



Multi-element analysis in beer cans using X-ray fluorescence

G. C. Ferreira¹, R. S. Santos¹, H. S. Gama Filho¹, D. F. Oliveira², C. C. G. Leitão¹ and M. J. Anjos¹

¹ Physics Institute, State University of Rio de Janeiro

R. São Francisco Xavier, 524 - 20550-900 Maracanã - Rio de Janeiro, RJ, Brazil

gabriel.cferreira@hotmail.com; ramonziosp@yahoo.com.br; hamiltongamafilho@hotmail.com; davi@lin.ufrj.br; catarine.cgl@gmail.com; marcelin@uerj.br

² Nuclear Instrumentation Laboratory, Federal University of Rio de Janeiro

Av. Horácio Macedo, 2030 – Ilha do Fundão, 21945-970, Rio de Janeiro, RJ, Brazil

davifoliveira82@gmail.com

1. Introduction

Beer consumption has become moderate to high in several countries, being a drink known worldwide [1]. Consumption of soda and beer in aluminum cans reaches 2×10^{11} cans every year [2, 3]. Trace metals in beer may originate from natural sources (soil, water, cereal, hops, and yeast) as well as from environmental contamination due to fertilizers, pesticides, industrial processing, and containers [1, 4]. The maximum concentrations of trace elements in beers are controlled by legislation, as these elements might be essential or toxic in the human body depending on their concentration [5]. For instance, lead is a highly toxic element that accumulates in biological systems and has a long half-life and Zinc is an essential element during synthesis of proteins and energy metabolism [1, 6]. Thus, several metals, such as As, Pb, Fe and Cd, are subjected to careful control, not only related to beer production, but rather to the materials that come into contact (processing aids, additives, storage materials) [7].

Aluminum fits to be used as packaging of food and beverages due to its unique barrier and physical properties. Aluminum can effectively protect food and drink against the quality-reducing effects of oxygen, light, moisture, micro-organisms, and unwanted aromas even in its thinnest form. [3]

X-ray fluorescence is a multi-element analytical technique very popular and applied in many scientific and technological areas, and, in recent years has been used mainly in environmental sample analysis (air, sediment, water, soil, plants). Its main advantages over other techniques are non-destructive chemical analysis, fast qualitative analysis, little interference between X-ray fluorescence lines, simplicity in the preparation of samples, a wide range of elements that can be analyzed (Al - U) and the detection limits from percentage to $\mu\text{g/g}$ (in some cases it may reach ng/g) [8, 9, 10].

In this study, it was analyzed 23 cans of beer from 4 different nationalities to create a concentration profile of the beer cans and try to correlate in the future, the presence of these elements with their presence in the beer liquid.

2. Methodology

In this study, it was analyzed the elemental concentrations of 23 cans of beer. The beers are from 4 different nationalities, most of them Brazilian beers (20 beers can), 1 beer can from Germany, 1 beer can from the United Kingdom and 1 beer can from Colombia. Of the 20 Brazilian beers, a total of 12 different national breweries were analyzed.

XRF analysis of the aluminium can was performed using the internal side of the can cut out in a square with an area of 9 cm^2 (Figure 1a). The analyzed areas were cleaned with 70% alcohol to remove the remaining beer in them. The internal side of the can was analyzed so that the paint or film used on the outside side of the can would not influence the XRF measurement. The Brazilian beer cans were the thickness of $(118 \pm 31) \mu\text{m}$ while other nationalities were $(106 \pm 4) \mu\text{m}$. Samples were analyzed in triplicate.

XRF analysis of the beer cans was performed using the commercial equipment Epsilon 1 (Malvern Panalytical) with silver anode (Ag) and SDD detector (Silicon Drift Detector) (Energy resolution < 135 eV for Mn-K α) (Figure 1b). Two different experimental conditions were used in the analysis of the samples. First experimental condition was used for a better excitation of low Z elements (Mg to Ca K-lines), using 10 kV, 500 μ A and an acquisition time of 180 s. Whereas, the second experimental condition was used to excitation of the high Z elements (V to Zr K-lines and Pb L-lines), using 50 kV, 100 μ A, 300 s and a Cu filter (500 μ m). Quantitative analyses were carried out by the own software of Epsilon 1.

