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Determination of brominated vegetable oils in soft drinks using combustion ion chromatography

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ABSTRACT

Purpose: To demonstrate determinations of brominated additives, specifically brominated vegetable oils (BVO), in carbonated beverages using pyro-hydrolytic combustion ion chromatography.

Methods: Fifty-µL aliquots of carbonated beverage samples were pyro-hydrolytically combusted at 900 to 1000 °C in argon and oxygen-argon atmospheres. The resultant bromine was absorbed in 30 mg/L hydrogen peroxide solution, after which a 100-µL aliquot was analyzed for anions. Bromine as bromide was separated by anion-exchange chromatography on a 4 mm i.d. Thermo Scientific™ Dionex™ IonPac™ AS18-4µm column using electrolytically generated 23 mM KOH at 30 °C and 1 mL/min. Using overlap mode for the 5 min combustion, the total analysis time is 13 min after the first sample, which requires 18 min.

Results: The method had good accuracy with recoveries within 90–102% and good reproducibility with <3% RSDs. The LOD was determined using the 0.5 mg/L bromide standard (n = 7, 3 × S/N) and found to be 0.34 mg/L. The linearity was determined by triplicate injections of standards from 0.5 mg/L to 25 mg/L bromide, the results showed a linear relationship with a coefficient of determination, r2 = 0.998. The method was applied to three carbonated beverages and two ginger beer samples. Bromide from total BVO was found at expected levels in one of the carbonated beverages and unexpectedly found at trace levels in another carbonated beverage. BVO was not detected in the other three samples.

INTRODUCTION

Brominated vegetable oil (BVO), is a food additive used to emulsify citrus flavoring and provide a stable mixture in carbonated beverages. BVO is a heterogenous fatty acid composed of plant-based oils which are brominated at the previously unsaturated bonds.[1]

Analytical methods are needed for BVO determinations to maintain the beverage quality and to meet labeling requirements. In addition, the use of BVO as an additive is controversial, banned in many Asian and European countries and is limited to 15 mg/L with increasing public scrutiny in the U.S.

However, the determinations are challenging because BVO exists as a non-polar suspension in an ionic sample matrix. Pyrolytic combustion ion chromatography is an ideal approach to eliminate the sample matrix and increase sample homogeneity.

This poster demonstrates a method to determine brominated compounds in juice and carbonated beverages.

MATERIALS AND METHODS

Reagents

ACS Grade acetone, used as the diluent for BVO.

Brominated vegetable oil (BVO), food grade (Fisher Scientific P/N NC0415602), S.G. 1.325-1.335. No assay or Formula Weight was provided.

Sample Preparation

Samples: The carbonated beverages and ginger beer samples were purchased locally. Carbonated beverages 1, 2, and 3 are transparent without color, slightly opaque with yellow-green hue, and slightly opaque with a white hue, respectively. The ginger beer beverages were slightly opaque without color.

Initially, the samples were degassed by filtration with applied vacuum which was found to remove the BVO suspension. Samples shown here were analyzed after degassing applied by ultrasonic agitation.

Method

Equipment

- Mitsubishi Chemical Analytech™ Automatic Combustion Unit Model AQF-2100H system, including: Automatic Boat Controller Model ABC-210, Liquid Sample Changer Model ASC-250L, Horizontal Furnace Model HF-210, Gas Absorption Unit GA-210, External Solution Selector ES-210
- Thermo Scientific™ Dionex™ Integrion™ HPIC™ system, RFIC model including Detector Compartment Temperature Control, Eluent Generation, Integrion IC Conductivity Detector

Conditions

Pyrolysis/combustion conditions: AQF-2100H system	
Sample size combusted:	50 µL
Sample boat:	Quartz with quartz wool
Pyrolysis tube:	Quartz tube with ceramic insert and quartz wool at exit
Combustion run time:	5 min in overlap mode
Absorption solution:	30 mg/L hydrogen peroxide in ASTM Type I deionized (DI) water
Mode:	Constant volume
Ion Chromatography conditions: Dionex Integrion HPIC system	
Columns:	Dionex IonPac AG18-4µm guard, Dionex IonPac AG18-4µm, 4 mm i.d.
Eluent:	23 mM KOH from Thermo Scientific™ Dionex™ EGC 500 KOH eluent generator cartridge, Thermo Scientific™ Dionex™ CR-ATC 600 trap column, and high pressure degas device
Flow rate:	1 mL/min
Injection volume:	100 µL aliquot from collected, combusted sample in GA-210 Gas Absorption Unit
Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ ADRS 600 dynamic anion suppressor, 4 mm, 57 mA, constant current and recycle modes
Mode:	Constant volume
Temperatures:	Column: 30 °C, Detection/suppressor: 15 °C
Run time:	IC: 9 min, total run time: 13 min in overlap

Data Analysis

- Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.2 SR9
- Mitsubishi NSX-2100 version 2.1.6.0.

