Comparison of Potentiometric and ETAAS Determination of Copper and Iron in Herbal Samples

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The metal content (iron and copper) was potentiometrically analyzed in 44 tea samples. The analyzed samples included chamomile (*Matricaria chamomilla*), green tea (*Camellia sinensis*), sage tea (*Salvia officinalis* L.), linden (*Tilia* L.) and mint (*Mentha piperita*) in tea bags and bulk purchased at local supermarkets and marketplaces in Split, Croatia. Tea samples digestion was performed in microwave oven by using nitric acid and hydrogen peroxide mixture. Potentiometric determination was performed by using FISE for Fe^{3+} and CuISE for Cu^{2+}, respectively, by using potentiometric methods previously developed in our laboratory. The measured results were compared with atomic absorption spectrometric measurements from our previous research and showed notable statistical superposition.

Keywords: iron, copper, tea, potentiometric determination, ion-selective electrode

1. INTRODUCTION

It is very difficult to enumerate all the chemical species that can be detected in the herbs used for preparation of beverage. The chemical composition of tea can be classified into several groups: polyphenols, proteins and amino acids, carbohydrates, pectins, fiber, organic acids, lipids, pigments (chlorophylls and carotenoids), vitamins and minerals. There are many scientific papers about polyphenols in tea and their impact on human health [1-3]. Recently, scientists increasingly pay

attention to the determination of metals in tea. Although the metals in tea are less represented than other chemical species, their level of intake by living organisms is particularly important, especially when it comes to metals that are highly toxic and accumulate in organisms such as cadmium, lead and mercury. Elements, that are considered as biogenic, can be found in tea in significant amounts are fluoride, potassium, calcium and magnesium, while manganese, iron, and phosphorus, copper and nickel, sodium, boron, and molybdenum can be found in small amounts[4]. Most of studies concluded that essential metals can produce toxic effects when the metal intake is in high concentrations, whereas non-essential metals are toxic even in very low concentrations [5]. Polyphenols in tea are able to complexing cations and may be used as excellent chelating agents. The large number of phenolic hydroxyl groups provides a great number of potential active complexation sites [4]. The evaluation of metals in tea is of great importance considering the potential health risk to habitual tea drinkers if the quantity of these metals is not within the safe limits [6]. The tea-consuming manner has significantly changed in the past few decades by making tea more available through instant formulations such as packed tea, powdered tea, and both bottled and canned tea. Tea is widely consumed around the globe because of its aroma, taste, smell, variety of types and most especially due to its multiple health-promoting effects [6]. Frequent and prolonged intake of metals through tea leads to the chronic accumulation of metals which causes various health problems [5].

The aim of this study is to find a simple method for monitoring a concentration of essential (Fe and Cu) metals present in various brands of herbal teas: chamomile (*Matricaria chamomilla*), green tea (*Camellia sinensis*), sage tea (*Salvia officinalis* L.), linden (*Tilia sp.* L.) and mint (*Mentha piperita*) in tea bags and bulk purchased at local supermarkets and marketplaces in Split, Croatia. Iron is an essential element for humans and animals and is also an essential component of hemoglobin for oxygen transport [7]. The level of iron (overload or deficiency) in blood is associated with the incidence and severity of microbial infection [8]. Copper is an essential to the function of many key enzymes but can be toxic at excessive levels as well as iron [9]. Concentrations of iron and copper have been studied in our previous research using electrothermal atomizer atomic absorption spectrometry (ETAAS) and flame atomizer atomic absorption spectrometry (FAAS) [10-12]. It is very important to find a simple method for monitoring the metal concentrations in daily intake of food and drink.

In this paper we have analyzed iron and copper contents in five different plants using a very simple potentiometric method with ion-selective electrodes. It could be said that this work represents our efforts for developing and applying new potentiometric methods which are very useful, inexpensive and, above all, very simple for use [13,14].

Fluoride ion-selective electrode (FISE) was used for determination of iron based on the formation of FeF^{2+} complex in acidic solution as described in previous research [14]. Copper ion-selective electrode (CuISE), Orion, was used for determination of copper. These results were compared with our previous research using ETAAS and FAAS atomic absorption spectrometric measurements with the same samples [10-12].

