The influence of style and origin on mineral composition of beers retailing in the UK

S. Rodrigo[a,*], S.D. Young[b], M.I. Talaverano[c], M.R. Broadley[b]

[a] Agricultural Engineering School, University of Extremadura. Avda. Adolfo Suárez s/n,
06007 Badajoz, Spain

[b] School of Biosciences, University of Nottingham, Sutton Bonington Campus,
Loughborough, LE12 5RD, UK

[c] CICYTEX-Technological Institute of Food and Agriculture-INTAEX (Government of
Extremadura) Av. Adolfo Suárez, s/n 06071 Badajoz, Spain

*Tel: +34 924 289 300; Fax: +34 924 286 201. E-mail: saramrodrigo@gmail.com

ABSTRACT

Beer has high nutritional values in terms of energy, and is also a dietary source of antioxidants, carbohydrates and minerals among others. In Europe, 53 Mt of beer are produced annually, and with an average supply of 68.2 kg *capita*$^{-1}$ year^{-1} among adults. In this study, the mineral composition of 125 commercial beer samples retailing in the UK, but originating from 10 countries, was determined; such detailed information is lacking in UK food composition tables. Beer composition data are reported for Al, As, Ba, Ca, Cd, Co, Cr, Cs, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Se, Sr, U, V and Zn, following analysis by inductively coupled plasma-mass spectrometry. ANOVA results showed higher concentrations of Mo, Pb and Sr (0.160; 491.70×10^{-5}; 0.38, mg L^{-1} respectively) for stout/porter style and a significant higher amount of minerals such as Al (3.835 mg L^{-1}), Cd (8.64×10^{-5} mg L^{-1}), Mn (1.02 mg L^{-1}) or Ni (0.312 mg L^{-1}) among others for lambic beer. Regarding the country of origin, higher Se concentrations were reported from beer brewed in the USA (0.110 mg L^{-1}). It is concluded that beer style was determined to have a greater effect on beer mineral composition than origin or container type.

Keywords:
Alcoholic beverage
Nutrients
Chemometrics
ICP-MS

1. Introduction

The last data recorded by FAO (2011) stated that Europe produced ~53 Mt of beer, with an average reported supply of 68.2 kg *capita*$^{-1}$ year^{-1} for adults. The Russian Federation and Germany (9.9 Mt and 8.9 Mt, respectively) had the highest beer production, followed by UK, Spain, Poland and Ukraine, each with production of 3-4.5 Mt. The Russian Federation, Czech Republic and Ireland have the greatest *per capita* beer supply in Europe, with >130 kg *capita*$^{-1}$ year^{-1}. According to the FAO[1] data, the UK and Spain have an annual supply of 75–79 kg *capita*$^{-1}$ year^{-1}. All these figures highlight the importance of beer in Europe, in both trade and food supply.

Beer contributes significantly to energy intake due to its ethanol content (7 kcal mL^{-1} FW) but also due to protein (4 kcal mL^{-1}) and carbohydrate (3.75 kcal mL^{-1}) which includes starch partially degraded in a non-fermentable form[2]. Beer also contains a range of antioxidants, polyphenols, phenolics, folates, carbohydrates, soluble fibre, vitamins and minerals[3-7]. There is considerable ongoing debate about potential health benefits arising from moderate alcohol consumption, such as reduced coronary heart disease or ischemic stroke risk[8] and improved immune response[9]. Moderate alcohol consumption is defined as an alcohol intake of 10-12 mL d^{-1} for women and 20-24 mL d^{-1} for men according to Díaz et al.[10], which is equivalent to 1 - 3 drinks d^{-1} for studies carried out in the UK by Rimm et al.[11]. Currently, there is limited information in the literature regarding the influence of beer style or origin on beer mineral profiles[7]. In the UK, the Food Standards Agency[12] periodically publishes Food Composition tables, with information about beer among other foods and beverages. In these tables some entries correspond to ale, stout or lager, the beer types most widely consumed in the UK. For these entries, concentrations of Ca, Cl, Cu, Fe, I, K, Mg, Mn, Na, P, Se and Zn are reported, but not all minerals are reported for all beer types. Therefore, the aim of this study is to determine a wider mineral composition of a range of domestic and imported beers currently retailing in the UK.

2. Materials and methods

2.1. Beer samples

Beers (n = 125) were purchased from UK-based stores or obtained directly from UK-based breweries. Beers originated from 10 countries (Belgium, China, Czech Republic, Germany, Holland, Ireland, Italy, Mexico, UK and USA), according to the label. Alcohol contents given in the label ranging between 2.8 and 10.1%. Ale style was represented by 67 samples, lager style by 58 samples including 4 specifically classified as pilsner. Within ale style, 7 beers were specifically classified as bitter, 6 as India pale ale (IPA), 4 as lambic and 10 as stout/porter. More information about the samples can be found in Rodrigo et al.[13]. Sample containers were bottles (n=104), aluminium cans (n=16) or brewery barrels of varying capacities (n=5).

