532	997 ± 60 / 1242 ± 50^a
Ineu	<i>Unio crassus</i>	56.0 ± 6.1 / 80.0 ± 3.1^a	16000 ± 640 / 15000 ± 150^b	596 ± 42 / 560 ± 60
Fresh muscles				
Brad	-			
Almas	<i>Unio crassus</i>	9 ± 1.0 / 13 ± 1.1	340 ± 15 / 350 ± 18	87 ± 10 / 117 ± 7
Ineu	<i>Unio crassus</i>	16.0 ± 1.5 / 20.3 ± 0.8	410 ± 18 / 390 ± 18	109 ± 11 / 139 ± 14
Fish fillet				
Brad	<i>Gobio albipinatus</i>	11.5 ± 0.8 / 12.3 ± 0.7	40.0 ± 2.2 / 40.3 ± 2.2	130 ± 13 / 94.0 ± 7.5
Almas	<i>Alburnus alburnus</i>	< LD / 3.0 ± 0.2	21.5 ± 1.2 / 22.6 ± 1.0	53 ± 2.6 / 69 ± 2.8
Ineu	<i>Alburnus alburnus</i>	13.2 ± 0.6 / 9.0 ± 0.4	34.5 ± 1.8 / 31.1 ± 1.1	95 ± 4.1 / 85 ± 5.0
Sediment				
Brad		370 ± 15 / 385 ± 18	2100 ± 45 / 1995 ± 45	1120 ± 22 / 1140 ± 25
Almas		< LD / 6.1 ± 0.9	225 ± 12 / 205 ± 9	44.5 ± 2.5 / 42.0 ± 2.2
Ineu		217 ± 15 / 202 ± 11	460 ± 33 / 668 ± 23^a	314 ± 7 / 328 ± 8
Chisineu Cris		35.3 ± 11 / 28.0 ± 9	367 ± 12 / 350 ± 10	70.0 ± 3.5 / 60.0 ± 2.5

TABLE III (cont.)

Black Cris					
	Fresh water gills				
Borz	<i>Unio crassus</i>	30.0 ± 1.7 / 26 ± 1.6	10300 ± 580 / 9500 ± 550	390 ± 16 / 350 ± 12	
Tinca	<i>Unio crassus</i>	20.5 ± 2.8 / 17.5 ± 2.1	11000 ± 660 / 10900 ± 763	432 ± 17 / 480 ± 3^b	
	Freshwater muscles				
Borz	<i>Unio crassus</i>	< LD / 6.1 ± 0.2	225 ± 27 / 205 ± 27	139 ± 5 / 109 ± 4	
Tinca	<i>Unio crassus</i>	13 ± 2.5 / 8.4 ± 2.1	434 ± 30 / 713 ± 71^a	68.5 ± 6.9 / 52.5 ± 5.3	
	Fish fillet				
Borz	<i>Alburnus alburnus</i>	< LD / 2.8 ± 0.3	21.0 ± 1.1 / 8.0 ± 0.4	30.0 ± 2.1 / 35.0 ± 1.8	
Tinca	<i>Alburnus alburnus</i>	< LD / 2.8 ± 0.3	< LD / 5.0 ± 0.4	47.5 ± 3.6 / 42.8 ± 3.8	
	Sediment				
Borz		15.0 ± 2.0 / 18.5 ± 1.8	270 ± 30 / 236 ± 33	23.4 ± 1.8 / 20.5 ± 1.5	
Tinca		51.0 ± 4.8 / 50.0 ± 3.7	700 ± 30 / 680 ± 35	220 ± 10 / 243 ± 13	

^a Average values significantly different; ^b Standard deviation values significantly different.

^c Typical concentration as mass fraction ($w_{dm} \times 10^6$) for Cu, Mn and Zn in aquatic animal tissue: 4–50, 1–60 and 6–1500, respectively.²⁷

difference. The bias was appreciated from the mean difference and the limit of agreement was calculated considering a 95% normal range of the differences. The confidence interval (CI) of the mean difference was established considering a 95% confidence level.

Data in Table III show that the contents of Cu, Zn and especially Mn in the analyzed samples vary in a wide concentration range. Moreover, in the case of Mn, the results are concentrated in two groups, at low and high concentrations, and this is not ideal for the regression analysis, which requires an even spread of data.

