Zsóka Kárpáti[1], Eszter Luca Benes[2], Marietta Fodor[3]

Received: October 2017 – Accepted: June 2018

Nutritional analysis of coffee dregs for utilization purposes using classical, ICP-OES and FT-NIR techniques

Keywords: coffee dregs, coffee consumption, nutritional values, ICP-OES, FT-NIR, principal component analysis (PCA), linear discriminant analysis (LDA)

1. Summary

Coffee dregs are a byproduct left behind in significant amounts after brewing coffee. Several researches have dealt with its utilization possibilities and have proven, in certain cases, its positive effect. In our study, the applicability of coffee dregs as a soil improver was investigated. The pH, dry matter and water-soluble total salt content of coffee dregs, produced as the byproduct of coffee beverages prepared by the espresso method were determined. The mineral content of the samples was measured using the ICP-OES technique. The FT-NIR spectra of the samples were recorded and pattern recognition was carried out according to growing site and preparation method (French Press and Espresso) by the chemometric evaluation of the spectral data.

2. Literature overview

Coffee has become an increasingly popular luxury good: according to the annual statistics of the International Coffee Organization, on average, around 9,000 tons of green coffee per has been grown annually in recent years worldwide. Due to the continuous increase in the amount of coffee consumed, increasing amounts of the byproduct of brewing coffee, of coffee dregs are produced. According to data from the Hungarian Central Statistical Office (KSH), the annual per capita consumption of coffee in Hungary is 2.2 kg on average, and the weight of the coffee dregs produced is even greater because of the water bound to the particles. The dregs are usually treated as municipal waste. Many possibilities have risen regarding the use of the large amounts of coffee dregs produced, utilizing its physico-chemical characteristics (small particle size, large specific surface area, nutritional values, etc.) during drainage cleaning, scrubbing, deodorization or soil improvement.

The fruit of the coffee plant is the so-called coffee cherry whose pulp is removed during various processing steps, and the pit is packaged and transported after drying as green coffee beans. The cell wall of green coffee beans consists of cellulose, hemicellulose, pectins containing varying amounts of lignin, tannic acids, gum, proteins, minerals, pigments, fats, waxes and oils, as well as volatile components. During roasting, several physical and chemical processes take place. Physical changes include an increase in volume, weight loss, loss of water and color change. The main chemical components of green coffee and roasted coffee are summarized in ***Table 1***.

Valuable active ingredients and flavors are released from roasted and then ground coffee due to hot water extraction. The byproduct of the process are coffee dregs. Coffee dregs is a brown-colored, porous substance with a small particle size and a characteristic odor. When investigating its nutritional values it can be stated that it is mainly characterized by a high hemicellulose content. It contains smaller amounts of pectin, lignin, caffeine, tannin, fatty acids, minerals, proteins and polysaccharides. The nutritional parameters of coffee dregs are naturally influenced by the variety, the growing area, the soil and the climate **[3]**. Coffee beverages made from beans coming from different growing areas can be easily distinguished by sensory, electronic tongue and GC-MS methods as well **[4]**. Accordingly, we can rightly assume that these differences can also be detected in the case of the residual dregs.

[1] Certified bioengineer BSc, Szent István University, Faculty of Food Science
[2] Food safety and quality engineer MSc student, Szent István University, Faculty of Food Science
[3] Szent István University, Faculty of Food Science, Department of Applied Chemistry

Many international publications have appeared regarding the application of coffee dregs. A study published in 2001 presented the possibilities of producing biodiesel from coffee dregs. The raw material was collected from local cafes and then it was dried in a kitchen oven. Coffee dregs are rich in oil which was extracted using Soxhlet extraction, and then the oil was separated from the solvent by a rotary evaporator **[5]**. Biodiesel was produced by the transesterification of the oil thus obtained. Based on their measurements, the biodiesel met the requirements of the relevant European standard **[6]**.

In a recent research, coffee dregs were used in bakery products as food additives. Their results proved that coffee dregs is a natural antioxidant and a source of essential amino acids and low glycemic index carbohydrates, which is resistant to heat treatment and digestion processes **[7]**.

