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Determination of trace elements in Brazilian beers by ICP–AES

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The levels of Co, Cr, Cu, Fe, Pb and Zn were determined simultaneously in several brands of bottled and canned beer, by inductively coupled argon plasma atomic emission spectrometry, with previous mineralization with conc. HNO_3/H_2O_2 (30%). The results showed the good quality of the beers with respect to their metal contents. An alternative digestion method, with conc. HNO_3 and O_3, was also studied.

INTRODUCTION

During preparation of beer, iron and copper levels are critical, because they are interferents in the brewing process. In the presence of high levels of these metals, retardation of the brewing process occurs (Martins, 1987).

The importance of several metals in beer is now well recognized and it is subject to legislation; for example the limits in Brazil are shown in Table 5 (MDUMA, 1965). For instance, Pb, Cd, Hg and As have toxic properties and there are no homeostatic mechanisms in the body than can operate to regulate the levels of these metals (Carter & Fernandus, 1979).

The normal levels of the elements that are considered essential in the human body at trace levels (Fe, Cr, Co, Mn, Cu) are maintained by homeostatic mechanisms and the toxic action of most of these elements is a result of chronic or acute exposures or ingestion of a large quantity of one of these elements.

Several techniques of analysis are used for the determination of metals in beer samples. Weiner and Taylor (1969) have estimated the trace metals Cu, Fe, Zn and Pb in beers by atomic absorption spectrophotometry and also carried out a survey of the magnesium content of beer and brewing materials. Borriello and Sciaudone (1980) determined Fe, Cu and Zn by flame atomic absorption and Pb by electrothermal atomization in bottled and canned beers. Ward (1977) used the inductively coupled plasma atomic emission spectrometry for determining twenty elements in beer samples and tested three different sample preparations: filtration through a Whatman No. 40 filter paper, followed by heating and acid digestion of the sample with HNO_3.

In the present work, Co, Cr, Cu, Fe, Pb and Zn were determined in Brazilian beer using inductively coupled plasma atomic emission spectrometry (ICO-AES) and two different wet/oxidation/sample dissolution procedures, taking into account the time spent for the preparation of the samples with a routine method of analysis in mind. The direct aspiration of beers into the ICP was not possible, because the plasma was extinguished.

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MATERIALS AND METHODS

Twenty-two samples of beer were analysed, twelve samples of bottled beer, six samples of canned beer from Brazil and four samples of beer from other countries. Acids and other reagents used in this work were analytical grade (Merck).

Stock solutions (1000 mg litre^{-1}) of Cr(VI), Pb(II), Fe(III), Co(II), Zn(II) and Cu(II) were prepared from appropriate amounts of $K_2Cr_2O_7$, $Pb(NO_3)_2$, Fe_2O_3, Co_2O_3 and ZnO (Aldrich) and CuO (Spex) in 20% HNO_3 (v/v).

High-purity water was produced by passing distilled water through a deionising system (Permution Deionizador).

The glassware was cleaned with 1 M HNO_3 and deionized water. A home-made ozonizer was built according to Rheinboldt (1950), in which ozone is produced by electrical discharge through an oxygen gas flux.

A model ICP900, inductively coupled plasma atomic emission spectrometer (Jarrel-Ash) was used for wavelength determinations, and instrumental conditions are presented in Table 1.

Sample preparation

(a) Digestion with conc. HNO_3/H_2O_2 (30%): a sample (50·00 ml) is digested with HNO_3 (10 ml), heated at 75°C following by dropwise addition

Table 1. Instrumental conditions—ICP 900 Jarrel-Ash spectrometer

Rf forward power	1.1 kW
Plasma gas flow	20 litres min^{-1}
Auxiliary gas flow	Zero
Carrier gas flow	0.45 litres min^{-1}
Observation height	14 mm above the load coil
Sample flow	1·1 ml min^{-1}
Wavelengths	Co = 228·17 nm; Cr = 267·72 nm; Fe = 239·55 nm; Pb = 283·51 nm; Cu = 327·40 nm; Zn = 334·50 nm.

of H_2O_2 (30%) until the solution is clarified, heated until 10 ml of solution remains and, after cooling, is transferred to a volumetric flask and the volume brought to 25 ml with 20% HNO_3. A blank solution is prepared under the same conditions. This procedure takes about 4 h to treat each sample.

