

On the possibilities of ICP-AES for analysis of archaeological bones

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Abstract: The possibility of using inductively coupled plasma atomic emission spectrometry (ICP-AES) to determine the elemental composition of archaeological bones elements was evaluated and discussed. The interferences of the major elements (Ca, P, K, Na, Al and Fe) on the microelements (Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sr, Zn) were investigated and the appropriate analytical lines were selected. The role of different nebulizers (cross-flow, Babington and Meinhard) on detection limits were investigated. The applicability of the proposed procedure was demonstrated analyzing IAEA-SRM-H-5 (Animal bone); and authentic bone sample dating back to the 4th century BC. These results were compared to ETAAS and ICP-MS.

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1 Introduction

The concentrations of elements in archaeological bones, especially trace elements, can serve as useful indicators of dietary habits, nutrition and disease [1-7]. The variations in the concentration of elements such as Sr, Ba, Cu, Zn, V may be used to estimate the type of food and its importance in the daily diet. The content of Ca and P indicates the conditions of preservation of the bone material. Mn, Fe, Al, K, Na and other elements are indicative of the extent of soil effects and effects post mortem. Due to burial, the effects of digenesis, and different dietary habits, the elemental composition of the archaeological bones may be very different compared to the bones of today [e.g. 8, 9]. The increase

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in the concentration of elements, such as Al, Fe, Mn is typical while the concentrations of trace elements, such as As, Cd, Cu, Ni, Zn may be higher or lower depending on the conditions of the burial place and dietary habits.

Several analytical techniques are used in the analysis of archaeological bones: (a) inductively coupled plasma atomic emission spectroscopy (ICP-AES) (see [3, 5, 10]); (b) atomic absorption spectroscopy (AAS) (see [11-14]); (c) instrumental neutron activation analysis (INAA) [see 15-18]; (d) inductively coupled plasma mass spectroscopy (ICP-MS) [19], (e) and more often the combinations of AAS/ICP-AES [20-23] and ICP-AES/XRF [1, 2, 7]. The ICP-AES technique (see [1-3]) is gaining popularity in the analysis of bone materials. Very little has been reported on the determination of all elements in bones, which are important in the reconstruction of ancient diets (see e.g. [1, 2, 13, 14]). Reports devoted to the methodological aspects of ICP-AES in the analysis of archaeological bones are not well documented with the exception of [24, 25]. Despite good detection limits obtained using the ICP-AES technique, there are limitations because it is hard to determine many trace elements in bone. One reason could be their concentrations lie below the lowest level of detection, another reason because the limits of detection for some elements are degraded by matrix interferences, by background changes, and by stray light effects arising from major bone constituents. Such effects may be found in the bone where the matrix element is Ca and the major elements are K, Na, Fe, Mn etc., all of which create spectral problems in the analysis. Spectral interferences have not been adequately investigated or evaluated. The lack of investigation is justified by the fact that Sr and Ba primarily have been determined in archaeological bones fall off using the ICP-AES technique.

The main objective of this research is to estimate the real applicability of the ICP-AES technique in the analysis of archaeological bones for dietary reconstruction.

2 Experimental

2.1 Instrumentation.

Samples are measured using a Spectroflame ICP-D spectrometer (Spectro Analytical Instruments, Kleve, Germany), nebulizers type Meinhardt, V- groove and cross-flow.

The measurement settings are listed in Table 1.

2.2 Samples and sample preparation.

Information regarding the analyzed samples and standard reference material is listed in Table 2. For the interferences investigations of the elements Ca, P, Na, K, Al and Fe, the model solutions containing the matrix elements in varying concentrations and microelements (Ba, Cu, Co, Pb, Cd, Cr, Ni, Sr, Zn) ranging from 0.27–25 mg/l were analyzed.

