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ORIGINAL PAPER

SOME MICRO- AND TRACE ELEMENTS IN SELECTED BOTTLED NATURAL WATERS FROM THE POLISH MARKET EVALUATED BY ELECTROCHEMICAL METHODS

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Abstract

Although beneficial properties of mineral waters are acknowledged by law in many countries, the use of water for medicinal purposes is not universally accepted. Notably numerous waters (especially mineral and curative ones) have high concentrations of mineral and trace elements. These mineral waters are common on the market and their availability is not regulated by law. Due to the hazard of overdosing, quantification of trace elements and minerals seems to be necessary. The World Health Organization, European Standards and Polish Standards recommend different methods for elemental determination, i.e. spectrometry, photometry for zinc determination, colorimetry or spectrometry for copper, and ionic chromatography for calcium, chloride and fluoride. In this paper, alternative, electrochemical methods have been applied to determine zinc, copper, calcium, chloride and fluoride in most popular natural and curative waters from southern Poland. The determined elemental content varied between 3.85-33.54 μg L^{-1} for zinc, 85-15.33 μg L^{-1} for copper, 2.8-2433.63 mg L^{-1} for chloride, 0.4-1.66 mg L^{-1} for fluoride and 11.05-478.48 mg L^{-1} for calcium. The voltammetric method was tested according to the validation procedures, taking into account the following parametes: linearity range, limit of detection and limit of quantification and precision. The results show that the applied electroanalytical methods are suitable for determination of the selected elements in waters of natural origin, ensuring low instrumental and analysis costs while providing results comparable with ones achieved with recommended methods.

Keywords: natural waters, stripping voltammetry, potentiometry, trace elements, microelements.

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INTRODUCTION

Natural waters have a long tradition of being used in treatment of various afflictions (Bender et al. 2014). Both Polish and European legislation (Directive 80/777/EEC) provide definitions of each type of natural water. According to the Polish law, natural mineral spring water should come from documented sources of underground water, extracted through one or few openings. This type of water should be chemically and microbiologically clean, have constant composition and produce beneficial effects on physiological functions of the human organism, no clinical or pharmacological tests are required (Dz.U. 2011, No. 85, 163). Natural spring water is chemically and microbiologically clean water and generally does not differ from water used for general consumption. Table water is obtained either by mixing natural spring water with mineral water or by adding mineral salts, one or more physiologically active compounds to spring water or normal tap water. The Polish Law (Dz.U. 2011, No. 85, 163) also specifies salts which can be used in table water production: calcium chloride, magnesium chloride/sulphate and sodium and potassium chlorides, sulphates and hydrogenocarbonates. Furthermore, the ministry specifies the required accuracy of each measurement of these substances, which in turn determines what analytical methods can be applied for each assay.

Water is essential for life and has been recognized as such since ancient times, but its use for medicinal purposes is not universally accepted. Most national legislations acknowledge that mineral waters have beneficial properties (Fricke 1993). For the human organism, water is one of the main sources of many elements, such as calcium, magnesium, chloride, fluoride (almost a fourth of fluoride intake in children and a half in adults) and trace elements (Berg et al. 2011, Varga 2012, Salomon, Regulska-Ilow 2013). Water treatment seems to play a promising role in nephrology (Wang et al. 2013), in the prevention of iron deficiency in patients with different types of anaemia (Kochański 2002, Halksworth 2003), or in the improvement of gastric and pancreatic secretion (Varga 2012, Salomon, Regulska-Ilow 2013). Rybeczka-Gacek et al. (2015) suggest that curative water can mitigate type C hepatitis symptoms. However, due to adverse effects inducible by components of curative waters during uncontrolled consumption, it is advised that these waters should be used in the same manner as pharmaceuticals (Salomon, Regulska-Ilow 2013). On the other hand, pharmaceutical preparations have to fulfil strict pharmacopoeia guidance rules and have a precisely determined composition. Fricke (1993) suggests that curative waters do not tend to be inspected so rigorously; furthermore, their standards are more lenient than even the ones set for mineral waters. Drobnik et al. (2011) note that numerous known waters deserve special attention.

