

## Determination of Ca, K, and Na in Soft Drinks Using MP-AES

“Dilute and shoot” method that includes one-step sample preparation and replaces argon with cost effective nitrogen to fuel the plasma



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### Introduction

Soft drinks are among the most common beverages consumed in the United States. Fifty percent of young adults report drinking one or more soft drinks per day (1). Regulations issued by the United States Food and Drug Administration (FDA) require reporting of the Ca and Na content of packaged foods and beverages [2], while K content reporting is optional. FDA regulations for package labeling dictate that K and Na concentrations in the 5 to 140 mg/serving range should be rounded to the nearest 5 mg. For values over 140 mg/serving, the label can be rounded to the nearest 10 mg. Calcium is reported to the nearest 10 % of the “recommended daily value” of 1000 mg (2). These labeling requirements, as well as the typical quality control analyses carried out by manufacturers, demonstrate the need for simple, cost-effective, sensitive, accurate, precise, and high sample throughput methods for soft drink analyses.

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Current FDA guidelines suggest using microwave-assisted digestion (MAD) and inductively coupled plasma optical emission spectrometry (ICP-OES) for soft drink elemental analysis (3). MAD is recommended due to the complexity of this type of sample. The combination of carnation, dye additives, artificial flavoring, and high sugar content contribute to significant matrix effects. These effects are difficult to overcome for most analytical techniques (4). Although effective, MAD is a labor-intensive, expensive, and time-consuming process, especially due to sample handling and the time required for sample cool down after digestion.

This application note describes a “dilute and shoot” method for soft drink elemental analysis. The method is based on microwave-induced plasma atomic emission spectrometry (MP-AES) using the Agilent 4200 MP-AES. Sample preparation is not required, eliminating the need for an expensive digestion apparatus as well as the time-consuming procedures associated with them. The 4200 MP-AES is less expensive to buy and operate than an ICP-OES as it uses N<sub>2</sub> rather than Ar to fuel the plasma. If the optional nitrogen generator is bought, N<sub>2</sub> can be produced in situ from a supply of clean, dry, oil-free compressed air. The N<sub>2</sub> microwave-induced plasma is cooler than an Refueled inductively coupled plasma (5,6). This produces lower background signals in the visible region of the spectrum, allowing for lower limits of detection (LODs). These limits vary on an element-by-element basis, but in the visible region (>300 nm) they are comparable with the detection limits of ICP-OES.

The 4200 MP-AES records emission signals sequentially. Therefore analytical conditions can be optimized for each specific element within the same experiment, which maximizes efficiency and may minimize potential interferences.

## Experimental

### Instrumentation

All determinations were carried out using the Agilent 4200 MP-AES. A liquid N<sub>2</sub> Dewar was used to provide N<sub>2</sub> gas to run the microwave-induced plasma. No sample preparation other than simple dilution with 1 % v/v HNO<sub>3</sub> was required. The sample introduction system is composed of an SPS 4 automatic sampler, solvent resistant tubing, a double-pass cyclonic spray chamber, and an inert Flow Blurring nebulizer (OneNeb).

Nebulizer flow rate and plasma viewing position were adjusted for each individual analyte to optimize recovery. Operating conditions were optimized by selecting one of the spiked samples, then running the “optimize nebulizer

flow” followed by “optimize viewing position” features in MP Expert. One of the samples was chosen for optimizing the instrumental operating conditions to match matrix conditions and improve accuracy. The viewing position used in this case was 0 for all elements. The nebulizer flow rates were 0.90, 1.00 and 1.00 L/min for Ca, K and Na, respectively. Table 1 and 2 list the instrument operating parameters.

**Table 1.** Element-Specific Operating Parameters.

Element	Wavelength (nm)	Nebulizer Flow Rate (L/min)
Ca	393.366	0.9
K	766.491	1
Na	588.995	1

**Table 2.** Instrument parameters.

Parameter	Setting
Number of replicates	3
Peristaltic pump speed	15 rpm
Uptake time	45 s
Rinse time	30 s
Stabilization time	15 s
Background correction	Auto
No. of pixels	3
Read time (all elements)	3 s
Spray chamber	Double pass glass cyclonic
Nebulizer	OneNeb Flow-Blurring
Sample pump tubing	Orange/Green
Waste pump tubing	Blue/Blue
Autosampler	SPS 4

### Standards and sample preparation

All solutions were prepared using distilled-deionized water (18 M Ω cm, Milli-Q, Millipore, Bedford, MA, USA) and trace metal grade nitric acid (Fisher, Pittsburgh, PA, USA). Single-element stock solutions containing 1000 mg/L of Ca, K, or Na (SPEX CertPrep, Metuchen, NJ, USA) were used to prepare standard reference solutions for calibration and to carry out spike experiments.

