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DETERMINATION OF THE ANTIOXIDANT ACTIVITY OF DIFFERENT TYPES OF COFFEE BY MEANS OF BRIGGS-RAUSCHER ANALYTICAL METHOD

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ABSTRACT. The antioxidant activity of coffee brews was determined in batch conditions by means of a Briggs-Rauscher oscillating system. This method consists of the measurement of the inhibition time caused by the addition of a diluted coffee sample to the oscillating system. The inhibition time vs. the relative concentration of the diluted coffee sample shows linear dependence. The slope of these lines was used to calculate a relative antioxidant activity for each sample. It was concluded that the method of preparation greatly influenced the resulting coffee brew, with the filtering method showing the best results with up to 50% higher antioxidant activity. As such, it was chosen as a standard to compare activity values. It can also be noted that decaffeinated coffee samples show significantly lower activity than caffeine-containing ones.

Keywords: *Briggs-Rauscher oscillating reaction, inhibitory effect, analytical method, coffee extract, antioxidant activity*

INTRODUCTION

One of the most consumed beverages worldwide is coffee due to its flavor and several health benefits. According to the International Coffee Organization, the annual consumption in the world is around 9.8 billion kg/year [1]. The two most popular species are *Coffea arabica* and *Coffea robusta*. The coffee beans have a complex composition containing lipids, proteins, soluble fibers, minerals, antioxidants and volatile compounds. This depends on

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genetic aspects, degree of maturation, soil composition, cultivation practices, climate, etc. When comparing the two main species, it can be noted that, generally, Coffea robusta has a higher content of caffeine and antioxidants while Arabica provides a better aroma [2, 3]. It should be noted that the high level of antioxidants in Robusta has several benefits for the plant (e.g. increased resistance to plant diseases, UV-radiation). Nevertheless, this difference in antioxidant content disappears during the roasting process [3].

The health benefits of coffee are attributed to its high antioxidant content [4]. Several compounds with antioxidant properties are already present in raw coffee beans, such as chlorogenic acids (CGA), which are mainly responsible for scavenging free radicals and interactions with reactive species [5, 6, 7].

During the roasting process, due to several chemical reactions like hydrolysis, degradation, isomerization, and incorporation into melanoidins, *ca.* 99% of the CGA decomposes [8]. Nevertheless, the melanoidins and different metabolites formed during the process also show significant antioxidant properties [9, 10].

It is well known, that processing conditions (e.g. temperature, dry or wet conditions, organic solvents, water, or vapor) affect the chemical composition of the coffee beans and subsequently change their antioxidant activity too. Similarly, the quality of the coffee extract is also greatly affected by the brewing process [11]. There are several brewing techniques, such as infusion, decoction, and percolation. During infusion, the almost boiling water is passed through the roasted and ground beans under pressure and espresso coffee is obtained. In the case of decoction, to obtain the extract, the raw material is boiled, resulting in Turkish-style coffee. The beverage can be obtained by percolation too, which consists of filtering hot water through the coffee powder, dissolving the soluble compounds. The question that arises is how the preparation method influences the antioxidant activity of the coffee brew.

Several methods are used in order to determine antioxidant activity. Most of them are based on measuring the trolox equivalent antioxidant capacity (TEAC), the total radical-trapping antioxidant parameter (TRAP), the oxygen radical absorbance (ORAC) [12], and the 2,2-Diphenyl-1-picrylhydrazyl radical scavenging activity (DPPH) [13]. All these methods are based on the generation of free radicals that react with the antioxidant. Because of the different nature of the radicals, the varying pH of the environment, and the solvent used, the results obtained with different methods are not comparable [14]. A method based on the inhibition of the Briggs-Rauscher (BR) oscillating system was developed by R. Cervelatti & al., and