2.2. Elemental analysis

Concentrations of Al, As, Ba, Ca, Cd, Co, Cr, Cs, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Se, Sr, U, V and Zn in the beers were determined by ICP-MS (X-Series^{II}, Thermo Fisher Scientific Inc., Waltham, MA, USA), using a H_2 reaction cell to enhance resolution of Se, and diluting the samples 1-in-6 with 1% Trace Analysis Grade (TAG) HNO_3. Samples in duplicate were introduced from an autosampler (Celtac ASX-520, Omaha, ME, USA) at 1 mL min^{-1} through a concentric glass venturi nebuliser and Peltier-cooled (3 ºC) spray chamber (Thermo Fisher Scientific Inc.). The instrument (Thermo XSeries(II)) has a hexapole with 'kinetic energy discrimination in order to reduce polyatomic interferences. The XSeries(II) uses a 7% hydrogen in helium gas as the 'collision-reaction' gas in the hexapole chamber. Internal standards were introduced to the sample stream via a T-piece and included Sc (50 ng mL^{-1}), Rh (10 ng mL^{-1}) and Ir (5 ng mL^{-1}) in 2% TAG HNO_3. An acid-digested wheat flour standard (NIST 1567a; National Institute of Standards and Technology, Gaithersburg, MD, USA) was used as reference material. Two sets of multi-element standards were used: 0, 10, 20, 30 ppm (mg/L) for Ca, Mg, Na and Mg (PlasmaCAL, SCP Science, France) 0, 20, 40, 100 ppb for all other elements (Claritas-PPT grade CLMS-2 from Certiprep/Fisher, UK). The limit of detection (LOD) for the analysis was calculated by substituting three times the standard deviation of the blank into the equation operational blank samples (ten replicates).

2.3. Statistical analysis

Mineral element concentrations and alcohol content were subjected to two 1-way analysis of variance (ANOVA) including beer style (ale, bitter, India pale ale, lager, lambic, pilsner and stout/porter) and country of origin (Belgium, China, Czech Republic, Germany, Holland, Ireland, Italy, Mexico, UK and USA) in the models. Moreover, the influence of the container type (barrel, bottle and can) on mineral elements concentration was also assessed using a 1-way ANOVA. When significant differences were found in ANOVA, means were compared using Fisher’s protected least significant difference (LSD) test at $p \leq 0.05$. Pearson correlation tests were performed between the different parameters. Principal component analysis (PCA) and discriminant analysis (DA) were conducted on the 22 elemental composition traits for each beer style and country of origin with the aim of determining the most explanatory variables in the method. All these analyses were performed with the XLStat (Addisoft, USA) ‘add-on’ for Microsoft Excel.

3. Results and discussion

3.1. Beer mineral content

The elements present at highest concentrations in beers were K, Mg, Ca and Na (means of 451, 78, 52 and 41 mg L^{-1} respectively) (Table 1), fact that perfectly agrees with the results given by Montari et al.[14]. Most elemental concentrations in the current survey are similar to data reported in the literature, except K and Mg, whose values are lower than those reported by Rubio et al.[15] and Alcázar et al.[16], in their surveys with 28 and 32 beer samples respectively. In the UK food composition tables, Ca, Cu, Fe, Mn, Na and Zn concentrations are smaller than those in our survey[12], that could be explained by the higher number of entries of the survey here presented with reference to the one done by the Food Standard Agency (FSA). Moreover, FSA survey does not reflect any classification by beer styles or origin, while this paper presents all the complete data for describing any beer including in the study. These two reasons could explain the differences found between the FSA data and the presented data.

Alcázar et al.[16] also found lower Zn values in Portuguese beers than the values obtained from our survey. As expected, toxic elements were present at the lowest concentrations; the average concentrations of Cd, Cs, Pb and U were <0.1 mg L^{-1}.

The Food and Nutrition Board of the Institute of Medicine has established the TUL (Tolerable Upper Intake Level) for Cu, Fe, Mn, Mo, Se and Zn, as 10, 45, 11, 2, 0.4 and 40 mg day^{-1}, respectively and the RDA (Recommended Dietary Allowance) for Cu, Fe, Mo and Se as 0.9, 18, 0.045, 0.055 respectively and for Zn, 11 and 8 mg day^{-1} for males and females, respectively. The AI (Adequate Intake) for Cr is 0.025 and 0.035 mg day^{-1} for males and females respectively, while the NOAEL (No-Observed Adverse Effect Level) is 1.468 mg kg^{-1} day^{-1}. Meanwhile, AI is established for Mn in 2.3 mg day^{-1}. If we compare literature values with our results, drinking 1 L day^{-1} of beer (all styles excluding lambics), could cover between 10% - 50% and 20% - 50% of the RDA for Fe and Zn respectively, while 100% of the RDA for Mn, Se and Cr would be accommodated. The Cu RDA could be achieved from consumption of just 100 mL day^{-1} of beer. In the case of lambic beers, Fe intake could exceed the TUL when drinking 1 L day^{-1}.

3.2. Effect of beer style and place of origin on mineral and alcohol contents

There was a significant effect of beer style on mineral composition for all elements except Na, Cu, Se and Cs ($p \leq 0.05$; Table 1). The IPA beers had the highest, and lager beers the lowest, concentrations of Ca, K and Mg (Table 1). One hypothesis that could explain this fact could be the use of various yeasts to brew the varied beer styles; thus, as explained previously in another matrixes[17] different fungal strains could behave completely different regarding to the same raw material having contrary tendencies in the uptake of the minerals contained in the matrix. Lambic beers had the highest Al, Cd, Co, Cr, Fe, Mn, Ni and Zn concentrations; stout/porter beers had the highest Sr and Mo concentrations. Bacteria (i.e. lactic acid bacteria) growth in lambic beer worts produce higher concentrations of amine derivate compounds[18], which probably increases the amine-based ligands and accordingly heavy metal concentration[19] in lambic beer. It should be noted that all the lambic beers analyzed in this study were brewed in Belgium, so the higher concentration of heavy metals could be not completely defined by beer style but also by the mineral profile of the raw material. Ale, IPA and stout/porter beers typically had higher alcohol contents than bitter, lager, pilsner and lambic beers, which confirms the influence of beer style in beer alcohol content stated previously by Willaert and Nedovic[20].

