Application Note

Analysis of Beer

H. Daidoji,
HORIBA Ltd, Japan

Keywords: food, beverage, method development
Elements: Al, Ca, Cd, Cu, Fe, Mg, Mn, Na, Zn

1 Introduction

The analysis of beer is important to the brewery industry, both for production purposes as well as to the final consumer. The analysis can pose several problems due to both the CO_2 gas dissolved in the beer and the dissolved and undissolved protein. This report demonstrates several approaches and compares the results obtained.

2 Principle

2.1 Technique used

The elemental analysis of these samples was undertaken by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The sample is nebulized then transferred to an argon plasma. It is decomposed, atomized and ionized whereby the atoms and ions are excited. We measure the intensity of the light emitted when the atoms or ions return to lower levels of energy. Each element emits light at characteristic wavelengths and these lines can be used for quantitative analysis after a calibration.

2.2 Wavelength choice

The choice of the wavelength in a given matrix can be made using the profile function, or by using "Win-Image", which is rapid semi-quantitative analysis mode using multiple wavelengths. The principle is the same in either case: record the scans of analytes at low concentration, and of the matrix. By superimposing the spectra, we see possible interferences.

3 Sample Preparation

The analysis of beer is affected by CO_2 and organic materials such as protein. The CO_2 must be degassed, otherwise CO_2 breaks out of solution during the pumping stage and nebulization. There are several methods to achieve this including bubbling N_2 into the solution, ultrasonic vibration and heating.

We tried three methods for the analysis.

A) Typical calibration curve
B) Internal standard method
C) Standard addition method

A) Typical calibration curve

To each 20 g or 40 g sample of beer, about 5 ml of concentrated HNO_3 was added to dissolve organic materials. It was heated at 80 °C for 3 minutes. The action of HNO_3 and heat is to degas the CO_2. Distilled water was added to a total volume of 50 mL.
The standards for the calibration, for all elements, were made from Spex Certiprep Mix standard solutions.

B) Internal standard method

A vessel containing 20 g of beer was kept in an ultrasonic vibration bath (80W) for 1 hour to degas the CO_2 in the beer. Due to the alcohol content the specific gravity can change, so it is important to weigh the sample, rather than pipette a volume. Then, 5 ppm Yttrium was added as an internal standard element in this solution and distilled water was added to make a total weight of 50 g. The standards for calibration curves, for each element, was made from Spex Certiprep Mix standard solutions and 5 ppm Yttrium was added at the same concentrations as the samples. An alternative to adding the Y to the samples directly is to introduce 5ppm using a

"Y" piece. This ensures all solutions have identical concentration of internal standard.

C) Standard addition method

Five vessels containing 20 g of beer were kept in an ultrasonic vibration bath (80 W) for 1 hour. Due to the alcohol content the specific gravity can change, so it is important to weigh the sample, rather than pipette a volume. After degassing of CO_2, mixed standard solutions were added in these solutions to prepare 0, 0.02, 0.05, 0.1 and 10 ppm spikes of each element. Background corrections were done for all elements.

4 Instrument specification

The work was done on a JY ULTIMA and is also applicable to a JY ULTIMA 2 ICP spectrometer. The specifications are listed below.

Table 1: Specification of spectrometer

Parameters	Specifications
Mounting	Czerny-Turner
Focal length	1 m
Thermoregulation	Yes
Variable resolution	Yes
Nitrogen purge	Yes
Grating number of grooves	2.400 gr/mm
Orders	2
1st order resolution	0.005 nm
2nd order resolution	0.010 nm

Table 2: Specification of RF Generator

Parameters	Specifications
Type of generator	Solid state
Observation	Radial
Frequency	40.68 MHz
Control of gas flowrate	By computer
Control of pump flow	By computer
Cooling	Air

The operating conditions of the spectrometer are listed in Table 3.

Table 3: Operating conditions

Parameter	Condition
Generator power	1000 W
Plasma gas flowrate	12 L/min
Auxiliary gas flowrate	0.4 L/min
Sheath gas flowrate	0.25 L/min
Nebulizer	1 L/min
Sample uptake	1 mL/min
Type of nebulizer	Tangential (Burgener)
Type of spray chamber	Cyclonic
Argon humidifier	No
Injector tube diameter	3.0 mm

5 Wavelength selection and analytical conditions

Table 4: Analytical conditions

Mode of calculation	Entrance Slits (µm)	Exit Slits	Integration time (sec)	Replicates
Maximum Mode	20 µm	15 µm	3 s	3

6 Results

Profiles for each element in beer dissolved with HNO_3 (first method) are shown in Figure 1.