In research aimed at agricultural application, coffee dregs are mixed with other natural substances for soil improvement, and used this way. In a previous study, biooil was produced from coffee dregs, the residual byproduct of the process was defatted, and from the remaining material biochar was produced by slow pyrolysis. The biochar thus obtained was mixed with a fertilizer and used as a potential soil improver **[8]**.

Cruz et al. mixed coffee dregs with biomass used as soil in different ratios, and investigated how the amount of the coffee dregs influenced the carotene and chlorophyll concentrations of lettuce grown on the mixed biomass. As a result of the experiment, it was found that by increasing the ratio of the coffee dregs, both the concentrations of carotene and chlorophyll in the samples increased. Although this could be considered a positive effect, but it should be noted that by increasing the amount of coffee dregs the amount of caffeine introduced into the soil also increases and this can have a significant stress effect on the plants (a 20 V/V % mixture is already toxic) **[9]**.

3. Goal of the research

The goal of our research was to investigate the applicability of coffee dregs as a soil improver. Our main hypotheses were as follows:

There is a correlation between:

- brewing methods (French Press és Espresso) and the nutritional values of coffee dregs;
- the growing area and the nutritional values of the coffee dregs.

During our investigations, the following questions were addressed specifically:

- Is there any difference between the two procedures in terms of the observable nutritional values?
- Determination of the pH value of coffee dregs obtained after the Espresso brewing method – can the application of coffee dregs as soil improvers or soil conditioners cause the acidification of the soil?
- Determination of the salt content of coffee dregs obtained after the Espresso brewing method – can the application of coffee dregs as soil improvers or soil conditioners cause salinization?
- Is there a difference between the mineral contents of coffees coming from different growing areas?
- What kind of quality relationships can be observed between the FT-NIR spectra of finely ground coffee and the two types of coffee dregs obtained by the different brewing methods?

4. Materials and methods

4.1 Materials used and sample preparation

During the study, *Coffea arabica* coffees from five different rowing areas were used: Brazil, Panama, Ethiopia, New Guinea and Costa Rica. Vienna and French roasting procedures were used and, of the brewing methods, the French Press and Espresso brewing methods were selected.

For the FT-NIR analyses, roasted coffee beans were ground to a coarse, lumpy particle size by an Imat Inox LUX (Nemox International S.R.L, Italy) coffee grinder for the French Press procedure, while a finer, semolina-like meal was needed.

Roasted coffee beans, brews and coffee dregs were provided by SemiramiS Kft. Brews were prepared according to the following recipes:

- During ***French Press*** brewing, roasted beans are ground coarsely (1,200 – 1,250 μm) to achieve a large grain size. The coffee maker is a glass vessel into which an up and down movable metal contraption with a filter is immersed. According to the recipe, 500 ml of water with a temperature of 90 to 95 °C is required for 30 g of coarsely ground coffee. The mixture is stirred, allowed to stand for 4 minutes by placing on the top of the vessel the compression device with the lid and the filter. After the 4 minutes are over, it is pressed down with a firm action.
- During ***Espresso*** brewing, finely ground meal (400 - 450 μm) should be used. The temperature of the water used for brewing is 90 to 95 °C, extraction is carried out with a pressure of 1 to 1.5 bar. The amount of finely ground coffee is 16 to 20 g. Hot water passes through the compressed meal over 25 to 30 seconds. During Espresso brewing, 50 ml of coffee beverage is prepared **[10]**.

4.2. Measurement methods

4.2.1. Classical analysis procedures

Determination of the nutritional values (pH, dry matter content, water-soluble total salt content) were carried out in accordance with FVM decree 6/2006. (V. 18.) about the authorization, storage, marketing and use of crop enhancers, using classical analysis methods **[11]**.