2.2.1 Sample digestion.

The bones were rinsed with tap water, brushed clean and rinsed with deionized water. The samples for analyses were drilled using a diamond disc. These samples were treated in an ultrasonic bath with deionized water and finally dried in an oven at 105° C. About 1 g of the bone sample and IAEA SRM H-5 (Animal bone) were ashed (7h, 725 °C). A sample of 0.4–0.5 g was taken for analysis and dissolved in conc. HNO₃. After evaporation to dryness the residue was dissolved in 2% HCl and diluted to 25 cm³. The solution was analyzed using the ICP-AES analytical technique.

2.3 Calibration of the spectrometer.

The spectrometer was calibrated with multi-element standard stock solutions of Ba, Cu, Co, Pb, Cd, Cr, Ni, Sr, Zn. Single stock solutions (1000 mg/l) of all determined elements were prepared by dissolving their oxides (Merck) in HCl (1:1) (Merck). Then five mixed standard stock solutions were made using the concentration ratios of the determined elements which matched the normal concentrations found in the archaeological bones.

2.4 Ion-exchange procedure for isolation of Cu.

The sample solution was passed through a column (h = 8 cm, d = 0.5 cm) using a 100–200 mesh Dowex 1x10, Cl⁻ form anion resin, preequilibrated with 2.5% HCl. The sample rate was 2ml/min. The elution of Cu was conducted using 2.5M HCl.

3 Results and discussion

The choice of analytical lines to determine the presence of Ba, Cu, Co, Pb, Cd, Cr, Ni, Sr, Zn in bones is complicated by the expected interferences from matrix and major elements such as Ca, P, Fe, K, Na, Al and Fe. Their concentrations are orders of magnitude higher than the trace element concentrations.

Investigations [24] have been conducted on the interference of Ca, Mn, Al, Fe in the determination of B, Cu, P, S; however, concentration intervals and ratios are generally very different from those observed in archaeological samples; the reported results are often contradictory. Besides, these are not the typical elements determined in a dietary study.

3.1 Major element interferences

Whenever possible several analytical lines of the elements were investigated due to expected interferences of major elements. The lines are presented in Table 3.

Solutions of the major interfering elements Ca (1000–10000 mg/l), P (500–10000 mg/l), K (50–5000 mg/l), Na (70–7000 mg/l), Al (50–1000 mg/l) and Fe (40–800 mg/l)

were measured to investigate the signals indicated at the analytical lines of the determined elements (apparent concentrations). First, interferences were established for all determined elements at the following concentrations of the major elements: P – 500mg/l; Ca and Na – 1000 mg/l; Al – 80 mg/l; K – 500 mg/l and Fe – 80 mg/l. A further increase in the concentrations of the major elements led to an accumulative effect. No apparent concentrations were observed from:

- Ca on Cd and Ni;
- Fe on Cd, Cu, Ni and Pb;
- Al on Cd.

Second, a mixed model solution of the microelements (concentrations of Sr and Zn – 25 mg/l; Ba – 15 mg/l; Pb – 2.5 mg/l; Cd, Cr and Ni – 1.5 mg/l; Cu – 0.5 mg/l; Cd – 0.27 mg/l) was added to the solutions of major elements, and measurements were performed to establish the error in the determination.

Of course, the highest errors are established in the solutions with the highest concentrations of the major elements. Figure 1–3, however, presents the results for those concentrations of matrix elements (Ca (1000 mg/l), P (500 mg/l), K (500 mg/l), Na (1000 mg/l), Al (80 mg/l) and Fe (80 mg/l)) where first interferences were established. Thus the errors in Fig. 1–2 are minimal.

The analytical lines of Ba (445.40 nm), Co (238, 89 nm), Sr (477.71 nm) and Zn (213.86) are in general not seriously disturbed by any of the major elements (overall error not higher than 10 %). The error introduced by Ca and P in the determination of Ba is about 11–13% and from Ca on Co is – 8%.

On the other hand, the errors in the determination of Cu using analytical line 324.752 nm, led to the assumption that it cannot be used for direct determination. The error introduced by Ca only, exceeds 20 % (Fig. 1).

