

Acrylamide in industrial potato crisp manufacturing: a potential tool for its reduction

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1 **Abstract**

2 This paper considers the potential for identifying industrial manufacturing conditions that
3 will lead to high acrylamide formation in potato crisp manufacture. Considering the available
4 historical industrial processing data, initial tests were undertaken to identify the degree of
5 variability and confidence in the data. Following data visualisation which indicated data
6 ‘fingerprints’ characteristic of high acrylamide, Partial Least Squares (PLS) Discriminant
7 Analysis (DA) was implemented to provide indications of the probability that high
8 acrylamide product would be produced. It was determined that in a third of instances, high
9 acrylamide could be predicted while maintaining a low level of false predictions. The
10 predominance of fructose concentration in the prediction along with the need for asparagine
11 were indicated and aligned well with prior literature mechanistic model indications. The
12 ability to identify a third of high acrylamide occurrences provides the process operators with
13 a good opportunity to make process modifications that would comply with increasingly
14 stringent regulation.

15

16 **Keywords**

17 Acrylamide; crisps; Food Processing; Maillard Reaction; Partial Least Squares

18

19 **1. Introduction**

20 Acrylamide is a product of the Maillard Reaction, which occurs when foods containing
21 protein and reducing sugars are heated to high temperatures (Parisi and Luo 2018). The
22 formation of acrylamide during cooking and/or processing was first reported in 2002 by the
23 Swedish National Food Administration (SNFA) and the University of Stockholm (Tareke,
24 Rydberg, Karlsson, Eriksson, & Törnqvist, 2002).

25 Acrylamide is a known carcinogen in rodents (Friedman, Dulak, & Stedham, 1995; Capuano
26 & Fogliano, 2011) which has led to its classification as a probable human carcinogen by the
27 International Agency for Research on Cancer (1994).

28 The European commission has set benchmark levels of acrylamide acceptable to find in
29 manufactured and processed foods. For potato crisps the indicative value was set at 750
30 $\mu\text{g}/\text{kg}$ in 2018 (Commission European, 2017). For food production this means having a clear
31 understanding of the amount of acrylamide in their products but also having an appreciation
32 of raw material characteristics and processing operations that lead to increased levels.
33 FoodDrinkEurope have published a toolbox which outlines process changes to be adopted by
34 manufacturers to reduce the formation of acrylamide in food (FoodDrinkEurope, 2013).
35 Within the European Union, a more formalised requirement was put in place with
36 Commission Regulation (EU) 2017/2158 that came into force in April 2018 that required
37 companies to take mitigation measures and track success via routine measurement. The
38 guiding principle behind this is, by applying best practice in operation, a reduction in
39 acrylamide will follow. Notably it is stated that *'the level of acrylamide in 10 % to 15 % of*
40 *the production with the highest levels can usually be lowered by applying good practices'*.
41 Food business operators are expected to implement measures to reduce acrylamide in their
42 final product to a level "As Low As Reasonably Achievable" (ALARA), including a risk-
43 benefit analysis. Namely a mitigation strategy that reduces acrylamide at the detriment of the
44 overall nutrition of the product is not a desirable outcome (Seal et al., 2008).

45 Acrylamide formation, quantification (Elbashir, Omar, Ibrahim, Schmitz, & Aboul-Enein,
46 2014) and mitigation (Vinci, Mestdagh, & De Meulenaer, 2012; Salazar, Arámbula-Villa,
47 Hidalgo, & Zamora, 2012) has received significant research subsequently.

48 The formation of acrylamide requires asparagine and reducing sugars, and is affected by
49 time, temperature, pH and moisture (De Vleeschouwer, Van der Plancken, Van Loey, &

50 Hendrickx, 2008a). The kinetics of the formation of acrylamide has been investigated
51 extensively in model systems (De Vleeschouwer, Van der Plancken, Van Loey, & Hendrickx,
52 2008b; Knol, Linssen, & van Boekel, 2010; Knol, van Loon, Linssen, Ruck, van Boekel, &
53 Voragen, 2005a).

54 There has been much research into the mitigation of acrylamide formation for potato crisps.
55 Strategies includes selection of potato variety (Elmore, et al. 2015), inclusion of additives in
56 the hot wash such as acids (citric acid) (Kita, et al. 2004), salts (CaCl) (Mestdagh, et al. 2008)
57 or enzymes (asparaginase) (Pedreschi, et al. 2011), monitoring of the colour (Serpen and
58 Gökmen 2009) and controlling the fryer conditions (Matthäus and Haase 2014). Mitigation
59 strategies tested at laboratory scale, when scaled to industry the reduction in acrylamide is
60 reduced. It is also important to note that these studies analysed crisps that have both a flat
61 shape and uniform thickness, and that crisps with a varying thickness and ridge shape (as in
62 this case study) are affected differently by the treatments.

63 Predicting and preventing the formation of acrylamide, opposed to detection following
64 formation is preferable to the food industry. Segtnan et al. modelled acrylamide formation
65 using multiple linear regression (MLR), partial least squares regression (PLSR) and design
66 variables to identify the key parameters affecting acrylamide formation in crisps (Segtnan,
67 Kita, Mielnik, Jørgensen, & Knutsen, 2006). Knol and co-workers employed empirical
68 models and logistic exponential models to acrylamide formation and found the logistic-
69 exponential model initial reducing sugar concentration and parameter a, to be most
70 promising, however the predictive capacity of the model was not tested extensively (Knol,
71 Viklund, Linssen, Sjöholm, Skog, & van Boekel, 2009).

72 This paper describes a study that considered data currently available from a production-line
73 making crisps, to better understand factors arising that cause high acrylamide. With such
74 understanding, operators can act in a more informed manner on the processing conditions to

75 reduce acrylamide formation. It is argued that since this study only considered data that is
76 routinely available, this falls within the ALARA requirement. A critical consideration is that
77 in reviewing historical data is it possible to ascertain the percentage instances of high
78 acrylamide, it is explainable and whether they exceed the 10%-15% EU regulation aim. If so
79 then the scope for achieving reduction beyond EU regulation targets is achievable. In this
80 paper we use industrial production line data alongside pre and post testing for initial reducing
81 sugars concentrations and acrylamide content as inputs for partial least squares regression
82 analysis (PLS). Data from one year was used as a training set and a subsequent year as a
83 validation set.

