Analysis of Elemental Contaminants in Beverages using the Thermo Scientific iCAP 6200 ICP-OES

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Key Words
Beverages, Directive (EN 1134:1994), Commission Regulation (EC) No 1881/2006, iCAP 6200, Method template, Internal Standard.

Benefits in Brief

- Duo viewing for optimal method conditions using axial view for traces and radial view for major elements
- Pre-loaded template for rapid, simple method development
- Optimized application specific sample handling kits

Introduction

In recent years, several investigations around the world have captured global media attention by highlighting excessive contamination of foodstuffs and beverages. This has prompted local authorities in many countries to increase the legislation and testing of many foodstuffs, including beverages. Most method directives involving the analysis of beverages, including those in Europe, are based on acid digestion and subsequent analysis by atomic absorption spectroscopy (AAS) and have yet to be updated to include optical ICP.

The analysis of contaminants in beverages in Europe is based on the recommendation of a European Union "Reports on tasks for Scientific Cooperation" (SCOOP, Task 3.2.11) and the Committee on Toxicity (COT; Chemicals in Food, Consumer Products and the Environment, 2004) which researched and established the average human intake and absorption of contaminants and nutrients from liquids. The elements ordinarily analyzed, both contaminants and major constituent elements are displayed in Table 1.

Table 1. Elements commonly analyzed in beverages

Elements/Nutrients in beverages			
Al	Cu	Mn	Zn
As	Fe	Na	
Ca	K	Pb	
Cd	Mg	Sn	

The method most commonly used for fruit juices is EN 1134:1994 which was developed for AAS and includes microwave digestion of samples. Optical ICP can process these samples directly, so EN 1134 method has been adapted to allow for removal of the digestion step, thus saving time and materials and reducing method development.

Instrumentation

The Thermo Scientific iCAP 6200 ICP was used for the direct analysis of a range of beverages. The iCAP 6200 is a new compact, dual view ICP instrument based on the innovative and powerful core technologies of the iCAP 6000 Series ICP spectrometers. The instrument achieves powerful analyte detection and provides a highly cost effective solution for routine analysis of liquids in laboratories with standard sample throughput requirements. The iCAP 6200 software, iTEVA, incorporates pre-loaded method templates (see Figure 1) for common methods, simplifying normal method development and providing an option of immediate analysis.

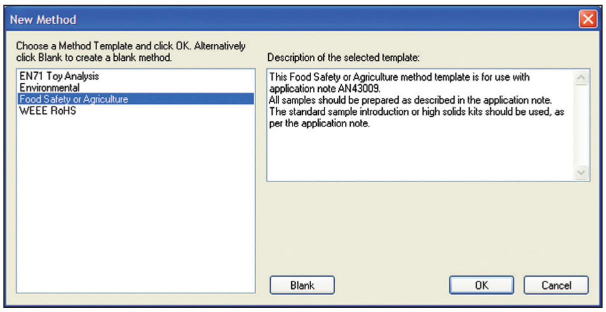

Figure 1. Food Safety/Agriculture Method Template selection

Sample and standard preparation

Three different beverages below were analyzed:

- Blackcurrant squash concentrate – normally consumed as a 1:4 diluted liquid with water
- Beer – a British ale was used, one drop of a silicone anti-foaming agent was added to reduce the influence of the dissolved CO_2 gas on nebulization and transport
- Pure cranberry juice (smooth) – consumed undiluted

The samples were prepared as follows:

- The individual sample containers were shaken and a 20g aliquot mass weighed into a glass volumetric flask
- An additional 2g aliquot mass was also weighed into a volumetric flask to determine higher concentration elements
- A duplicate sample was produced for each beverage, which was spiked with a small concentration of aqueous standard for recovery testing
- All samples were diluted to 100 ml volume with deionized water

Calibration standards were prepared by diluting traceable 1000 mg/kg aqueous, single element standards to the concentrations listed in Table 2. All solutions were made to volume in deionized water, although 0.5% high purity nitric acid may be used to improve long-term solution stability.

Table 2: Calibration standard concentrations.

Standard Concentrations (mg/L)

Element	Blank	Standard 1	Standard 2	Standard 3
Al	0	0.5	1	2
As	0	0.5	1	2
Ca	0	2	5	10
Cd	0	0.5	1	2
Cu	0	0.5	1	2
Fe	0	0.5	1	2
K	0	2	5	10
Mg	0	2	5	10
Mn	0	0.5	1	2
Na	0	2	5	10
Pb	0	0.5	1	2
Sn	0	0.5	1	2
Zn	0	0.5	1	2

Method Development

The *Food Safety* method template was opened in iTEVA – this contains all of the required method parameters and standard concentrations' as listed in this note. The standard sample introduction kit was used for the analysis as per the recommendations in the method notes. The instrument was calibrated and the samples analyzed in a single run. Table 3 shows the instrument parameters used for the method.