There are different recommendations on analytical methods of soluble components in water samples, depending on the legislative body that has issued the standards, but generally spectroscopic methods or, less often, ionic chromatography are recommended. None of these methods is free from interferences, e.g. due to high salinity of therapeutic water. Therefore, it may seem that application of simple electroanalytical methods should improve the analytical performance. The objective of this work has been to determine zinc, copper, calcium, chloride and fluoride in most popular natural and curative waters from southern Poland by stripping voltammetry and potentiometric analysis.

MATERIAL AND METHODS

The investigated waters were purchased in shops or obtained directly from spa resorts. The set of samples included:

- curative/medical waters: Słotwinka, Jan, Zuber (Spa Krynica-Żegiestów), Franciszek, Józef, Henryk (Spa Wysowa S.A.), Wielka Pieniawa (Kłodzko Spas S.A.);
- mineral waters: Krynica Minerale (Mineral Complex Sp. z o.o.), Muszynianka (Spółdzielnia Pracy Muszynianka), Staropolanka 2000 (Kłodzko Spas S.A.), Kryniczanka (Krynica Żegiestów S.A. Spa), Cisowianka (Nałęczów Zdrój S.A.), Polanicka (Wytwórnia Wód Mineralnych MINERAL Sp. J.);
- spring waters: Kropla Beskidu (Coca-Cola Poland Sp. z o.o.), Żywiec Zdrój (obtained from Żywiecki Park Krajobrazowy)

Reagents

Standard solutions of $Zn(NO_3)_2$ and $Cu(NO_3)_2$ were prepared by proper dilution of 1000 mg L^{-1} stock standard solutions (OUM, Łódź, Poland). HNO_3 65% (Merck, Suprapur®), HCl 36% (Merck, Suprapur®), KNO_3 (Merck, Suprapur®), KCl (Merck, Suprapur®), NaCl (POCH, Poland), $CaCO_3$ (Merck CertiPur®), CH_3COOH (POCH, Poland), EDTA (Merck Titripur®), NaOH (POCH, Poland), NaF (Reachem, Russia) were purchased from local suppliers. All solutions for voltammetry were prepared using quadruple distilled water from a quartz distiller (S2-97A, Chemland, Poland).

Calcium standard stock solution (1000 mg L^{-1}) was prepared by dissolving 2.499 g of dried $CaCO_3$ in 50 mL of 1M HCl, in a beaker, followed by quantitative transfer of the solution to a volumetric flask, replenished up to the volume of 1 L. The stock solution was then stored in an HDPE bottle. Chloride stock standard solution (1000 mg L^{-1}) was prepared by dissolving 1.649 g of dried NaCl in a 1 L volumetric flask. Fluoride stock standard solution (100 mg L^{-1}) was prepared by dissolving 0.2210 g of dried anhydrous NaF (Reachem pure) in a 1 L HDPE volumetric flask. The fluoride stock solution was refrigerated in an HDPE bottle and used before 3 months. Working standard solutions were made by diluting appropriate amounts of the stock solutions. Total ionic strength adjustment buffer I (TISAB I – 4M KCl) for calcium determination was prepared by dissolving 74.55 g KCl in a 250 mL volumetric flask. Total ionic strength adjustment buffer II (TISAB II – NH_4CH_3COO/CH_3COOH) was prepared by dissolving 77.8 g of ammonium acetate (POCH) in 250 mL of double distilled water and then adding 57 mL of glacial acetic acid. Total ionic strength adjustment buffer III (TISAB III – CH_3COOH/NaCl/Disodium EDTA) was prepared by dissolving 57 mL of glacial acetic acid, 58 g of NaCl and 4 g of disodium EDTA in a 500 mL beaker. Then, after pH adjustment to 5.3, the solution was filled up to 1 L and kept in a refrigerator. All solutions were made with double distilled water.

Apparatus

The voltammetric measurements were performed on a M161 multi-functional electrochemical analyser with an M164 electrode stand and EA-GRAPH 6.0 software (mtm anko, Poland), The working cell consisted of three electrodes: CGMDE (controlled growth mercury drop electrode) with the working surface of 1.4 mm^2 as a working electrode, a double junction silver/silver chloride electrode as a reference electrode and platinum wire as an auxiliary electrode. Potentiometric analysis was done on an OPB2 electrochemical values meter (mtm anko, Poland), with appropriate ion selective electrodes (ISE): calcium ISE (PCV membrane; Sentek, USA), Fluoride ISE (monocrystalline LaF_3 membrane; Detektor, Poland) Chloride ISE (polycrystalline membrane (AgCl/AgS); Detektor, Poland) and reference electrodes: single junction silver/silver chloride electrode (Detektor, Poland). A double junction silver/silver chloride electrode (outer junction filled with 3M KNO_3; Detektor, Poland) was used for fluoride and chloride determination.