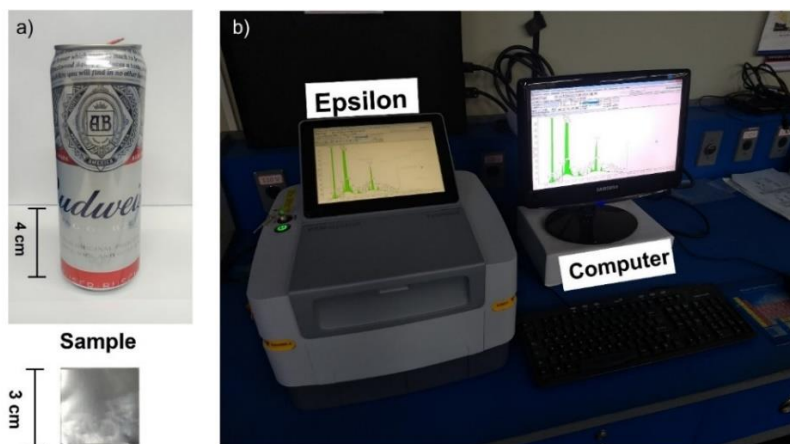


Figure 1 – Materials and Methods; a) Example of one of the samples beers can analyzed; b) Epsilon 1.

3. Results and Discussion

Figure 2 shows the X-ray spectra of aluminium samples from different nationalities, Brazilian and German. It was possible to determine the concentrations of 15 elements (Mg, Al, Si, S, Cl, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Zr and Pb) for all 4 nationalities.

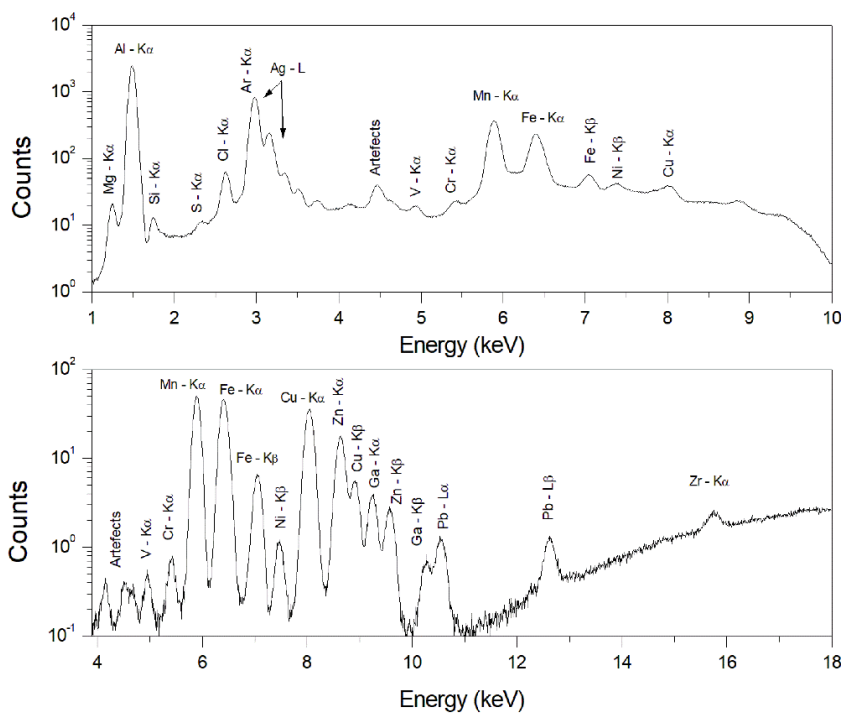


Figure 2 – XRF spectra of a beer can sample (low Z and high Z experimental conditions)

Table 2 shows the average, minimum and maximum concentrations found in beer can samples. All 23 aluminium samples analysed presented the Al element as the majority (approximately 94%). On the other

hand, one sample of Brazilian beer showed an Al concentration of 74%. However, other cans from the same brewery had Al concentrations of 94%. This difference in concentration may be related to the aluminium recycling process, which in Brazil represents about 97% of the cans that entered the market for consumption.