used for the first time to put in evidence soybean antioxidants [15]. The BR reaction consists of the oxidation of an organic substrate by iodate in an acidic medium and Mn catalyst in the presence of H_2O_2. During the reaction, free radicals are generated, among them hydroperoxyl (HOO·) and hydroxyl (HO·), which also occur naturally in the human body [16]. The BR method is based on the cessation of the oscillation due to the interaction of the radicals with the antioxidants. The total consumption of the antioxidants added to the BR active mixture cause the regeneration of the oscillatory regime. The elapsed time between the cessation and regeneration of the oscillation (*i.e.* the inhibition time) is proportional to the concentration of the antioxidant. The main advantage of the BR method, compared to other techniques, is the acidic pH of the testing system (pH≈2) appropriate to that of the human stomach fluid, which is a great opportunity to obtain information on the behavior of antioxidants in such conditions. It is well known, that the antioxidant activity of the species is dependent on the pH of the systems [16].

The aim of this work is to determine the antioxidant activity of different coffee samples with the Briggs-Rauscher method.

The novelty of the study consists in the types of commercial coffees chosen, as they are among the most widely consumed in Romania, which increases the regional significance of the findings. Additionally, as the sample preparation method (coffee brewing process) can greatly influence the antioxidant activity of the systems, a comparative study was realized to study this aspect. It should also be noted that even though the Briggs-Raucher method was previously used successfully to determine antioxidants that are present in raw and roasted coffee beans [17], information on its effective use for the coffee beverage is limited in the literature [18].

RESULTS AND DISCUSSION

Impact of the brewing method on the antioxidant activity of coffee

To determine the most effective brewing method (*i.e.* the one that results in the highest antioxidant activity), four types of coffee were studied: espresso, filtered, turkish and moka pot.

The inhibition time was determined for several dilutions and calibration curves were fitted on them [19]. Variation of the inhibition time in function of the relative antioxidant concentration was found to be linear, as can be seen in Figure 1.

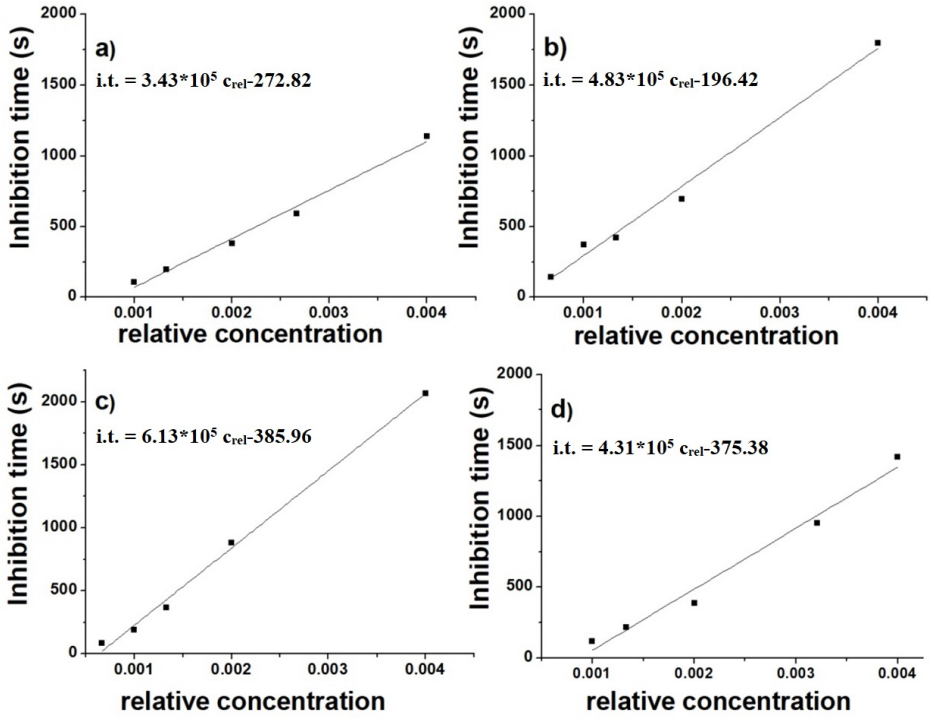

Figure 1. The calibration curves of the different types of coffee brew:
a) Espresso; b) Turkish; c) Filtered; d) Moka pot
*i.t. is the abbreviated form of inhibition time

The qualitative analytical information is the slope of the calibration curve, a higher slope gives a higher antioxidant activity.