4.2.2. Fourier transform near infrared (FT-NIR) method

FT-NIR measurements were carried out using a Bruker MPA FT-NIR (Bruker, Ettlingen, Germany) instrument. Spectra of the ground samples (before brewing) and the coffee dreg samples obtained after the two brewing methods were recorded. In the latter case, given that the spectral image is adversely affected by the moisture content of the sample, the moisture content of the sample was reduced by drying to a constant value before recording the spectrum.

Spectra were recorded using a diffuse reflection measurement procedure and a rotating quartz sample holder with a diameter of 85 mm in the 12,500 to 4,000 cm^{-1} wave number range. For the recording of the spectra, the instrument's own OPUS 7.2 (Bruker, Ettlingen, Germany) program was used.

4.2.3. Statistical evaluation methods

Chemometric evaluation of the spectral data was carried out using principal component analysis (PCA) and linear discriminant analysis (LDA). Statistical analyses were performed using the Statistica 12.0 (StatSoft, Tulsa, Oklahoma, USA) software.

PCA is a multivariate data analysis procedure based on eigenvalue calculation. Original data are combined based on correlations, and so a smaller number of new, non-correlated principal components are created. The advantage of this method is that by reducing the number of variables, variables that provide less information than desirable can be eliminated **[12]**.

It is recommended that LDA analysis is performed after a preliminary principal component analysis. The method allows us to review the groups previously created by us and their separation. To achieve this, discriminant functions are sought that provide the best separation for the groups. Whether a certain direction becomes a coordinate axis in the discriminant space is determined by the discriminating effect **[13]**.

4.2.4. Inductively coupled plasma emission optical spectroscopy (ICP-OES) method

Determination of the mineral components released from the coffee dregs was carried out using the ICP-OES method. During the extraction procedure, standard MSZ 21470-50:2006 was used and a Lakanen-Erviö solution was used as the extraction agent **[14]**. Dissolvable element content of the samples was determined by an ICP-OES (PerkinElmer Optima 8000, Waltham, Massachusetts, USA) optical emission spectrometer. The wavelengths for the components tested are summarized in ***Table 2***.

Due to the wide linear range of the technique, a two-point calibration was used. The first point was the blank solution, and the second point was a multielement standard. Two types of multielement standard calibration solutions were used and three parallel measurements were carried out in each case. The first solution contained alkaline and alkaline earth metals (Na, K, Mg, Ca), while the second solution contained all the other elements to be measured (Al, Cr, Cu, Fe, Mn, Mo, Pb, P, Zn). The acid content of both the calibration solutions and the sample solutions was 0.2 mol/L nitric acid.

5. Results and evaluation

5.1. Nutritional value results - pH, dry matter content, water-soluble total salt content

pH, dry matter content and water-soluble total salt content measurement results of coffee dregs obtained as byproducts after brewing coffee beverages from coffee samples coming from five different growing areas using the Espresso procedure are shown in ***Table 3***.

From the pH value results (in 10% aqueous suspension) of the three parallel measurements it can be concluded that the byproduct after brewing of the samples coming from Ethiopia nd Costa Rica exhibits a more acidic character. In view of the experimental results, in the case of these two products, their more acidic characteristic should be taken into consideration during agricultural application.

There was a significant difference between the dry matter contents of the samples. The difference between the samples with the two extreme values (Panama, Costa Rica) can be explained by the geographic and climatic characteristics of the growing areas. The coffee from Panama with the highest dry matter content is typically produced at a lower altitude (200 m on average), under relatively rainy conditions (3,500 mm/year). Thus, it can be characterized by a more robust structure. In contrast, the coffee from Costa Rica with the lowest dry matter content is produced at an altitude of 1,500 m, under less rainy conditions (1,500 to 3,000 mm/year).

In terms of the water-soluble total salt content, no difference between the samples was found. Typically, very low concentrations were measured, so no salinization related to the salt content can be expected when used for soil improvement.

5.2. Analytical results of the FT-NIR spectra

FT-NIR spectra of the coffee dreg samples after the different brewing procedures of coffees coming from the five different growing areas are shown in ***Figure 1***. Characteristic peaks are marked in the figure with numbers, and their qualitative evaluation is summarized in ***Table 4***. For the identification of the peaks, literature data were used **[15]**.