2. EXPERIMENT

2.1. Reagents and chemicals

All needed solutions were prepared by solving a certain amount of chemicals in ultrapure water. Ultrapure water (declared conductivity of 0.04 μS cm^{-1}) was prepared by Millipore Simplicity (USA). The following chemicals were used: Sodium nitrate, $NaNO_3$, p.a., Sodium acetate, CH_3COONa, p.a., Sodium hydroxide, NaOH, p.a., Acetic acid, CH_3COOH, p.a., Copper (II) nitrate×3 H_2O, p.a., Iron (III) nitrate×9 H_2O, p.a., perchloric acid, p.a. which were obtained from Kemika (Croatia).

The ionic strength of buffer solutions was adjusted by dissolving a needed mass of $NaNO_3$ to reach the value of 0.1 M.

Tea samples digestion was described in our previous research [10-12].

2.2. Apparatus

The indicator electrode used was a combined fluoride ion-selective electrode (FISE) DC219 purchased from Mettler Toledo (USA) and copper ion-selective electrode (CuISE) Orion 94-29A from Orion (USA). Reference electrode used for both measurements was Orion 90-02 double junction reference electrode (Orion, USA). Potentiometric measurements were conducted in the double-wall glass vessel and the data were recorded with a millivoltmeter (Seven Excellence Mettler Toledo, USA) connected to a personal computer.
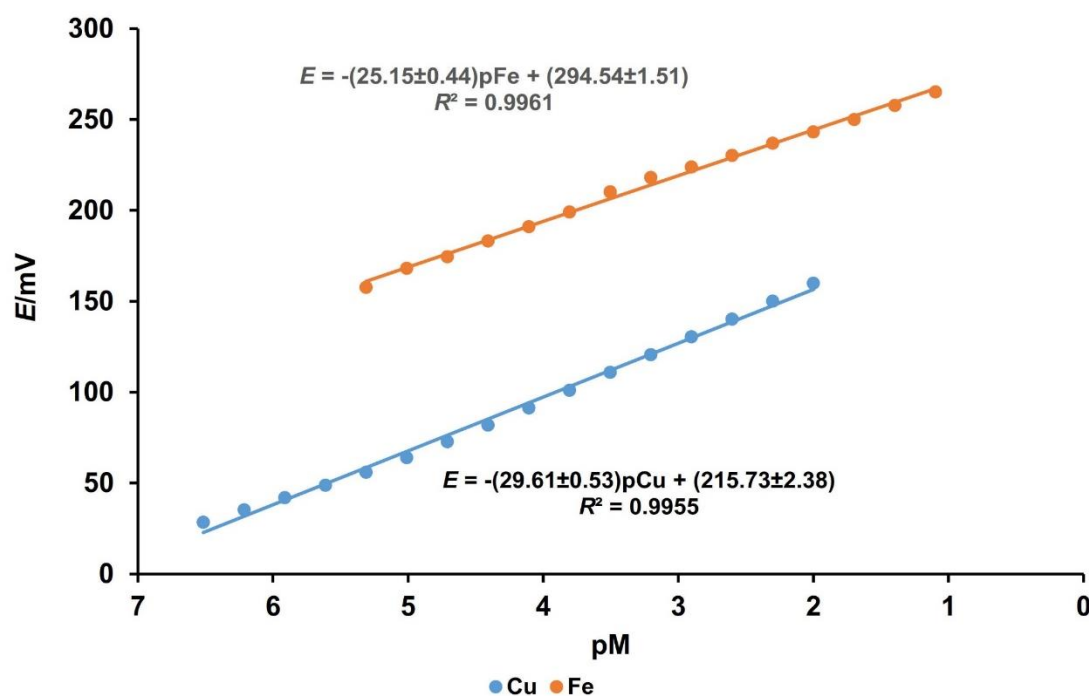
Figure 1. Response of FISE and CuISE for iron at pH = 3.0 and for copper ions at pH = 4.75

Figure 1 provides a response of FISE used in our experiment to Fe^{3+} at pH = 3.0 and response of CuISE to Cu^{2+} at pH = 4.75.