Calibration curves for Mn for the three methods are given Figure 2.

The results are shown in Table 4 for the three types of calibration.

Table 4: Results for three types of calibration

Element	Wavelength nm	A (ppm) a	A (ppm) b	B (ppm)	C (ppm)
Al	396.1	0.080	0.082	0.078	0.072
Ca	422.6	28.8	29.4	29.6	27.2
Cd	228.8	< 0.0001	< 0.0001	< 0.0001	< 0.0001
Cu	324.7	0.042	0.040	0.042	0.050
Fe	259.9	0.056	0.051	0.059	0.066
Mg	285.2	48.1	52.2	53.5	53.7
Mn	257.6	0.075	0.074	0.076	0.071
Na	588.9	29.9	31.0	30.7	30.5
Zn	213.9	0.0052	0.0035	0.0050	0.0058

7 Conclusion

To analyze beer, it was shown in this Application Note that the three types of methods used to eliminate the CO_2 and protein gave equivalent results.

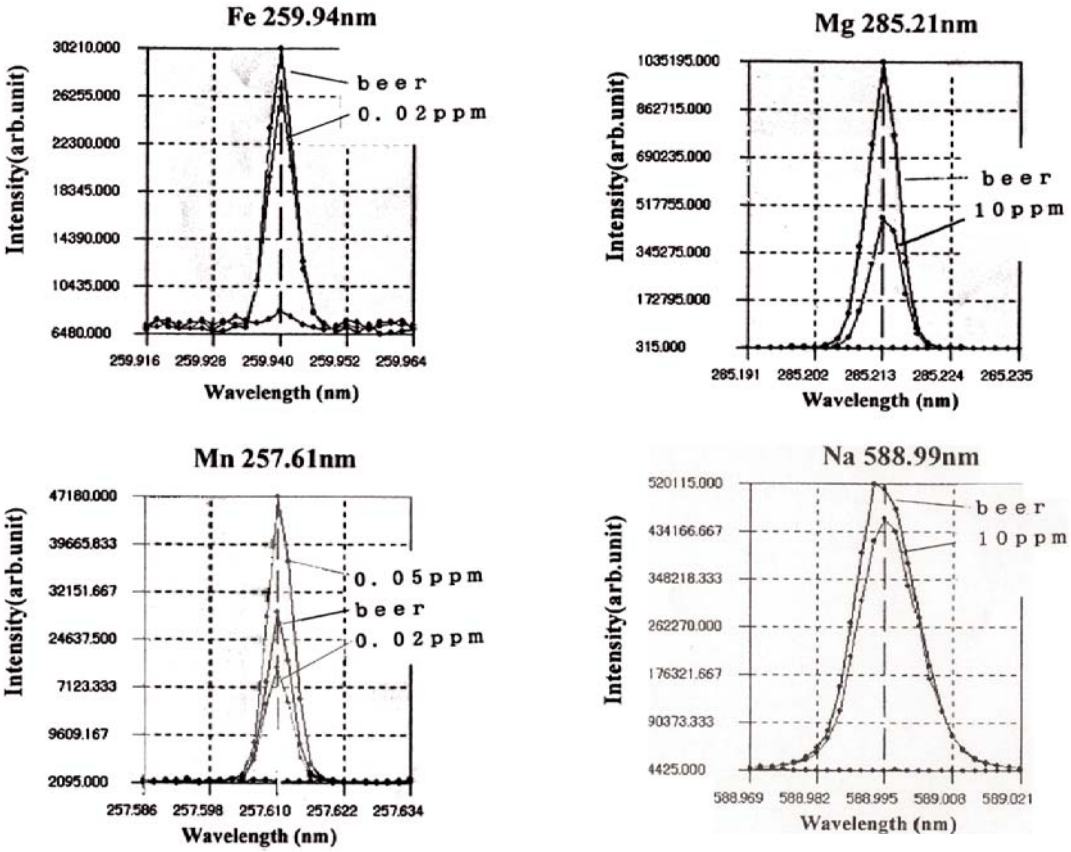
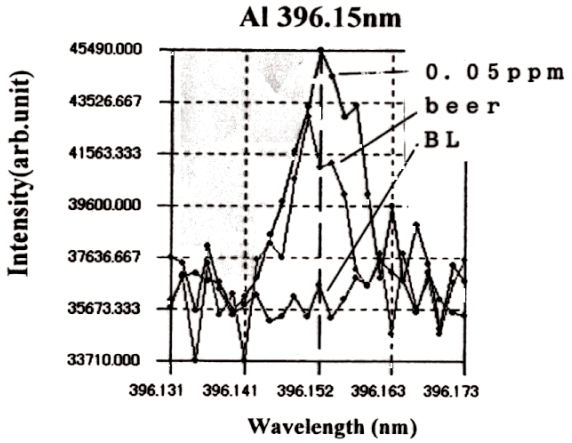
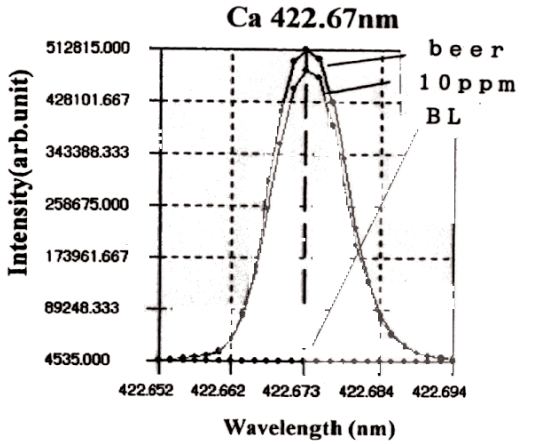
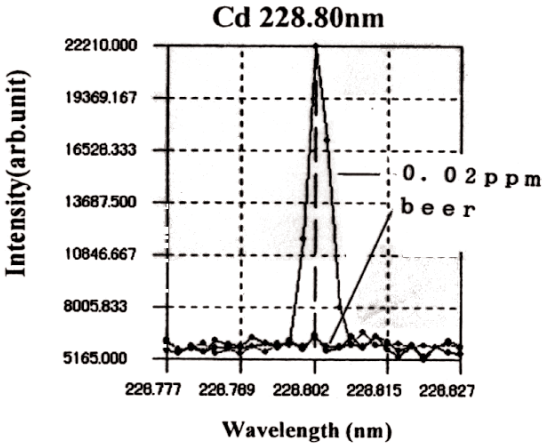
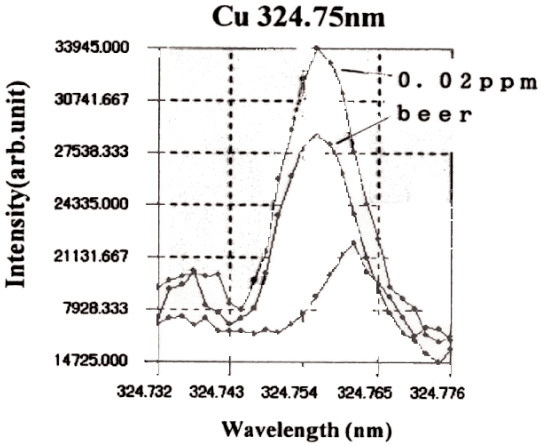


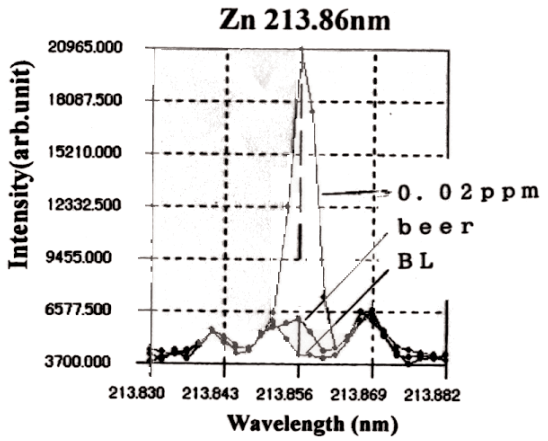
Figure 1: Profiles of elements in beer. Dissolution with HNO_3


Al 396.15nm
Intensity(arb.unit)
45490.000
43526.667
41563.333
39600.000
37636.667
35673.333
33710.000
396.131
396.141
396.152
396.163
396.173
Wavelength (nm)
0.05ppm
beer
BL


