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STUDY OF ACRYLAMIDE PRECURSOR'S LEVEL IN POTATO TUBERS CORRELATED WITH ACRYLAMIDE LEVEL IN CRISPS

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ABSTRACT
Potato crisps are a popular snack due to their unique sensory properties and their nutritional value. Wide variations of acrylamide concentration in finished products are caused by different levels of precursors (asparagine and sugars) of acrylamide in the potato's tubers and the conditions of thermal process. The aim of this study was to assess the content of precursors of acrylamide from potatoes tubers, prediction of the amount of acrylamide based on precursors quantity and correlation of predicted values with the acrylamide level from crisps. The principle of the method used to measure reducing sugars and asparagine from potato tubers were based on an enzymatic reaction which is detectable by photometric measurement while the acrylamide level in potato crisps was determined using HPLC system. The relationship between concentration of precursors and acrylamide formation is very important and the prediction of acrylamide level can provide to crisps manufacturer warnings on potatoes batches in which is expected to arise high level of acrylamide concentration, thus allowing to make adjustments in process to mitigate acrylamide formation in potato crisps.

1.Introduction

Many of the food products require thermal processing. Deep-fat frying is one of the oldest and most common cooking method used in the preparation of potato crisps that creates unique texture and flavor of final product (Moreira *et al.*, 1999).

An important quality parameter for potato crisps is the acrylamide content. Acrylamide levels in foods have been subject to a benchmarking system. Based on the monitored results, the European Commission has implemented the Regulation 2017/2158 and establish benchmark levels for the reduction of the presence of acrylamide in food. For potato crisps, recommendation to mitigate the formation of acrylamide as contaminant, include selecting suitable potato varieties, controlling potato storage and transport, monitoring recipe and process conditions, and the indicative value for the presence of acrylamide was set at 750 µg kg^{-1} (parts per billion) (EU 2017/2158).

Acrylamide is formed as a result of reaction between amino acids, namely asparagine and reducing sugars, particularly glucose and fructose as part of the Maillard reaction (Mottram *et al.*,2002, Stadler *et al.*, 2002). During the heating process of potato products at high temperature (>120 °C) and low moisture conditions acrylamide is developed. The amount which is developed is depending on the applied energy (heat) and the quantity of precursors in potato (Moreira *et al.*, 1999, Tareke *et al.*, 2002).

Lipid oxidation, the Maillard reaction and the absorption of oil during deep-fat frying process play an important role in the acrylamide formation. The Maillard reaction is also known as non-enzymatic browning, which is responsible for flavor and aroma in potato crisps. As L-asparagine is the dominant amino acid in potato tissue, the acrylamide formation depends to the levels of fructose and glucose (Biedermann *et al.*, 2002).

Sugar reduction is an important processing step, as reducing sugars as glucose and fructose together with asparagine are acrylamide precursors and can impact on its production during the deep-frying process (Knol *et al.*, 2005). Reducing sugar content is used to predict potato tuber suitability for potato crisps processing, since it is often an indicator of color development (Marquez *et al.*, 1986).

Since 2002 many researches have been done with focus on acrylamide formation and detection. Studies showed that higher levels of acrylamide in deep-fat fried products may be due to the different composition of potatoes in acrylamide precursors and also this level may be influenced by the storage condition and the conditions of thermal process (Abt *et al.,* 2019, Andačić *et al.*, 2020, Yang *et al.*, 2016, EFSA, 2015, Keramat *et al*., 2011, Becalski *et al*., 2003, Zyzak *et al*., 2003, Haase *et al.,* 2004, Palazoglu *et al.*, 2010, Williams, 2005).

Potatoes may accumulate high levels of reducing sugars during the storage conditions even though the sugar levels were accepted at harvest, therefore the contents of these precursors in potato tubers before processing are important and have to be controlled (Williams, 2005, Martinez et al., 2019).

In literature already there are an important number of strategies to reduce acrylamide (AA) level, and limiting the content of reducing sugars and asparagine is a common goal of all crisps manufacturer.