There was a significant effect of geographical origin on beer mineral concentration for half of the elements, except Ba, Ca, Cd, Co, Fe, Mn, Mo, Ni, Pb and V ($p \leq 0.05$; Table 2). Beers from USA typically had higher Mg and K concentrations, while Mexican beers had lower concentrations of these elements. Arsenic concentrations were higher in beers from Mexico and the USA, while USA beers had the highest concentrations of Se (Table 2). Previous studies have reported the relationship between Se availability in soil and Se content of cereal grains[13, 21-23] which could explain the higher Se concentration in beers coming from the USA. Regarding to the alcohol content, significant differences were only detected between beers originated in Czech Republic, Mexico and UK, showing the beer originated in the two first countries a lower alcohol content that the one registered from beers brewed in UK (Table 2).

3.3. Influence of container type on beer mineral contents

There was relatively little effect of container type on beer mineral composition for most elements. Only the concentrations of As ($p \leq 0.001$), Mg ($p \leq 0.01$), Na ($p \leq 0.01$) and V ($p \leq 0.01$) in beer were significantly affected by container type (Table 3). Concentrations of As and Na were highest for beers stored in metal barrels and V concentrations were lowest when stored in cans. It is known that metallic elements can be extracted from the container surface due to complex formation between metal ions and chelating agents. Thus, Al[24] and Sb[25] were reported to be transferred from cooking or storage container surfaces into food. However, the common use of inox containers, except in the case of lambic beers, where other materials are used, reduces considerably the possibility of transferring constituents from the container to the beer[26]. This suggests that the trends seen in our work could reflect ingredients, mainly water, characteristics and quality (every barrel is from the same area) rather than the use of different containers.

3.4. Principal Component Analysis (PCA)

PCA was applied to evaluate trends in the data taking into account both the beer style and its origin. Only elements significantly affected by beer style or beer origin were included in PCA studies.

In the first application of PCA (style), two principal components (PCs) explained 75% of the total variance; PC1 explained up to 54% and PC2 up to 21% (Fig. 1). In Fig. 1 it can be seen that Al, Ba, Cd, Co, Cr, Fe, Mn, Ni and Zn and, are located at positive values of PC1, and Mo, Pb and Sr, at positive values of PC2; these elements had the highest loadings (> 0.85; data not shown). Elements in the first group (+ve PC1) are clustered very tightly suggesting that they provide similar information, reflecting a similar underlying cause, such as similar water characteristics[27], meanwhile V appeared opposite this first group (in –ve PC1), which was expected due to the opposite relation between Mn and Ni with V reported by Fargašová and Beinrohr[28] in metal accumulation in plants. Manganese, Mg and K were identified by Alcázar et al.[29] as the most important variables for beer classification purposes but only Mn shows a strong underlying trend in the present study. There is greater variability in Mg and K values in our survey because of the inclusion of different beer styles, whereas in Alcázar et al.[29] most of analyzed beers were lager.

At the bottom-left in the observations plot (Fig. 1), a group of four out of the seven beer styles appear together, suggesting some similar characteristics, due to the slight separation between observations. Lambic and stout/porter beers appear in the bottom-right side and the upper-left part of the figure respectively, showing a clear separation from the other beer styles. Differences between beers arise from different methods of processing raw material[30] (i.e. fermentation). This could explain the differences found between beer styles in this study regarding the mineral profile, due to the different behavior of the mineral elements during brewing process showed by Kayodé et al.[31] for Zn and Fe.

In the second PCA (origin), variables are more poorly explained than in the first PCA (style); there was a lower two principal components (PCs) explanation of the total variance (56%). PC1 explained up to 35% and PC2 explained 21% of the variance (Fig. 1). Chromium, Mn, Fe, Co and Cd, with loadings higher than 0.83 (data not shown) and at positive values in PC1, seem to be the most dominant variables, together with U and Cs, at positive values of PC2 (Fig. 1) and loadings higher than 0.84, respectively (data not shown).

Belgium, USA and Italy, appear clearly separated in the observations plot (Fig. 1), a group of seven out of the ten places of origin studied are clustered together, showing some kind of consistent trend, due to the slight separation between observations. Recognition of Belgian beers based on multivariate analysis was previously described by Cajka et al.[32]; this arose due mainly to unusual traditional brewing practices such as

Trappist and lambic monastic brewing recipes and spontaneous fermentation respectively.

3.5. Supervised learning methods: Discriminant Analysis (DA)

Discriminant analysis (DA) to identify differences between beers was undertaken both for beer style and beer origin. DA regarding beer style (Fig. 2) showed a prediction ability higher than 81%, while DA for beer origin place showed a lower prediction ability (76%) which means that only 76% of the beers are placed by the method in the correct style group (Fig. 2). For the first DA (beer style) five out of the seven beer styles were predicted with a success rate higher than 70% (ale 78%, lager 90%, lambic 100%, pilsner 75% and stout/porter 70%) while bitter and India pale ale showed success rates of 57% and 50% respectively. IPA beers re-categorized by the analysis were placed in the Ale group. Lambic beers, with a 100% of the success rate (every lambic beer was included by the method in the correct beer group), reveal special characteristics of this beer style in terms of its mineral profile, probably due to its unique fermentation using wild yeast and uncontrolled amounts of bacteria[33]. Unlike our results, significant differences were not found by Blanco et al.[34] when analyzing Al in different beer types.

