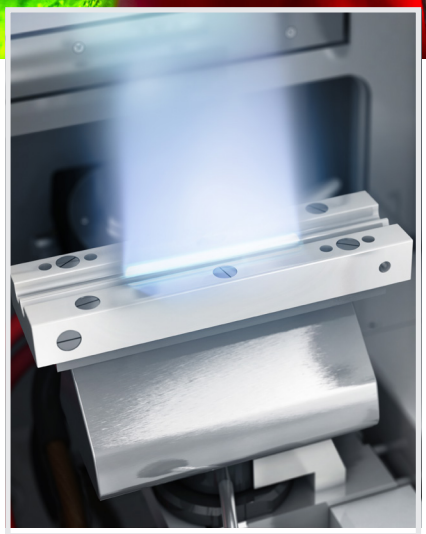


Challenge

Direct analysis of minerals (Ca, Mg, Na, K, Fe) in juice, mineral water, table water and cola

Solution

Simple and fast flame AAS with automatic dilution function of the novAA 800F/D, ZEEnit 700P and contrAA 800 F/D, latter with best detection limits and side pixel evaluation.

Determination of Mineral Contents in Non-Alcoholic Beverages

Introduction

The testing of beverages such as mineral water, fruit juice and soft drinks for element contents is a common application in industrial quality control laboratories of beverage producers. Of particular interest are elements such as Ca, Fe, K, Mg and Na, as they are also shown on beverage packaging.

The concentration of these minerals typically ranges from low mg/L to a few g/L depending on element and beverage. Apple juice for example contains usually about 1g/L of potassium and 5 mg/L of iron as essential nutrients. In mineral waters potassium levels are expected to be below 5 mg/L though, and for iron only trace levels are expected to avoid coloring of mineral waters. The working range of the flame AAS technique matches the concentration for the elements of interest; hence, most beverage samples are analyzed by flame AAS directly after sample dilution.

The note describes a simple and fast flame AAS routine for quality control of beverage samples applicable for the novAA 800, ZEEnit 700P and contrAA 800 series from Analytik Jena. To improve the ease of use and to increase productivity, the autosampler AS-FD was used for (i) the preparation of calibration standards from a stock solution and for (ii) automatic dilution of different beverage samples (up to a factor of 1:500) to bring the element concentrations into the typical calibration range of the flame AAS technique. Further flame accessories like the SFS 6.0, the switching valve technology for AAS, improve the analytical precision in daily routine work.

analytikjena
An Endress+Hauser Company

Especially with the High Resolution Continuum Source AAS contrAA 800 all analytes can be easily quantified within one method. Due to the generally available spectral information next to the element line, the side pixel evaluation enables the measurement of high element concentration.

Materials and Methods

Samples and Reagents

The following non-alcoholic beverage samples were analyzed:

Juice	Mineral water	Further beverage
■ Apple juice 1 ■ Apple juice 2 ■ Grape juice ■ Cherry juice	■ Mineral water 1 ■ Mineral water 2 ■ Table water	■ Cola

Sample Preparation

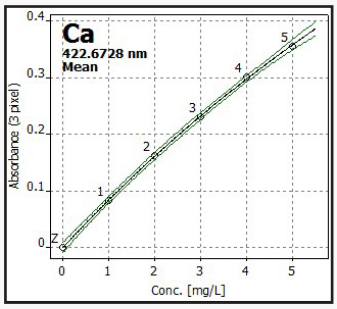
The samples were always diluted 1:10 with 1% (v/v) HCl and 0.1% CsCl/$LaCl_3$ buffer. If necessary, further intelligent sample dilutions were automatically performed by the AS-FD autosampler. For iron analysis the mineral and table water samples did not require any dilution. These samples were just acidified with 1% (v/v) HCl.

Calibration

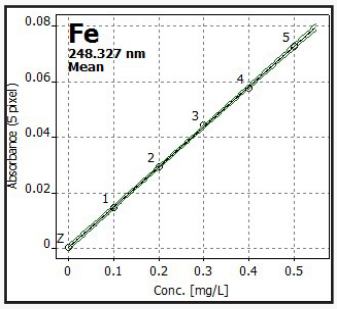
The calibration was performed from a multi-element stock solution, containing 1 mg/L of Fe and 20 mg/L of Ca, K, Mg and Na. The calibration standards were automatically prepared by the autosampler applying a diluent solution of 1% (v/v) HCl and 0.1% CsCl/$LaCl_3$. Table 1 shows the concentrations of the calibration standards.