2. Materials and methods

2.1. Materials

2.2.1. Samples

36 samples from three potatoes varieties were analyzed, Hermes, Opal and Pirol. Potatoes varieties were selected for crisps production due to their low levels of reducing sugars. All the potato varieties were harvested in 2022 and were analyzed from December 2022 till February 2023. The samples were stored in a carefully controlled environment, protected for light and stored at temperature between 8 – 10 °C. For deep-fat frying the vegetable sunflower oil was used.

2.2.2. Precursor analysis

Reducing sugars (glucose and fructose) and asparagine concentrations in potatoes tubers were quantified using Konelab Arena 20 biochemical analyzer. The method is based on an enzymatic reaction which is detectable by photometric measurement. In order to determine the initial reducing sugars and asparagine a 5 kg samples were washed and blended. After blending, 50 g blended potato pulp was mixed with 50 mL of water and approximate 0.3 ml Octanol was added. The solution was homogenized after adding 4 mL of potassium hexacyanoferrate and 4 mL zinc sulfate heptahydrate. The pulp was filled into the 250 mL volumetric flask and flask stand for at least 10 minutes, then filtered. The filtrate was analyzed with Konelab Arena 20 analyzer. 5 analyses were made on each potato sample, and for results interpretation was used the average of the values. As reference material standard solution of D-fructose, D-glucose and L-asparagine from Thermo Fisher were used.

2.2.3. AA quantification in crisps

Before frying, potatoes were peeled, sliced at 1.6 mm average thickness. After peeling they were rinsed in water and the excess water from the potato sliced was removed using absorbent paper. Samples of potatoes were fried using a temperature-controlled fryer AEG FR 5548 fryer with two unites with capacity of 15 L. Potatoes were fried at temperature between 164 – 178 °C. During frying process fryer temperature (inlet and outlet) were recorded and moisture and fat content were analyzed. Sample cooled were grounded in order to analyze the AA level from potato crisps.

The AA level in crisps was determined using an Agilent 1200 model HPLC system.

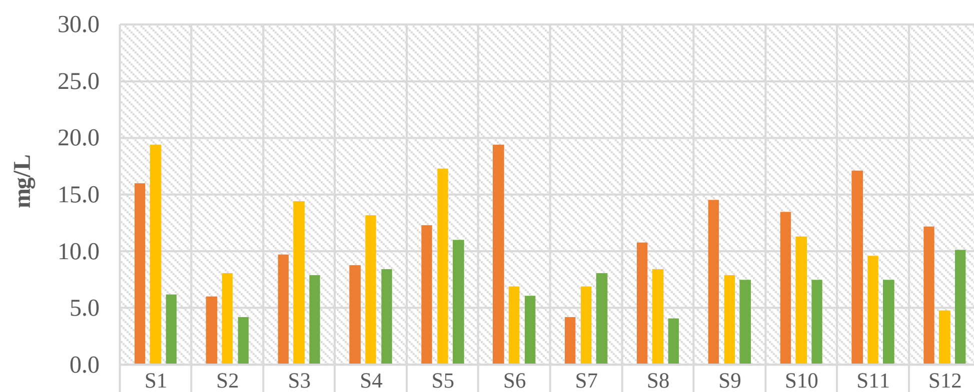
Thus, 2 grams of potato chips were weighed and grounded into a fine powder, then putted into a 50 mL centrifuge tube. Over grounded sample was added 30 mL ultrapure water, samples were vortex oscillated and ultrasonic vibrated for at least 10 minutes, then centrifuged at 6000 rpm. The resultant 15 mL supernatant solution was collected and putted into a new 50 mL centrifuge tube mixed with 5 mL n-hexane, followed by vortex oscillated for 1 minute. Then the mixture was centrifuged at 6000 rpm for 10 minutes followed by pipette out of the upper layer of n-hexane. The centrifuge and n-hexane extraction steps were repeated one more time. The resultant 15 mL sample solution was used for determination of AA content using HPLC method. Reagents, solvents and reference materials used were analytical grade.

