INTERNATIONAL JOURNAL OF CURRENT RESEARCH IN CHEMISTRY AND PHARMACEUTICAL SCIENCES

(p-ISSN: 2348-5213: e-ISSN: 2348-5221)

www.ijcrcps.com Coden: IJCROO (USA)

Research Article

ASSESSMENT OF TRACE METALS USING FAAS IN ALCOHOLIC BEVERAGES FAVORABLY CONSUMED IN AGRA REGION, INDIA

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Abstract

There are many issues related to alcoholic beverages over the world. So a critical review, in which the different sources, concentrations, effects, removal methods, speciation and analysis of some metals (e.g. Cr, Cu, Fe, Ni, Ca, Na) present in some alcoholic beverages, is discussed in this paper.

Keywords: Trace metals, Alcoholic Beverages, alcoholic content

1. Introduction

The concentration of metals in many alcoholic beverages can be a significant parameter affecting their consumption and conservation. This derives from the negative and positive effects caused directly or indirectly by the presence of metals. Negative effects include beverage spoilage and hazing, as well as sensorial and health consequences.

Positive effects include the removal of bad odors and tastes, participation in fermentative processes, provision of pathways for dietary intake of some essential minerals, and usefulness for authentication purposes.

Because of all this, many metals are carefully monitored and regulated, which has resulted in the development of a plethora of analytical techniques for their analysis. Metals in alcoholic beverages are often determined by atomic absorption or emission techniques; however, the high cost of the instruments involved and the long sample-preparation times required often preclude their widespread use. Electrochemical methods are an option for such analyses. But FAAS is more reliable.

In the manufacturing process employed for most alcoholic beverages we distinguish between fermentation and distillation. In the second process, the distillate is sometimes obtained directly from a previously fermented product, which carries over the volatile compounds (water, alcohols, aromatic substances like acids, aldehydes, ketones, esters, etc.) and modifies the composition previously existing in the raw product. Due to the low volatility of the seven elements considered in this project (Fe, Cu, Ni, Cr, Pb, Ca, Na), their levels in the resulting distilled alcoholic Beverages have to be lower. In the distillation process copper still is usually employed because copper is very malleable, a good heat conductor, and resistant to corrosion, as well as playing a role as catalyser in certain chemical reactions and of complexing molecules unpleasant from the organoleptical point of view.

Consequently, an increase in the Cu levels of the resulting distilled brandy would be expected.

Additionally, it is known that in the ageing of brandies obtained via distillation, the activation of chemical reactions that require oxygen are probably enhanced by the existence of ions of heavy metals like Cu.

Several techniques have been employed for the determination of minerals in wines and beverages: inductively coupled plasma mass spectrometry (ICP-MS) using a double-focusing sector fields; AAS with flame or electro thermal atomization; or electro analytical methods such as differential pulse anodic stripping voltammetry (DPASV).

In the available food composition and nutrition tables, the levels of the essential minerals studied, especially

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those for the trace elements Cu and Ni are not usually collected.

Therefore, the aim of this project was to review the various sources and concentrations of metals (e.g., Ca, Cr, Cu, Fe, Pb, Ni and Na) in 6 alcoholic beverages (Whisky, Vodka, Rum, Brandy, Spirit and Deshi liquors), most commonly consumed in India and over the world their effects, speciation, removal methods and detection by FAAS technique and flame photometer.

2. Sampling

The samples of alcoholic beverages analysed in the present study (n = 6) were purchased from the locality of Agra, Uttar Pradesh. Distilled alcoholic beverages (n = 6) were selected from the most popular brands consumed by the local inhabitants taking into consideration their food habits. The samples were brought to the laboratory of the Department of Chemistry of St. John's College, Agra where they were stored at 18 0C until analysed.

3. Materials and Methods

Apparatus

A Perkin-Elmer AAnalyst100 double beam atomic absorption spectrophotometer (Perkin-Elmer corp., CT) was used at a slit width of 0.7 nm, with hollow cathode lamps for mineral measurements by FAAS. Samples were atomized for Cr, Cu, Fe, Pb, and Ni. All analyses were performed in peak height mode to calculate absorbance values.

SYSTRONICS Flame photometer 130 was used for the estimation of Ca and Na.

Sample preparation

All solutions were prepared from analytical reagent grade reagents, for e.g., Commercially available 1,000 µg/mL Cu [prepared from $Cu(NO_3)_2.3H_2O$ in 0.5 M HNO_3] were used. The water employed for preparing the standards for calibration and dilutions was ultra pure water with a specific resistivity of 18 m_ cm-1 obtained by filtering double-distilled water through a Milli-Q purifier (Millipore, Waters, Mildford, MA) immediately before use.

Sample treatment and analysis

Cu, Fe and other elements in spirits, gin, vodka, whisky, rum and similar beverages can be analysed by atomic absorption. It is accurate, fast and needs no special sample preparation. The samples are aspirated directly and standards are made up in alcohol to match the content of the particular sample.

Calcium and sodium can be easily analysed by Flame Photometer.

Standards can be prepared as follows-

1. Calcium – 1000 ppm
Dissolved 2.497 g $CaCO_3$ in approx 300 ml glass distilled water and added 10 ml conc. HCl diluted to 1 litre.