Sample preparation

Aliquots (20-25 mL) had been drawn from each of the water samples, transferred to quartz test tubes and 1 mL of HNO_3 (Merck, Suprapur®) was added for every 5 mL of the sample. Test tubes were set into a UV R8 Digestion unit (Mineral, Poland). Digestion was carried for 12-16 hours. Next, the samples was quantitatively transferred to quartz evaporating dishes and evaporated to almost dry residue on a hot plate at 130°C. The residue was dissolved in quadruple distilled water and quantitatively transferred to 5 mL volumetric flasks; the volume was made up to 5 mL.

Validation of the methods

The voltammetric and potentiometric methods were tested according to the validation procedures criteria (ICH, 2005) and the following parameters were established: linearity range, limit of detection (LOD) and limit of quantification (LOQ) and precision. The results are shown in Table 1.

Linearity range

4 mL 0.1 M KNO_3 solution was added directly to the voltammetric cell and deaerated for 5 min with argon. Next, the signal from electrolyte was recorded and 10 additions of 10 µL of proper 1 mg L^{-1} standard were added and measured. The measurements were made with the DP ASV (Differential Pulse Anodic Stripping Voltammetry) technique at the following parameters: for zinc(II) deposition potential (E_{acc}) -1200 mV, deposition time (t_{acc}) 20 s, pulse amplitude (d_E) -20 mV, potential step amplitude (E_s) 4 mV, sampling time (t_p) 20 ms; for copper(II) deposition potential (E_{acc}) -300 mV, deposition time ($t_{acc)}$ 40 s, pulse amplitude (d_E) -20 mV, potential step amplitude (E_s) 4 mV, sampling time (t_p) 20 ms. The relationships of the peak current and standard concentration in the range of 2.5-25 µg L^{-1} were linear both for zinc(II) and copper(II).

Using an OPB2 apparatus, the potential between appropriate ISE and the reference electrode was measured; anodic and cathodic area were connected by an electrolytic junction filled with saturated KNO_3 solution.

Limit of detection (LOD) and limit of quantification (LOQ)

Limit of detection (LOD) and limit of quantification (LOQ) for zinc(II) and copper(II) were established using the slope for regression line (a) and standard error of estimation (S_y).

Limit of detection (LOD) and limit of quantification (LOQ) for the investigated ions were estimated based on the background signal of 1M KNO_3 solution in the case of chloride and calcium(II), as well as total ionic strength adjustment buffer III in the case of fluoride.

Precision

Precisions were estimated by multiple analysis of a 400 µL sample of Franciszek water fortified by 5 µL of the standard solution at the concentration 1 mg L^{-1}. All conditions were the same as above. The measurements were repeated 6 times for both zinc(II) and copper(II). Precision estimations for the potentiometric method were performed in the same manner.

Accuracy

Accuracy was estimated based on standard recovery. The measurements were performed on a Krynica mineral water sample spiked with standard additions at 80%, 100% and 120% of the analyte (Table 1). The accuracy of the potentiometric method was assessed analogously to that of the voltammetric method but using samples of Zuber, Wielka Pieniawa and Żywiec Zdrój waters.

Interferences

The surface-active compounds cause strong interference effects on the proposed voltammetric method and were thoroughly destroyed by the dige-