(a_1) Study of recovery was performed in each sample of beer and 50 ml of distilled and deionized water. The beer sample and 50 ml of water were spiked with 5·0 μg of each metal and both samples were treated according to (a).

(b) Digestion with conc. HNO_3/O_3: a sample of beer (50·00 ml) is digested with HNO_3 conc. (10 ml) and $O_3 + O_2$ allowed to bubble through for 30–40 min until the sample is clarified (colorless or light yellow) and the sample is evaporated to 10 ml and transferred to a 25-ml volumetric flask and the volume brought to 25 ml with 20% HNO_3. This procedure was performed with four samples, and takes about 75 min to treat each sample. A blank solution in the same conditions is prepared.

Following the sample preparation methods (a) and (b), the beer samples are pre-concentrated twice.

Table 2. Parameters of the calibration curves and detection limits for the elements

Element	A	B	r^2	LD (μg ml^{-1})
Co	0·190	0·816	1·000 0	0·005
Cr	0·703	1·180	0·999 9	0·020
Cu	0·332	0·962	0·999 7	0·010
Fe	0·221	0·997	0·999 8	0·025
Pb	0·658	0·672	0·999 4	0·010
Zn	0·332	0·852	0·999 5	0·025

$I = A + B.C$, where

I = relative intensity
C = concentration
r^2 = correlation coefficient
LD = detection limit

Table 3. Results for beer samples for the conc. HNO_3/H_2O_2 (30%) dissolution procedure