84

85 2. Material and methods

86 2.1 Chemicals

87 Methanol (LC-MS grade), acetonitrile (HPLC), hexane (HPLC grade) and sodium chloride
88 (NaCl, 99.5%) were purchased from Fisher Scientific. Magnesium sulphate (MgSO₄, 97%)
89 was purchased from Acros Organics. Primary Secondary Amine sorbent (PSA) was
90 purchased from Agilent Technologies (CA, USA). Acrylamide (98%) was purchased from
91 Fluka. [2,3,3-*d*₃]-acrylamide (98%) was purchased from Sigma Aldrich (UK). D-Fructose, D-
92 Glucose, Sucrose (Total Glucose) and L-Asparagine/L-Aspartic Acid (system reagents) were
93 purchased from Thermo-Scientific.

94

95 2.2 Production line data collection

96 For each sample the potato variety, initial glucose, fructose, total sugars and asparagine
97 concentrations were recorded. The potatoes variety used were *Lady Claire* and *Taurus*. From
98 the production process, line number, fryer temperature (inlet and outlet), hot wash

99 temperature and moisture content were recorded on-line. Final acrylamide content
100 determined off-line.

101 Data was collected over a period of 30 months from the manufacturing line of KP Snacks
102 from late 2016. While more than one line is used to produce the product of interest, only one
103 line was considered to remove between line variability. On-line data was recorded 1/minute.
104 Off-line data determination (acrylamide and potato composition) varied in frequency with
105 1/day being typical. Acrylamide was quantified by LC-MSMS. Glucose, fructose, sucrose
106 and asparagine concentrations in the potatoes was quantified by Konelab (Arena 30).

107

108 **2.3 Precursors analysis**

109 Precursor analysis was performed as the potatoes arrive on site with a 27.5 tonne load
110 typically processed within 24 hours of arrival. The load composition was determined to be
111 stable for the duration of processing period.

112 The analysis approach involved taking a subsample of 5 kg which was washed and blended
113 for initial analysis. Glucose, fructose, total sugars and asparagine were measured using the
114 Konelab 20 biochemical analyser (Thermo Fisher Electron Corporation, Courtaboeuf,
115 France). Blended potato (50g) was mixed with 50mL of water. Carrez 1 and 2 (4 mL of each)
116 and octanol (2-3 drops) were added and the solution homogenised. The sample was diluted to
117 250 mL, allowed to stand for 10 minutes then filtered. The filtrate was analysed with the
118 Konelab analyser. The accuracy of the results was determined by processing five replicate
119 samples of the same stabilised solution, using potatoes of different varieties and sugar
120 content. The average confidence boundary is displayed in Table 1, showing the method
121 accuracy according to Friedel et.al. (2013).

122

123 **2.4 Acrylamide analysis**

124 Acrylamide quantification was carried out using the three-phase extraction method described
125 by Mastovska & Lehotay (2006) with modifications. Briefly 1 g of blended fried crisps was
126 combined with [2,3,3-*d*₃]-acrylamide (10 µL, 0.2 mg/mL), 10 mL water, 10 mL acetonitrile
127 and 5 mL hexane, 4g MgSO₄ and 0.5 g NaCl. The mixture was vigorously shaken for 1
128 minute and then centrifuged (5000 rpm for 10 mins). One ml of the acetonitrile layer (middle
129 layer) was transferred to a 2ml Eppendorf tube containing 50 mg of PSA and 175 mg of
130 MgSO₄, this was vortexed for 1 min and centrifuged (1000 rpm for 1 min). The supernatant
131 was transferred to a HPLC vial for analysis by LC-MS/MS.

132 Acrylamide quantification was performed on a Thermos Fisher Scientific, San Jose, CA,
133 USA) consisting of a degasser, a quaternary pump, a thermostatic autosampler, a column
134 oven and a TSQ Mass spectrometer. Chromatographic separation was achieved with ultra-
135 pure water containing 0.1 % formic (mobile phase A) acid and methanol containing 0.1 %
136 formic acid (mobile phase B). The gradient was 98% A at 200µl/min for 3.5 min, the flow
137 rate increased to 300 µL/min and 75% B over 2 mins and held for 2 mins before re-
138 equilibration to initial conditions for 16.7 mins. Sample (10µL) were injected on a Synergi
139 Hydro RP column (250 mm x 4.6 mm x 4 µm, 80 Å pore size) (Phenomenex, UK).

140 The mass spectrometer electrospray ionisation (ESI) in positive mode. Multiple reaction
141 monitoring (MRM) transitions were *m/z* 72.07→55.1 and 44.0 for acrylamide and
142 75.2→58.0 and 44.0 for 2,3,3-*d*₃]-acrylamide (Internal standard) with a dwell time of 100 ms.
143 The MS source conditions were spray voltage 3500 kV, capillary temperature 270 °C,
144 nitrogen was used as a nebulizer gas. Acrylamide and the internal standard eluted from the
145 column at 2.8 mins. Acrylamide was quantified using a linear calibration with a 1/x fitting
146 with a range 10-1000 ng/mL (*r*² > 0.99), with a method detection limit of 26.7 ppb
147 (equivalent to 267 µg/kg).

148

149 **2.5 Crisp Processing Line**

150 The crisp processing follows a standardized protocol. The ACR precursors were analysed
151 during storage (Figure 1) following different unit operations they reach the fryer, temperature
152 of the oil was monitored and taken into consideration on the PLS analysis as well as the off
153 line ACR measurements values. Following a system engineering approach to assess the line
154 behaviour it is necessary to understand the fundamental reactions occurring during the
155 process as far as possible, the behaviour of the processing plant and operators and the
156 variability that can occur within a factory scenario. Previous kinetic studies tackled lab scale,
157 not considering the added complexity of a food processing plant. This study aimed to build a
158 predictive tool applicable in factory settings using food factory data.

159

160 **2.6 Statistical analysis**

161 Principal Component Analysis (PCA) was carried out using the PCA toolbox for Matlab as
162 described by Ballabio (2015). The PLS-DA was performed using the Classification toolbox
163 for Matlab as described by Ballabio and Consonni (2013). ACR analysis was performed in
164 order to consider biological and technical repetition (four observations per sample). The
165 analysis was carried out using Matlab R2018b.