Table 1: Concentration of the calibration standards

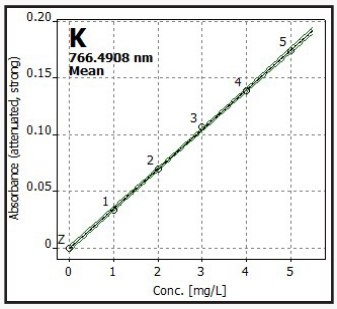
Standard solution	Analyte concentration [mg/ L]				
	Ca	Fe	K	Mg	Na
Cal. std. 0	0	0	0	0	0
Cal. std. 1	1.00	0.10	1.00	1.00	1.00
Cal. std. 2	2.00	0.20	2.00	2.00	2.00
Cal. std. 3	3.00	0.30	3.00	3.00	3.00
Cal. std. 4	4.00	0.40	4.00	4.00	4.00
Cal. std. 5	5.00	0.50	5.00	5.00	5.00



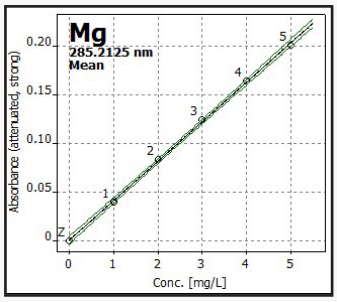
nonlinear; R^2 (adj.)=0.9992



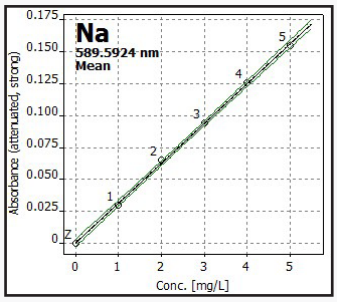
linear; R^2 (adj.)=0.9995



linear; R^2 (adj.)=0.9995



linear; R^2 (adj.)=0.9992



linear; R^2 (adj.)=0.9992

Figure 1: Resulting calibration functions and correlation coefficients

Instrumentation

All instrument parameters and method settings are listed in table 2 and table 3.

Table 2: General instrument parameters and accessories

Parameter	Specification
Instrument	contrAA800 F
Burner type	50 mm
Flame type	Air/ Acetylene
Burner angle	0°
Autosampler	AS-FD
Injection switch	SFS 6.0

To combine the determination of elements in low and high concentrations in one method, it can be challenging to find suitable element lines. The side pixel evaluation of the AspectCS software allows to attenuate strong absorbance signals by measuring on the wing of the respective resonance line. Several attenuation options allow to individually optimize the spectral evaluation parameters for each analyte and application. Finally, the strongest attenuation was used for the elements K, Mg and Na. As the Ca measurement in the air/acetylene flame is not as sensitive as in the nitrous oxide flame, an attenuation of the signal is not required. The resonance line is measured in the center of the absorption profile.

Table 3: Instrument and evaluation parameters

Element	Wavelength [nm]	Meas.time [s]	Burner height [mm]	Fuel gas flow [L/h]	No. of eval. Pixels/attenuation	Baseline correction
Ca	422.6728	3.0	6	50	3	IBC
Fe	248.3270	3.0	6	55	5	IBC
K	766.4908	3.0	6	45	Strong attenuation	IBC
Mg	285.2125	3.0	6	45	Strong attenuation	IBC
Na	589.5924	3.0	5	40	Strong attenuation	IBC

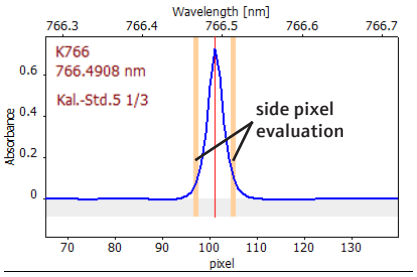
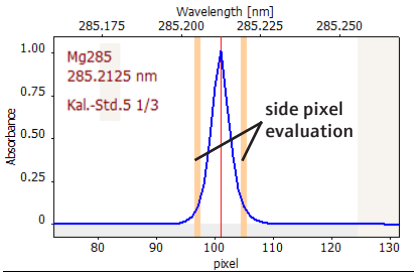
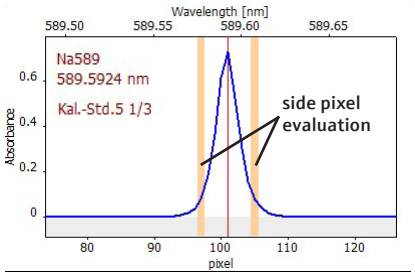
IBC: Iterative Baseline Correction

Results and Discussion

Typical spectra and spectral vicinity

Table 4 shows characteristic spectra and spectral vicinity of the applied analyte lines K, Mg and Na. In the enlarged view of the spectrum the evaluation pixels are set onto the wings of the signal.

Table 4: Characteristic spectra and spectral vicinity of the applied analyte lines with side pixel evaluation

K 766 enlarged spectrum	Mg285 enlarged spectrum	Na 589 enlarged spectrum
		

Measurement results

The automatic overrange dilution function of the autosampler AS-FD was used to handle the different concentration of the individual minerals. The autosampler will automatically perform several dilutions steps, until the analyte concentration of the sample is in the calibration range. Table 5 shows the automatically generated dilution factors.