For calibration 20, 40, 60, 80 and 100 ppm solutions were prepared from the stock solution.

2. Sodium- 1000 ppm
Dissolved 2.5416 g NaCl in one litre of glass distilled water.
For calibration 20, 40, 60, 80 and 100 ppm solutions were prepared from the stock solution.

Determination of Heavy Metals

Reagents

1. Air- cleaned and dried through a filter air.
2. Acetylene- standard, commercial grade
3. Metal free water- all the reagents and dilutions were made in metal free water
4. Methyl isobutyl ketone (MIBK)- Reagent grade MIBK is purified by re-distillation before use.
5. Ammonium pyrrolidine dithiocarbamate (APDC) solution- 4 g APDC is dissolved in 100 ml water.
6. Conc. HNO_3
7. Standard metal solutions: Five standard solutions of 0.01, 0.1, 1,
10 and 100 mg/L concentrations of metals such as Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb for instrument calibration and sorption study are prepared by diluting their stock solution of 1 g/l, i.e., 1 ml = 1 mg metal.

4. Results and Discussion

Levels of measured metals (Ca, Cr, Cu, Fe, Pb, Ni and Na) in alcoholic beverages from Agra are shown in table VII. A variability in the concentrations of the seven elements analysed can be noted. This finding can be related to the drink type, manufacturing and bottling process.

Drinks of high alcoholic content

Ca, Cr, Cu, Fe, Pb, Ni and Na levels in the whisky, vodka, rum, spirit, deshi-liquor, and brandy samples analysed are summarized in table VII, where a variation can be observed among the different samples.

The variability is even more pronounced in the case of Cu and Fe. In drinks of high alcoholic content, Cu and Fe concentrations determined in the present study are considerably higher in Brandi and whisky samples

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(table VII). In liquors, although the Calcium contents measured by us are higher than those shown in table-8. It is interesting to note that many of the food composition and nutrition tables included in table-8 contain measurements of mineral content for spirits, although they only collect trace or 0.01µg L-1 levels for Ca.

Due to the different manufacturing processes used to produce the liquors and complex brandies.

We found that Cu level measured in liquor and vodka was lower than those found in the group of complex brandies (table VII). This result could be related to the use of copper stills for complex brandies (whiskies, rums and brandies) which increases Cu concentrations. Since Cr and Pb both are very hazardous to health and their concentration must be low and it was found correct also.

Table VII shows the very less concentration of both the elements in all the beverages studied. A little bit amounts of these metals would have been added due to processing steps like bottling, aging / storage and adulteration etc.

All the metal concentrations were under the DL, PL and MAL limits. Even Brandi was found to be a good source of Fe and Cu.

Table-1 Recommended DDI of Copper by WHO

Nutrient	Life Stage Group	RDA/AI (µg/d)	UL (µg/d)
Copper	Males		
	14-18 y	890	8,000
	19-50 y	900	10,000
	Females		
	14-18 y	890	8,000
	19-50 y	900	10,000
	Pregnancy		
	19-30 y	1000	10,000
	31-50 y	1000	10,000
	Lactation		
	19-30 y	1300	10,000
	31-50 y	1300	10,000

Table-2 Chromium level in DDI recommended by WHO

Nutrient	Life Stage Group	RDA/AI (µg/d)	UL (µg/d)
Chromium	Males		
	14-18 y	35	ND
	19-50 y	35	ND
	Females		
	14-18 y	24	ND
	19-50 y	25	ND
	Pregnancy		
	19-30 y	30	ND
	31-50 y	30	ND
	Lactation		
	19-30 y	45	ND
	31-50 y	45	ND

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Table-3 Iron level in DDI recommended by WHO

Nutrient	Life Stage Group	RDA/AI (µg/d)	UL (µg/d)
Iron	Males		
	14-18 y	11	45
	19-50 y	8	45
	Females		
	14-18 y	15	45
	19-50 y	18	45
	Pregnancy		
	19-30 y	27	45
	31-50 y	27	45
	Lactation		
	19-30 y	9	45
	31-50 y	9	45

Table-4 Calcium level in DDI recommended by WHO

Nutrient	Life Stage Group	RDA/AI (µg/d)	UL (µg/d)
Calcium	Males		
	14-18 y	1,300	2,500
	19-50 y	1,000	2,500
	Females		
	14-18 y	1,300	2,500
	19-50 y	1,000	2,500
	Pregnancy		
	19-30 y	1,000	2,500
	31-50 y	1,000	2,500
	Lactation		
	19-30 y	1,000	2,500
	31-50 y	1,000	2,500

Table-5 Nickel level in DDI recommended by WHO

Nutrient	Life Stage Group	RDA/AI (µg/d)	UL (µg/d)
Nickel	Males		
	14-18 y	ND	1.0
	19-50 y	ND	1.0
	Females		
	14-18 y	ND	1.0
	19-50 y	ND	1.0
	Pregnancy		
	19-30 y	ND	1.0
	31-50 y	ND	1.0
	Lactation		
	19-30 y	ND	1.0
	31-50 y	ND	1.0