Standard metal solutions were prepared by dissolving a required mass of iron and copper salts in ultrapure water, respectively 0.01 M Cu^{2+} and 0.1 M Fe^{3+} solutions were used for construction of the calibration curves by successive dilution method by certain pH solution (3.00 for iron ions and 4.75 for copper, respectively) with constant ionic strength, figure 1.

Potential change of 25.15 mV per decade of iron concentration, with correlation coefficient of 0.9961 and potential change of 29.61 mV per decade for copper concentration, with correlation coefficient of 0.9955 were recorded which is very much in line with theoretical Nernstian slope for divalent ions.

LOD (limit of detection), LOQ (limit of quantification) for iron and copper standard solutions used for preparing calibration curves were calculated using the following equations:

$$\text{LOD} = \frac{3\sigma}{S} \qquad \text{LOQ} = \frac{10\sigma}{S}$$

where:

σ means standard deviation of the slope of calibration curve for each metal,

S means slope of calibration curve for each metal.

Calculated limit of detection (LOD) for iron is 4.34×10^{-6} mol L^{-1} and limit of quantification (LOQ) is 7.31×10^{-6} mol L^{-1}. LOD for copper standard solution is 2.69×10^{-7} mol L^{-1} and LOQ is 4.60×10^{-7} mol L^{-1}. Linear range for iron is $4.9 \times 10^{-6} - 8.0 \times 10^{-2}$ mol L^{-1} and for copper is $3.0 \times 10^{-7} - 1.0 \times 10^{-2}$ mol L^{-1}.

2.3. The analyzed samples

All samples of analyzed tea were purchased at supermarkets and local marketplaces. 14 different samples of mint tea (*Mentha piperita* and *Melissa officinalis*), 8 samples of green tea (*Camellia sinensis)* and 16 samples of chamomile tea (*Matricaria chamomilla*), 3 samples of sage tea (*Salvia officinalis* L.) and 3 samples of linden tea (*Tilia sp.* L.) were analyzed.

All information collected about analyzed tea, such as type of tea, name and country of packaging are presented in Table 1.

Table 1. Characteristic of analyzed tea samples

Sample name	Package type	Plant species (Tea type)	Latin name of the herb	Country of packaging
K-1	bags	mint	*Mentha piperita*	Austria
K-2	bags	mint	*Mentha piperita*	Croatia
K-3	bags	mint	*Mentha piperita*	Croatia
K-4	bags	mint	*Mentha piperita*	Croatia
K-5	bags	mint	*Mentha piperita*	Croatia
K-6	bags	mint	*Mentha piperita*	Germany
K-7	bags	mint	*Mentha piperita*	UK
V-1	bulk	mint	*Mentha piperita*	Croatia
V-2	bulk	mint	*Mentha piperita*	Croatia
V-3	bulk	mint	*Mentha piperita*	Croatia
V-4	bulk	mint	*Mentha piperita*	Croatia
V-5	bulk	mint	*Mentha piperita*	Croatia
V-6	bulk	mint	*Melissa officinalis*	Croatia
V-7	bulk	mint	*Melissa officinalis*	Croatia
A-1	tea bags	sage	*Salvia officinalis* L.	Croatia
A-2	tea bags	sage	*Salvia officinalis* L.	Croatia
A-3	tea bags	linden	*Tilia sp.* L.	Croatia
A-4	tea bags	linden	*Tilia sp.* L.	Croatia
A-5	tea bags	linden	*Tilia sp.* L.	Croatia
A-6	tea bags	sage	*Salvia officinalis* L.	Croatia
A-7	tea bags	chamomile	*Matricaria chamomilla* L.	Croatia
A-8	bulk	chamomile	*Matricaria chamomilla* L.	Croatia
A-9	bulk	chamomile	*Matricaria chamomilla* L.	Croatia
A-10	bulk	chamomile	*Matricaria chamomilla* L.	Croatia
A-11	tea bags	chamomile	*Matricaria chamomilla* L.	Croatia
N-1	tea bags	chamomile	*Matricaria chamomilla* L.	Macedonia
N-2	tea bags	chamomile	*Matricaria chamomilla* L.	Poland
N-3	tea bags	chamomile	*Matricaria chamomilla* L.	Poland
N-4	tea bags	chamomile	*Matricaria chamomilla* L.	Germany
N-5	tea bags	chamomile	*Matricaria chamomilla* L.	Croatia
N-6	tea bags	chamomile	*Matricaria chamomilla* L.	Croatia