Seven different soft drink samples were analyzed. Various popular beverages were chosen to sample a range of different flavors and types (for example: diet versus. regular, cola, orange, ginger ale, and so on). Approximately 2.0 mL aliquots

of each of these samples were weighed in 15 mL graduated polypropylene centrifuge tubes using an analytical balance (Mettler AE 100, Hightstown, NJ, USA). For K determination in Diet Dr. Pepper, and Na determination in Diet Dr. Pepper, Mountain Dew, and Schweppes, the same procedure was employed using 0.2 mL sample aliquots. Sample mass was adopted rather than volume to minimize any potential bias introduced by residual gas bubbles in the soft drink or inaccuracies due to viscosity caused by high sugar content. The samples were then diluted to 10.0 mL with 1 % v/v HNO<sub>3</sub>. Five standard reference solutions (0.2 to 10 mg/L) and a blank, all prepared in 1 % v/v HNO<sub>3</sub>, were used to build the calibration curves. A traditional external standard calibration method was used for all determinations, rather than using a more complicated calibration method, such as standard additions. This simplified the analysis and made it less labor intensive. A similar approach to calibration could be achieved by using the standard calibration function within the MP Expert software, with background correction set to 'none'.

Spike experiments were carried out to evaluate the procedure's accuracy. Samples used in this study were prepared in the same way as the unspiked samples. Adequate volumes of stock solution were added to the samples such that the final concentrations were 1.00 mg/L for Ca, and 2.00 mg/L for K and Na. An intermediate stock solution of 10 mg/L Ca and 20 mg/L K and Na was prepared from the same standards used to create the calibration curve. 1 mL was added to the weighed 2.0 mL soft drink aliquots, which were then completed to 10.0 mL using 1 % HNO<sub>3</sub>.

## Results and Discussion

### Limits of detection and accuracy

The limits of detection for determinations using the Agilent 4200 MP-AES were calculated according to IUPAC's recommendations as three times the standard deviation of the blank signal ( $S_B$ ) divided by the calibration curve slope ( $m$ ):  $LOD = 3S_B / m$ . Twelve consecutive blank solution (1 % v/v HNO<sub>3</sub>) measurements were used to calculate  $S_B$  for each instrumental condition. The detection limits for Ca, K, and Na were 30, 3 and 20 µg/L, respectively.

The procedure's accuracy was evaluated by spike experiments. Recoveries were calculated by comparing expected (concentrations added) and measured (spiked - unspiked) values. The results for each analyte and sample are presented in Table 3.

Recoveries were within 91 to 110 % using the optimized conditions. The spike recoveries were excellent with simple external calibration, which are good indicators of the method accuracy.

The method also takes advantage of the MP's tolerance to high carbon-content matrices, as the regular (nondiet) drinks included a substantial concentration of sugar. The external gas control module (EGCM) air injection was not used in this study, but significant carbon build-up was not found to be a problem on the torch.

**Table 3.** Soft drink analysis with the 4200 MP-AES. Values are the recoveries (%) for spike experiments with 1.00 mg/L Ca, and 2.00 mg/L K and Na.

Sample	Ca	K	Na
Cheerwine	95	91	105
Diet Dr. Pepper	100	106	102
Fanta	110	107	106
Mountain Dew	99	96	100
Pepsi	96	95	100
Schweppes	91	104	103
Sprite	91	106	108

### Soft drink concentrations

The same procedure used in the addition and recovery experiment was used to determine the concentrations of Ca, K, and Na in the original (nonspiked) samples. The results are shown in Table 4. Calcium concentrations were more varied across the samples. Schweppes ginger ale presented a significantly higher Ca value, which may be related to the high concentrations of Ca found in the Ginger root (*Zingiber officinale*) (6). Sodium and potassium also had wider variations, possibly due to some products using a Na or K salt as a preservative, as disclosed on the individual labels.

**Table 4.** Ca, K, and Na concentrations in soft drinks determined by the 4200 MP-AES. Results are the mean ± 1 standard deviation (mg/L, n = 3).

Sample	Ca	K	Na
Cheerwine	6.09 ± 0.10	6.07 ± 0.04	18.15 ± 0.14
Diet Dr. Pepper	3.06 ± 0.02	31.27 ± 0.41	58.58 ± 0.31
Fanta	6.17 ± 0.02	54.63 ± 0.46	3.28 ± 0.18
Mountain Dew	6.28 ± 0.06	21.20 ± 0.23	84.72 ± 0.52
Pepsi	3.30 ± 0.04	14.69 ± 0.20	20.08 ± 0.11
Schweppes Ginger Ale	23.49 ± 0.07	3.16 ± 0.02	62.47 ± 0.58
Sprite	7.22 ± 0.12	1.03 ± 0.01	79.73 ± 0.51

## Conclusions

The method described in this application note is an interesting alternative to the MAD and ICP-OES method recommended by the FDA for determining Ca, K, and Na in Soft Drinks. It is a fast, cost effective, and efficient strategy that can be applied by manufacturing laboratories in routine quality control analyses and determinations associated with package-labeling regulations.

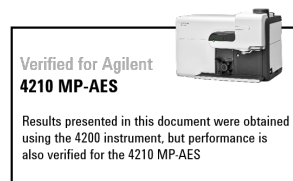
The method also demonstrates the ability of MP-AES to handle complex sample matrices without time-consuming, expensive sample preparation steps.

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