The second DA (beer origin) produced prediction success rates for the origin place, higher than 63%, except beers brewed in Belgium (42%), whose characteristics made the analysis place them in Germany or Holland groups, among others. Alcázar et al.[16] found in their study about beer chemical descriptors higher predictions success rate (99%), although only three countries were studied in their work.

As expected by the multivariate analysis results presented in sections above, average data for each beer style and mineral element (Table 1), showed the highest Mg, Mo, Pb and Sr in stout/porter and Al, Ba, Cd, Co, Fe, Mn, Ni and Zn values in lambic beers, which was expected due to the correlation ($r > 0.60$ in the first group and $r > 0.64$, in the second group respectively) between the element except for Fe with Ba, Cd, Mn, Ni and Zn. Regarding stout/porter beers, their higher Mg content could be explained by the correlation existing between Mg and polyphenols described by Vitali et al.[35], where polyphenols decrease the mineral binding to fermentable compounds and thus the yeast's mineral consumption. This leads to an increase in the Mg concentration in beer after fermentation[36]. The higher amount of polyphenols in stout/porter beer can be inferred by the fact of including in the brewing process a slightly higher amount of hops[37], which contains important concentration of polyphenols according to Nagasako-Akazome et al.[37] study.

The most important result to highlight regarding the DA with respect to the country of origin is found in the relationship between Se and beers brewed in the USA. USA beers showed the highest Se values in the whole survey. Moreover, high Ni and Fe concentration were detected for Belgian beers, and high Cs concentration in beers manufactured in Italy (Table 1). Several elements such as U and Cs are well explained by factor 1 (data not shown) with loadings of -0.72 for U and-0.89 for Cs. Selenium, on the other hand is very well explained by factor 2 with loading of 0.92. Aluminium, Cd, Co, Mn, Ni and Zn are correlated ($r^2 > 0.50$) to each other, but their loadings are lower than 0.18 in both factor 1 and 2. However, Al, Cd, Co, Mn, Ni and Zn loadings are higher than 0.5 in factor 6 (data not shown), even when the program did not chose this factor as one of the most important ones.

4. Conclusions

The mineral concentration of beer can be differentiated by style and place of origin place using a chemometric approach. Beer style had a greater effect on beer mineral composition than place of origin; higher Mg, Sr, Mo and Pb concentrations classified stout/porter beer while higher Al, Mn, Fe, Co, Ni, Zn, Cd and Ba clearly described lambics. The Se concentration of beers from the USA highlights the likely higher concentration of this element in USA cereal grains due to prevailing soil geochemical characteristics.

Acknowledgments

The authors would like to acknowledge the financial support provided by COST FA-0905 which supported Dr. Rodrigo’s stay in the University of Nottingham and for samples provided by Philip Darby from The Nottingham Brewery.

References

1. FAO (2014) FAOSTAT: Food supply, Available at: http://faostat3.fao.org/faostat-gateway/go/to/home/E. Accessed 31 December 2014
2. Bamforth CW (2002) Nutritional aspects of beer—a review. Nutr Res 22: 227–237
3. Forsander OA (1998) Dietary influence on alcohol intake: A review. J Stud Alcohol 50 (1): 26–31
4. Mayer O, Simon J, Roslova H (2001) A population study of beer consumption on folate, and homocysteine concentrations. Eur J Clinl Nutr 55: 605–609

5. Romeo J, Díaz L, González-Gross M, Wärnberg J, Díaz LE, Marcos A (2008) Effect of moderate beer consumption on blood lipid profile in healthy Spanish adults. Nutr Metab Cardiovas 18: 365–372
6. Walker C, Freeman G, Jugdaohsingh R, Powell JJ (2009) Silicon in beer: origin and concentration. In: Víctor R. Preedy (Ed.), Beer in Health and Disease Prevention (pp. 367-371). Academic Press, London
7. Rodrigo S, Santamaría O, Chen Y, McGrath SP, Poblaciones MJ (2014) Selenium speciation in malt, wort, and beer made from selenium-biofortified two-rowed barley grain. J Agr Food Chem 62(25): 5948–5953
8. Movva R, Figueredo VM (2013) Alcohol and the heart: To abstain or not to abstain?. Int J Cardiol 164: 267 – 276
9. Romeo J, Wärnberg J, Nova E, Díaz L, Gómez-Martínez S, Marcos A (2007) Moderate alcohol consumption and the immune system: A review. Brit J Nutr 98(1): 111–115
10. Díaz LE, Montero A, González-Gross M, Vallejo AI, Romeo J, Marcos A (2002) Influence of alcohol consumption on immunological status: a review. Eur J Clin Nutr 56: 50-53
11. Rimm EB, Klatsky A, Grobbee D, Stampfer MJ (1996) Review of moderate alcohol consumption and reduced risk of coronary heart disease: is the effect due to beer, wine, or spirits?. Brit J Med 312: 731-736
12. Food Standard Agency (2014) McCance and Widdowson's the Composition of Foods. Seventh Summary Edition. Royal Society of Chemistry, Cambridge
13. Rodrigo S, Young SD, Cook D, Wilkinson S, Clegg S, Bailey EH, Mathers AW, Broadley MR (2015) Selenium in commercial beer and losses in the brewing process from wheat to beer. Food Chem 182: 9-13