N-7	tea bags	chamomile	*Matricaria chamomilla* L.	Croatia
N-8	tea bags	chamomile	*Matricaria chamomilla* L.	Croatia
N-9	tea bags	chamomile	*Matricaria chamomilla* L.	Croatia
N-10	tea bags	chamomile	*Matricaria chamomilla* L.	Croatia
N-11	tea bags	chamomile	*Matricaria chamomilla* L.	Croatia/
N-12	tea bags	green tea	*Camellia sinesis*	Croatia
N-13	tea bags	green tea	*Camellia sinesis*	Ukraine
N-14	tea bags	green tea	*Camellia sinesis*	Croatia
N-15	tea bags	green tea	*Camellia sinesis*	Croatia
N-16	tea bags	green tea	*Camellia sinesis*	Croatia
N-17	tea bags	green tea	*Camellia sinesis*	Austria
N-18	tea bags	green tea	*Camellia sinesis*	Croatia
N-19	tea bags	green tea	*Camellia sinesis*	Russia

Ultrapure water was used for all measurements in order to be certain that measured metals come from tea. Sampling and pretreatment of examined tea samples was described earlier [10].

Due to the high acidity of microwaved samples (pH ≈ 0.5), 1.0 mL of each samples was partially neutralized by adding 0.52 mL of 10% NaOH and subsequently diluted by acetic buffer, pH = 4.75 for copper measurement mixed with 0.1 M $NaNO_3$ in 50 mL flask to keep both ionic strength and pH constant. In case of iron potentiometric measurements, 0.001 M perchloric acid was used with 0.1 M $NaNO_3$. During the measurement, solutions were constantly mixed, and temperature was kept constant at 25 °C. Measurements were finished as soon as potential had obtained a constant value. Final value given in an article represents a mean of five consecutive measurements.

3. RESULTS AND DISCUSSION

The collected potentiometric (POT) data for copper and iron contents in analyzed herbal samples are presented in Table 2, while atomic absorption spectroscopy (AAS) data were taken from our previous researches [10-12]. After collecting all data, a statistical evaluation of collected data was performed.

Table 2. Collected potentiometric (POT) and atomic absorption spectroscopy (AAS) data of copper and iron contents in herbal samples, Δ represents difference between metal content measured by POT and AAS

Sample	POT $c(Cu^{2+})$ /mol L^{-1}	AAS $c(Cu^{2+})$ /mol L^{-1}	Δ	%	POT $c(Fe^{3+})$ /mol L^{-1}	AAS $c(Fe^{3+})$ /mol L^{-1}	Δ	%
K-1	4.63×10^{-3}	4.54×10^{-3}	9.06×10^{-5}	2.00	5.35×10^{-3}	5.39×10^{-3}	4.25×10^{-5}	0.79
K-2	6.20×10^{-3}	6.50×10^{-3}	2.97×10^{-4}	4.57	6.26×10^{-3}	6.30×10^{-3}	3.23×10^{-5}	0.51
K-3	4.78×10^{-3}	4.88×10^{-3}	1.07×10^{-4}	2.19	6.53×10^{-3}	6.46×10^{-3}	7.23×10^{-5}	1.12
K-4	4.89×10^{-3}	4.99×10^{-3}	9.56×10^{-5}	1.92	3.20×10^{-3}	3.21×10^{-3}	6.77×10^{-6}	0.21