Table I: Elemental concentrations of the beer can
(Mean value \pm standard deviation and minimum to maximum values)

Elements	Brazil ^a	Germany	United Kingdom (UK)	Colombia
Mg (%)	2.3 \pm 0.4	2.2 \pm 0.1	2.6 \pm 0.3	2.5 \pm 0.2
	1.2 - 3.4	2.1 - 2.4	2.2 / 2.9	2.4 / 2.7
Al (%)	93 \pm 5	95.1 \pm 0.2	94.9 \pm 0.3	95.1 \pm 0.7
	74 - 96	94.9 - 95.3	94.6 - 95.2	94.4 - 95.6
Si (%)	0.46 \pm 0.05	0.53 \pm 0.01	0.49 \pm 0.01	0.41 \pm 0.01
	0.35 - 0.61	0.52 - 0.54	0.49 - 0.50	0.41 - 0.42
S ($\mu\text{g g}^{-1}$)	325 \pm 227	124 \pm 5	157 \pm 8	155 \pm 27
	96 - 1050	120 - 127	149 - 165	124 - 174
Cl ($\mu\text{g g}^{-1}$)	1257 \pm 584	1427 \pm 257	1014 \pm 347	804 \pm 155
	327 - 3320	1130 - 1580	763 - 1410	711 - 984
V ($\mu\text{g g}^{-1}$)	160 \pm 27	133 \pm 11	157 \pm 4	126 \pm 5
	111 - 221	121 - 142	152 - 161	120 - 130
Cr ($\mu\text{g g}^{-1}$)	159 \pm 20	183 \pm 8	186 \pm 9	155 \pm 8
	107 - 211	174 - 190	181 - 197	149 - 165
Mn (%)	1.0 \pm 0.1	1.1 \pm 0.1	0.99 \pm 0.01	0.86 \pm 0.02
	0.8 - 1.5	1.0 - 1.1	0.98 - 0.99	0.84 - 0.88
Fe (%)	0.51 \pm 0.09	0.66 \pm 0.04	0.64 \pm 0.01	0.42 \pm 0.01
	0.39 - 0.83	0.61 - 0.69	0.64 - 0.65	0.42 - 0.44
Ni ($\mu\text{g-g}^{-1}$)	70 \pm 11	75 \pm 5	79 \pm 2	62 \pm 2
	55 - 102	68 - 79	78 - 82	60 - 63
Cu (%)	0.17 \pm 0.03	0.19 \pm 0.01	0.16 \pm 0.01	0.16 \pm 0.01
	0.13 - 0.25	0.18 - 0.20	0.16 - 0.17	0.16 - 0.17
Zn ($\mu\text{g g}^{-1}$)	611 \pm 120	342 \pm 23	466 \pm 10	480 \pm 10
	431 - 1050	317 - 361	460 - 477	474 - 491
Ga ($\mu\text{g g}^{-1}$)	94 \pm 15	103 \pm 7	92 \pm 2	77 \pm 1
	75 - 145	95 - 108	90 - 94	76 - 78
Zr ($\mu\text{g g}^{-1}$)	7 \pm 2	21 \pm 3	16.6 \pm 0.6	5.3 \pm 0.2
	5 - 14	18 - 23	16 - 17	5.1 - 5.5
Pb ($\mu\text{g g}^{-1}$)	37 \pm 6	18 \pm 1	22.9 \pm 0.7	31.5 \pm 0.4
	27 - 51	17 - 19	22 - 24	31 - 32

a. Average, minimum and maximum values of 20 samples of Brazilian beers.

The beer cans of the 4 nationalities showed similar concentrations of the elements Mg, Al, Si, V, Mn, Fe, Ni and Cu. The average concentration of S found in Brazilian beers cans was approximately 2 times higher than the average found in the beer cans from other nationalities, with a maximum concentration of S approximately 6 times higher than beer cans of other nationalities (1050 $\mu\text{g g}^{-1}$ and 174 $\mu\text{g g}^{-1}$, Brazilian and Colombian beer cans, respectively). In addition, Brazilian beer cans showed higher average concentrations of Zn (27% to 78% higher) and maximum values of at least 2 times higher. Brazilian and Colombian beer cans had higher average concentrations of Pb, with the average concentration being at least 35% higher than European beer cans, German and UK.