Table 1

Validation parameters of voltammetric and potentiometric method

Element	Zinc	Copper	Calcium	Chloride	Fluoride
LOD (μg L^{-1})	0.020	0.330	0.031	0.046	$7.63 \cdot 10^{-4}$
LOQ (μg L^{-1})	0.059	1.000	0.095	0.140	$2.31 \cdot 10^{-3}$
Recovery (%)	101.00	99.55	99.75	100.8	108.82
SD	1.59	1.34	2.28	1.40	3.79
RSD (%)	1.57	1.34	2.29	1.40	3.49
Precision (μg L^{-1})	33.22	10.84	$5.70 \cdot 10^{-3}$	$2.01 \cdot 10^{-3}$	$2.18 \cdot 10^{-5}$
SD	0.27	0.34	$9.50 \cdot 10^{-5}$	$2.94 \cdot 10^{-5}$	$7.8 \cdot 10^{-7}$
RSD (%)	0.81	3.12	1.67	1.46	3.57
Linear equation	$I = 2.7 c + 180$	$I = 0.14 c + 1200$	$E = 56.4 \lg c + 267.1$	$E = -116 \lg c - 11.67$	$E = -95.7 \lg c - 119.1$
r	0.99989	0.998	0.9989	0.9989	0.9913

SD – standard deviation, I – current (nA), c – concentration (μg L^{-1}), r – correlation coefficient

stion procedure prior to analysis. In zinc and copper analyses, 1000-fold excess of Fe^{3+}, and 100-fold excess of Pb^{2+}, Cd^{2+}, Mn^{2+} did not interfere. In potentiometric analyses, the selectivity method was tested by the fixed interference method (FIM) and the selectivity coefficients (K_{ij}^{pot}) were calculated. Increasing calcium concentrations were measured by calcium ISE in the presence of a constant background solution of Mg^{2+}, K^+, Na^+, or Cl^- (for Ca^{2+}: 0.100 M KCl, 0.016 M NaCl and 0.001 M $MgCl_2$) (Merck, Suprapur®). The procedure was used in the same manner for chloride and fluoride ions. Under these conditions, the calculated values of selectivity coefficients were low and suggested that the proposed surfactants did not change the potential of an electrode significantly.

The developed methods were used for the determination of ions of zinc(II), copper(II), chloride, fluoride and calcium(II) in selected mineral, spring and healing waters.

Zinc(II) and copper(II) determination

The measurements were performed using the DP ASV technique in 4 mL of supporting electrolyte with 0.05M of KNO_3. Oxygen was removed from the electrolyte by an argon flow maintained for 5 minutes. The background current was registered and 400 μL of the selected sample was added and registered. According to the method of standard addition, 5 μL of the standard (1 mg L^{-1}) was added three times and measurements were performed for each addition.

The investigated water samples were analysed 6 times: three samples prepared by nitric acid evaporation to the dry residue from 20 mL of a water sample and three samples by nitrate evaporation of 25 mL of a water sample. The results are shown in Table 2.

Table 2

Content of elements (mean value ± SD, *n* = 6) in the investigated bottled natural waters from the Polish market

Natural water	Zinc (μg L^{-1})	Copper (μg L^{-1})	Chloride (mg L^{-1})	Fluoride (mg L^{-1})	Calcium (mg L^{-1})
Słotwinka	11.05 ± 0.45	14.54 ± 0.88	9.6 ± 0.76 %E = 131.50	0.09 ± 0.016 %E = 108.43	271.70 ± 6.67 %E = 122.61
Jan	22.60 ± 1.01	2.80 ± 0.15	18.00 ± 0.49 %E = 101.52	0.31 ± 0.007 %E = 170.18	163.30 ± 6.65 %E = 107.22
Zuber	17.40 ± 0.76	8.42 ± 0.63	988.99 ± 0.15 %E = 101.43	0.70 ± 0.025 %E = 174.47	30.36 ± 2.251 %E = 23.00
Franciszek	33.54 ± 0.35	10.84 ± 0.37	2433.63 ± 41.97 %E = 112.52	1.66 ± 0.072 %E = 296.36	169.92 ± 8.444 %E = 96.55
Józef	8.37 ± 0.37	7.09 ± 0.49	200.23 ± 11.35 %E = 94.14	0.31 ± 0.011 %E = 123.25	11.09 ± 1.134 %E = 98.31
Henryk	16.95 ± 0.90	15.15 ± 0.88	572.15 ± 32.17 %E = 97.78	0.56 ± 0.012 %E = 113.41	134.76 ± 2.45 %E = 86.00
Wielka Pieniawa	7.76 ± 0.51	7.39 ± 0.43	3.70 ± 0.08 %E = 102.21	0.34 ± 0.013 %E = 93.01	237.97 ± 7.33 %E = 103.24
Krynica Minerale	4.84 ± 0.23	3.84 ± 0.28	8.63 ± 0.19 %E = 97.40	0.13 ± 0.015 %E = 98.46	478.48 ± 21.55 %E = 109.525
Muszynianka	4.68 ± 0.39	4.26 ± 0.18	8.98 ± 0.29 %E = 149.66	0.05 ± 0.006 ND	200.22 ± 7.03 %E = 97.67
Staropolanka 2000	23.67 ± 0.49	1.85 ± 0.06	2.86 ± 0.04 %E = 80.91	0.58 ± 0.01 %E = 102.25	322.48 ± 5.77 %E = 99.34
Cisowianka	3.01 ± 0.16	3.65 ± 0.30	2.8 ± 0.18 %E = 2.79	0.11 ± 0.012 ND	151.31 ± 6.82 %E = 117.935
Polanicka	5.07 ± 0.10	2.34 ± 0.17	26.00 ± 0.99 %E = 90.87	0.17 ± 0.008 %E = 60.71	170.35 ± 9.55 %E = 105.74
Kropla Beskidu	4.25 ± 0.28	15.33 ± 1.22	4.40 ± 0.18 %E = 137.93	0.04 ± 0.004 ND	50.00 ± 1.86 %E = 113.40
Żywiec Zdrój	3.85 ± 0.19	6.16 ± 0.29	5.88 ± 0.07 %E = 103.74	0.12 ± 0.002 %E = 155.26	44.18 ± 1.06 %E = 103.67
Kryniczanka	57.40 ± 2.12	8.78 ± 1.41	9.57 ± 0.12 %E = 107.99	0.32 ± 0.01 %E = 242.40	378.95 ± 5.99 %E = 86.74