A vertical shift in the spectra can be observed clearly, which can be explained by the different particle sizes. No characteristic difference could be found between the spectra of ground coffee samples coming from different growing areas.

Coffee dreg samples prepared by the same brewing method but coming from different growing areas were compared (***Figures 2 and 3***). In the case of coffee dreg samples obtained after the application of the French Press procedure (***Figure 2***), a minimal baseline shift could be observed. A significant difference in the spectra could be found in the characteristic vibration range of proteins (5,000-4,800 cm^{-1}) and lipids (4,600-4,300 cm^{-1}).

This can be explained by the solubilities of the different organic components. The French Press can be considered a very gentle preparation technique, so the characteristic difference between the residual coffee dreg samples indicates that the samples coming from different growing areas contain varying amounts of easily soluble components.

When using the Espresso brewing technique, the characteristic difference between the spectra of the residual coffee dreg samples (***Figure 3***) is not as significant as in the case of the French Press brewing method.

Compared to the French Press procedure, the Espresso procedure is a more powerful preparation technique. Thus, the delicate difference between the components with different solubilities cannot be detected due to the more intense extraction conditions.

Following this, dreg samples of coffees coming from the same growing area but prepared in different ways were compares. Spectra of the samples coming from Brazil are shown as an example. The spectra of the original ground sample and the coffee dreg samples were compared (***Figure 4***), as well as the first derivative of the spectra. The most obvious difference between the spectra of the coffee dreg samples and of the ground coffee can be seen in the absorption range of water (5,200-5,100 cm^{-1}), which was expected, since the moisture content of the roasted sample is certainly lower than that of the dried dreg samples. A difference can also be observed in the 7,100-7,000 cm^{-1} range, which is primarily the absorption range of aliphatic hydrocarbons and fats and oils. Based on the spectra, quantitative conclusions cannot be drawn, only the fact that there is a difference can be established.

5.3. Chemometric evaluation of FT-NIR data

As the first step of chemometric evaluation, principal component analysis (PCA) was performed. The goal of this was to determine spectral outliers. Spectral outlier can be a sample because of incorrect recording of the spectrum or because it really does not fit the sample population.

During PCA, it was determined how many principal components are needed for the description of the data set (***Figure 5***), and to what extent these components explain the variance of the data set. It can be stated that 99.8% of the variance of the properties can be explained by the first three principal components (PC1=92.4 %, PC2=6.2%, PC3=1.2%).

Accordingly, PCA results were studied in the context of three principal components. The data set is explained to the largest extent by the first and second principal components. As an illustration, their relationship is shown in ***Figure 6***. The ellipse represents the 95% confidence interval.

As a result of the PCA it can be stated that, taking into account the 95% confidence interval, al samples can be classified into a single set, so the spectra examined can later be regarded as a single matrix. No faulty or spectral outlying spectrum was identified.

For the pattern recognition of ground coffees according to the growing area, linear discriminant analysis (LDA) was used (***Figure 7***). Grouping of the ground coffee samples according to the growing area was successfully completed. Of the five growing areas, only the New Guinea one shows an overlap with other areas (Ethiopia and Brazil). Based on our results, it was shown that the method is suitable for the identification of the growing aera. The results of the LDA model were validated by random grouping. If the original grouping cannot be explained by chance, then a jumbled pattern is obtained during a random type check. Since random grouping resulted in a jumbled pattern, it can be stated that the original LDA model is satisfactory.

LDA results of the coffee dreg samples analyzed according to the brewing method are shown in ***Figure 8***. The figure shows the grouping according to the different brewing methods and the ground coffee. The three groups are perfectly separated from each other. In this case, checking by randomization was also performed, and it confirmed the success of the original grouping.