Can samples from German and UK beers showed similar concentrations of all elements. These two beers had the highest Zr concentrations (21 \pm 3 $\mu\text{g g}^{-1}$ and 16.6 \pm 0.6 $\mu\text{g g}^{-1}$, Germany and UK, respectively) when compared to the others. On the other hand, the Colombian beer can sample presented Zr

concentration similar to the Brazilian can samples. In addition, the Colombian can sample had lower concentrations of Cl and Ga when compared to the other samples.

4. Conclusions

Through the XRF technique, it was possible to calculate the concentration of 15 elements in the beer cans samples. A majority concentration of Aluminum of around 94% was obtained. The other elements can be considered trace elements, being the highest concentrations of them for Mg (approximately 2%) and Mn (approximately 1%). Some elements showed differences between cans from different nationalities, with Zn being much higher in samples from Brazil. The Zr element showed similarities between German and UK beer cans. In addition, the beer can sample from Colombian had lower concentrations of Cl and Ga. The presence of some elements in the human body can have toxic effects depending on their concentration. The presence of elements in beer liquid can be a consequence of the aluminum can and could influence the concentration of some elements in the beer. Therefore, this work has as a future perspective the analysis of the liquid of these beers using the technique of Total Reflection X-Ray Fluorescence (TXRF) to investigate and compare the results obtained from the cans with the beer liquid, and thus identify possible transitions from one to the other.

Acknowledgements

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001, project Qualitec – Bolsas para profissionais nas Unidades de Desenvolvimento Tecnológico (UERJ), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ) and Financiadora de Estudos e Projetos (FINEP).

References

- [1] C.C. Nascentes, M. Y. Kamogawa, K. G. Fernandes, M. A. Z. Arruda, A. R. A. Nogueira, J. A. Nóbrega, "Direct determination of Cu, Mn, Pb, and Zn in beer by thermospray flame furnace atomic absorption spectrometry," *Spectrochimica Acta Part B*, vol. 60, pp. 749–753 (2005).
- [2] - The World Counts. We use a lot of aluminium," http://www.theworldcounts.com/counters/world_food_consumption_statistics/aluminium_cans_facts. (2014).
- [3] V. Y. Risonarta, J. Anggono, Y. M. Suhendra, S. Nugrowibowo, Y. Jani, "Strategy to Improve Recycling Yield of Aluminium Cans", *E3S Web of Conferences*, vol. 130, pp. 01033 (2019).
- [4] Y. Li, J.C. Van Loon, R.R. Barefoot, "Preconcentration of trace elements in potable liquids by means of a liquid membrane emulsion for flame atomic absorption determination, *Fresenius' J. Anal. Chem.*, vol. 345, pp. 467– 470 (1993).
- [5] E. M. Gama, C.C. Nascentes, R. P. Matos, G.C.Rodrigues, G.D.Rodrigues, "A simple method for the multi-elemental analysis of beer using total reflection X-ray fluorescence". *Talanta*, vol. 174, pp. 274-278 (2017).
- [6] P.C. Onianwa, A. O. Adeyemo, O. E. Idowu, E. E. Ogabiela, "Copper and zinc contents of Nigerian foods and estimates of the adult dietary intakes". *Food Chem.*, vol. 72, pp. 89-95 (2001).
- [7] S. Moreira et al., "Analysis of beers from Brazil with synchrotron radiation total reflection X-ray fluorescence," *Journal of Radioanalytical and Nuclear Chemistry*, vol. 270, pp. 167–171 (2006).
- [8] D. H. S. Richardson, M., Shore, R. Hartree, et al., "The use of X-ray fluorescence spectrometry for the analysis of plants, especially lichens, employed in biological monitoring." *Sci. Total Environ*, vol. 176, pp. 97–105 (1995).
- [9] G. S. Banelos, H. A., Ajwa, "Trace elements in soils and plants: an overview," *J. Environ. Sci. Health*, vol. A34, pp. 951–974 (1999).
- [10] E. Marguá, I. Queralt, M. Hidalgo, "Application of X-ray fluorescence spectrometry to determination and quantification of metals in vegetal material," *Trends Anal. Chem.*, vol. 28, pp. 362–372 (2009).