3.Results and discussions

3.1. Precursor analysis

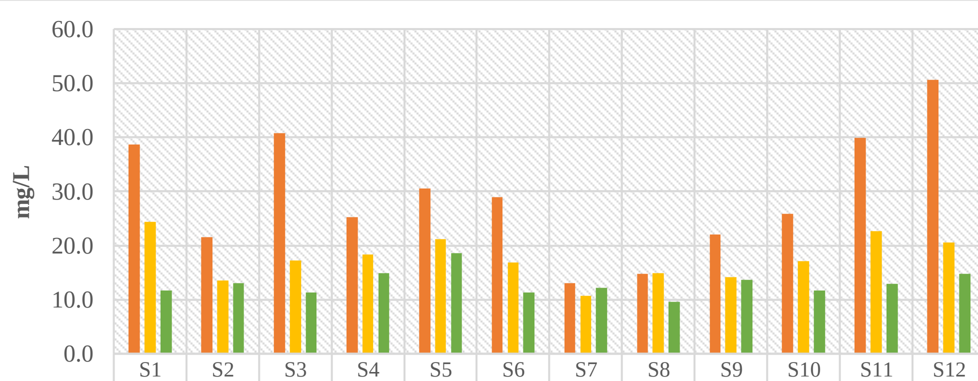
Controlling of reducing sugar it is a measure to reduce AA level in potato crisps. The results are given in Figure 1, Figure 2 and Figure 3.

Analyzed samples give us information on the state of potatoes samples. Reducing sugars (glucose and fructose) levels were low for all samples from the three varieties analyzed. Fructose levels ranged from 4.1 mg/L for Opal potato variety to 19.4 mg/L for Hermes variety while in case of glucose content ranged from 9.6 mg/L in case of Opal variety to 50.6 mg/L in case of Pirol variety.



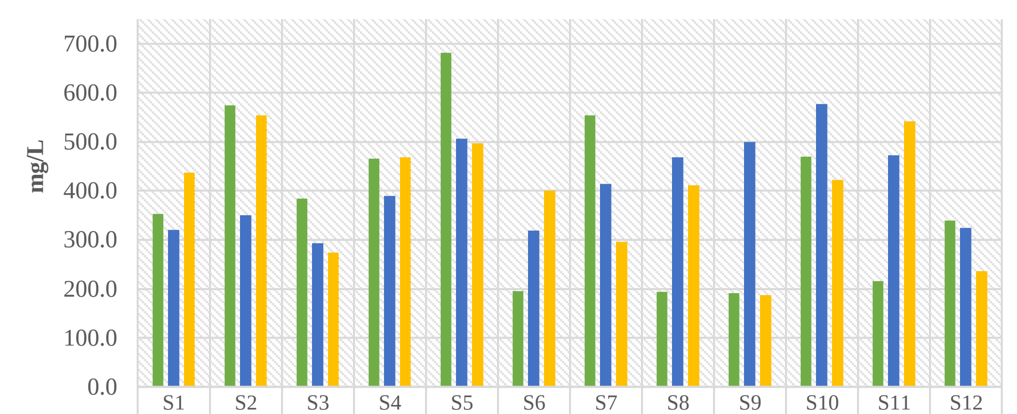
	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12
Pirol	16.0	6.0	9.7	8.8	12.3	19.4	4.2	10.8	14.5	13.5	17.1	12.2
Hermes	19.4	8.1	14.4	13.2	17.3	6.9	6.9	8.4	7.9	11.3	9.6	4.8
Opal	6.2	4.2	7.9	8.4	11.0	6.1	8.1	4.1	7.5	7.5	7.5	10.1

Figure 1. Fructose concentration in potato tubers



	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12
Pirol	38.7	21.5	40.7	25.2	30.5	28.9	13.0	14.8	22.0	25.9	39.9	50.6
Hermes	24.4	13.5	17.2	18.4	21.2	16.9	10.7	14.9	14.2	17.1	22.6	20.5
Opal	11.7	13.0	11.3	14.9	18.6	11.3	12.2	9.6	13.6	11.7	12.9	14.8