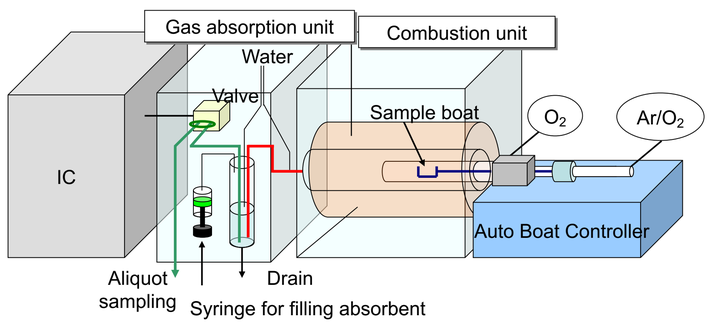

Figure 1. Combustion IC Diagram.

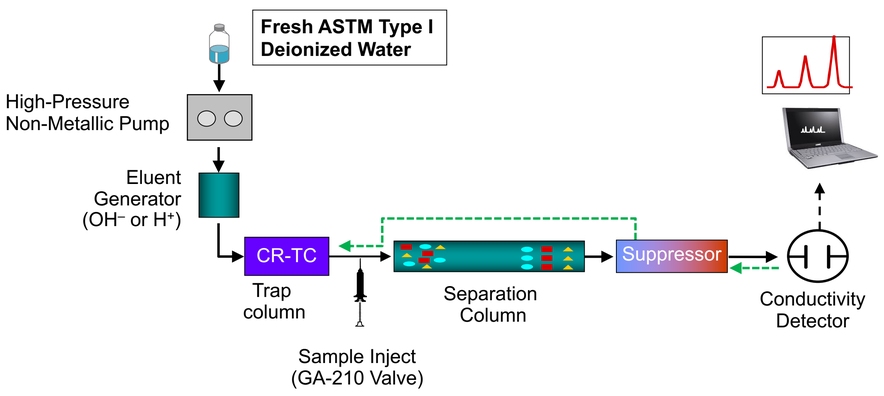

Figure 2. Flow Diagram for a Dionex Reagent-Free IC System in recycle mode.

RESULTS

BVO Composition

BVO is a heterogenous triglyceride composed of three plant-based fatty acids (colloquially called oils), which are brominated at the previously unsaturated bonds. The BVO chemical composition varies due to the types of fatty acids, plant source, and local and seasonal variations of the crop. As a result, three compositions of BVO have been reported.[1] Figure 3 shows one of the possible chemical structures of BVO.[2] In the U.S., BVO is commonly made from soybean oil, which typically contains: >50% as linoleic (C18:2) or α-linolenic (C18:3)), 15 to 20% as oleic (C18:1), and 15 to 20% as palmitic (C18:0)). BVO based on the structure shown in Figure 3 contains ~21% bromine.

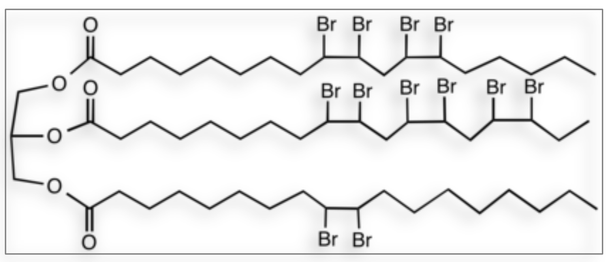

Figure 3. One of proposed chemical structures of BVO.

A BVO reagent was obtained but without assay and molecular composition, however it was used in method development to estimate the response of BVO. The BVO was diluted in acetone for the stock standard and found to remain in solution when further diluted in DI water. Figure 4 compares the response of BVO and bromide.