Ca 422.67nm
Intensity(arb.unit)
512815.000
428101.667
343388.333
258675.000
173961.667
89248.333
4535.000
422.652
422.662
422.673
422.684
422.694
Wavelength (nm)
beer
10ppm
BL


Cd 228.80nm
Intensity(arb.unit)
22210.000
19369.167
16528.333
13687.500
10846.667
8005.833
5165.000
226.777
226.789
228.802
228.815
228.827
Wavelength (nm)
0.02ppm
beer


Cu 324.75nm
Intensity(arb.unit)
33945.000
30741.667
27538.333
24335.000
21131.667
7928.333
14725.000
324.732
324.743
324.754
324.765
324.776
Wavelength (nm)
0.02ppm
beer

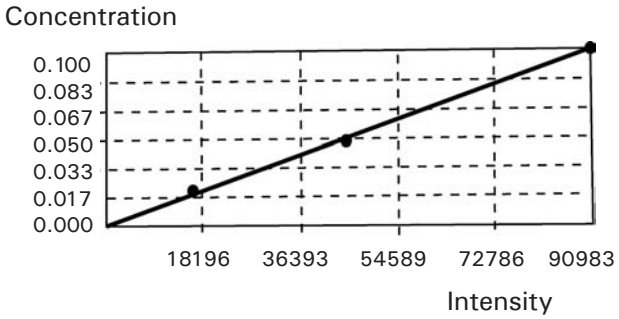

Zn 213.86nm
Intensity(arb.unit)
20965.000
18087.500
15210.000
12332.500
9455.000
6577.500
3700.000
213.830
213.843
213.856
213.869
213.882
Wavelength (nm)
0.02ppm
beer
BL

Typical calibration curve

s: 0.014988

BEC: 938 ng/l

Correlation: 0.9998

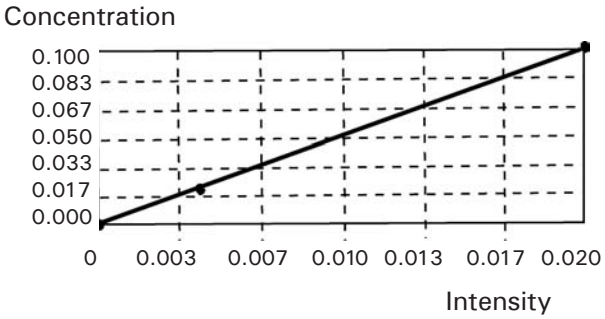


Internal standard method

s: 0

BEC: 49.7 ng/l

Correlation: 1



Standard addition method

s:0

BEC: 15.4 μg/l

Correlation: 1

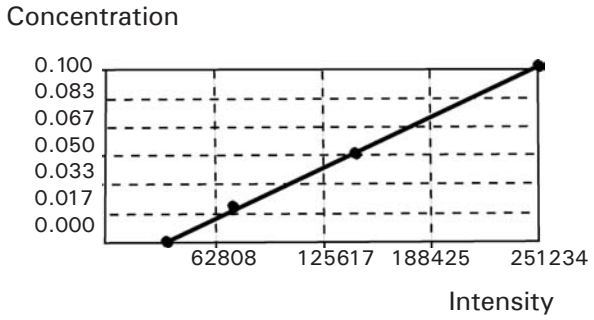


Figure 2: The calibration curves Mn 257.610 nm

In the USA:
Jobin Yvon Inc.
3880 Park Avenue
Edison, NJ 08820
Tel: 1-732-494-8660
Fax: 1-732-494-8796
E-mail:
emission@jyhoriba.com

In France:
Jobin Yvon S.A.S.
16-18, rue du Canal
91165 Longjumeau Cedex
Tel: (33) 1/64 54 13 00
Fax: (33) 1/69 09 90 88

Germany: (49) 89/46 23 17-0
Italy: (39) 2/57 60 56 90
U.K.: (44) 20/82 04 81 42

In Japan:
Horiba Ltd.
2 Miyanohigashi, Kisshoin
Minami-ku, Kyoto 601-8510
TEL: (81) 75 313 8121
FAX: (81) 75 321 5725
www.horiba.com

China: (86) 10/6849 2240
Spain: (34) 91/724 16 57
Other Countries: Contact JY S.A.S.

1-877-JYHORIBA