14. Montari L, Mayer H, Marconi O, Fantozzi P (2009) Minerals in beer. In: Beer in Health and Disease Prevention. Ed. Victor R. Preedy. Academic Press, California, USA

15. Rubio C, Ravelo A, Gutiérrez AJ, González Séller D, Hardisson A (2013) Nutricional interest of Na, K, Ca, Mg, Fe, Mn, Cu, Zn, Cr and Mo levels in dark beers. Ann Nutr Metab 63 (suppl.): 1475–1476

16. Alcázar A, Jurado JM, Palacios-Morillo A, de Pablos F, Martín MJ (2012) Recognition of the geographical origin of beer based on support vector machines applied to chemical descriptors. Food Control 23: 258–262

17. Lledó S, Rodrigo S, Poblaciones MJ, Santamaría O (2015) Biomass yield, mineral content, and nutritive value of *Poa pratensis* as affected by non-clavicipitaceous fungal endophytes. Mycol Progress 14:67

18. Izquierdo-Pulido M, Mariné-Font A, Vidal-Carou MC (2000) Effect of tyrosine on tyramine formation during beer fermentation. Food Chem 70: 329–332

19. Obuseng V, Nareetsile F, Kwaambwa HM (2012) A study of the removal of heavy metals from aqueous solutions by *Moringa oleifera* seeds and amine-based ligand 1,4-bis[N,N-bis(2-picoyl)amino]butane. Anal Chim Acta 730: 87–92

20. Willaert R, Nedovi VA (2006) Primary beer fermentation by immobilised yeast: a review on flavour formation and control strategies. J Chem Technol Biot 81(8): 1353–1367

21. Broadley MR, Alcock J, Alford J, Cartwright P, Foot I, Fairweather-Tait SJ, Hart DJ, Hurst R, Knott P, McGrath SP, Meacham MC, Norman K, Mowat H, Scott P, Stroud JL, Trovey M, Tucker M, White PJ, Young SD, Zhao F-J (2010)

Selenium biofortification of high-yielding winter wheat (*Triticum aestivum* L.) by liquid or granular Se fertilization. Plant Soil 332: 5–18

22. Rodrigo S, Santamaría O, López-Bellido FJ, Poblaciones MJ (2013) Agronomic selenium biofortification of two-rowed barley under Mediterranean conditions. Plant Soil and Environment 59 (3): 115–120
23. Joy EJM, Broadley MR, Young SD, Black CR, Chilimba ADC, Ander EL, Barlow TS, Watts MJ (2015) Soil type influences crop mineral composition in Malawi. Sci Total Environ 505: 587-595
24. Veríssimo MIS, Oliveira JABP, Gomes MTSR (2006) Leaching of aluminium from cooking pans and food containers. Sensors Actuator B 118: 192–197
25. Jiang X, Wen S, Xiang G (2010) Cloud point extraction combined with electrothermal atomic absorption spectrometry for the speciation of antimony(III) and antimony(V) in food packaging materials. J Hazard Mater 175: 146–150
26. Repetto M (1995) Toxicología avanzada. Ediciones Díaz de Santos, Madrid, Spain
27. Szabó E, Sipos P (2014) Mineral and polyphenol contents of self-brewed and commercial beer samples. J MacroTrends Appl Sci 2 (1): 1-9
28. Fargašová A, Beinrohr E (1988) Metal-metal interactions in accumulation of V^{5+}, Ni^{2+}, Mo^{6+}, Mn^{2+}, and Cu^{2+} in under- and above-ground parts of *Sinapsis alba*. Chemosphere 36: 1305-1317
29. Alcázar A, Pablos F, Martín MJ, González AG (2002) Multivariate characterisation of beers according to their mineral content. Talanta 57: 45–52
30. Bamforth CW (2000) Beer: an ancient yet modern biotechonolgy. The Chemical Educator 5 (3): 102–112

31. Kayodé APP, Hounhouigana JD, Noutb MJR (2007) Impact of brewing process operations on phytate, phenolic compounds and in vitro solubility of iron and zinc in opaque sorghum beer. LWT 40: 834–841

32. Cajka T, Riddellova K, Tomaniova M and Hajslova J (2010) Recognition of beer brand based on multivariate analysis of volatile fingerprint. J Chromatog A 1217:, 4195–4203

33. De Keersmaecker J (1996) The mystery of lambic beer. Sci Am, Aug. 74–80

34. Blanco CA, Sancho D, Caballero I (2010) Aluminium content in beers and Silicon sequestering effects. Food Res Int 43: 24432–2436

35. Vitali D, Vedrina Dragogević I, Ševečić B (2008) Bioaccesibility of Ca, Mg, Mn and Cu from whole grain tea-bicuits: impact of protein, phytic acid and polyphenols. Food Chem 110: 62–68