K-5	4.70×10^{-3}	4.89×10^{-3}	1.91×10^{-4}	3.90	8.95×10^{-3}	9.02×10^{-3}	7.81×10^{-5}	0.87
K-6	8.85×10^{-3}	9.18×10^{-3}	3.29×10^{-4}	3.58	4.50×10^{-3}	4.45×10^{-3}	4.53×10^{-5}	1.02
K-7	2.50×10^{-3}	3.00×10^{-3}	5.00×10^{-4}	16.69	2.74×10^{-2}	2.85×10^{-2}	1.09×10^{-3}	3.85
V-1	6.98×10^{-3}	7.33×10^{-3}	3.49×10^{-4}	4.76	4.11×10^{-3}	4.19×10^{-3}	8.58×10^{-5}	2.05
V-2	5.55×10^{-3}	5.69×10^{-3}	1.42×10^{-4}	2.49	1.30×10^{-3}	1.24×10^{-3}	6.03×10^{-5}	4.87
V-3	9.74×10^{-3}	9.80×10^{-3}	6.28×10^{-5}	0.64	4.11×10^{-3}	4.17×10^{-3}	6.57×10^{-5}	1.58
V-4	9.00×10^{-3}	9.50×10^{-3}	5.04×10^{-4}	5.31	1.54×10^{-3}	1.61×10^{-3}	6.41×10^{-5}	3.98
V-5	7.50×10^{-3}	7.61×10^{-3}	1.15×10^{-4}	1.51	1.95×10^{-2}	1.92×10^{-2}	3.03×10^{-4}	1.58
V-6	8.12×10^{-3}	8.65×10^{-3}	5.38×10^{-4}	6.21	4.61×10^{-3}	4.69×10^{-3}	8.22×10^{-5}	1.75
V-7	9.00×10^{-3}	9.31×10^{-3}	3.10×10^{-4}	3.33	9.47×10^{-4}	9.57×10^{-4}	9.47×10^{-6}	0.99
A-1	4.14×10^{-4}	4.78×10^{-4}	6.36×10^{-5}	13.31	2.46×10^{-3}	2.54×10^{-3}	8.67×10^{-5}	3.41
A-2	4.63×10^{-4}	4.74×10^{-4}	1.15×10^{-5}	2.43	7.21×10^{-3}	7.32×10^{-3}	1.11×10^{-4}	1.52
A-3	5.25×10^{-4}	5.39×10^{-4}	1.43×10^{-5}	2.65	8.80×10^{-3}	8.83×10^{-3}	3.06×10^{-5}	0.35
A-4	5.59×10^{-4}	5.83×10^{-4}	2.40×10^{-5}	4.12	7.77×10^{-3}	7.77×10^{-3}	1.82×10^{-6}	0.02
A-5	5.13×10^{-4}	5.27×10^{-4}	1.43×10^{-5}	2.71	2.56×10^{-3}	2.50×10^{-3}	6.33×10^{-5}	2.53
A-6	3.74×10^{-4}	3.91×10^{-4}	1.76×10^{-5}	4.52	2.83×10^{-3}	2.94×10^{-3}	1.12×10^{-4}	3.82
A-7	4.24×10^{-4}	4.34×10^{-4}	9.54×10^{-6}	2.20	2.71×10^{-3}	2.78×10^{-3}	6.86×10^{-5}	2.47
A-8	3.98×10^{-4}	4.07×10^{-4}	9.12×10^{-6}	2.24	2.69×10^{-3}	2.72×10^{-3}	3.08×10^{-5}	1.13
A-9	4.04×10^{-4}	4.16×10^{-4}	1.16×10^{-5}	2.78	2.69×10^{-3}	2.63×10^{-3}	5.74×10^{-5}	2.18
A-10	4.31×10^{-4}	4.35×10^{-4}	4.54×10^{-6}	1.04	3.51×10^{-3}	3.54×10^{-3}	3.61×10^{-5}	1.02