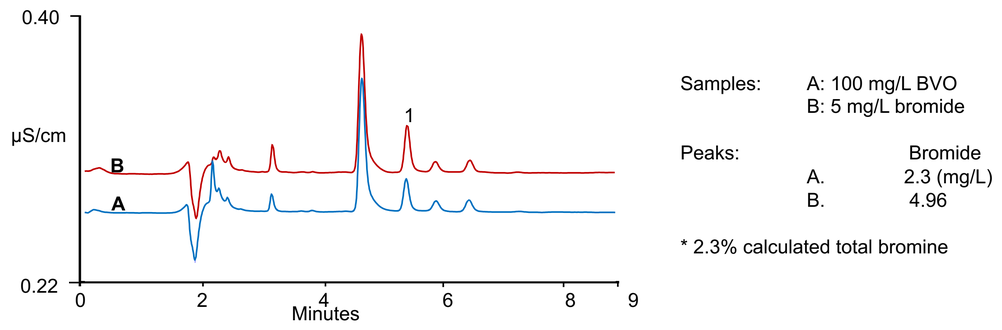

Figure 4. Comparison of a) 100 mg/L BVO in acetone and B) 5 mg/L bromide.

Method Linearity and MDL

The peak area response to concentration was determined using the responses of six standards (n =3) from 1 to 20 mg/L bromide and found to be linear with a coefficient of determination r^2 = 0.998. MDL was determined using a 0.5 mg/L standard (n=7, at 3x S/N), estimated at 0.34 mg/L.

Sample Analysis

The method was applied to three carbonated beverages and two ginger beer beverages. Sample C noted the presence of BVO additive on the label. Figure 5 shows the chromatogram of Sample C and with 2 mg/L bromide added. Recoveries were determined in the carbonated beverages. The results are shown in Table 1.

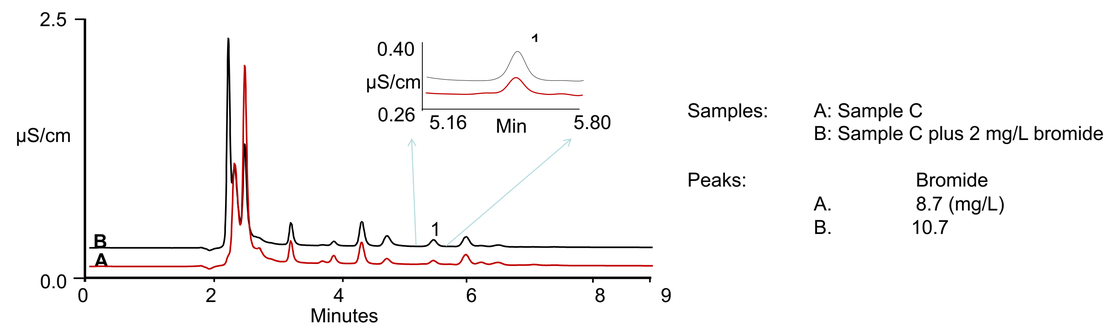

Figure 6. Comparison of A) Sample C and B) Sample C with 2 mg/L bromide added.

Table 1. Summary of Recovery Results.

Carbonated Beverage Sample	Free Bromide (mg/L)	Total Measured (mg/L)	RSD (%)	Added (mg/L	Recovery		
					(mg/L)	RSD	(%)
A (clear)	ND	ND	--	0.5	0.45	2.2	90
B (Opaque, white)	0.007	< LOD	--	0.5	0.51	2.8	102
C* (yellowish-green)	0.049	8.7	2.5	2	10.7	1.9	100

*BVO was listed on the label

CONCLUSIONS

- Combustion IC (CIC) provides an automated and fast method to determine total and free halides in complex and challenging sample matrices, such as an oil-based food additive in carbonated beverages, by eliminating the sample matrix.
- In this application, mg/L determinations of bromide from BVO were applied to the analysis of three carbonated beverage samples.
- This technique could be used to profile incoming lots of BVO for the bromination as well as to determine BVO in carbonated beverage formulations.
- More information on CIC and CIC applications can be found on the Thermo Scientific website and on the Thermo Fisher Scientific AppsLab Digital Library.[2,3]

REFERENCES

1. Bendig, P.; Maier, L.; Lehnert, K.; Knapp, H.; Vetter, W. Mass spectra of methyl esters of brominated fatty acids and their presence in soft drinks and cocktail syrups. Rapid Commun. Mass Spectrom. 2013, 27, 1083–1089.
2. Thermo Scientific Application Note AN72917 Fast determinations of brominated compounds in carbonated beverages using oxidative pyrolytic combustion and ion chromatography
3. https://appslab.thermofisher.com

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