166

167 **3. Results and discussion**

168 In analysing system data it is important to build on qualitative and semi-quantitative
169 understanding of the underlying system to underpin and verify the results provided by the
170 data analytic methods. Prior fundamental knowledge of reaction mechanisms and their
171 drivers is thus important in assessing the results

172 **3.1 Implications of known reaction mechanisms**

173 It is widely known that the initial step of the Maillard reaction is between a reducing sugar
174 and any amino acid (or nitrogen source) and that it occurs more rapidly with fructose than
175 glucose (Dills Jr, 1993) and that the open chain form of both are necessary for this reaction.
176 The resulting Schiff's base rearranges to give either an Amadori rearrangement product
177 (ARP), from glucose or a Heyns rearrangement product (HRP), from fructose. These
178 dehydrate and fragment, regenerating the free amino acid and forming a group of highly
179 reactive dicarbonyl compounds, deoxyosulose, dicarbonyl, and hydroxycarbonyl (Figure 2).
180 These intermediates undergo a classical Strecker degradation with an amino acid to form
181 flavour and colour compounds (Mottram, Wedzicha, & Dodson, 2002; Wedzicha, Mottram,
182 Elmore, Koutsidis, & Dodson, 2005).

183 The importance of temperature controlling the rate of reaction from fructose to ultimately
184 acrylamide was reported by Knol *et al* (2005b) and the activation energy as considered by
185 Parker *et al* (2012). According to Knol, above 160°C the rate constant to convert glucose to
186 fructose increases significantly. The increasing of temperature impacts also on rate constants
187 between reactants where the reaction of asparagine with fructose is preferred, compared to
188 the reaction with glucose (at temperature >140°C).

189 The impact of temperature on rate of reaction is shown in Figure 3. Figure 3a shows the
190 experimental data fit and Figure 3b is expanded to highlight the typical range of temperatures
191 experienced in the production fryer. The implications of this from an industrial operational
192 perspective are that for the temperature range of the fryer (150°C to 170°C) there is a four-
193 fold increase in rate constant, clearly demonstrating tight control of the fryer temperature is
194 vital if acrylamide is to be reduced.

195

196 3.2 Initial data screening and Pattern Recognition

197 Once the variability of individual samples was established, the next step was to understand
198 the behaviour of the important process inputs and outputs to appreciate the breadth of
199 operation and where possible quantify the distribution characteristics. Visualisation of the
200 distribution additionally highlights potential outliers and verifies the data validity of those
201 samples. Before plotting the data distributions as shown in Figure 4, a number of outliers
202 were removed, that were due to human entry errors (for example, data a factor of 100 out due
203 to decimal point errors), training set $n=111$, test set $n=111$. In Figure 4 all the data available
204 over the two-year period of operation is considered. Such plots are useful to consider both at
205 an early stage of analysis to understand the extent of variation but also subsequently, once the
206 impact of variation is clearer.

207 Crucially important is the assessment of the acrylamide variation in the product as shown in
208 Figure 4. Here a normal distribution and non-parametric distribution have been fitted to the
209 data using the Matlab Statistics toolbox. As expected the data is not normally distributed and
210 the fitted standard deviation of 290ppb over-estimates the extent of variation and a mean of
211 560ppb over-estimates the mean operating value. The cumulative probability density function
212 of the non-parametric fit (not shown) indicates a 50% probability at 490ppb and a 93%
213 probability of being less than 1000 ppb

214 Applying Parallel Coordinates Analysis as shown in Figure 5, allows a useful visual approach
215 to gain initial insight into the relationships within the data set.

216 The parallel coordinates plot takes process values, applies auto-scaling to each variable and
217 plots each variable position on the Y-axis scale. For each time point, the values of all
218 variables are joined by lines. The utility of the parallel coordinates plot comes from the
219 colour coding strategy, where, in this case the variable on the far right, acrylamide
220 concentration is colour coded based on magnitude. In this case four colours are chosen,
221 below the 750ppb threshold, between 750ppb and 1000ppb legal threshold and two that are

222 greater than 1000ppb. The spread of colours found for fryer inlet temperature shows no high
223 ACR is found below 170°C and fryer outlet temperature is below 153°C. Above those
224 temperatures a mix of colours is observed but without a clear pattern, so these temperatures
225 alone do not lead to high ACR. For precursors, glucose, fructose and asparagine, a colour
226 pattern is more apparent for high ACR. Variety indications are that *Taurus* (the third node in
227 the plot) typically leads to higher ACR than other varieties. Typically in such analysis, a clear
228 single variable to variable of interest relationship is not observed, but several variables are
229 indicated as having some impact.

230 An interesting observation relating to online colour measurement is apparent. While the
231 literature suggests that the 'A' value correlates to ACR (Gökmen, Açar, Arribas-Lorenzo, &
232 Morales, 2008), the online measurement indicates some correlation to high ACR but it is not
233 sufficiently sensitive in the industrial environment to distinguish by itself as a surrogate
234 measurement of ACR.

235

236 **3.3 Principal Component Analysis**

237 In analysing the behaviour of a system, the ultimate objective is improving control, the first
238 step is typically to apply Principal Component Analysis (I.T., 2002). The purpose of PCA in
239 this case is to compress high dimensional process data into a low dimensional graphical
240 representation that allows 'abnormal' conditions to be identified and the combination of
241 process variables that cause them to be indicated as 'abnormal' to be determined. The
242 compressed information can then be interrogated to assess deviations from standard or
243 desired behaviour. The compressed information forms new 'variables' – the principal
244 component scores, which are weighted summations of all the original process variables.
245 Patterns are identified in the scores plots to detect deviations from typical behaviour. In this
246 case process data from samples where ACR was less than 750ppb were used to generate the

247 PCA model (class 1). The inputs used are the same as those considered in the parallel
248 coordinates with the exception of potato variety which cannot be quantified. Subsequently
249 data from, higher than 750ppb ACR (class 2), was plotted on the same scores plot. Figure 6
250 shows scores plot for PC1 against PC2 generated.

251 It is observed that the points corresponding to higher ACR are shifted towards the right hand
252 side of the plot compared to the blue, lower ACR blue points. The important interpretation
253 from this plot is that there are combinations of variables that are in the data that are
254 descriptive of different levels of ACR given the varying location in the scores plot. In this
255 case, the two PC's explain 39% of the overall data variance. While this is less than half of the
256 overall variance, the key finding at this stage of the data analysis is that there are patterns in
257 the data that indicate information is present to distinguish high and low ACR. This therefore
258 suggests that the information could be used for predictive modelling purposes. In the
259 subsequent modelling of the data, in Section 3.4, considerably more of the data variance is
260 used to build the model. It is important to realise that while patterns are apparent in the PCA
261 plot, the quality, capability and reliability of the model can only be judged on the model
262 itself, with PCA indicating potential but it is not an end in itself.