A-11	3.74×10^{-4}	3.88×10^{-4}	1.42×10^{-5}	3.65	2.22×10^{-3}	2.29×10^{-3}	6.65×10^{-5}	2.91
N-1	1.14×10^{-4}	1.46×10^{-4}	3.21×10^{-5}	21.98	7.15×10^{-3}	7.22×10^{-3}	6.46×10^{-5}	0.90
N-2	1.10×10^{-4}	1.24×10^{-4}	1.33×10^{-5}	10.74	4.14×10^{-3}	4.21×10^{-3}	6.97×10^{-5}	1.66
N-3	6.92×10^{-5}	7.21×10^{-5}	2.85×10^{-6}	3.95	8.44×10^{-3}	8.48×10^{-3}	3.88×10^{-5}	0.46
N-4	2.00×10^{-4}	2.01×10^{-4}	9.88×10^{-7}	0.49	1.04×10^{-2}	1.07×10^{-2}	3.24×10^{-4}	3.02
N-5	1.41×10^{-4}	1.58×10^{-4}	1.73×10^{-5}	10.92	8.80×10^{-3}	8.72×10^{-3}	8.37×10^{-5}	0.96
N-6	7.86×10^{-5}	1.11×10^{-4}	3.19×10^{-5}	28.89	5.81×10^{-3}	5.85×10^{-3}	3.73×10^{-5}	0.64
N-7	9.89×10^{-5}	1.66×10^{-4}	6.72×10^{-5}	40.46	3.94×10^{-3}	3.96×10^{-3}	2.18×10^{-5}	0.55
N-8	9.73×10^{-5}	1.60×10^{-4}	6.24×10^{-5}	39.06	4.04×10^{-3}	4.20×10^{-3}	1.63×10^{-4}	3.89
N-9	9.81×10^{-5}	1.41×10^{-4}	4.27×10^{-5}	30.35	9.56×10^{-3}	9.63×10^{-3}	6.65×10^{-5}	0.69
N-10	8.99×10^{-5}	1.28×10^{-4}	3.79×10^{-5}	29.64	2.60×10^{-3}	2.68×10^{-3}	7.44×10^{-5}	2.78
N-11	9.21×10^{-5}	1.50×10^{-4}	5.76×10^{-5}	38.48	1.35×10^{-3}	1.38×10^{-3}	3.04×10^{-5}	2.20
N-12	2.88×10^{-4}	3.17×10^{-4}	2.95×10^{-5}	9.30	9.96×10^{-3}	1.03×10^{-2}	3.30×10^{-4}	3.21
N-13	2.70×10^{-4}	2.86×10^{-4}	1.54×10^{-5}	5.41	5.31×10^{-3}	5.43×10^{-3}	1.19×10^{-4}	2.19
N-14	3.56×10^{-4}	3.67×10^{-4}	1.03×10^{-5}	2.82	4.61×10^{-3}	4.70×10^{-3}	9.02×10^{-5}	1.92
N-15	1.98×10^{-4}	2.22×10^{-4}	2.37×10^{-5}	10.68	4.93×10^{-3}	4.69×10^{-3}	2.40×10^{-4}	5.12
N-16	1.43×10^{-4}	1.65×10^{-4}	2.14×10^{-5}	12.98	3.31×10^{-3}	3.26×10^{-3}	4.90×10^{-5}	1.50
N-17	3.80×10^{-4}	3.98×10^{-4}	1.88×10^{-5}	4.71	6.37×10^{-3}	6.87×10^{-3}	5.05×10^{-4}	7.35
N-18	2.42×10^{-4}	2.45×10^{-4}	3.23×10^{-6}	1.32	5.18×10^{-3}	5.40×10^{-3}	2.25×10^{-4}	4.16
N-19	2.90×10^{-4}	3.05×10^{-4}	1.49×10^{-5}	4.88	3.81×10^{-3}	3.96×10^{-3}	1.48×10^{-4}	3.74