Sample	Co (μg ml^{-1})	Cr (μg ml^{-1})	Cu (μg ml^{-1})	Fe (μg ml^{-1})	Pb (μg ml^{-1})	Zn (μg/ml^{-1})
1 B clear	0·031 ± 0·003	0·66 ± 0·03	0·034 ± 0·004	0·11 ± 0·03	0·015 ± 0·003	0·034 ± 0·003
2 B clear	0·028 ± 0·003	0·67 ± 0·04	0·079 ± 0·006	0·10 ± 0·01	0·018 ± 0·003	0·047 ± 0·004
3 B clear	0·035 ± 0·004	0·57 ± 0·03	0·014 ± 0·004	0·044 ± 0·005	0·015 ± 0·005	0·015 ± 0·003
4 B clear	0·030 ± 0·003	0·57 ± 0·03	0·053 ± 0·005	0·076 ± 0·006	0·039 ± 0·005	0·043 ± 0·005
5 B clear	0·035 ± 0·004	0·59 ± 0·04	0·011 ± 0·003	0·040 ± 0·003	—[a]	0·013 ± 0·002
6 B clear	0·029 ± 0·002	0·56 ± 0·04	0·019 ± 0·003	0·15 ± 0·04	—[a]	0·021 ± 0·002
7 B medium	0·030 ± 0·003	0·72 ± 0·05	0·021 ± 0·003	0·11 ± 0·03	0·014 ± 0·004	0·036 ± 0·003
8 B medium	0·029 ± 0·003	0·68 ± 0·04	0·052 ± 0·004	0·11 ± 0·01	0·017 ± 0·003	0·060 ± 0·005
9 B dark	0·030 ± 0·003	0·48 ± 0·03	—[a]	0·15 ± 0·05	0·045 ± 0·004	0·028 ± 0·002
10 B dark	0·033 ± 0·004	0·54 ± 0·03	0·076 ± 0·007	0·21 ± 0·03	0·050 ± 0·005	0·040 ± 0·003
11 B dark	0·033 ± 0·003	0·47 ± 0·02	0·014 ± 0·004	1·2 ± 0·1	0·028 ± 0·004	0·040 ± 0·004
12 B dark	0·033 ± 0·003	0·43 ± 0·02	0·040 ± 0·004	1·1 ± 0·1	0·033 ± 0·004	0·048 ± 0·005
1 C clear	0·049 ± 0·003	0·84 ± 0·05	0·049 ± 0·005	0·45 ± 0·02	0·013 ± 0·003	0·044 ± 0·003
2 C clear	0·074 ± 0·004	0·77 ± 0·04	0·049 ± 0·004	0·35 ± 0·02	0·025 ± 0·003	0·068 ± 0·004
3 C clear	0·048 ± 0·003	0·58 ± 0·03	0·052 ± 0·005	0·55 ± 0·03	0·039 ± 0·004	0·034 ± 0·004
4 C clear	0·050 ± 0·003	0·73 ± 0·04	0·074 ± 0·005	1·2 ± 0·1	0·052 ± 0·005	0·057 ± 0·005
5 C clear	0·060 ± 0·004	0·66 ± 0·03	0·047 ± 0·003	0·56 ± 0·02	0·014 ± 0·04	0·050 ± 0·005
6 C clear	0·055 ± 0·003	0·56 ± 0·04	0·045 ± 0·005	0·52 ± 0·03	0·017 ± 0·03	0·050 ± 0·004
C Portugal	ND	0·88 ± 0·02	0·060 ± 0·002	0·24 ± 0·02	0·032 ± 0·02	0·060 ± 0·003
C German	ND	0·82 ± 0·02	0·059 ± 0·003	1·3 ± 0·1	0·021 ± 0·03	0·022 ± 0·002
C Holland	ND	0·78 ± 0·02	0·061 ± 0·002	0·091 ± 0·005	0·024 ± 0·02	0·054 ± 0·003
C Chile	ND	0·98 ± 0·03	0·078 ± 0·003	0·33 ± 0·03	0·047 ± 0·04	0·084 ± 0·004
Recovery of 0·100 μg ml^{-1} metal in 20% nitric acid	0·100 ± 0·002	0·100 ± 0·001	0·100 ± 0·001	0·100 ± 0·001	0·100 ± 0·002	0·100 ± 0·001
Recovery of 0·100 μg ml^{-1} metal in 20% beer	0·100 ± 0·004	0·100 ± 0·005	0·100 ± 0·006	0·100 ± 0·004	0·100 ± 0·006	0·100 ± 0·004

B = bottled, C = canned, (1 B same trade mark as 1 C, etc.).
ND = Not determined.
[a] Values below the detection limit.
[b] Average of 4 samples.

Table 4. Results for four beer samples using two different dissolution procedures[a]

Sample	Treatment	Cr (μg ml^{-1})	Cu (μg ml^{-1})	Fe (μg ml^{-1})	Pb (μg ml^{-1})	Zn (μg ml^{-1})	Co (μg ml^{-1})
1		0·57 ± 0·03	0·053 ± 0·005	0·076 ± 0·006	0·039 ± 0·005	0·043 ± 0·005	0·030 ± 0·003
2	HNO_3	0·68 ± 0·02	0·052 ± 0·004	0·11 ± 0·01	0·017 ± 0·003	0·060 ± 0·005	0·029 ± 0·003
3	H_2O_2	0·43 ± 0·02	0·004 ± 0·004	0·25 ± 0·02	0·033 ± 0·004	0·048 ± 0·005	0·033 ± 0·003
4		0·73 ± 0·04	0·074 ± 0·005	0·54 ± 0·02	0·052 ± 0·005	0·057 ± 0·005	0·050 ± 0·004
1		0·64 ± 0·06	0·057 ± 0·006	0·12 ± 0·01	0·037 ± 0·005	0·040 ± 0·006	0·033 ± 0·004
2		0·60 ± 0·05	0·043 ± 0·004	0·16 ± 0·08	0·019 ± 0·003	0·057 ± 0·005	0·028 ± 0·003
3		0·45 ± 0·04	0·014 ± 0·002	0·16 ± 0·05	0·038 ± 0·004	0·047 ± 0·004	0·035 ± 0·004
4		0·74 ± 0·05	0·072 ± 0·005	0·13 ± 0·01	0·052 ± 0·005	0·053 ± 0·005	0·048 ± 0·003

[a] The dissolution procedures are described in the Material and Methods section.