As can be observed from Table 1., the filtering method yields a brew with the highest antioxidant activity. As such, it was chosen as the standard for further studies.

The relative antioxidant activity (R.A.S.) was also calculated as the ratio of the slope of each preparation method and that of the chosen standard (*i.e.* filtered coffee).

R.A.S. = slope(method)/slope(standard). Equation (1)

Table 1. Analytical parameters of the calibration curves obtained with different coffee brew preparation methods

Brewing method	Equations of the calibration curve	R^2
Espresso	$3.43*10^5$ c_{rel}-272.82	0.9879
Turkish	$4.83*10^5$ c_{rel}-196.42	0.9912
Filtered	$6.13*10^5$ c_{rel}-385.96	0.9965
Moka pot	$4.31*10^5$ c_{rel}-375.38	0.9951

The R.A.S. values obtained for the brewing methods are compared in Figure 2.

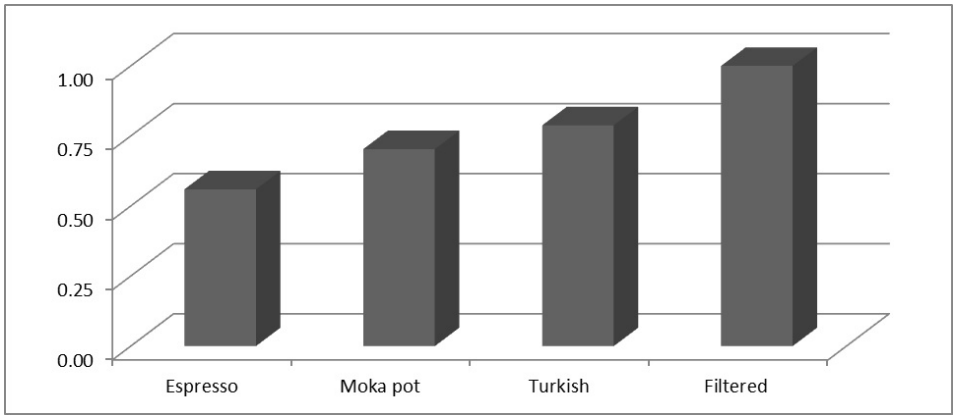

Figure 2. The R.A.S. values of the coffee brew

According to the R.A.S. values, the filtered coffee has 25-50% greater antioxidant activity than the samples prepared by other methods (Figure 2.). For example, the coffee made with an espresso machine had almost 50% less antioxidant activity. The higher antioxidant activity of the filtered coffee can be explained by the longer extraction time (approximately 10 minutes longer compared to other methods), as well as the lower extraction temperature. These results are in good accordance with literature data, which show a reduced antioxidant potential for a brew prepared with an Espresso machine compared to the Drip (Filtered) or Turkish methods [20, 21]. In the case of the filtering method, it should be noted that due to differences in the flow of hot water, results may vary significantly in the case of different brewing apparatuses [20, 21].

The antioxidant activity of different types of coffee, the effect of decaffeination

As filtering proved to be the method that yields the highest antioxidant activity, it was used for further studies regarding commercially available coffee samples.

Six types of popular commercially available coffee were studied: Lavazza, Lavazza (decaffeinated), Jacobs, Jacobs (decaffeinated), Fort, Tchibo.

The resulting calibration curves are presented in Figure 3.