The determination of Cr is strongly interfered by the elements Fe and K using 267.716 nm line (see Fig. 2), introducing error over 20 %. The interferences of major elements in the determination of Pb are less than 10%, with the exception of Fe introducing – 20 % error when the 220.35 nm line of Pb is used. For further investigations, this line was used after background correction.

The analysis of the solution containing the highest concentrations of the investigated major elements, proved that the detection of Cu, P, Cd and Ni was not possible. The errors that were introduced exceeded 30 %. (Fig.3).

The investigations on the lines of Al, Mg and Cd, proved the possibility to use the lines at 308.21 nm (Al), 226.50 nm (Cd), after background corrections on the right, and of 220.35 nm for Mg. In comparison to the other investigated lines the results obtained in this way showed much better precision.

The natural ratios of major elements versus the microelements in bones have to be considered in order to evaluate the significance of the results. Table 4 presents these ratios in conjunction with the investigated ratios and the estimation of error. With an increase in the concentration of the macrocomponent (increase of the ratio) the errors increase as well.

The values in Table 4 indicate that in real samples serious interferences are to be expected from:

- Ca on Cr, Cu and Zn;
- K on Cu and Ni;
- Na on Co, Cr, Cu and Ni;
- P on Cr, Cu, Zn (and to a certain extent on Ba and Sr);
- Fe on Cd and Cr;
- Al on Cr, Cu, Ni, Pb and Zn.

The investigations of model solutions at varying concentration intervals compared to expected concentration intervals in real samples, indicate an inability to correctly determine the presence of Cu, Co, Cd, Ni as well as Zn at lower concentrations. However, all elements considered relevant for dietary reconstruction (except Cu) may be determined by using the ICP-AES technique with a Meinhard nebulizer.

3.2 Investigation on the influence of nebulizer type.

Essentially three types of pneumatic nebulizers are used in ICP-AES: the concentric flow [26], the cross-flow [27] and the Babington type nebulizer (V-groove version) [28]. The Meinhard nebulizer which has a limited salt tolerance, is the most popular. The other two types of nebulizers have a greater salt tolerance. Since the salt content in bone samples is normally above 4.5%, the efficiency of the three types of nebulizers was tested for analysis of the archaeological bones.

Table 5 presents the results from the analysis of IAEA SRM H-5 (Animal Bone) using the three nebulizers under the experimental conditions described above. The results indicate that because of the lower degree of dilutions necessary for V-groove and cross-flow nebulisers, the number of determined elements increased to a range of 10–14 including Cu, Cr and Fe. The determination of Ca and P is possible at dilution 1:10, while for the Meinhard nebulizer dilution 1:100 is necessary. In respect to the dietary important elements Ba, Mg, Sr, Ca, Zn and P no differences were detected among the nebulizers.

Thus for dietary reconstruction Meinhard nebulizer may be used not permitting only the determination of Cu from all important trace elements. If the purpose of the investigation is to determine the diagenetic effects (content of Mn, Fe, Al etc) of some specific diseases (Pb) or some traditional habits (Ti, Pb, Fe), then the V-groove and cross flow nebulizers should be preferred.

3.3 Ion-exchange separation of Cu.

When the Meinhard nebulizer is used and the instrumental determination of Cu is not possible in the remains, or when the concentration of Cu is below the detection limit as in individuals on milk diet [29, 30], a procedure for the isolation and concentration of the sample prior to the measurement should be applied.

For this purpose, an anion exchange procedure was developed, described in the ex-

perimental section of this paper.. Two concentrations of the eluent were tested – 6M and 2.5M. Figure 4 illustrates the elution curves which indicate the quantitative elution of Cu from the resin both with 6M and with 2.5M HCl in final volumes of 10 and 13 ml respectively (see Fig. 4).

Additionally, 2.5M HCL has been found to be more suitable for the following measurements.

This procedure was tested in the analysis of the bone samples as well as in the analysis of IAEA SRM H-5 (Animal bone). The results are presented in Table 6 in conjunction with the results from ETAAS and the certified value for H-5. The overall uncertainty is evaluated using the SR-criterion [31] and is below 25% (i.e. excellent agreement between methods). The data for the Student's t-criterion indicate no systematic errors.