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Table-6 Concentration of elements in studied alcoholic beverages mostly Consumed in Agra region, India

Element / Beverage	Calcium (mg/L)	Chromium (mg/L)	Copper (mg/L)	Iron (mg/L)	Nickel (mg/L)	Sodium (mg/L)
Brandi	12	0.118	0.056	2.727	-1.135	29
Rum	37	-0.011	0.009	0.474	-1.069	ND
Spirit	16	0.177	0.045	1.371	-0.468	ND
Whisky	20	-0.144	0.024	0.791	-1.169	18
Vodka	02	-0.078	0.016	-0.105	-0.797	ND
Deshi liquor	34	-0.144	0.025	-0.229	-1.383	ND

Table-7 Metal concentration limits for selected beverages

Metal Beverage Concentration limit, mg/L Obligatorietya Reference

Cu Wine 0.5 Recommended Green et al. (1997)
Pb Wine 0.2 Recommended Green et al. (1997)
Cu Brandi 0.05 Recommender Mayer et al. (2003)
Cu Rum 0.1 Recommended Richter et al. (2001)
Cu Vodka 0.02 Recommended Green et al. (1997)
Cu Whisky 0.04 Recommended Salvo et al. (2003), Dugo et al. (2005)
Pb Brandi 0.01 MAL Dugo et al. (2005)
Pb Rum 0.01 MAL Dugo et al. (2005)
Pb Vodka 0.01 MAL Dugo et al. (2005)
Pb Whisky 0.01 MAL Dugo et al. (2005)
Cr Brandi 0.02 MAL Soufleros et al. (2004)
Cr Rum 0.01 MAL Salvo et al. (2003), Dugo et al. (2005)
Cr Vodka 0.01 MAL Soufleros et al. (2004)
Cr Whisky 0.01 MAL Richter et al. (2001)
Fe Brandi 3.0 Recommended (Almeida Neves et al., 2007)
Fe Rum 0.8 Recommended (Almeida Neves et al., 2007)
Fe Vodka 0.1 Recommended (Almeida Neves et al., 2007)
Fe Whisky 1.0 Recommended (Almeida Neves et al., 2007)
Cu Beer 0.05 Recommended Mayer et al. (2003)
Cd Wine 0.1 MAL Salvo et al. (2003), Dugo et al. (2005)
Cu Wine 1.0 MAL Richter et al. (2001)
Pb Wine 0.2 MAL Commission of the European Communities (2006),
Dugo et al. (2005)
Cu Brandi 0.8 MAL Richter et al. (2001)
Zn Wine 0.5–5 MAL Salvo et al. (2003), Dugo et al. (2005)
Cu Cachaza 5 MAL Richter et al. (2001)
Cu Fruit distillate 5 MAL Soufleros et al. (2004)
MAL = maximum acceptable limit.

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Table-8 Ca content in alcoholic beverages in the most frequently used food composition and Nutrition tables in different countries

Reference (country)	Drinks of high alcoholic content	Ca (µg L-1)
Souci et al. (1989, Germany)	Whisky	15.0
Favier et al. (1995, France)	Liquor	60.0
Mataix Verdu and Carazo Martin (1995, Spain)	Liquor	0.000
Muñoz et al. (1999, Spain	Liquor	0.000
Holland et al. (2001, United Kingdom)	Spirit	Trace
USDA (2005, USA)	Liquor Spirit	26.2 0.000
Farran et al. (2004, Spain)	Liquor Spirit	60.0 Trace
Spanish Ministry of Agriculture (2004,Spain)	Spirit	0.000
Food Institute Informatics (2005, Denmark)	Whisky Gin Rum	0.000 0.000 0.000
Ministry of Health (2005, Canada)	Liquor Spirit	0.000 0.000

5. Conclusion

Levels of iron, copper, chromium, nickel, lead, calcium and sodium were measured in alcoholic beverages (Whisky, vodka, rum, brandy, wine and deshi liquors) using flame atomic absorption spectrometry (FAAS) and flame photometer. A critical review is offered concerning the different sources, effects, concentrations, removal methods, speciation, and analysis of metals (e.g., Ca, Cr, Cu, Fe, Pb, Ni and Na) present in a variety of alcoholic beverages.

Mineral concentrations were found to be significantly different between the six alcoholic products studied. In distilled alcoholic beverages, Cu measured concentrations were statistically different for each of the 6 groups of alcoholic beverages studied. Contrarily, Cu concentrations were statistically lower. Remarkably, for Cu, the concentration determined in brandy was statistically higher.

From all studied elements, Cu was the one for which alcoholicbeverages constitute a significant source (more than 10% of recommended daily intake). These findings are of potential use to food composition tables.

Metals find their way into alcoholic beverages through many possible sources discussed here. Their effects on the beverages as well as on humans after consuming such beverages are quite varied. This then necessitates that metals be subject to regulations. FAAS offers distinct advantages for their analysis.

Caution: Consumption of liquor is injurious to health.

Acknowledgement

Authors are thankful to School of Chemical Sciences,Department of Chemistry, St. John's College, Agra for providing the analytical instrumentation facilities.

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