%E – relative error; ND – no data

Potentiometric analysis

Assays were conducted by the calibration curve method, measuring the difference in potential between a given ISE and a reference, single junction silver/silver chloride electrode (double junction in case of chloride). The ISEs were calibrated before measurements – equal ammounts of standard solutions were mixed with appropriate TISAB (in a 100:1 ratio for calcium, 10:1 ratio for chloride and 1:1 ratio for fluoride determination) and measured in a small beaker equipped with a magnetic stirrer. Each measurement was repeated 4 times, and afterwards the calibration curve was plotted. The electrode was recalibrated every 2 hours or when the drift of the electrode exceeded 1 mV. Subsequently, all samples were mixed with an appropriate TISAB and measured 3 times under the same conditions as the standards. Between measurements, all solutions and samples were kept at +4°C and were warmed before measurements to achieve equal, room temperature. The results are shown in Table 2.

RESULTS AND DISCUSSION

The World Health Organization (WHO 2011) recommends atomic absorption spectrometry (AAS) for zinc determination, whereas in compliance with the Polish Norm (PN) adopted to the International Organization for Standardization (ISO) standards (PN-90/C-04596/02, 1993) and European standards (PN-EN ISO 8288:2002), photometric and FAAS methods are recommended. For copper analysis, the WHO (2011) recommends AAS, whereas according to standards PN-EN ISO 8288:2002, PN-C-04611-2:1994 PN-EN ISO 15586:2005 the same samples should be measured by colorimetry and spectrometry (FAAS, ETAAS). Various methods are used for calcium determination, for example ionic chromatography (IC) is most suitable in line with the Polish Norm (PN-EN ISO 14911:2002). IC is also recommended for chloride and fluoride determination in water samples (PN-EN ISO 10304-1:2009). Direct determination of metals in samples with high salinity by atomic absorption spectrometry is not always possible due to the composition of the matrix, in which case liquid-liquid extraction, flow injection system and solid phase preconcentration techniques are applied (DASKALOVA, BOEVSKI 1999, MADRAKIAN et al. 2008).