263

264 **3.4 Acrylamide Prediction**

265 The aim of the modelling task is to provide the plant operators with a warning that
266 characteristics of the potatoes have an increased probability of high acrylamide in the final
267 product, thus allowing process adjustments to mitigate acrylamide formation. For the process
268 operators a 'traffic light' warning system would be the simplest to interpret and react to.

269 Given this requirement the modelling tasks requires prediction of membership of a class
270 (high ACR or not) based on the variables available to them at that time. This classification
271 task is firstly tackled using PLS-DA. Given that the operators need to predict, then the

272 variables available to them for the prediction becomes a subset used in the pattern recognition
273 task. Hence the use of precursor concentrations and fryer temperatures. PLS-DA analysis is
274 first considered on all the samples available from the production line. Subsequently, only the
275 most common variety is considered to investigate whether variety has an impact on
276 predictability.

277

278 **3.5 PLS Discriminant Analysis**

279 The development of the PLS algorithm to perform discriminant analysis was described by
280 Barker and Rayens (2003). Lee *et. al.* (2018) presents a review on the use of PLS-DA and the
281 practices that need to be adopted for its effective implementation. Here the PLS-DA
282 algorithm attempts to determine the probability that a sample belonging to either low
283 acrylamide or high acrylamide classes. Data from 2017 and 2018 were available. A common
284 approach in model building is to randomly sample from the available data to create model
285 building and validation sets. In this case, if inter year variation exists then this may act to
286 mask intra year variation. Furthermore, from a practical perspective, models are built on
287 available data and used on new data as it arrives. Thus, rather than randomly sampling, using
288 data from 2017 to construct the model and data from 2018 to test the model was considered
289 to be more realistic and appropriate. In Figure 7a, the circles represent the probability that a
290 sample will result in high acrylamide (class 2) for 2017 model building data and the stars
291 denote 2018 testing data. The clusters around 70 and 180 samples are the processing of new
292 potato crops when acrylamide tends to be low. Figure 7b shows the model coefficients for the
293 PLS-DA model. It is interesting to observe the significant impact that fructose and asparagine
294 have on the likelihood of high ACR. As expected, glucose is observed to have little impact
295 whereas sucrose has a negative impact. This negative impact arises as high sucrose is

296 characteristic of the new potato crop, low sucrose (high fructose) is typically observed when
297 sucrose is converted to reducing sugars by cold-induced sweetening (Sowokinos, 2001).
298 To use the information provided by the model, a boundary needs to be drawn in, probability,
299 above this threshold, predicts high acrylamide. The approach within the PLS-DA toolbox is
300 to set the threshold to reduce the incidence of misclassification. While this is theoretically
301 acceptable, in an industrial setting if actions are taken that have cost implications then the
302 cut-off that minimises misclassification is not necessarily the most appropriate. Table 2
303 considers the impact a threshold of probability has on the misclassifications of high and low
304 ACR on the 2018 testing data. It can be seen, that if a probability threshold is set at 0.75
305 roughly half of those potatoes that result in high ARC are identified. However, for the 13% of
306 potatoes that are incorrectly predicted as being high ACR, costly actions to mitigate ACR
307 formation could be unnecessarily implemented. By increasing the threshold to 0.95 this
308 misclassification problem can be reduced to 7% but at the expense of now only identifying
309 around a third of the high ACR occurrences. Of the 7% misclassification, around half of
310 those lie in the 600-750ppb ACR range so some degree of action would be appropriate.
311 Further industrial considerations are thus required to specify the appropriate location of the
312 threshold taking into account process costs.

313

314 **4. Industrial Implications of the Results**

315 Given recent EU Regulation, the onus is on companies to take actions to attain acrylamide
316 concentrations that are 'ALARA' with the target set to reduce concentrations in the top 10% -
317 15% of cases that violate guidance levels. To understand the scope of these targets it is
318 necessary to understand the performance and causes of high acrylamide as far as possible in
319 the process. The industrial collaborator had two years of raw potato and product

320 compositions logged on a routine basis to facilitate the assessment. Firstly, it was important
321 to understand the accuracy of the information provided in testing and the representative
322 nature of a sample from a potato load. It was found that while the errors were not
323 insignificant, they were accommodated by adopting an internal target of 750ppb as opposed
324 to the EU guidance of 1000ppb.

325

326 Analysis of the data routinely logged using data visualisation and pattern recognition
327 techniques demonstrated relationships were present in the data that could distinguish the
328 likelihood of high acrylamide in many instances but quantifying the percentage required
329 more detailed analysis. From an operator's perspective, a 'traffic light' system that warns of
330 potential issues with acrylamide based on current line settings and potato characteristics was
331 thus sought. PLS-DA was found to perform well in extracting the patterns contained within
332 the data, although further process consideration based on plant costs is required to set the
333 'optimal' choice of threshold of probability. Interestingly, the predominance of fructose
334 concentration in leading to the formation of acrylamide in the industrial production was in
335 agreement with existing mechanistic models (albeit those considering French fries) and
336 questioned the factory standard approach of considering the total reducing sugar
337 concentration. The 30% detection rate demonstrated aligns well with the EU regulation
338 targets of 10-15% of samples need to be reduced. The challenge resulting or the operators is
339 if 30% can be detected, can process conditions be modified to act effectively on half of those
340 being highlighted. Through more rigorous attention to fryer temperature control and the
341 effective use of the hot-wash to reduce sugar levels prior to the fryer it is hoped that this is
342 achievable. Work is currently addressing the control strategy, progressing the detection
343 studies reported in this paper.

344

345 Finally, while the PLS-DA technique is implemented without considering potato variety
346 clearly varieties have different precursor concentrations and behave in a different manner.
347 Initial analysis showed no benefit to variety specific models, due to limited data sets, further
348 process data is required to verify this finding

349 **5. Conclusion**

350 This paper has considered the variations in acrylamide concentration that arise in the
351 industrial manufacture of crisps. Analysis of available data from the manufacturing line has
352 been shown to provide insight into the causes of high ACR in 30% of the instances that arose.
353 These findings have focused the attention of operational staff on specific aspects of the
354 production line to allow action to be taken to address these known causes and achieve a
355 reduction in ACR levels. Importantly also, the analysis has suggested that 70% of the high
356 ACR values were not explainable by the available data. This finding has initiated an
357 industrial improvement programme focusing on unit behaviour, information availability and
358 measurement accuracy to reduce instances where high ACR occurrences arise for unknown
359 reasons and is the first step in further reducing the frequency of high ACR.