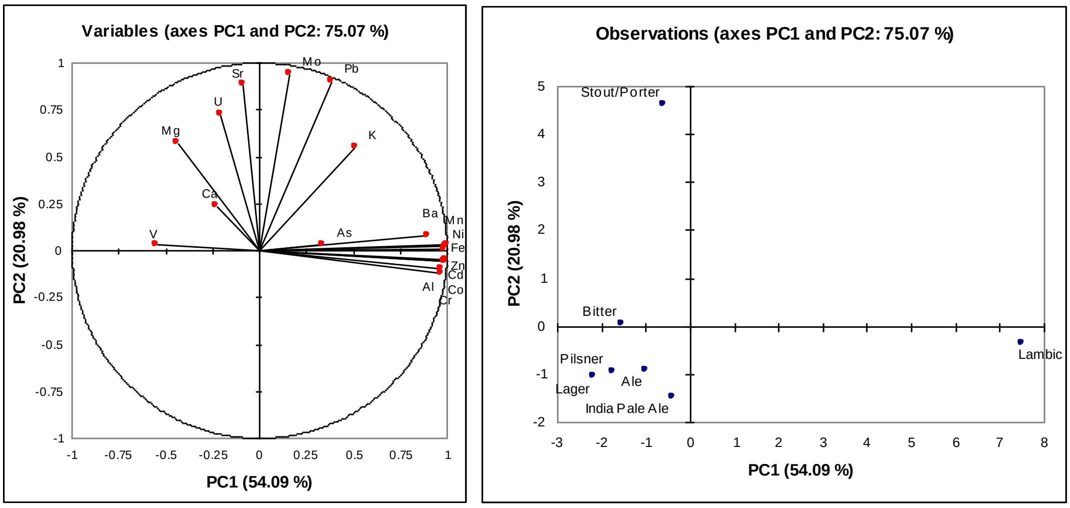
36. Edney MJ, Rossnagel BG, McCaig R, Juskiw PE, Legge WG (2011) Reduced phytate barley malt to improve fermentation efficiency. J I Brewing 117(3): 401-410

37. BJCP Style Guidelines (2008). http://www.bjcp.org/2008styles/style13.php

38. Nagasako-Akazome Y, Honma D, Tagashira M, Kanda T, Yasue M, Ohtake Y (2007) Safety evaluation of polyphenols extracted from hop bracts. Food Chem Toxicol 45: 1383–1392

Figure captions

Fig. 1. Correlation between loadings and factors (up-left) and observations plot (up-right) regarding the effect of style on beer mineral composition in the Principal Components Analysis (PCA), and correlation between loadings and factors (down-left) and observations plot (down-right) regarding the effect of place of origin on beer mineral composition in the Principal Components Analysis (PCA).



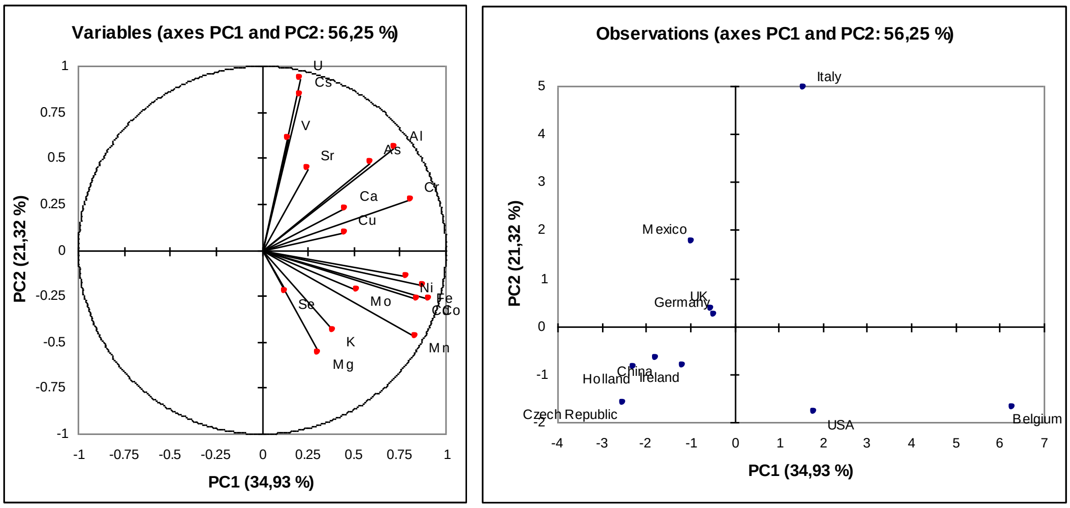
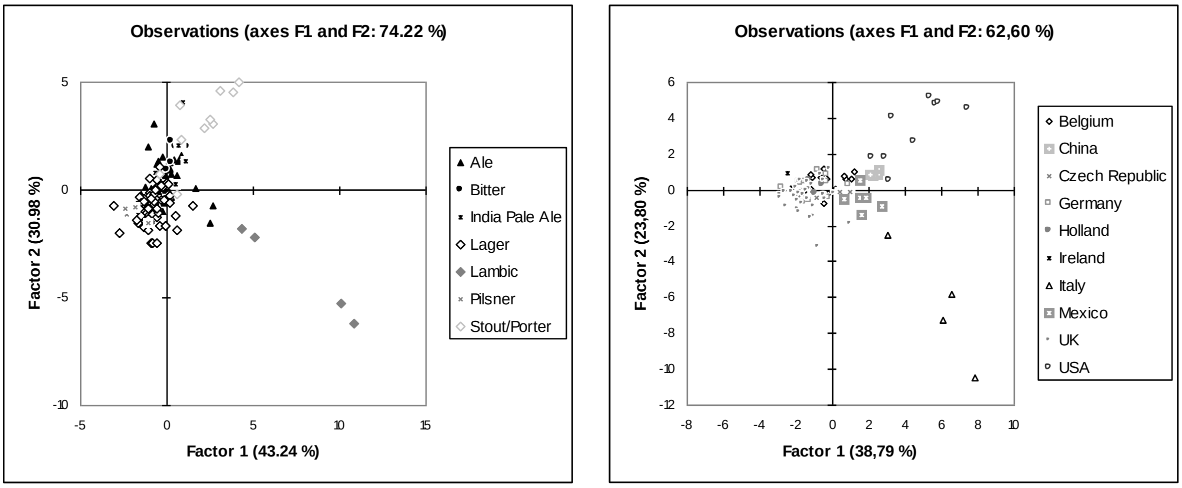


Fig. 2. Discriminant Analyses (DA) of beer mineral composition data for 22 elements,



regarding the style (left) and the place of origin (right)

Table 1. Mean mineral content (mg L^{-1}) and alcohol content (%) of beer samples as affected by beer style. Different letters mean significant differences ($p \leq 0.05$).