SCIENCE

NUTRITIONAL ANALYSIS OF COFFEE DREGS

5.4 ICP-OES results

In our work, quantitative determination of 13 elements was carried out, the results of which are summarized in ***Table 5***. There are significant differences in the analytical results of some of the elements, which suggests that the different elements are absorbed by the plants to varying degrees from the soil of the different growing areas. Knowing the limit values for application and the ICP-OES results, the dregs of not all coffee types can be recommended for soil improvement. To be able to make the final decision, further analyses are required according to FVM decree 36/2006. (toxic elements: As, Cd, Co, Hg, Ni, Se, total PAH, benzo[a]pyrene, petroleum hydrocarbons, biological tests, etc.).

6. Conclusions

In the course of our research, it was determined that there is a relationship between the residual nutritional value of coffee dreg samples coming from different growing areas and the brewing methods. Comparing the two brewing methods, the extract prepared by pressurized steam (Espresso) contained more valuable components from a phyto-physiological point of view (e.g., phosphorus) than the extract prepared by the French Press method at atmospheric pressure.

Ethiopian and Costa Rican coffee dreg samples exhibited a more acidic pH compared to the other samples. It is very important to take this into consideration during agricultural application, since the use of larger quantities could lead to the acidification of the soil, and so it is advisable to mix it with alkalizing additives.

In terms of the water-soluble salt content, it is worth noting that the measured concentrations were very low, so its role in triggering salinization is probably not significant.

Results of the FT-NIR analyses suggest that, based on a sufficiently large sample obtained from the producers or having proper certificates of origin, a database can be built based on the analysis of which the geographical origin of a commercial sample can be determined with a high degree of certainty. Another possibility may be the application of fast GC-MS measurements **[16], [17].**

Based on the results of our ICP-OES analyses, there is a significant difference between samples coming from different growing areas. This is quite likely to affect the recycling potential of the coffee dregs obtained after brewing. As a result, coffee dregs should be subjected to further soil microbiological tests in order for its recycling to be more solid and efficient.

However, evaluation of a number of different analyses requires the application of a complex chemometric method, the so-called multicriteria optimisation. The sum of ranking differences (SRD) method could mean a suitable alternative to evaluate multielement ICP-OES and FT-NIR results together with pH, dry matter content and water-soluble salt content measurements to be performed in accordance with FVM decree 6/2006. (V. 18.) and, in light of these, recommendations can be made for recycling options. The method has been successfully used for freshly consumed cocktail tomato varieties **[18],** basils **[19]**, as well as during sensory tests **[20]** and eye-tracking measurements **[21].**

7. References

[1] Spiller, M. A. (1997): The Coffee Plant and Its Processing, in *Caffeine*, G. A. Spiller, Ed. CRC Press, pp. 22–28.

[2] Clarke, R., Vitzthum, O. G. (2001): *Coffee: Recent Developments*. Wiley-Blackwell,.

[3] Campos-Vega, R., Loarca-Piña, G., Vergara-Castañeda, H. A., Oomah, B. D (2015): Spent coffee grounds: A review on current research and future prospects, *Trends Food Sci. Technol.*, vol. 45, no. 1, pp. 24–36.

[4] Várvölgyi E., Gere, A., Szöllősi, D., Sipos, L., Kovács, Z., Kókai, Z., Csóka, M., Mednyánszky, Zs., Fekete, A., Korány, K. (2014): Application of Sensory Assessment, Electronic Tongue and GC–MS to Characterize Coffee Samples, *Arabian Journal for Science and Engineering*, vol. 40, no. 1, pp. 125–133.

[5] Deligiannis, A., Papazafeiropoulou, A., Anastopoulos A., Zannikos, F. E., (2011): Waste Coffee Grounds as an Energy Feedstock. In *Proceedings of the 3rd International CEMEPE & SECOTOX Conference*.

[6] MSZ EN 14241 (2013): Folyékony ásványolajtermékek. Zsírsav-metil-észterek (FAME) dízelmotor-hajtóanyagként és fűtési célra. Követelmények és vizsgálati módszerek.