360

361

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Figure 1 – Unit operations in the industrial production process of crisps

Figure 2 – Reaction scheme for the formation of acrylamide. Adapted from Parker, Balagiannis, Higley, Smith, Wedzicha, & Mottram, 2012

Figure 3 – Impact of temperature on the rate of reaction of asparagine and fructose to acrylamide a) 120-200 °C b) 150-170 °C

Figure 4 – Frequency distributions for acrylamide and inset sucrose, glucose, fructose & asparagine,

Figure 5 – Parallel coordinates analysis plot for 2017 / 2018 data

Figure 6 – Scores plot considering whether higher level ACR is differentiable. PC1 against PC2 for class 1 (< 750ppb acrylamide), and class 2 (>750ppb acrylamide).

Figure 7 – Panel A: Probability of class 2 (>750ppb high acrylamide) prediction for training set (circles) and test set (stars). Panel B: Coefficients in PLS DA model for high acrylamide samples indicating extent of process variable contribution

Table 1 – Konelab accuracy

Table 2 – Analysis of misclassifications for varying the PLS DA probability threshold

Table 1 - Konelab Accuracy

Precursor Name	Avg. Confidence Boundary
Fructose	$\pm 0\%$
Asparagine	$\pm 1.29\%$
Total Glucose	$\pm 0.22\%$
Glucose	$\pm 1.26\%$
Sucrose	$\pm 0.15\%$

Table 2 – Analysis of misclassifications for varying the PLS DA probability threshold

Threshold at 0.75			Threshold at 0.95		
	Predict Low	Predict High		Predict Low	Predict High
Actual Low	58%	13%	Actual Low	64%	7%
Actual High	14%	15%	Actual High	18%	11%

Figure 1
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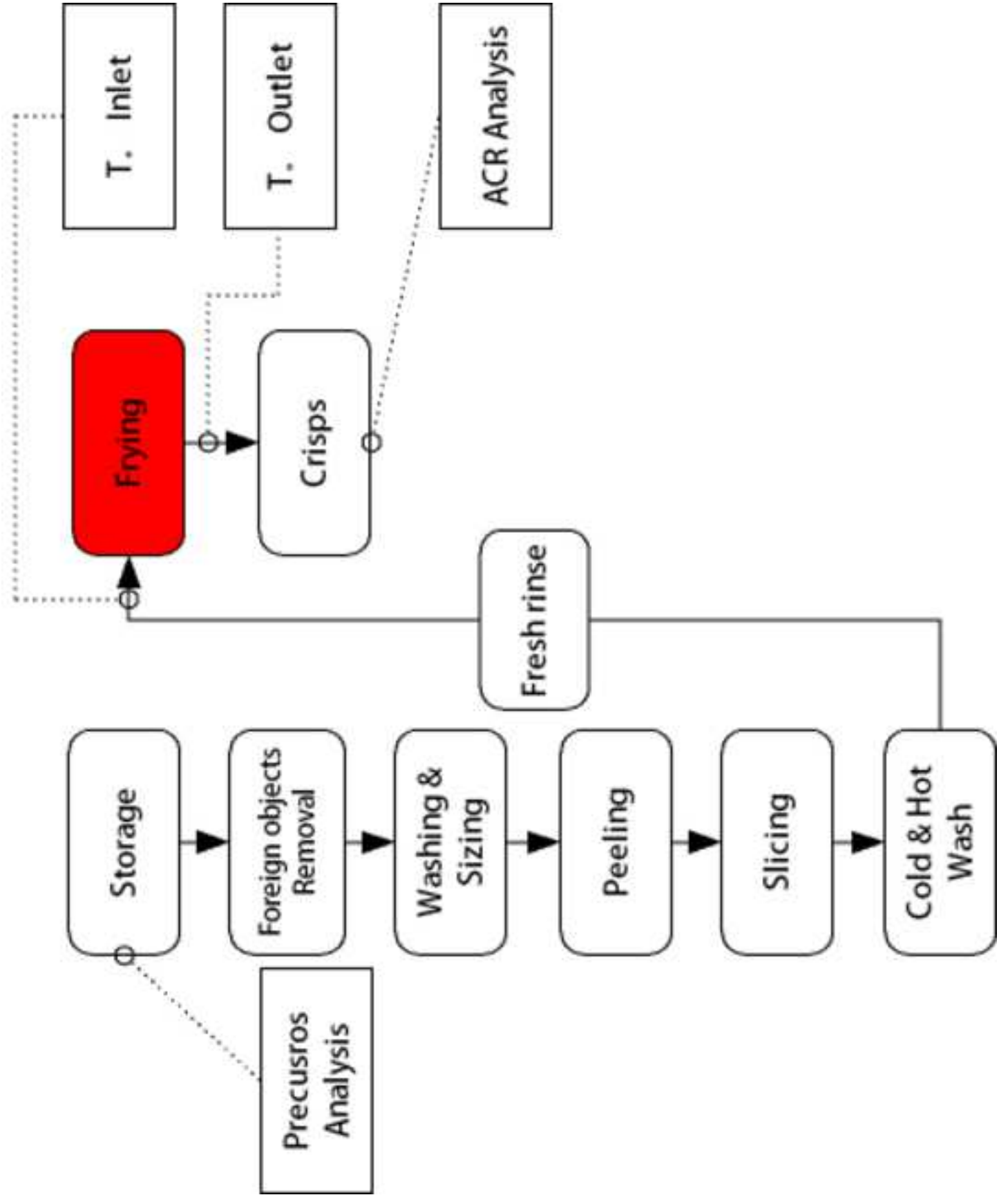


