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COMPOSITIONAL INVESTIGATIONS OF SOME ROMANIAN CEREALS

**R. VLĂDOIU[1] R.M. ION[1,2] S. TEODORESCU[3]
R.M. ŞTIRBESCU[3] I.D. DULAMĂ[3]**

Abstract: *The wheat, barley, rye, oat as grains, bran and flour are the most consumed cereals by humans. Cr, Fe, Co, Ni, Cu, Zn, Cd, Pb, were determined in this paper, by inductively coupled plasma atomic emission spectrometer (ICP-AES) and FTIR analytical technique. By ICP-OES, the minerals concentration have been identified and calculated, while by FTIR, the main compounds are identified, as follows: lipid lignin and carbohydrate. The highest Fe content was detected in barley fluor (61.233 ± 0.409 mg/kg), whereas the lowest content was determined in what flour (7.850 ± 0.029 mg/kg). Furthermore, the highest and lowest Cr contents were found in flour, too: oat, barley and rye, respectively.*

Key words: *flour, mineral determination, ICP-AES.*

1. Introduction

Cereals as member of the family, Gramineae, include rye, oats, barley, maize, triticale, millet and sorghum. At global level, wheat and rice are the most important crops, with over 50% of the world's cereal production [1]. All these cereals have similar structures, and are an important source of energy, protein, B vitamins and minerals for the world population.

The wheat is one of the most consumed cereals by humans, which belongs to the Triticum family [7], the hard wheat T. Durum being the most commercially used [14].

Barley is mainly grown for animal feed, especially for pigs, and also, in the manufacture of beer and for distilling in whisky manufacture [11].

Oat is mainly been grown for animal feed, and for breakfast cereals (Kent & Evers 1994). However, oats is used in cosmetics and adhesives [14].

Rye is a the major crop met in Russia, Poland, Germany and the Scandinavian countries, and is used for animal feed [7].

In spide of their low concentrations of sodium and potassium, all cereals contain considerable amounts of iron, magnesium and zinc, as well as low level of selenium [6].

[1] Doctoral School, *Valahia* University of Târgovişte.
[2] National Institute for Research and Development in Chemistry and Petrochemistry - ICECHIM, Nanomedicine Research Group.
[3] Institute of Multidisciplinary Research for Science and Technology, *Valahia* University of Târgovişte.

The flour is used for the bread, cookies and other bakery preparation, products. For this reason, many papers have been written, treating the characterization and nutritional evaluation of this cereal and its flour [10].

Cr, Fe, Co, Ni, Cu, Zn, Cd, Pb, were determined in this paper, by inductively coupled plasma atomic emission spectrometer (ICP-AES) and FTIR analytical technique.

Infrared (IR) spectroscopy is recognized as a useful technique for analytical examining the chemical composition of different samples. Different bonds absorb light at different frequencies giving very specific absorption patterns to various components.

A key advantage of infrared spectroscopy is that it is sensitive to the structure and concentration of all tissue components (proteins, lipid, carbohydrate, phosphate, carbonates, nucleic acids etc.) present in the sample. The vibrational spectrum collected from a specific tissue location has unique properties that provide detailed information for all cereals.

2. Material and Methods

2.1. Materials

In our experiments, have been used the following samples: wheat grains, Spelta wheat grains, barley grains, Spelta barley grains, rye grains, wheat bran, Spelta wheat bran, barley bran, oat bran, rye bran, wheat flour, Spelta wheat flour, barley flour, oat flour, rye flour. They have been processed in our laboratory after literature methods [2].

2.2. Methods

The heavy metals content in samples were determined using Thermo Scientific iCAP Qc ICP-MS system. All quantitative measurements in triplicates were performed in the standard mode (STD) using the instruments software Qtegra and the relative standard deviation (RSD) values was less than 10%. Several well-known isobaric interferences were automatic corrected.

To determine the heavy metals content, the samples were mineralized using the microwave digestion system, TOPwave (Analytik Jena) under extreme conditions of pressure and temperature.