Style	**Al*****	**As***	**Ba*****	**Ca***	**Cd*****	**Co*****	**Cr*****	**Cs**	**Cu**	**Fe*****	**K*****
Ale(n=35)	0.492^{b}	0.076^{a}	0.321^{b}	56.1^{b}	2.83×10^{-5b}	23.81×10^{-5b}	0.044^{b}	26.58×10^{-5}	0.512	0.884^{b}	474.3^{b}
Bitter(n=7)	0.655^{b}	0.092^{a}	0.364^{b}	86.0^{a}	1.40×10^{-5b}	22.76×10^{-5b}	0.038^{b}	28.71×10^{-5}	0.289	0.467^{b}	455.5^{bc}
IPA(n=6)	0.455^{b}	0.082^{a}	0.478^{ab}	76.1^{ab}	2.87×10^{-5b}	32.02×10^{-5b}	0.044^{b}	35.93×10^{-5}	0.395	0.264^{b}	647.8^{a}
Lager(n=59)	0.598×10^{-3b}	0.063^{a}	0.192^{c}	41.7^{c}	2.40×10^{-5b}	18.95×10^{-5b}	0.048^{b}	135.06×10^{-5}	0.428	0.461^{b}	379.9^{c}
Lambic(n=4)	3.835^{a}	0.042^{a}	0.674^{a}	39.3^{c}	8.64×10^{-5a}	279.85×10^{-5a}	0.141^{a}	98.35×10^{-5}	0.482	1.3^{a}	677.4^{a}
Pilsner(n=4)	0.395^{b}	0.007^{b}	0.230^{bc}	25.4^{c}	1.93×10^{-5b}	12.30×10^{-5b}	0.046^{b}	78.60×10^{-5}	0.576	0.208^{b}	462.6^{bc}
Stout/Porter (n=10)	0.411^{b}	0.064^{a}	0.380^{b}	74.2^{ab}	3.66×10^{-5b}	26.49×10^{-5b}	0.040^{b}	21.75×10^{-5}	0.432	0.15^{b}	592.6^{a}
Mean	0.977	0.061	0.501	56.9	3.39×10^{-5}	59.45×10^{-5}	0.057	60.71×10^{-5}	0.445	0.329	527.2

Style	**Mg*****	**Mn*****	**Mo*****	**Na**	**Ni*****	**Pb****	**Se**	**Sr****	**U***	**V***	**Zn*****	**Alcohol content*****
Ale	84.8^{bc}	0.18^{b}	0.053^{b}	44.9	0.061^{b}	41.90×10^{-5b}	0.039	0.15^{c}	4.06×10^{-5b}	0.174^{b}	0.443^{b}	5.35^{a}
Bitter	73.7^{cd}	0.17^{b}	0.040^{b}	52.7	0.041^{b}	48.19×10^{-5b}	0.013	0.23^{b}	11.87×10^{-5a}	0.209^{ab}	0.200^{b}	7.06^{bc}
IPA	95.3^{ab}	0.28^{b}	0.022^{b}	51.2	0.067^{b}	41.30×10^{-5b}	0.049	0.19^{c}	1.88×10^{-5b}	0.105^{b}	0.464^{b}	7.55^{ab}
Lager	67.9^{d}	0.10^{b}	0.055^{b}	33.0	0.045^{b}	36.99×10^{-5b}	0.022	0.14^{c}	10.24×10^{-5a}	0.386^{a}	0.178^{b}	5.11^{bc}
Lambic	63.6^{d}	1.02^{a}	0.074^{b}	53.3	0.312^{a}	263.73×10^{-5ab}	0.014	0.15^{c}	5.45×10^{-5ab}	0.109^{b}	3.545^{a}	4.25^{c}
Pilsner	92.7^{abc}	0.10^{b}	0.039^{b}	32.4	0.059^{b}	55.73×10^{-5b}	0.011	0.09^{c}	3.75×10^{-5b}	0.199^{ab}	0.251^{b}	5.05^{bc}
Stout/Porter	103.5^{a}	0.27^{b}	0.160^{a}	51.9	0.084^{b}	491.71×10^{-5a}	0.029	0.38^{a}	13.90×10^{-5a}	0.208^{ab}	0.428^{b}	4.93^{ab}
Mean	83.1	0.30	0.063	45.6	0.096	139.94×10^{-5}	0.025^{b}	0.19	7.31×10^{-5}	0.1.99	0.787	5.65

*, ** and *** significance at $p \leq 0.05$, 0.01 and 0.001 respectively following one-way ANOVA.