RESULTS AND DISCUSSION

Table 2, shows the parameters of the calibration curves and the detection limits for the elements studied. The detection limit is defined as that concentration of analyte which gives a response equal to three times the standard deviation of the blank.

Results obtained for the beer samples are presented in Table 3. Each result is the mean of at least three determinations and the respective standard deviation is given, with the precision expressed as a 95% confidence interval. For Co, Cr, Pb and Zn the values obtained for the canned beer are higher than those of bottled beers. The ICP results for Cr correspond to the total chromium content (CrVI highly toxic plus CrIII). The increase of Co, Cr, Pb and Zn in canned beer may be due to the release of such elements from the can or the solder, this seems likely because of the similar results obtained for Brazilian canned beers and for the four imported canned beers. The bottled dark beers showed a wide range of Fe levels in particular, probably due to the use of iron vessel for cooking the sugar that will confer the color to this kind of beer.

The values of copper and iron varied widely for the canned and bottled beers. This may be due to the different brewing process in Brazil (Martins, 1987). The last two lines of Table 3 show the good recovery of the method used for sample treatment.

Table 4, shows the results obtained for four beer samples, using the treatment with conc. HNO_3/H_2O_2 (30%) and conc. HNO_3/O_3. The values obtained using the two methods agree quite well, except for iron. The inconsistent results obtained for iron are probably due to incomplete dissolution of the samples, For Co, Cr, Cu, Pb and Zn, the use of conc. HNO_3/O_3 may be a quicker alternative method (75 min instead of 4 h).

Table 5, compares the results obtained in this work and literature values (Ward, 1977). The copper, iron and lead levels are higher and the zinc lower in the Brazilian beers compared with the literature values, probably due to the raw materials used in the production of the beers.

Table 5. Brazilian legislation, literature and the present work for the levels of elements studied

Element	Brazilian legislation (μg ml^{-1})	Literature values (Ward, 1977) (μg ml^{-1})	Present work (μg ml^{-1})
Co	0·2	—	0·029–0·074
Cr	1·0 (CrIII), 0·05(CrVI)	—	0·43–0·84 Cr (total)
Cu	5·0	0·030–0·50	0·011–0·079
Fe	5·0	0·080–0·70	0·044–1·2
Pb	0·5	0·030	0·014–0·052
Zn	5·0	0·070–0·15	0·013–0·068

CONCLUSION

The ICP–AES is a relatively simple technique for the simultaneous determination of trace elements in beer.

The two dissolution procedures studied were found to be suitable for determinating elements in beers, except for iron.

The results obtained for Co, Cr, Cu, Fe, Pb and Zn present in canned or bottled Brazilian beers can be considered to be below hazard levels (MDUMA, 1965).

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REFERENCES

Borriello, R. & Sciaudone, G. (1980). Zinc, copper, iron and lead in bottled and canned beer by atomic absorption spectroscopy. *Atomic Spectrosc.*, **1**(4), 131–2.

Carter, D. C. & Fernandus, Q. (1979). Chemical toxicology, Part II: Metal toxicity. *J. Chem. Education*, **56**(8), 490–5.

Martins, S. M. (1987). *Como Fabricar Cerveja*. Editora Icone, São Paulo, Brazil.

MDUMA (1965). Ministério do Desenvolvimento Urbano e Meio Ambiente, Decreto 55.871, 03/26.

Rheinboldt, H. (1950). *Chemische Unterrichtsversuche*. T. Steinkopff, p. 52 (ozone preparation).

Ward, A. (1977). Elemental analysis of beer using the inductively coupled plasma. Jarrel-Ash Division, Fischer Scientific Co.

Weiner, J. P. & Taylor, L. (1969). Determination of metals in beer and wine by atomic absorption spectroscopy. *J. Inst. Brewing*, **75**, 195–9.