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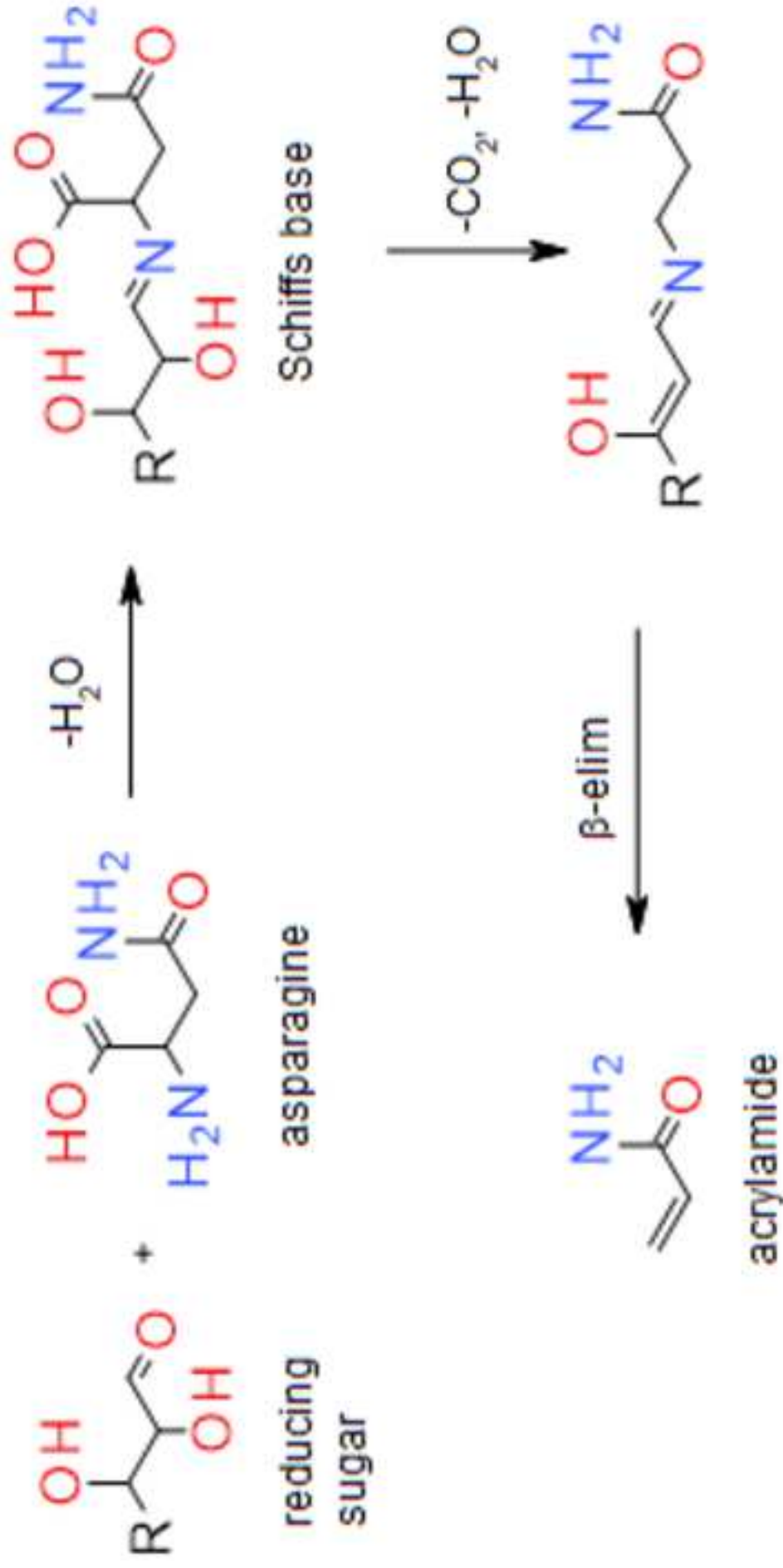


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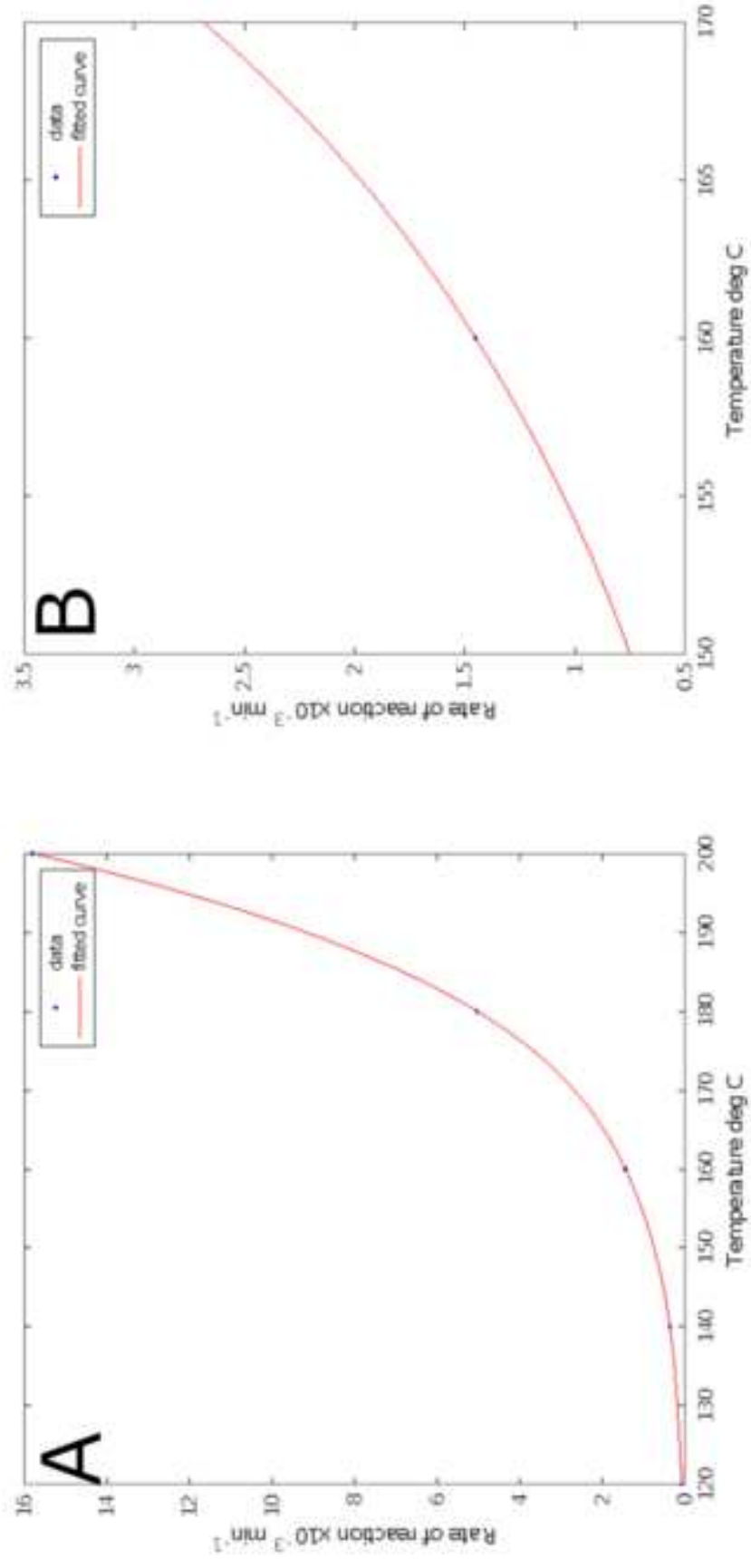