Table 2. Mean mineral composition (mg L^{-1}) and alcohol content (%) in the analyzed beer samples as affected by beer origin place. Different letters mean significant differences ($p \le 0.05$)

Country of origin	Al*	As*	Ba	Ca	Cd	Co	Cr*	Cs***	Cu*	Fe	K***	
Belgium(n=19)	0.13^{a}	0.080^{ab}	0.423	54.8	20.63×10^{-5}	79.77×10^{-5}	0.070^{a}	46.41×10^{-5b}	0.633^{a}	4.073	504.2^{b}	
China(n=4)	0.04^{b}	0.039^{bc}	0..93	35.1	1.23×10^{-5}	13.30×10^{-5}	0.038^{ab}	20.58×10^{-5b}	0.365^{bc}	0.252	298.9^{cd}	
Czech Republic (n=4)	0.03^{b}	0.024^{c} 0.074^{ab}	0.155	2.4.1	1.05×10^{-5}	9.95×10^{-5}	0.042^{ab}	80.80×10^{-5b}	0.532^{abc}	0.198	416.8^{bc}	
Germany(n=13)	0.05^{b}	0.055^{bc}	0.219	41.7	2.11×10^{-5}	18.02×10^{-5}	0.051^{ab}	35.68×10^{-5b}	0.400^{bc}	0.579	450.2^{b}	
Holland(n=4)	0.04^{b}	0.061^{abc}	0.089	29.7	1.95×10^{-5}	19.83×10^{-5}	0.033^{ab}	24.30×10^{-5b}	0.476^{abc}	0.487	506.0^{ab}	
Ireland(n=3)	0.03^{b}	0.091^{a}	0.240	55.2	2.63×10^{-5}	18.95×10^{-5}	0.027^{b}	17.20×10^{-5b}	0.232^{c}	0.850	475.3^{b}	
Italy(n=4)	0.17^{a}	0.093^{a}	0.304	44.0	1.50×10^{-5}	20.82×10^{-5}	0.071^{a}	1616.62×10^{-5a}	0.521^{abc}	0.843	412.8^{bc}	
Mexico(n=7)	0.04^{b}	0.060^{bc}	0.262	50.4	5.57×10^{-5}	22.29×10^{-5}	0.032^{b}	68.30×10^{-5b}	0.677^{a}	0.332	239.8^{d}	
UK(n=53)	0.05^{b}	0.088^{a}	0.268	61.5	2.36×10^{-5}	22.29×10^{-5}	0.043^{ab}	21.36×10^{-5b}	3.49×10^{-3c}	0.554	436.5^{b}	
USA(n=14)	0.05^{b}		0.307	38.7	3.66×10^{-5}	28.60×10^{-5}	0.059^{ab}	39.22×10^{-5b}	5.85×10^{-3ab}	0.489	626.2^{a}	

Country of origin	Mg**	Mn	Mo	Na**	Ni	Pb	Se***	Sr*	U***	V	Zn	Alcohol content
Belgium	83.3^{b}	0.35	0.070	49.7^{a}	0.111	94.03×10^{-5}	0.017^{d}	0.14^{ab}	4.28×10^{-5c}	0.200	0.987	4.99^{ab}
China	76.4^{b}	0.14	0.023	53.2^{a}	0.779	51.75×10^{-5}	0.058^{b}	0.23^{a}	1.73×10^{-5c}	0.093	0.145	4.82^{ab}
Czech Republic	89.1^{ab}	0.10	0.019	20.8^{ab}	0.547	53.92×10^{-5}	0.012^{d}	0.07^{b}	1.70×10^{-5c}	0.069	0.234	4.00^{b}
Germany	79.5^{b}	0.13	0.082	19.1^{b}	0.445	33.61×10^{-5}	0.009^{d}	0.09^{b}	6.30×10^{-5bc}	0.487	0.162	5.34^{ab}
Holland	68.5^{bc}	0.09	0.032	20.5^{ab}	0.345	25.00×10^{-5}	0.014^{d}	0.05^{b}	2.22×10^{-5c}	0.160	1.073	5.58^{ab}
Ireland	76.4^{b}	0.20	0.070	21.2^{ab}	0.330	31.57×10^{-5}	0.014^{d}	0.12^{ab}	7.27×10^{-5bc}	0.246	0.357	5.10^{ab}
Italy	72.6^{bc}	0.11	0.036	15.7^{b}	0.667	76.98×10^{-5}	0.019^{cd}	0.23^{a}	42.30×10^{-5a}	0.365	0.159	4.95^{ab}
Mexico	57.3^{c}	0.10	0.038	53.1^{a}	0.431	31.03×10^{-5}	0.042^{bc}	0.22^{a}	11.76×10^{-5b}	0.294	0.189	4.53^{b}
UK	73.6^{d}	0.14	0.060	48.3^{a}	0.504	120.48×10^{-5}	0.016^{d}	0.18^{a}	9.26×10^{-5b}	0.312	0.194	5.72^{a}
USA	99.8^{a}	0.25	0.080^{3}	26.8^{ab}	0.673	33.05×10^{-5}	0.110^{a}	0.22^{a}	3.47×10^{-5c}	0.153	0.853	5.61^{ab}

*, ** and *** significance at $p \le 0.05$, 0.01 and 0.001 respectively

Table 3. As, Mg, Na and V concentration as affected by container. Different lower case letters in the same column mean significant differences ($p \leq 0.05$)

Container	As (mg L^{-1})***	Mg (mg L^{-1})**	Na (mg L^{-1})**	V (mg L^{-1})**
Barrel	0.006^{b}	$7.8.1^{ab}$	82.7^{a}	0.014^{b}
Bottle	0.079^{a}	80.1^{a}	38.9^{b}	0.264^{b}
Can	0.071^{a}	605^{b}	3670^{b}	0.441^{a}

** and *** significance at $p \leq 0.01$ and 0.001 respectively