3.4 Analysis of archaeological bones using the proposed ICP-AES method

Table 7 presents the results from the analysis of archaeological bones from three individuals (man, woman and child) from Thrace – 4th c. BC. The results are compared to data from the ICP-MS analysis. A very good agreement between the results from both methods has been established using SR- criterion [31].

On the basis of the analytical data (Table 7) and the knowledge about the correlations between chemical composition of bones and the diet (see e.g. [32]) a conclusion about the dietary habits of the investigated individuals may be reached (more about is possible to find in [30]).

Since the high concentration of Sr is related to the consumption of foodstuff from plants we propose the vegetarian diet for the investigated adults (B-053.SOZ, B-054.SOZ). The very low data of $\log ([\text{Sr}]:[\text{Ca}])$ – lower than – 2.75 indicate consumption of corn. The determined concentration of Zn (~ 100 mg/kg) confirms the conclusion about a dominant vegetarian diet and very low part of meat in the diet. The low content of Ba indicate for consumption of sea food. An evidence for this conclusion is the low value of $\log ([\text{Ba}]:[\text{Sr}])$ (e.g. -1.1 for B-054.SOZ). That is quite logical concerning the location of Sozopol (on Black sea coast).

The concentration of copper confirms also the conclusion about a dominant vegetarian diet. But the suckling and small children (B-029.MAP) are individuals on milk diet and it may be presumed that low concentration of Cu is probably connected with milk consumption and that explain the very low concentration of Cu in the child's bone in comparison to the data for the adults.

4 Conclusion

The investigations described in the present paper prove that the ICP-AES technique used in conjunction with a Meinhard nebulizer can be successfully applied in the analysis of archaeological bones for dietary reconstruction. Of the important elements (Ba, Sr, Zn, Cu, Ca, P etc) only Cu presents a serious problem for the instrumental determination.

Therefore, a method for the anion exchange isolation of Cu is proposed. The results from the analysis of SRM and the comparison to other methods indicate the very good analytical characteristics of the proposed method and its applicability in archaeometric studies.

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Spectrometer	Spectroflame-D
Generator	27 MHz
Power	1200/1000 W
Coolant gas flow	14 l/min
Nebulizer gas flow	1 l/min
Auxiliary gas flow	0.8 l/min
Nebulizer	Meinhard TR-50-C1 concentric glass, Cross – flow and V-groove
Debit of sample	2.5 ml/min
Height	15 mm

Table 1 Measurement conditions.

Sample/SRM	Information
B-029.MAP	Malak Porovets-grave 1; 4 th c. BC, Child, 4–5 years
B-044.MAP	Malak Porovets-grave 16; 4 th c. BC, Woman, 35–40 years
B-053.SOZ	Sozopol-grave 43; 4 th – 3 rd c. BC, Woman, 40–50 years
B-054.SOZ	Sozopol-grave 154; end of 4 th c. BC, Man, 22–30 years
B-055.SOZ	Sozopol-grave 70; 4 th c. BC, Man, 22–30 years
B-058.SOZ	Sozopol-grave 67; end of 4 th c. BC, Woman, 40–50 years
B-061.SOZ	Sozopol-grave 186; 3 rd c. BC, Woman, 40–50 years
SRM	IAEA H-5 Animal Bone

Table 2 Description of the analyzed samples and reference materials.

Elements	Tested lines, λ ,nm	Chosen lines, λ ,nm
Al	308.215; 396.153;	308.215
Ba	455.40; 233.527	455.40
Ca	315.887; 393.37; 422.673	393.37
Cd	226.50	226.50
Co	228.80; 231.60; 238.89	238.89
Cu	324.75; 327.393	324.75
Cr	267.72	267.72
Fe	259.94; 238.204	259.94
K	766.490	766.490
Mg	280.27; 285.213; 279.077; 279.553	280.27
Mn	257.610	257.610
Na	588.99; 589.592	588.99
Ni	221.640; 231,651	231.651
Pb	220.353	220.353
P	213.619	213.619
Sr	407.771; 421.552	407.771
Ti	334.940	334.940
Zn	213.857	213.857

Table 3 Investigated analytical lines.