Each flour and bran sample (400 mg) was introduced to the digestion vessel, and then, was added 5 mL of 67% HNO_3 and 2 mL 30% H_2O_2. Whole cereals grains (1000 mg) were mixed with 10 mL of 67% HNO_3 and 2 mL 30% H_2O_2. The digestion parameters are presented in the following Table 1.

After digestion time (40 minutes) the vessels were cooled at room temperature and then, each solution was transferred to volumetric flask and filled to 50 mL with deionized water.

The calibration was achieved with a standard solution (Standard ICP-AES multielement standard solution IV, Merck, 1000 ppm), and by using bidistillated water. The validation method (including digestion and determination) was performed using a certified reference material of wheat flour furnished by National Institute of Standards & Technology (NIST).

The main parameters for samples digestion Table 1

Microwave digestion of flour and bran			Microwave digestion of cereals		
Step	1	2	Step	1	2
T [°C]	170	190	T [°C]	160	170
P [bar]	40	40	P [bar]	50	50
Power [%]	80	90	Power [%]	80	80
Ramp [min]	2	5	Ramp [min]	10	5
Time [min]	5	15	Time [min]	15	10

The FT-IR spectra have been recorded with a FT-IR spectrometer (VERTEX 80), in the following conditions: range 4000 cm^{-1} to 580 cm^{-1}, 32 scan, resolution 4 cm^{-1}. FT-IR spectra were achieved using Attenuated Total Reflectance (ATR) accessory with diamond crystal. The samples were investigated directly on ATR without special preparation.

The spectrometer has been achieved with a Vertex 80 FT-IR spectrometer, equipped with several features such as Automatic Accessory Recognition, which facilitate performing spectroscopic measurements. The standard configuration is designed for data acquisition in the mid IR region (8 000 to 350 cm^{-1}).

3. Results and Discussions

Figure 1 shows the mean value of the tested macro elements (Cr, Fe, Co, Ni, Cu, Zn, Cd, Pb) in cereal cultivars. All the elements have higher concentrations in flour than in bran and grain. The highest Fe content was detected in barley fluor (61.233 ± 0.409 mg/kg), whereas the lowest content was determined in what flour (7.850 ± 0.029 mg/kg). Furthermore, the highest and lowest Cr contents were found in flour, too: oat, barley and rye, respectively.

It should be mentioned the new and interesting rule, Spelta variety of wheat show higher concentrations at all the minerals in flour than in grain and bran.

During the last 20 years, methods based on vibrational spectroscopy in combination with chemometric techniques have resulted in the development of rapid methods to predict cereals biochemical and biophysical properties [13-15].

These tools include speed, ease-of-use, minimal or no sample preparation, and in some case the avoidance of sample destruction. Most of these features are characteristic of mid-infrared (MIR) and near-infrared (NIR) spectroscopy.

The use of Fourier transform infrared (FTIR) spectroscopy was used as tool to differentiate between patterns of components of cereals types. According to the authors, the IR spectrum of cereals samples was described by peaks near 3500, 3000, 1600, 1400, 1000, 800 and 500 cm^{-1}. The main signals in the mid-IR region are in 1800-1500 cm^{-1}. There is a band at about 1750 cm^{-1} which is associated with the C=O stretching of proteins. Beyond these remarks, C=O stretching band from amide I and N-H bending of amide II are both located in this spectral region.

By analyzing the FTIR spectra, could be concluded the following aspects:

The broad absorption band between 3400-3200 cm^{-1}, present in nearly all spectra is attributed to OH and NH stretching. They are not significant in selecting one or another cereal.

The presence of lipid is indicated by absorptions from the symmetric and asymmetric stretching vibrations of CH_2 (2922 and 2852 cm^{-1}) and CH_3 (2956 and 2874 cm^{-1}) groups of the acyl chains [15].