The statistical analysis was carried out using the RStudio ver. 1.1.383 [15] software. The data for each measurement method followed a lognormal distribution. For analyzing the difference between

two different measurement techniques (*N*=44) for the metal content (iron and copper), Passing-Bablok regression was chosen as a proposed model for comparison of methods based on robust, non-parametric model [16]. The linear relationship between the two methods was estimated using the Cusum test. The Pearson correlation coefficient was 0.99 (*p*<0.01) for Fe and 0.98 (*p*<0.01) for Cu. Inspection of the scatter diagram and regression equation shows that there is a small constant difference between two methods for measuring iron levels (figure 2) and copper levels (figure 3).
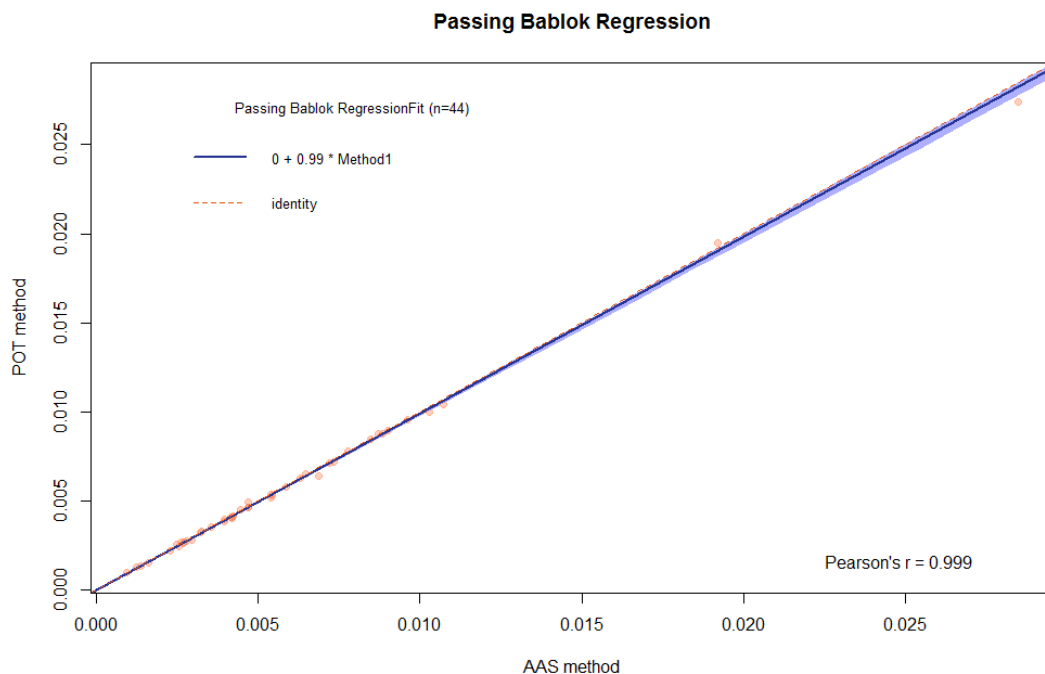
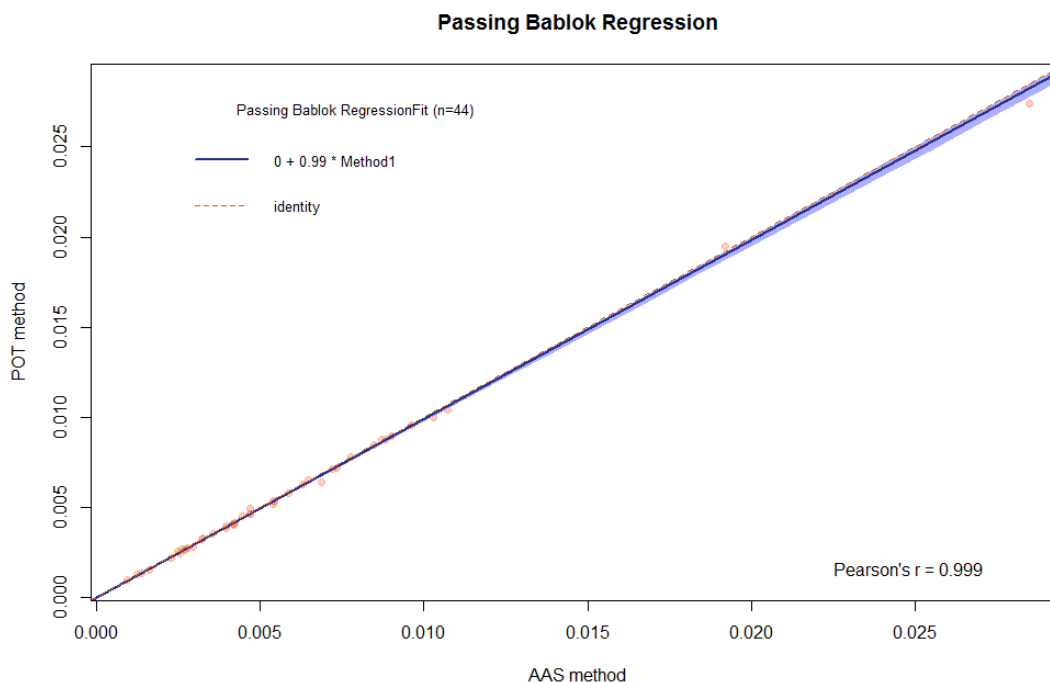**Figure 2.** Passing-Bablok regression analysis of two methods for iron measurements