In all cases, the slope m of the regression equation is not significantly different from unity, nor is the intercept significantly different from zero for

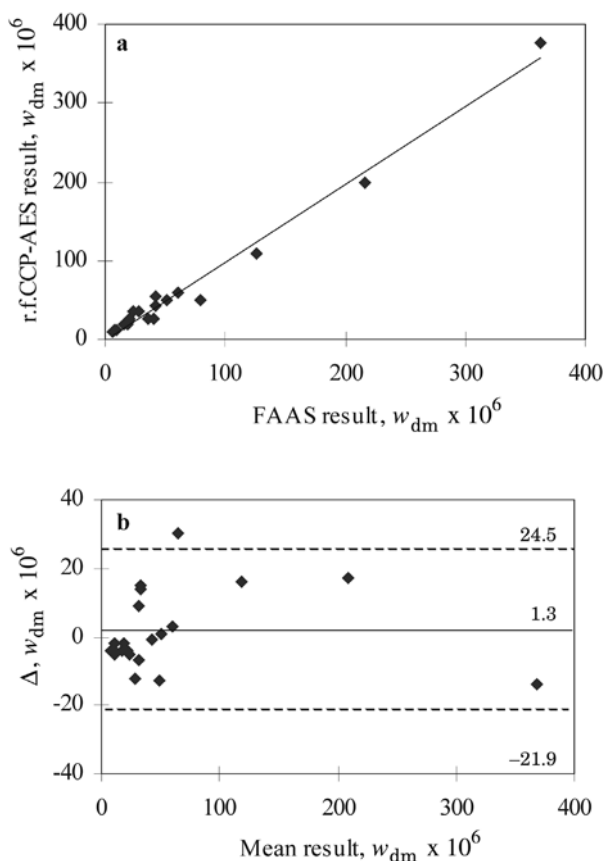


Figure 5. (a) Copper regression plot (21 samples: 8 sediment samples, 13 biological samples). Regression equation: $\text{Cu(r.f.CCP-AES)} = 0.99(\pm 0.06)\text{Cu(FAAS)} - 0.66(\pm 6.28)$. Correlation coefficient: $r = 0.991$. (b) Bland and Altman plot for Cu.

a 95% probability level. In the case of Cu (Figure 5), the mean difference or bias is 1.3 (± 5.2) $\mu\text{g g}^{-1}$ and it is not significantly different from zero. The limit of agreement is from -21.9 to 24.5 and includes all but one sample. As

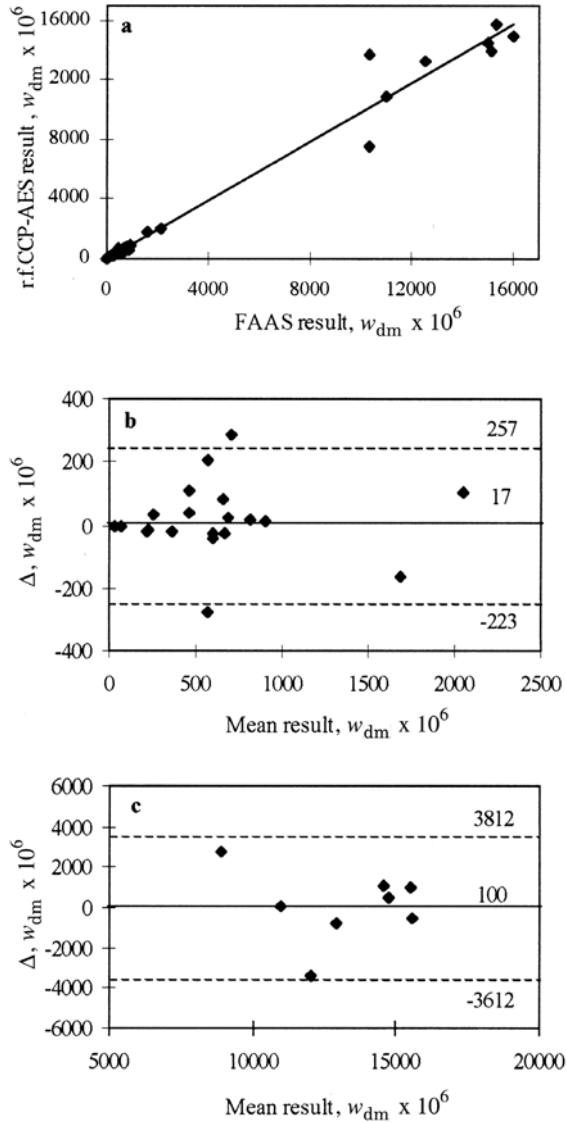


Figure 6. (a) Manganese regression plot (28 samples: 14 sediment samples, 14 biological samples). Regression equation: $\text{Mn (r.f.CCP-AES)} = 0.99(\pm 0.06)\text{Mn(FAAS)} + 17.4(\pm 432)$. Correlation coefficient: $r = 0.998$. (b) Bland and Altman plot for Mn $w_{dm} \times 10^6 < 2500$. (c) Bland and Altman plot for Mn $w_{dm} \times 10^6 > 5000$.