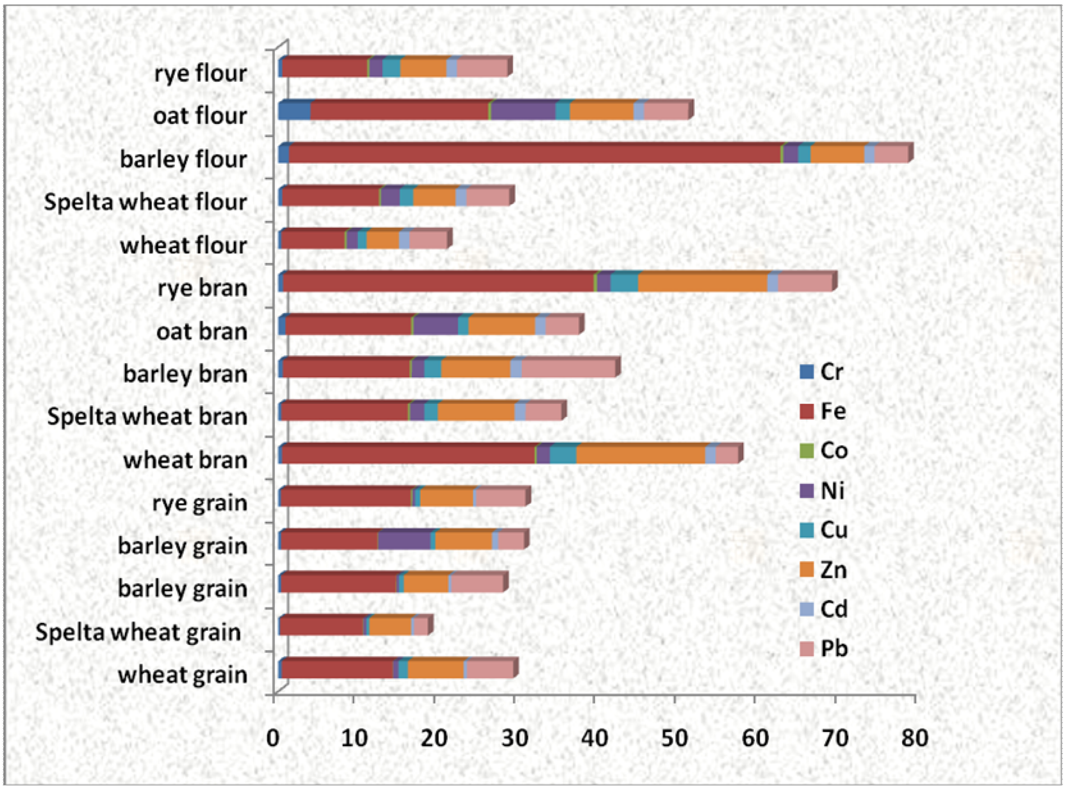

Fig. 1. *The mineral concentrations from cereals* [*mg/kg*]

The region of the IR spectrum between wave numbers 1750 and 2800 cm^{-1} is free from absorption of functional groups from biological materials.

The bands from 1735 cm-[1] is assigned to a strong absorption band at approximately arising from the stretching vibration of the C=O ester groups present in lipid molecules [8].

The peaks from 1650 cm^{-1} and 1550 cm^{-1} correspond to the protein absorption bands. The first located at 1650 cm^{-1} is assigned to the C=O stretching vibration of the amide C=O group, while the second one, between 1500 and 1560 cm^{-1}, is assigned to N-H bending vibrations coupled with C-N stretching within the protein molecule.

The band from 1510 cm^{-1} is attributed to the aromatic ring structures within lignin molecules [3].

The largest and broadest carbohydrate absorption peak is centered at approximately 1025 cm^{-1}, and is attributed to non-structural carbohydrate [4].

4. Conclusions

The wheat, barley, rye, oat as grains, bran and flour are the most consumed cereals by humans. Cr, Fe, Co, Ni, Cu, Zn, Cd, Pb, were determined in this paper, by inductively coupled plasma atomic emission spectrometer (ICP-AES) and FTIR analytical technique. By ICP-OES, the minerals concentration have been identified and calculated, while by FTIR, the main compounds are identified, as follows: lipid lignin and carbohydrate.

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