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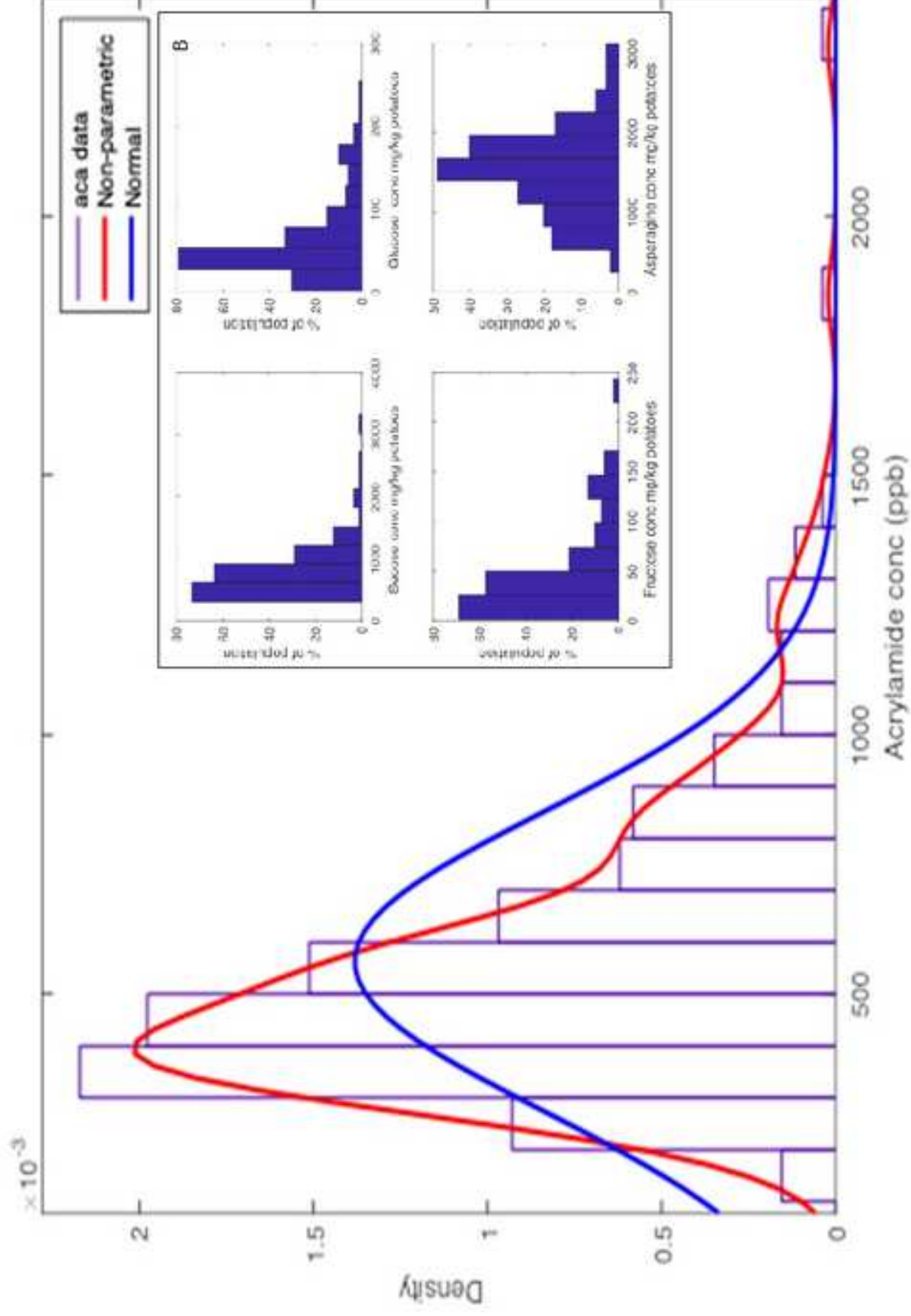