Based on the validation of the methods, it was found that the electrochemical methods were characterized by a wide linearity range: 2.5-25 μg L^{-1} for zinc(II) and copper(II), 0.1-6$\cdot$10^{-5}M for chloride, 5$\cdot$10^{-4}-2$\cdot$10^{-6}M for fluoride and 0.058-4.64$\cdot$10^{-4}M for calcium(II). Moreover, the methods achieved good precision, as the RSD was 0.81% for zinc, 3.12% for copper(II), 1.46% for chloride, 3.57% for fluoride and 1.67% for calcium(II). The recovery of the methods ranged from 99.55% to 108.82%. The developed methods were characterized by high sensitivity, with LOD values equal 0.02 μg L^{-1}, 0.33 μg L^{-1},

$7.63 \cdot 10^{-4}$ µg L^{-1}, 0.046 µg L^{-1} and 0.031 µg L^{-1} for zinc(II), copper(II), chloride, fluoride and calcium(II), respectively, whereas LOQ were 0.059 µg L^{-1}, 1.000 µg L^{-1}, 0.140 µg L^{-1}, $2.31 \cdot 10^{-3}$ µg L^{-1} and 0.095 µg L^{-1} for the same ions.

The investigations included 6 mineral waters, 2 spring waters and 7 curative waters. The waters were divided into 2 groups: the first one comprised curative waters whereas the other one was composed of mineral and spring waters. The zinc content in the first group varied between 7.76 and 33.54 µg L^{-1}. The highest zinc content in the first group was determined in the water called Franciszek (33.54 µg L^{-1}), while the lowest was in Wielka Pieniawa (7.76 µg L^{-1}). In the second group, the zinc content of waters was lower by one order of magnitude ($p < 0.05$) and ranged from 3.85 to 5.07 µg L^{-1}, except Staropolanka 2000, which characterized by the highest zinc concentration (23.67 µg L^{-1}). The copper content in the first group of waters was insignificantly higher than in the second group (7.09-15.15 µg L^{-1}), except the water named Jan, which was the lowest amount of Cu in this group (2.80 µg L^{-1}). In the second group, the copper content ranged from 1.85 to 6.16 µg L^{-1}, with the exception of Kropla Beskidu, which had the highest copper content at 15.33 µg L^{-1}. The chloride content was the most variable parameter in the first group and in the majority of water samples it was high, whereas spring and mineral waters contained between 3.7 and 2433.63 mg L^{-1} of this element. The highest copper content was in the water called Franciszek, which was also the richest in zinc. Moreover, the waters Franciszek, Henryk, Zuber and Jan differed significantly from the other tested water samples. In the first group of waters, the chloride concentration ranged from 2.80 to 26.00 mg L^{-1}, being the highest in Polanicka (26.00 mg L^{-1}) and the lowest in Staropolanka 2000 (2.86 mg L^{-1}) and Cisowianka (2.80 mg L^{-1}). The fluoride content was similar in both groups, regarding the ranges and the average content. The concentration of fluoride ranged from 0.09 to 1.66 mg L^{-1} and from 0.04 to 0.058 mg L^{-1} in the first and second group, respectively. The highest fluoride content was in Franciszek and the lowest one occurred in Muszynianka (0.05 mg L^{-1}) and Kropla Beskidu (0.04 mg L^{-1}). The calcium content was also one of the lowest variables, ranging from 11.05-478.48 mg L^{-1} in all the investigated water samples. The highest calcium content was in Krynica Minerale (478.48 mg L^{-1}) and the lowest in Józef (11.09 mg L^{-1}). Strong positive correlations were verified between chloride/fluoride (0.94, $p < 0.05$) and zinc/chloride (0.85, $p < 0.05$), being moderate at the most for the other pairs of ions. The scatterplot matrix of the content of individual elements in the tested waters is shown on Figure 1. Furthermore, a comparison between the values declared by manufacturers was made only for for calcium, chloride and fluoride determined by the potentiometric method. The zinc and copper content were not given by the manufacturers on the water bottle label. In most cases, our results were in an approximate agreement with the declared values. The biggest discrepancy occurred in the fluoride content, especially with respect to highly mineralized waters: Franciszek (296%), Jan (170%) and Zuber (174%), but also in the case of Żywiec Zdrój