Figure 2. Glucose concentration in potato tubers



	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12
Pirol	352.6	574.1	384.6	465.6	681.1	194.8	554.4	193.5	191.2	469.4	215.3	339.1
Hermes	320.0	349.7	293.5	390.1	506.8	318.8	413.9	468.1	499.7	577.0	472.8	323.7
Opal	437.1	554.4	274.2	468.1	496.4	400.3	295.6	411.6	186.6	422.7	541.6	236.6

Figure 3. Asparagine concentration in potato tubers

3.2. Acrylamide (AA) level in potato crisps

For AA determination the content obtained was expressed in μg kg^{-1}. The lowest concentration of AA that can be determined with an acceptable level of repeatability precision and trueness was 20 μg kg^{-1}.

The amount of acrylamide is strongly related to the moisture content of the product. Moisture content has a strong influence on crisps browning and acrylamide formation. The inside of crisp product is not as strongly exposed to high temperature and the outer layer is dried first. During frying process fryer temperature (inlet and outlet) were recorded and moisture and fat content were analyzed. Potatoes were fried at temperature between 164 – 178°C. For the analyzed samples the moisture content ranged from 1.3% to 1.8% and the fat content ranged from 30% to 39%.

The AA concentration in samples of potato crisps for each variety are shown in Figure 4, Figure 5 and Figure 6. All the crisps' samples analyzed contained AA levels higher than the limit of quantification (20 μg kg^{-1}).