Table 5: Automatically generated dilution factors

Sample	Ca	Fe	K	Mg	Na
Mineral water 1	26.8	1	10	10	26.8
Mineral water 2	47.0	1	10	10	393
Tap water	10	1	10	10	10
Apple juice 1	10	10	242	10	10
Apple juice 2	27.7	10	244	10	10
Grape juice	27.3	10	256	27.3	10
Cherry juice	26.9	10	234	26.9	10
Cola	10	1	20,9	10	20.9

	automatic overrange dilution
	manual pre-dilution
	no dilution

Table 6 shows the measurement results and the confidence range for the samples, calculated to the original undiluted samples. Relative standard deviation is provided for three replicate measurements.

Table 6: Measurement results

Sample	Ca		Fe		K		Mg		Na	
	Conc.	RSD	Conc.	RSD	Conc.	RSD	Conc.	RSD	Conc.	RSD
	[mg/L]	%	[mg/L]	%	[mg/L]	%	[mg/L]	%	[mg/L]	%
Mineral water 1	76.9	1.3	<0.009		8.5	1.6	17.0	0.2	102.9	0.6
Mineral water 2	111	0.9	<0.009		12.9	1.4	39.3	1.0	273	0.6
Tap water	49.0	0.9	<LOQ		1.29	1.7	7.90	1.9	5.7	2.1
Apple juice 1	52.3	0.8	4.09	1.9	1071	1.0	44.0	1.4	13.5	0.5
Apple juice 2	57.3	0.8	0.30	0.1	1061	0.7	43.08	1.3	12.6	0.6
Grape juice	115.2	0.5	3.35	1.3	1152	0.9	72.5	0.3	21.8	0.2
Cherry juice	69.9	0.5	3.44	0.5	1098	0.4	62.8	0.4	11.1	0.2
Cola	0.86	1.6	0.15	3.4	70.9	0.5	< 0.04		68.0	0.5

For two samples comparative values by the manufacturer or the water supply were available.

Table 7: Comparative values by manufacturer

Sample with known values	Ca	Fe	K	Mg	Na
	Conc.	Conc.	Conc.	Conc.	Conc.
	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]
Mineral water 2	107	-	13	39	258
Tap water	47	0.007	1.3	7.9	5.4

Conclusion

This application example can be easily performed using the flame mode of novAA 800 F/D, ZEEnit 700P or contrAA 800 F/D, each in combination with the autosampler AS-FD with automatic dilution function. The High Resolution Continuum Source AAS (HR-CS-AAS) of the contrAA 800 F/D enables additionally the fast sequential measurement of several analytes out of one sample solution as well as the side pixel evaluation on the wing of the respective resonance line. Finally, with this optimized method for the analysis of minerals in beverage the sample throughput of the latter is significantly higher. The total measurement time e.g. for ten beverage samples – that ought to be analyzed for all five elements with the described calibration protocol – will be about one hour on the continuum source AAS instrument contraAA 800. For the novAA 800 and ZEEnit 700P, that utilizes element-specific hollow cathode lamps, these measurements will take up to 90 minutes instead.

For further application, like additional determination of toxic elements or other trace elements, the novAA 800 D and contrAA 800 D with its dual atomizer concept can be easily adapted to the graphite furnace mode. The ZEEnit 700P with its ONE + ONE atomizer compartment is ready to use for flame and graphite furnace mode without any hardware adaptation. Furthermore, all devices can be equipped with a hydride system for the determination of mercury and hydride forming elements.

Table 8: Advantages and detection limits by device

Quality control of non-alcoholic beverages	novAA 800 F/D	ZEEnit 700P	contrAA 800 F/D
Advantages	■ Automatic dilution with AS-FD ■ Performance enhancing flame accessory	■ Automatic dilution with AS-FD ■ Performance enhancing flame accessory	■ Side pixel evaluation ■ Best detection limits ■ Automatic dilution with AS-FD ■ Performance enhancing flame accessory
Detection limits			
Ca	6 µg/L	6 µg/L	0.76 µg/L
Fe	8 µg/L	8 µg/L	1.6 µg/L
K	0.7 µg/L	0.7 µg/L	0.55 µg/L
Mg	1 µg/L	1 µg/L	0.15 µg/L
Na	1 µg/L	1 µg/L	0.2 µg/L

This document is true and correct at the time of publication; the information within is subject to change. Other documents may supersede this document, including technical modifications and corrections.

Headquarters
Analytik Jena GmbH+Co. KG
Konrad-Zuse-Strasse 1
07745 Jena · Germany

Phone +49 3641 77 70
Fax +49 3641 77 9279

info@analytik-jena.com
www.analytik-jena.com

Version 1.1 | Author: AnJu
en · 09/2023
© Analytik Jena GmbH+Co. KG | Pictures: © pixabay/ rawpixel