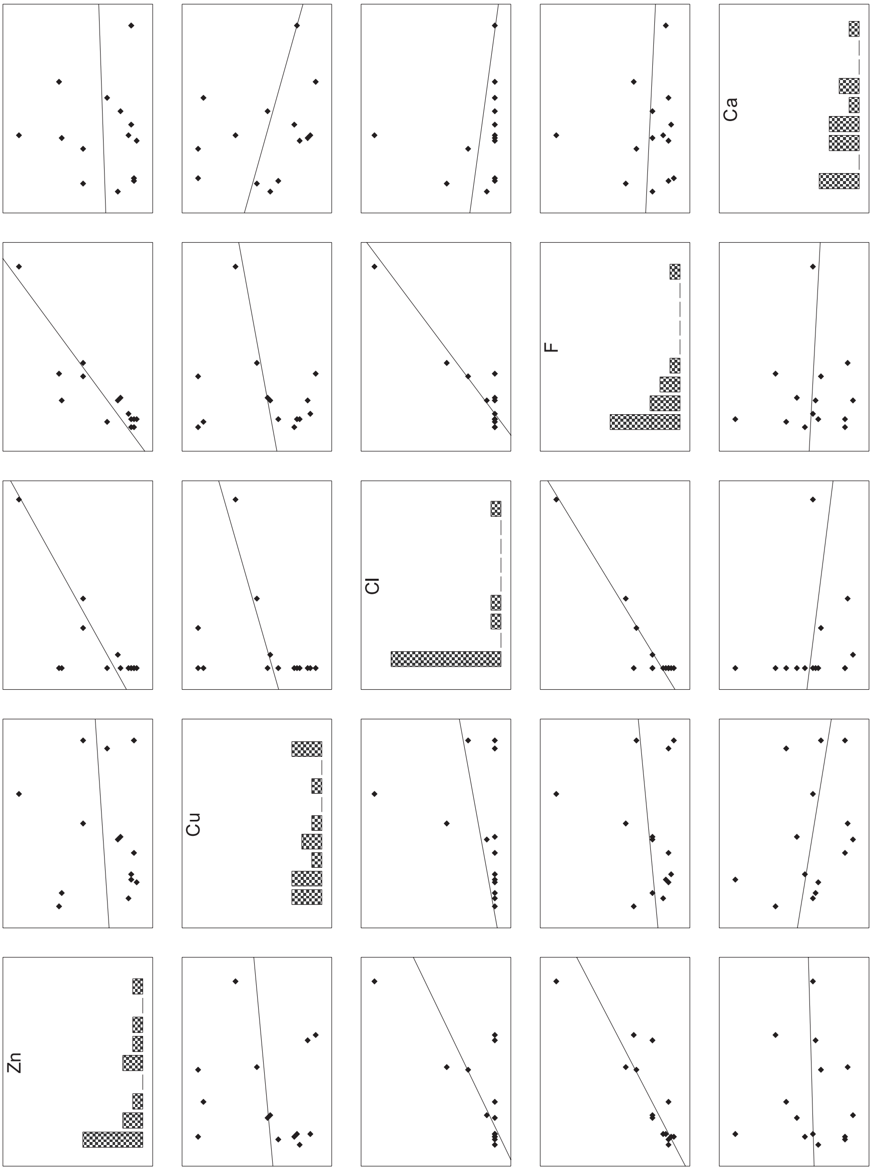

Fig. 1. The scatterplot matrix with histograms of the content of individual elements in the investigated bottled natural waters from the Polish market

(155%), which was the least mineralized water. The determined fluoride concentrations were higher than the declared ones, unlike the water Polanicka, which showed less fluoride than declared (61%). Regarding chloride, there were two waters which showed higher levels than declared by manufacturers, i.e. Muszynianka (150%) and Kropla Beskidu (138%). The calcium content in the tested waters was similar to the declared values, except Zuber, which contained less calcium (23%) than expected.

CONCLUSIONS

1. Methods for determination of zinc(II), copper(II), chloride, fluoride and calcium(II) have been developed and tested. The results have suggested that the proposed electroanalytical methods are suitable for determination of these ions in waters of natural origin.

2. The proposed methods incur low instrumental and analytical costs, but achieve results comparable with ones obtained with spectroscopic, chromatographic and colorimetric analysis recommended by the Polish Committee for Standardization, WHO, ISO and European standards.

3. The determined content of microelements differed from the manufacturer declared values. Fortunately, the determined concetrations of elements were relatively low and their daily intake with waters does not exceed the Tolerable Upper Intake Levels (www.nap.edu). Concerning chloride and copper, there is a certain risk of overdosing these elements by excessive consumption of the waters Jan, Zuber and Henryk.

4. It seems highly advisable to monitor the content of trace and mineral elements, and to perform their analytical quantification in water because of the important life functions played by water and a hazard of overdosing such elements with water.

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