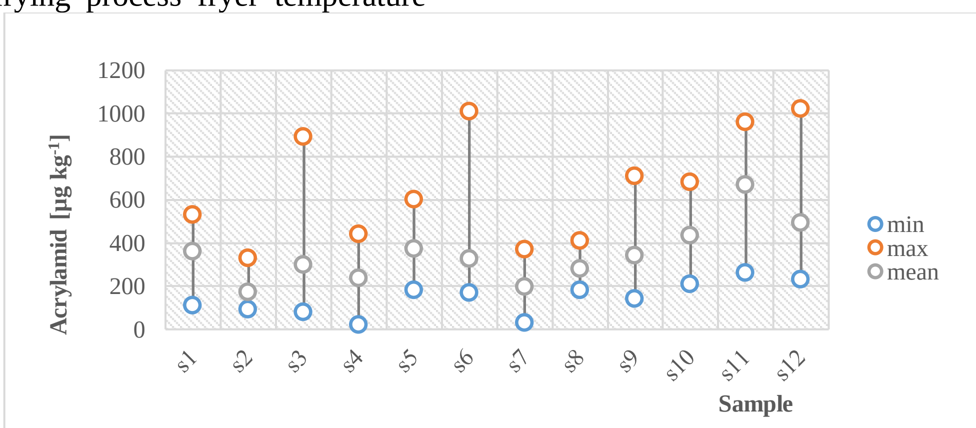


Figure 4. Concentration of AA in crisps samples from Pirol variety

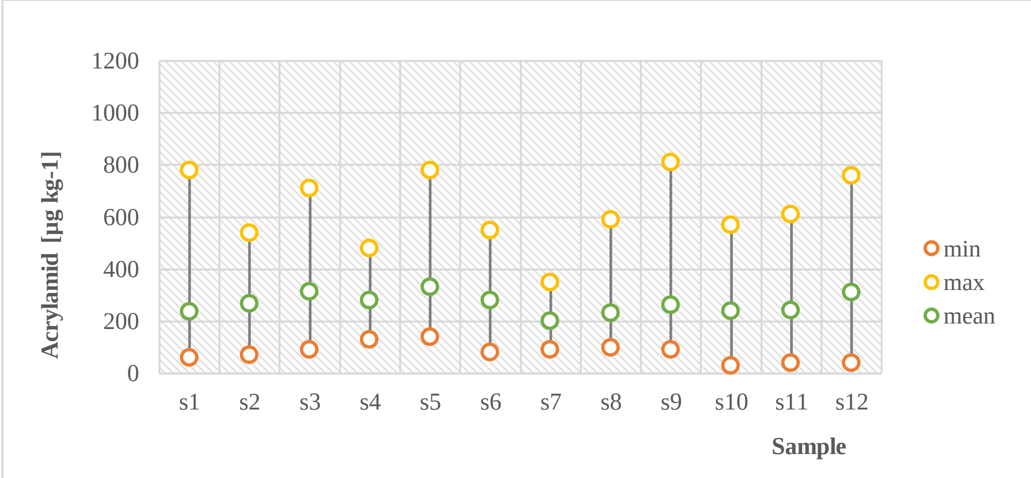


Figure 5. Concentration of AA in crisps samples from Hermes variety

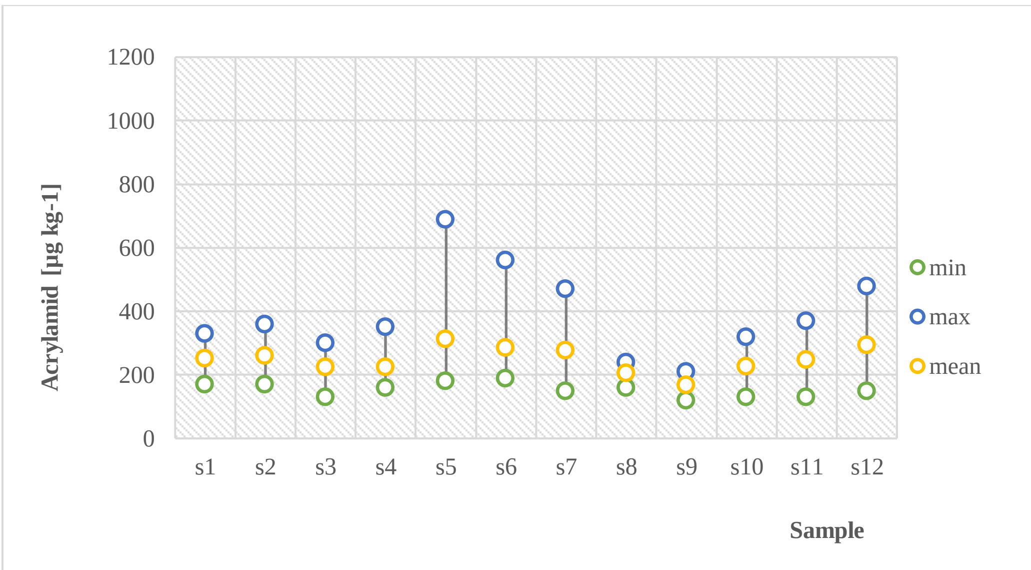


Figure 6. Concentration of AA in crisps samples from Opal variety

All the mean values obtained not exceed the acrylamide indicative value of 750 µg kg^{-1} recommended. Data distribution showed a variability in the AA content through samples and were registered some maximum values of AA (case of Pirol potato variety, samples s3, s6, s11, s12, and Hermes potato variety, samples s9 and s12) exceed the indicative level, values which may be due to the processing conditions applied.

Acrylamide level ranged from the minimum of 20 µg kg^{-1} to maximum 1020 µg kg^{-1} in case of Pirol potato crisps.

In case of Hermes potato crisps minimum value ranged from 30 µg kg^{-1} to maximum 810 µg kg^{-1}.

3.3. AA prediction and AA concentration

The reduction of AA concentration in case of potato crisps is based on reducing the precursors (reducing sugars and asparagine) present in the potato tubers. The reducing sugars level and the asparagine level may be reduced in manufacturing process by blanching the potatoes before deep frying process. The amount of acrylamide depends also by frying temperature which should be low and not higher than 175°C (EU 2017/2158) and the frying time.

The AA concentration correlated with predicted AA level in samples of potato crisps for each variety are shown in Figure 7, Figure 8 and Figure 9, where each value represents the mean.

The predicted AA level was calculated using the data presented in 3.1 for reducing sugars and asparagine from potato samples. Additional information about samples (moisture content, time and temperature of frying) was taken into account to establish a relationship with the acrylamide predicted level.