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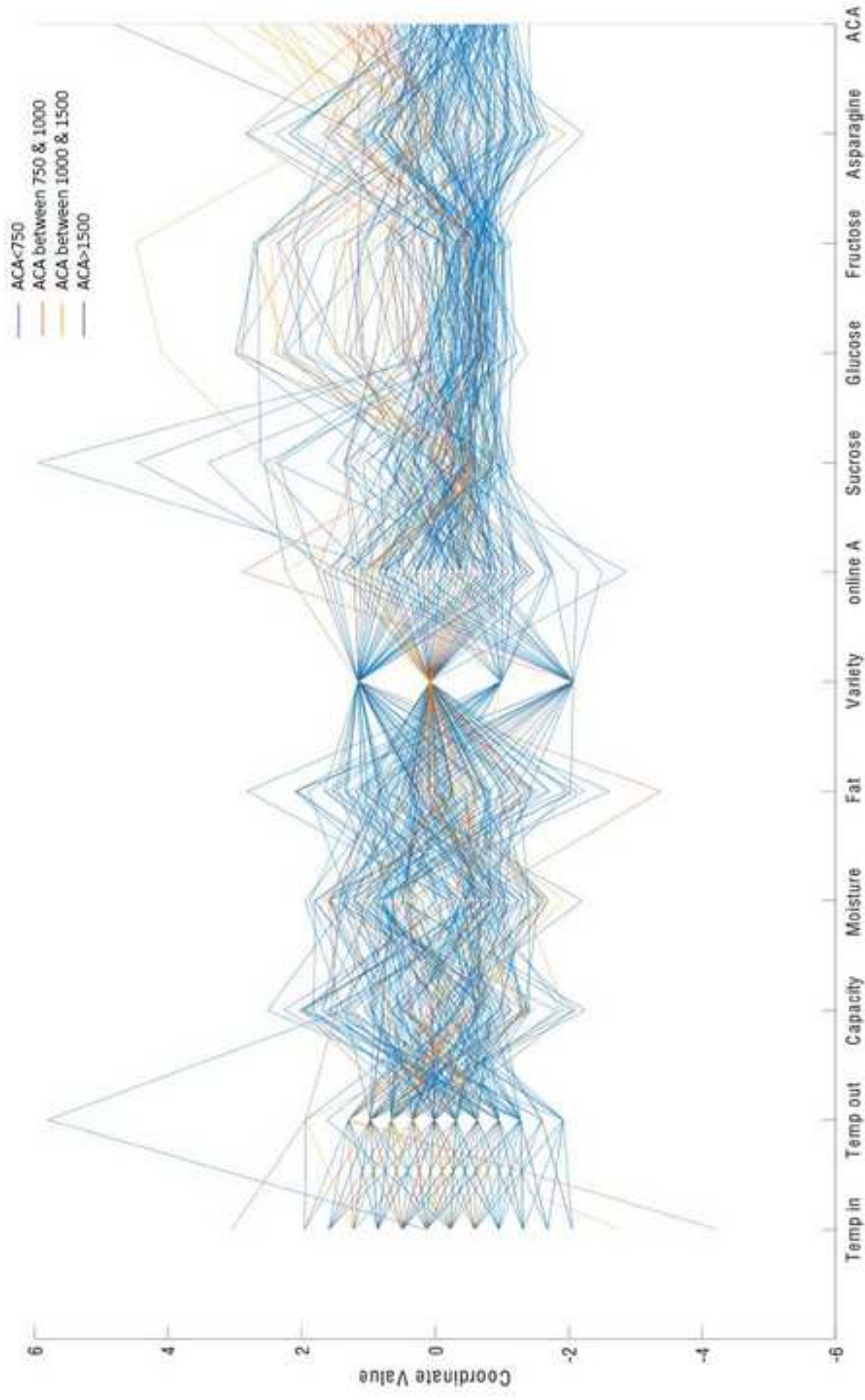


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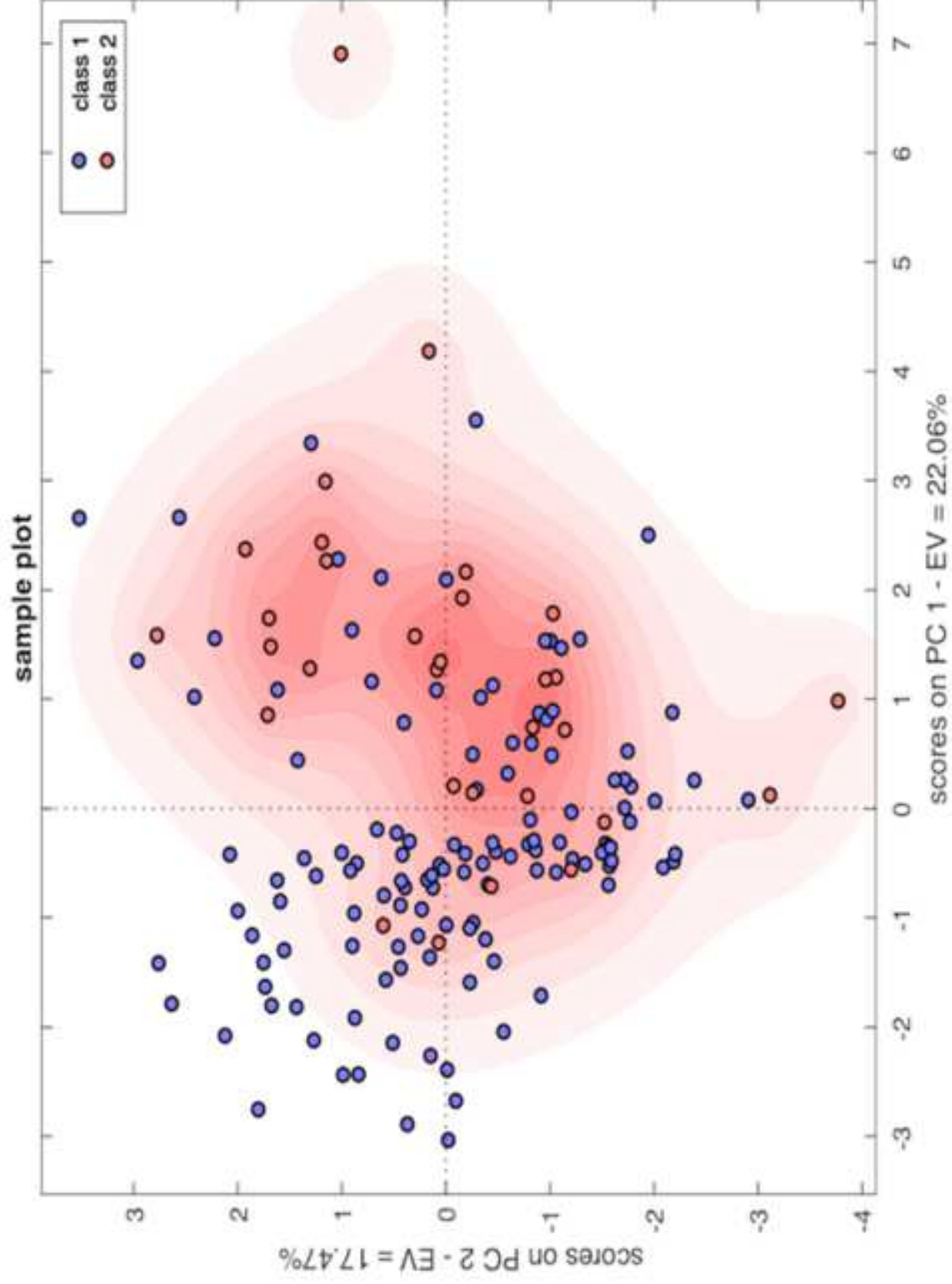


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