	Natural ratios	Investigated ratios	Ratios, where the first interference was established (%)
Ca/Ba	20–16500	70–670	70 (13)
Ca/Cd	1990–9600	3700–37000	18500 (> 100)
Ca/Co	118000–1180000	670–6700	–
Ca/Cr	4950–6256600	670–6700	3300 (70)
Ca/Cu	1000–2475000	2000–20000	2000 (22)
Ca/Ni	772000–1767800	670–6700	–
Ca/Pb	0–854000	400–4000	–
Ca/Sr	50–12000	40–400	200 (4)
Ca/Zn	40–12000	40–400	400 (7)
K/Ba	0.1–30	3–300	300 (29)
K/Cd	2.42–200	185–18500	18500 (19)
K/Co	144–2500	30–3300	3300 (55)
K/Cr	4.6–200	30–3300	330 (20)
K/Cu	1–42500	100–10000	10000 (10)
K/Ni	260–3000	30–3300	330 (13)
K/Pb	0–10	20–2000	–
K/Sr	0.4–28	2–200	200 (8)
K/Zn	0.4–20	2–200	200 (7)
Na/Ba	3–151	3–330	333 (20)
Na/Cd	35–1000	185–18500	3300 (22)
Na/Co	2000–13000	30–3300	3300 (17)
Na/Cr	66–5800	30–3300	330 (20)
Na/Cu	17–227000	100–10000	10000 (10)
Na/Ni	10000–16000	3–3300	330 (13)
Na/Pb	0–9	20–2000	–
Na/Sr	0.7–500	2–200	–
Na/Zn	6–110	2–200	200 (29)

Table 4 Natural ratios of major elements versus microelements, investigated ratios and estimation of error (%).

	Natural ratios	Investigated ratios	Ratios, where the first interference was established (%)
P/Ba	2–150	30–330	30 (17)
P/Cd	1150–49500	1850–37040	–
P/Co	6080–68500	330–6700	–
P/Cr	2200–27000	330–6700	6700 (13)
P/Cu	100–7100	100–2000	2000 (10)
P/Ni	440700–592000	330–6700	–
P/Pb	0–302	200–4000	–
P/Sr	24–24000	20–400	400 (10)
P/Zn	180–5200	20–400	400 (10)
Fe/Ba	0.03–80	3–50	50 (11)
Fe/Cd	0.4–530	150–300	150(11)
Fe/Co	24–6500	27–560	–
Fe/Cr	0.76–2900	27–560	50 (> 100)
Fe/Cu	0.2–114000	80–1600	–
Fe/Ni	120–8100	26.7–534	–
Fe/Pb	0–0.1	16–320	32 (20)
Fe/Sr	0.01–266	1.6–32	–
Fe/Zn	0.06–600	1.6–32	–
Al/Ba	0.02–150	4–80	80 (36)
Al/Cd	0.2–1024	200–22000	200 (11)
Al/Co	13–13000	40–4000	–
Al/Cr	0.4–5600	40–4000	400 (13)
Al/Cu	0.1–220000	0.5–2400	2400 (40)
Al/Ni	80–15700	40–400	240 (24)
Al/Pb	0–0.6	24–2400	240 (24)
Al/Sr	0.05–512	2.4–4.8	48 (12)
Al/Zn	0.4–100	2.4–48	48 (24)

Table 4 (Cont.)