Table 3. Instrumental parameters.

Parameter	Setting
Pump tubing	Sample tygon orange/white Drain tygon white/white
Pump rate	45 rpm
Nebulizer	Glass concentric
Nebulizer gas flow	0.15 MPa
Spraychamber	Glass cyclonic
Centre tube	2 mm
RF Power	1150 W
Coolant gas flow	12 L/min
Auxiliary gas flow	1 L/min
Integration times	Axial 15 seconds Radial 10 seconds

Results

The results, elements and wavelengths of the rapid analysis of the beverage samples is shown in Table 4 and are further highlighted in Figure 2. Each sample was spiked with the same 1000 mg/kg solutions used to make the calibration standards. These spiked samples were analyzed in the same run as the samples and all recoveries were within the acceptable range of +/-20 % relative to the added concentration. Method detection limits (MDL) were established for the trace elements by analyzing the cranberry juice, with ten replicates. This approach was chosen as the majority of the trace elements were very close to detection limit concentrations or slightly higher. The standard deviation of the result was multiplied by 3 to give a detection limit in mg/kg that equates to a confidence interval of approximately 98.5%.

Table 4. Results of the analysis of the beverages

Element and Wavelength (mm)	Spike value (mg/L)	Cranberry Undiluted (mg/L)	Cranberry % Spike Recovery	Cranberry 20g/100ml Detection/ limit (ug/L)	Squash Undiluted (mg/L)	Squash % Spike Recovery	Beer Undiluted (mg/L)	Beer % Spike Recovery
Al 396.152	0.5	0.0393	96.3	0.93	0.1305	96.8	0.1318	99.1
As 193.759	0.5	< DL	102.1	4.11	< DL	102.5	<DL	111.4
Ca 422.673	2	53.1	97.2		40.1	106.1	36.7	106.2
Cd 214.438	0.5	< DL	97.9	0.07	< DL	99.5	<DL	101.4
Cu 324.754	0.5	0.0425	98.8	0.85	0.0093	100.1	0.0100	99.6
Fe 259.940	0.5	0.44	104.4	6.08	0.2345	104.4	0.1338	104.9
K 766.490	2	190	83.8		484	96.5	532	96.0
Mg 279.079	2	21.1	103.7		7.72	107.1	89.4	104.0
Mn 257.610	0.5	0.3645	99.5	1.65	0.106	99.0	0.092	102.9
Na 589.592	2	40.9	101.3		156	107.9	28.2	109.2
Pb 220.353	0.5	< DL	91.1	1.28	< DL	95.5	< DL	94.4
Sn 283.999	0.5	< DL	99.7	5.11	< DL	107.3	0.0028	109.8
Zn 206.200	0.5	0.085	96.0	0.47	0.034	96.7	< DL	100.2

All of the trace contaminants detrimental to human health (As, Cd and Pb) were measured and found to be below the regulation limits (see Table 5 below).

The results show that the robust RF generator and the optimized sample handling kit easily handled the range of sample densities and viscosities. An internal standard may be added if the recoveries degrade below regulation levels. An online, internal standard mixing kit (p/n 8423 12051551) may also be used for ease of use or to reduce labor for higher sample numbers. iTEVA uniquely allows the analyst the ability to turn the internal standard on or off pre or post analysis, saving valuable method development time as only one analysis is required to generate two sets of results.

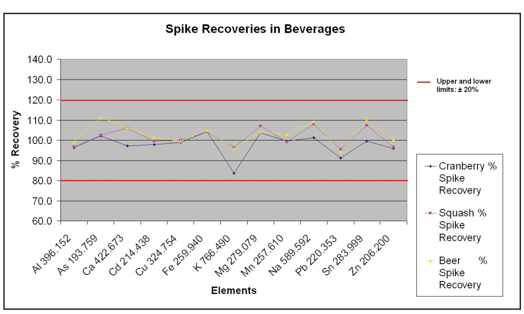

Figure 2. Percentage recovery of spikes in analyzed beverages

Table 5. Regulation maximum allowed concentrations in various beverages

Element	Maximum (mg/L)
As	< 0.2
Cd	< 0.1
Cu	< 2
Fe	< 7
Pb	< 0.5
Sn	< 100

Conclusion

The analysis of beverages is rapid and analyst friendly using the iCAP 6200 ICP-OES in conjunction with the pre-loaded iTEVA method template. This method template and the powerful, easy to use iCAP 6200 ICP-OES allows inexperienced and experienced users alike to vastly reduce the time for method development for these sample types, resulting in cost effective analyses. In addition to the time saving on method development, removal of the digestion stage and the use of internal standards produced an easy to use, versatile method capable of analyzing a wide variety of food and beverage samples.

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