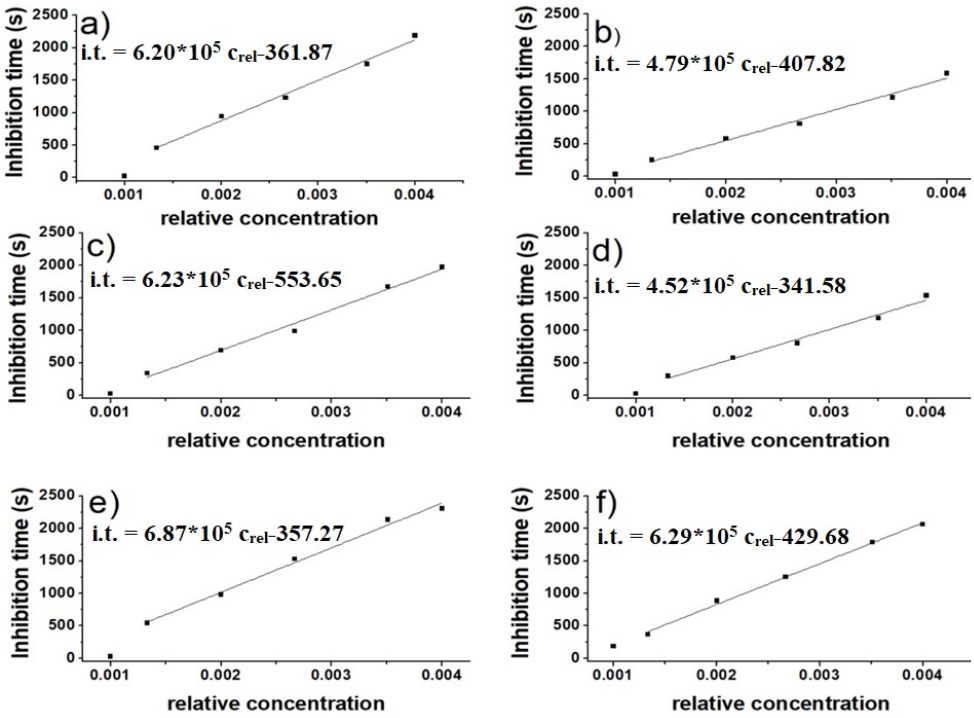

Figure 3. The calibration curves of coffee brews prepared by the filtering method from different commercially available coffees a) Lavazza; b) Lavazza (decaffeinated); c) Jacobs; d) Jacobs (decaffeinated); e) Fort; f) Tchibo
*i.t. is the abbreviated form of inhibition time

The obtained fitted calibration curves can be seen in Table 2.

Table 2. Analytical parameters of the calibration curves obtained for different commercially available coffees with the filtering method

Coffee type	Equations of the calibration curve	R^2
Lavazza	$6.20*10^5$ c_{rel}-361.87	0.9923
Lavazza (decaffeinated)	$4.79*10^5$ c_{rel}-407.82	0.9852
Jacobs	$6.23*10^5$ c_{rel}-553.65	0.9878
Jacobs (decaffeinated)	$4.52*10^5$ c_{rel}-341.58	0.9865
Fort	$6.87*10^5$ c_{rel}-357.27	0.9912
Tchibo	$6.29*10^5$ c_{rel}-429.68	0.9935

The relative antioxidant activity of each coffee brew was calculated using Equation (1), regarding the R.A.S. values. Results are compiled in Figure 4.