Elements	Type nebulizer			Certified value
	V-groove	Meinhard	Cross – flow	
Al	99 (5) ^b	99 (4)	98 (5)	101 (64)
Ba	72 (7)	85 (9)	95 (8)	72 (28)
Ca ^a	19.87 (5)	21.7 (8)	23.5 (2.5)	21.17 (2.4)
Cr	n.a.	n.a.	2.87 (0.15)	2.56 (1.06)
Cu	0.61 (0.03)	n.a.	< 1	0.64 (0.33)
Fe	82 (2)	n.a.	90 (15)	81 (11)
K	n.a.	n.a.	620 (35)	670
Mg	4100 (47)	3470 (19)	4040 (300)	3530 (250)
Mn	0.73 (0.05)	n.a.	< 1	0.76 (0.76)
Na	4100 (260)	n.a.	5300 (420)	4770 (47)
P ^a	9.0 (0.5)	9.98 (1.8)	11.4 (0.8)	9.58 (4.4)
Sr	110 (19)	102 (4)	119 (10)	105 (18)
Ti	n.a.	n.a.	< 1	n.a.
Zn	92 (1)	110 (4)	114 (9)	90 (15)

Table 5 Results from analysis of IAEA SRM H-5 Animal Bone (mg/kg) using three types of nebulizer.

^a = Results are in percentages.

^b = Standard deviation from the analysis 3 independent parallel samples.

Sample	Results from ICP-AES	Results from ETAAS	Student test	SR ^b [%]
B-055.SOZ	37.26 (1.86) ^d	40.95 (0.61)	3.43	18.1 ^c
B-058.SOZ	32.38 (1.62)	31.29 (0.97)	1.17	13.8 ^c
B-061.SOZ	53.66 (2.68)	50.78 (1.32)	1.86	16.2 ^c
B-044.MAP	63.56 (3.18)	65.32 (1.18)	0.96	12.4 ^c
SRM-IAEA H-5 ^a	n.d.	0.65 (0.08)	–	28.6 ^e

Table 6 Comparison of data for Cu from analysis with ICP-AES (after ion-exchange) and ETAAS, (mg/kg).

^a = certified value = 0.64 mg/kg

^b = SR is evaluated according [31]

$$SR = \frac{|C_{exp} - C_{st}| + 2U}{C_{st}} \cdot 100$$

C_{exp} = experimental value; C_{st} = certified value; U = uncertainty of experimental data.

SR < 25 % = excellent agreement

25 % < SR < 50 % = acceptable agreement

SR > 50 % = unacceptable agreement

^c = agreement to results obtained by ETAAS

^d = standard deviation from the analysis of 3 independent parallel samples

^e = agreement to certified value

Element	B-029.MAP (child, 4th c. BC)		B-053.SOZ (woman, 4th–3rd c. BC)		B-054.SOZ (man, end of 4th c. BC)				
	ICP-AES	ICP-MS	SR, %	ICP-AES	ICP-MS	SR, %	ICP-AES	ICP-MS	SR, %
Al	2380 ± 200 ^a	2450 ± 130	14.7	39 ± 5	38 ± 6	28.9	57 ± 6	50 ± 9	40
Ba	86 ± 7	92 ± 12	21.7	69 ± 7	92 ± 19	40.2	40 ± 5	43 ± 8	30.2
Ca (%)	33.6 ± 2.5			34.1 ± 3.5			30.2 ± 2.0		
Cr	2.9 ± 0.9			1.16 ± 0.90			0.82 ± 0.25		
Cu	0.08 ± 0.03			1.3 ± 0.4			12.1 ± 0.3		
Fe	1570 ± 250			35 ± 10			38 ± 4		
K	560 ± 80			171 ± 15			90 ± 10		
Mg	1660 ± 100	1725 ± 120	15.4	1330 ± 110	1450 ± 250	23.4	1500 ± 120	1600 ± 400	21.3
Mn	69 ± 4			3.8 ± 0.9			< 1		
Na	4050 ± 200			4500 ± 300			4700 ± 300		
P (%)	17.6 ± 1.2			15.8 ± 2.0			16.6 ± 1.5		
Sr	162 ± 5	165 ± 11	7.8	510 ± 50	445 ± 60	37	537 ± 36	456 ± 30	33.6
Ti	30 ± 4			< 1			< 1		
Zn	129 ± 5	133 ± 8	10.5	103 ± 9	94 ± 3	28.7	106 ± 10	97 ± 5	29.9