Figure 3. Passing-Bablok regression analysis of two methods for copper measurements

Table 3. Descriptives

	Method 1	Method 2
	AAS	POT
Fe levels		
Min-Max	9.566×10^{-4}-2.847×10^{-2}	9.471×10^{-4}-2.738×10^{-2}
Mean $\pm$ SD	$5.838 \times 10^{-3} \pm 4.83 \times 10^{-3}$	$5.760 \times 10^{-3} \pm 4.717 \times 10^{-3}$
Median (IQR)	4.569×10^{-3}	4.554×10^{-3}
Cu Levels		
Min-Max	7.208×10^{-5}-9.799×10^{-3}	6.923×10^{-5}-9.736×10^{-3}
Mean $\pm$ SD	$2.382 \times 10^{-3} \pm 3.321 \times 10^{-3}$	$2.288 \times 10^{-3} \pm 3.214 \times 10^{-3}$
Median (IQR)	4.115×10^{-4}	4.012×10^{-4}

Table 4. Passing-Bablok regression (AAS method and POT method) parameters

	Lower threshold 95%	Upper threshold 95%
Fe Levels		
Intercept	-7.358×10^{-5}	5.935×10^{-5}
Slope	9.728×10^{-1}	1.003
Cu Levels		
Intercept	-2.815×10^{-5}	-3.026×10^{-6}
Slope	9.635×10^{-1}	9.953×10^{-1}

In the end, it could be stated that the statistical difference between potentiometric and AAS results, Table 3 and Table 4, has not been found.

The aim of this work was to prove applicability of potentiometric determinations in comparison to AAS determination. Literature search [17] shows that even in the last decade there was only one paper that dealt with the comparison between the mentioned methods. In that paper [17] AAS was used for validation of newly "homemade" membranes for ion-selective electrodes (ISE). Herein we proposed, statistically checked and approved the use of commercially available ISEs for control and implementation in quality control of technological process. On the other hand, it is important to explain why we have decided for commercially available ISEs. The reason is very simple, due to the guarantee and technical support behind the commercially available ISEs, big producers should buy them instead of preparation and use of "home-made" ISEs. Implementation of "home-made" ISEs in complex technological process is often demanding and could have unexpected and unpredictable results during the work.

Nevertheless, it is notable to mention and establish that potentiometry is inexpensive, simple, fast, not requiring a specifically trained operator. This information is very valuable. On the other hand, potentiometric methods could be automated and could significantly increase the number of determinations per time unit by implementing in various flow injection methods, e.g. [18, 19].

4. CONCLUSION

A comparison of various herbal samples ($N = 44$), used for the preparation of hot drink and tea, was presented in this paper. All samples were analyzed for metal content using both potentiometry and AAS. Cu and Fe were selected for the test. Cu was selected as an example for direct determination by using CuISE. On the other hand, Fe was selected as an example of indirect potentiometric determination by using FISE. In both cases, results collected through potentiometric measurements were similar and without statistically significant difference for all samples. Since the potentiometry is a simple-to-use, inexpensive and fast analytical method, this work proves the possibility of using potentiometry in wide range of analytical applications.

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