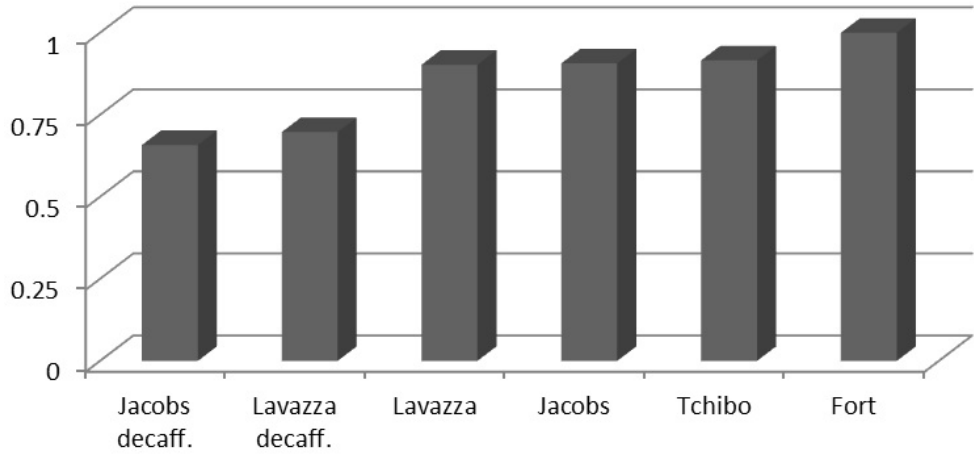

Figure 4. Comparative study of the R.A.S. values of coffee brews prepared by the filtering method from different commercially available coffees.

Results show that Fort brand coffee has the highest antioxidant activity, however, the difference between coffee brands is relatively small in the case of caffeine-containing samples (less than *ca.* 10%). This can be explained by the fact that all ground coffee was prepared in similar conditions. These results are in good accordance with literature data, which show similar antioxidant contents for coffees even if the place of origin is different, both when comparing green and roasted beans [3].

According to the two-sample t-test (95% confidence level), results show that decaffeinated coffee has a statistically significantly lower antioxidant activity (calculated t value of 6.91, with a critical t value of 2.78) compared to caffeine-containing samples. This effect of decaffeination meant that these samples had an antioxidant strength of up to *ca.* 35 % lower than the corresponding caffeine-containing coffees even though caffeine does not inhibit the active BR system. The results are probably due to the caffeine extraction process which decreases the concentration of antioxidants in the coffee beans [22]. This is in good accordance with data from the literature, showing that decaffeinated brews have *ca.* 30% lower antioxidant activity [3].

CONCLUSIONS

One purpose of this work was to study the influence of the coffee brewing method on the antioxidant activity. For this, we compared four types of brews: filtered, moka pot, turkish and espresso. It was determined that the brewing method significantly affects the antioxidant activity of the resulting coffee brew, and that the highest antioxidant activity can be obtained by the filtering method.

This was followed by a comparative study of several commercially available coffee samples. It can be concluded that in the case of caffeine-containing samples, the antioxidant activity is similar regardless of the brand. In comparison, the decaffeination process significantly reduced antioxidant activity compared to the corresponding caffeine-containing samples.

Results show similar trends to data in literature obtained by other methods, proving the effectiveness of the BR method to determine the antioxidant activity of coffee samples. The fact that the pH of the testing environment is similar to that of stomach acid constitutes an advantage when analyzing samples meant for human consumption.

EXPERIMENTAL SECTION

The proposed method was implemented by connecting a double-walled vessel with a volume of 10 mL to a FALC FA 90 thermostat. Water circulation through the temperature jacket provided a constant temperature of 20°C [19]. The oscillations were monitored electrochemically with a handmade Ag/AgI indicator electrode. The cell also contained a Pt-wire counter electrode. The system was connected to a computer through a PCI 6036 E data-acquisition interface.

The coffee brew was prepared in all cases from 10 g of ground, roasted coffee (used immediately after opening the commercial packaging) and 200 ml of distilled water. The resulting coffee brew was also used immediately after preparation. Several dilutions were prepared from this stock solution. The relative concentrations of these were calculated as the reciprocate of the dilution factor.

Chemicals and procedure

All chemicals were of analytical grade and were used without further purification. Stock solutions with the following concentration were made: $[H_2SO_4]_0$=220 mM, $[KIO_3]_0$=180 mM, $[MA]_0$=200 mM, $[MnSO_4]_0$=260 mM, $[H_2O_2]_0$=5.28 mM by using double distilled water.

The mixing order was: malonic acid, $MnSO_4$, H_2SO_4, KIO_3, and H_2O_2. Oscillations start after the addition of H_2O_2. At the third oscillation, 0.250 mL of diluted coffee brew was added to the reactor using an automatic pipette [19].

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