Table 7 Results from analysis of archaeological bones with ICP-AES and ICP-MS [mg/kg].
a = Standard deviation from the analysis of 3 independent parallel samples

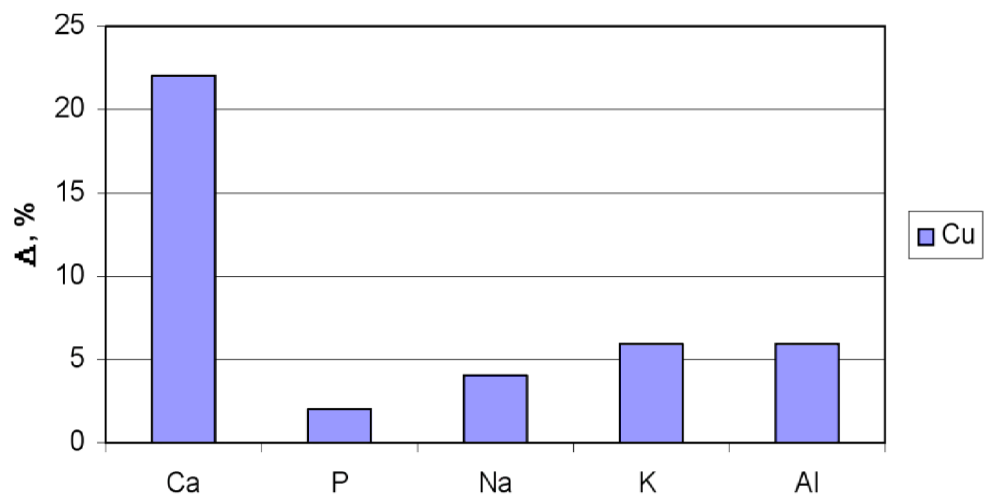


Fig. 1 Influence of the matrix elements Ca and Na (1000 mg/l), P (500mg/l), K (500mg/l), Al (80mg/l), Fe (80mg/l) on the accuracy of the analysis of Cu, 324.75 nm.
 Δ =percentage error in determination.

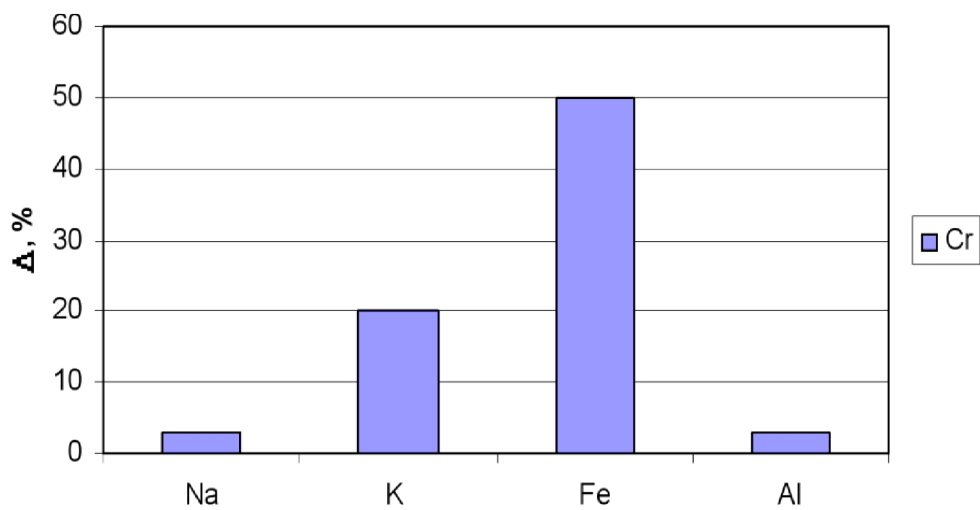


Fig. 2 Influence of the matrix elements Na (1000 mg/l), K (500mg/l), Fe (80 mg/l), Al (80 mg/l), Fe (80mg/l) on the accuracy of the analysis of Cr, 267.72 nm.

Δ =percentage error in determination.