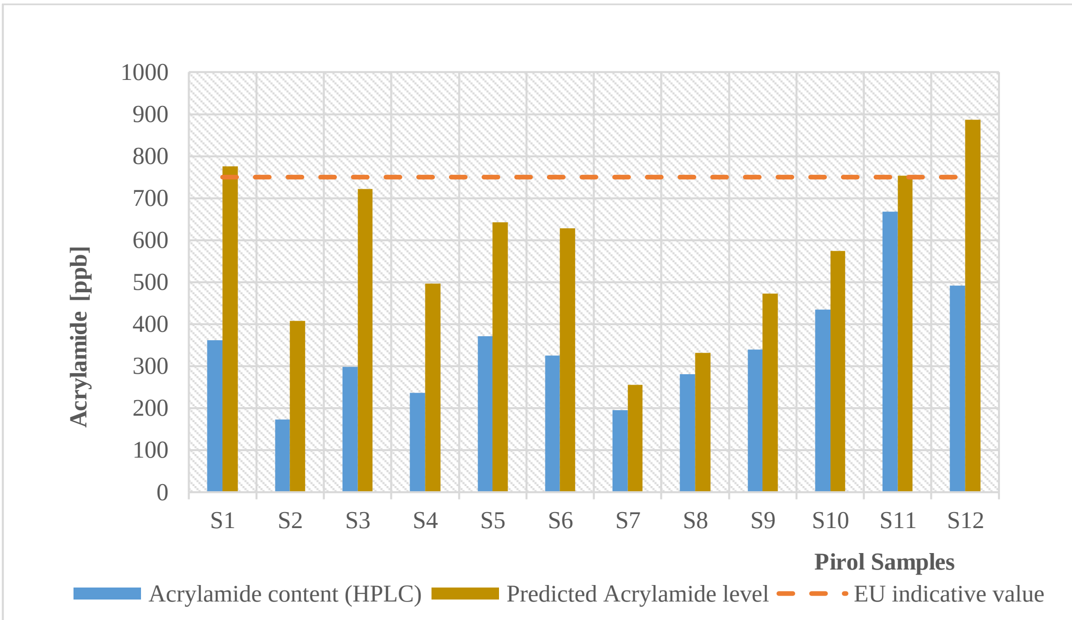


Figure 7. AA concentration and predicted AA level - Pirol variety

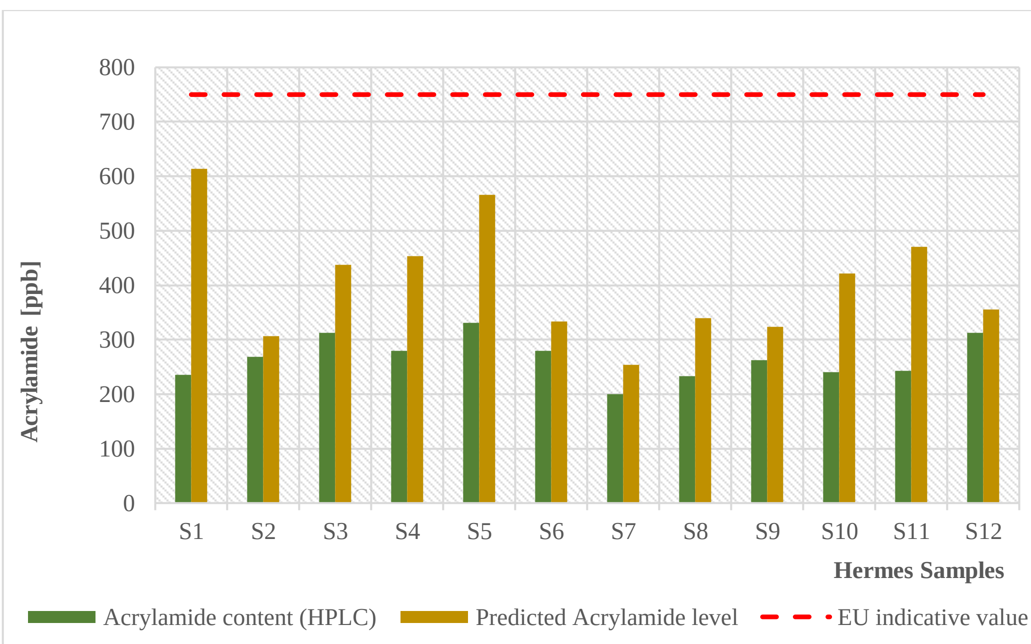


Figure 8. AA concentration and predicted AA level - Hermes variety

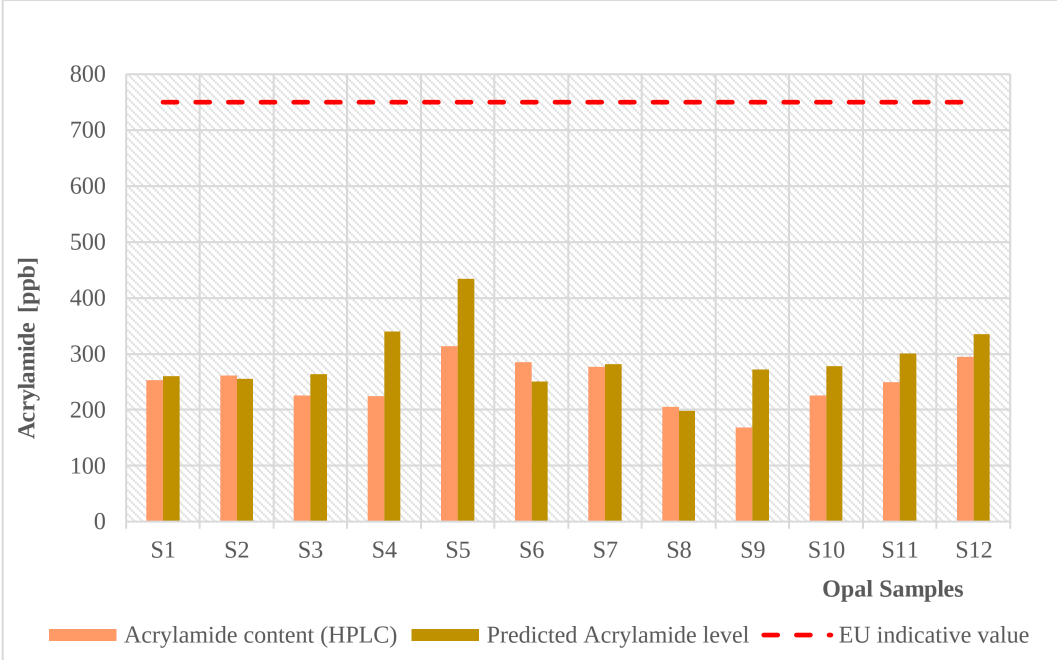


Figure 9. AA concentration and predicted AA level - Opal variety

The obtained values for the predicted AA level were higher with 5% to 20% than acrylamide concentration determinate with HPLC and this can provide warnings that characteristics of the potatoes tubers which will be used in process have an increased probability of high acrylamide in crisps, and thus this information allowing process adjustment (e.g., blanching before frying, adjustment of frying temperature, time of frying) to mitigate acrylamide formation in finished product.

4. Conclusions

Concerns related to concentration of AA in potato crisps are well known. Levels of reducing sugars and asparagine in potato tubers are the main factors contributing to the formation of AA in crisps.

For determination and detection of AA in potato crisps are available methods based on the principles of chromatography and mass spectrometry including high performance liquid chromatography (HPLC), gas chromatography (GC), liquid chromatography tandem mass spectrometry (LC-MS/MS), and gas chromatography-mass spectrometry (GC-MS) (Andrzejewski *et al.*, 2004, Chen et al., 2012). All these methods are used to provide information about acrylamide concentration in finished product, so the purpose of this study was to analyze the content of acrylamide precursors in potato tubers and in the case of a batch of potatoes likely to develop acrylamide to be able to adjust the process.

Potato tubers and potato crisps analyzed al laboratory scale contained no excessive amount of acrylamide. The study results showed useful information about AA prediction and can be used as a mitigation measure to prevent, predict and reduce the presence acrylamide in potato crisps.

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