[7] Martinez-Saez, N., García, A. T., Pérez, I. D., Rebollo-Hernanz, M., Mesías, M., Morales, F. J., María A. Cabrejas, M., Dolores del Castillo, M. (2017) : Use of spent coffee grounds as food ingredient in bakery products. *Food Chem.*, Vol. 216, pp. 114–122.

[8] Vardon, D. R., Moser, B. R., Zheng, W., Witkin, K., Evangelista, R. L., Strathmann, T. J., Rajagopalan, K., Sharma, K. B. (2013): Complete Utilization of Spent Coffee Grounds To Produce Biodiesel, Bio-Oil, and Biochar. *ACS Sustain. Chem. Eng.*, vol. 1, no. 10, pp. 1286–1294, 2013.

[9] Cruz, R., Baptista, P., Cunha, S., Pereira, J. A., Casal, S. (2012): arotenoids of lettuce (Lactuca sativa L.) grown on soil enriched with spent coffee grounds. *Molecules*, vol. 17, no. 2, pp. 1535–1547, Feb.

[10] Moldvaer, A. (2014): *Coffee Obsession*. New York: DK Publishing.

[11] 36/2006. (V. 18.) FVM rendelet - a termésnövelő anyagok engedélyezéséről, tárolásáról, forgalmazásáról és felhasználásáról.

[12] Csambalik L., Divéky-Ertsey, A., Pap, Z., Orbán, Cs., Stégerné M., Gere M. A., Stefanovits-Bányai E., Sípos L. (2014): Coherences of instrumental and sensory characteristics: case study on cherry tomatoes. *Journal of Food Science*, vol. 79, no. 11, United States, pp. C2192-202, Nov-2014.

[13] Sipos, L., Gere, A., Szöllősi, D., Kovács, Z., Kókai Z., Fekete A. (2013): Sensory evaluation and electronic tongue for sensing flavored mineral water taste attributes. *Journal of Food Science*, vol. 78, no. 10, pp. S1602-8.

[14] MSZ 21470-50 (2006): szabvány- Környezetvédelmi talajvizsgálatok. Az összes és az oldható toxikuselem-, a nehézfém- és a króm(VI)tartalom meghatározása

[15] Workman, J., Weyer, L. (2012): *Practical Guide and Spectral Atlas for Interpretive Near-Infrared Spectroscopy*, 2nd ed. CRC Press.

[16] Radványi D., Gere A., Jókai Zs., Fodor P. (2014): Rapid evaluation technique to differentiate mushroom disease-related moulds by detecting microbial volatile organic compounds using HS-SPME-GC-MS. *Analytical and Bioanalytical Chemistry*, vol. Published, no. 2, p. 407, 22-Nov-2014.

[17] Radványi D., Gere A., Sipos L., Kovács S., Jókai Zs., Fodor P. (2016): Discrimination of mushroom disease-related mould species based solely on unprocessed chromatograms. *Journal of Chemometrics*. (30) p. 197-202.

[18] Csambalik L., Divéky-Ertsey, A., Pusztai P., Boros F., Orbán Cs., Kovcs S., Gere A., Sipos L. (2017): Multi-perspective evaluation of phytonutrients Case study on tomato landraces for fresh consumption. *J. Funct. Foods*, vol. 33, pp. 211–216.

[19] Sipos L., Bernhardt B., Gere A., Komáromi B., Orbán Cs., Bernáth J., Szabó K. (2016): Multicriteria optimization to evaluate the performance of Ocimum basilicum L. varieties," *Ind. Crops Prod.*, vol. 94, pp. 514–519.

[20] Gere A., Sipos L., Kovács Z., Kókai Z., Héberger K. (2017): Which just-about-right feature should be changed if evaluations deviate? A case study using sum of ranking differences. *Chemom. Intell. Lab. Syst.*, vol. 161, no. June 2016, pp. 130–135.

[21] Gere A., Danner L., Nino de A., Kovács S., Dürrschmid K., Sipos L. (2016): Visual attention accompanying food decision process: an alternative approach to choose the best models. *Food Qual. Prefer.*, vol. 51, pp. 1–7.