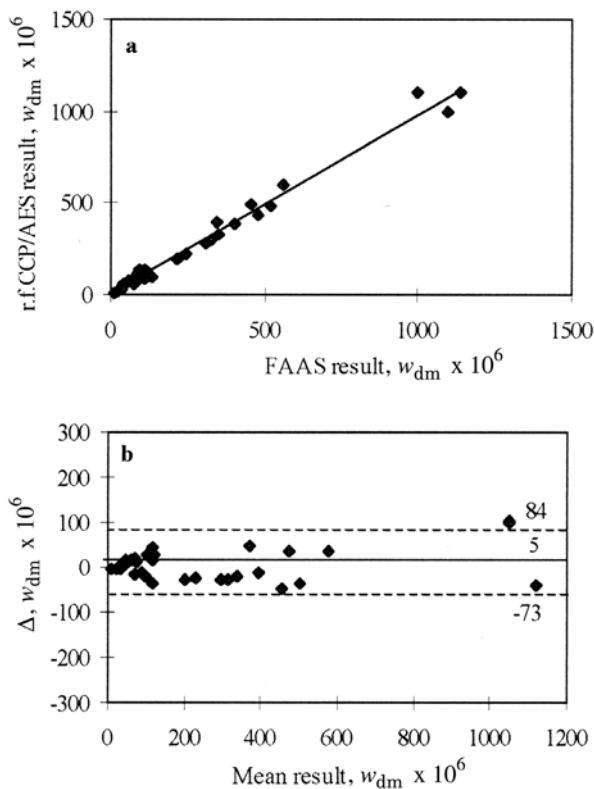


Figure 7. (a) Zinc regression plot (31 samples: 14 sediment samples, 17 biological samples). Regression equation: $Zn(r.f.CCP-AES) = 0.98(\pm 0.06)Zn(FAAS) + 5.31(\pm 18.00)$. Correlation coefficient: $r = 0.993$. (b) Bland and Altman plot for Zn.

in the case of Mn, the differences fall into two populations; Bland and Altman plots were separately represented for the two ranges (Figure 6). In the range up to $2500 \mu g g^{-1}$, the mean difference is $17 (\pm 56) \mu g g^{-1}$ and it is not significantly different from zero. The limit of agreement is from -223 to 257 and includes 18 out of 20 samples. For mean values higher than $5000 \mu g g^{-1}$, the mean difference is $100 (\pm 1552) \mu g g^{-1}$. The limit of agreement is from -3612 to 3812 and includes all samples. For Zn (Figure 7), the mean difference is $5 (\pm 14) \mu g g^{-1}$ while the limit of agreement is from -73 to 84 and includes all but one sample.

The results in TRT r.f.CCP-AES and FAAS significantly different according to the Bland and Altman test are shown boldface and given as footnote (a) in Table III. This is attributed to a more depressive matrix effect in TRT r.f.CCP-AES as compared to FAAS.

CONCLUSIONS

The analytical performance of the new method TRT r.f.CCP-AES in the determination of Cu, Mn and Zn in sediments and biological samples was evaluated and the results were statistically compared with those obtained by FAAS.

Although the real limits of detection in TRT r.f.CCP-AES were higher than those in FAAS, most of the analyzed samples showed Cu, Mn and Zn contents above the limit of determination and analysis by TRT r.f.CCP-AES was possible.

Statistical analysis (F-test, regression analysis, Bland and Altman test) has shown a satisfactory agreement for Cu, Mn and Zn determinations by the two methods, both in accuracy and reproducibility. This suggests that TRT r.f.CCP-AES could be an alternative to FAAS in the analysis of some metals in environmental samples. The studied plasma source offers the advantage of a low Ar consumption and the possibility of a simultaneous determination compared to atomic absorption spectrometry.

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SAŽETAK

Tragovi Cu, Mn i Zn u vodenim životinjama i sedimentu iz korita rijeke Cris – zapadna Rumunjska

Dio I: Statistička ocjena podataka dobivenih atomskom emisijskom spektrometrijom s radiofrekventnim kapacitivno spregnutim izvorom plazme i plameno-atomskom apsorpcijskom spektrometrijom

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Prikazana je ocjena atomske emisijske spektrometrije s radiofrekventnom kapacitivno spregnutom plazmom s dvije prstenaste elektrode (TRT r.f. CCP-AES) u radu kod 275 W i 0,4 L min⁻¹ Ar, u usporedbi s plamenom atomskom apsorpcijskom spektrometrijom, i to pri određivanju Cu, Mn i Zn u sedimentima i vodenim životinjama. Granice detekcije Cu, Mn i Zn u r.f. CCP-AES bile su 2, 6 i 3 µg g⁻¹. Statistička ocjena rezultata temeljila se na 31 uzorku sakupljenom u koritu rijeke Cris, Rumunjska. Nakon uklanjanja uzoraka, čija je koncentracija metala bila ispod granice određivanja u TRT r.f. CCP-AES, F-test (95% pouzdanosti) pokazao je sličnu preciznost obje metode, sa po jednim izuzetkom u slučaju Mn i Zn. Temeljem 21, 28 i 31 određivanja Cu, Mn i Zn, statistička korelacija i regresija, kao i analiza po Blandu i Altmanu (95% pouzdanosti) pokazale su sustavne pogreške u TRT r.f. CCP-AES u odnosu na FAAS samo u jednom slučaju za Cu, u dva slučaja za Mn i u jednom slučaju za Zn. Sadržaj metala određen je u područjima: 10–400 µg g⁻¹ (Cu), 20–16000 µg g⁻¹ (Mn) i 20–1200 µg g⁻¹ (Zn).