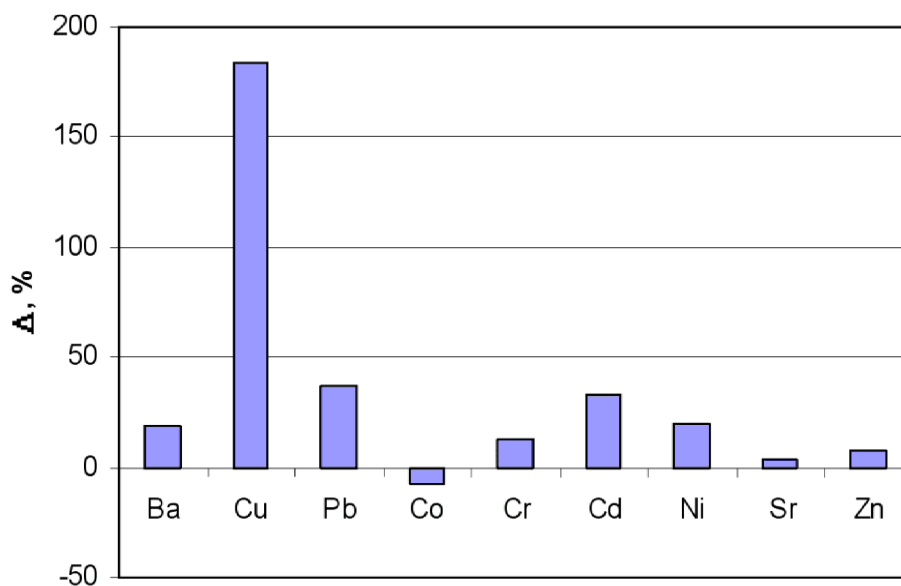


Fig. 3 Influence of the matrix elements K (5000 mg/l), Na (7000 mg/l), Al (1000 mg/l), Fe (800 mg/l), Ca (10000 mg/l), P (5000 mg/l) on the accuracy of the analysis of Ba, Cu, Pb, Co, Cr, Cd, Ni, Sr and Zn.

Δ = percentage error in determination.

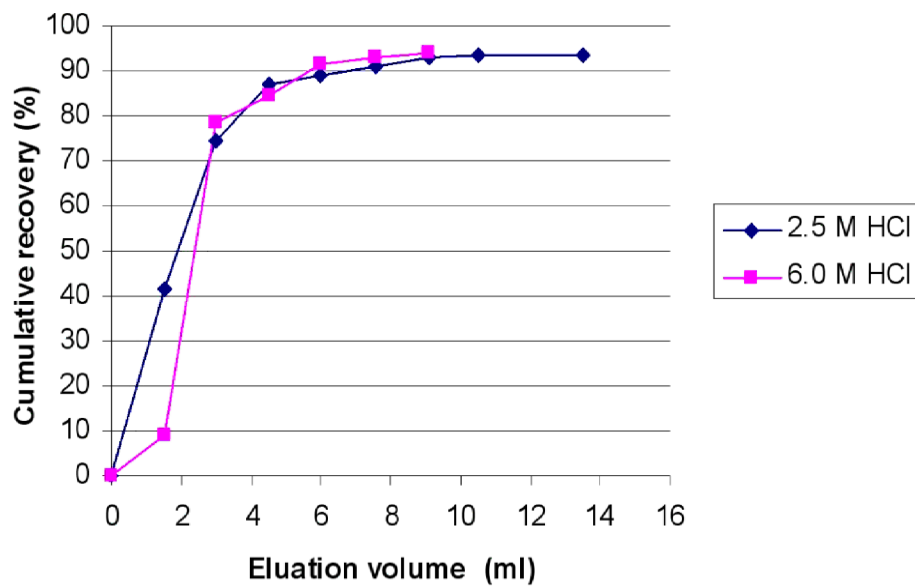


Fig. 4 Elution profile for Cu after elution with 2.5 M and 6.0 M HCl from Dowex 1x10 anion-exchange column.