Application Note 251

Screening foods and beverages for butylated hydroxytoluene (BHT) using automated headspace–trap GC–MS

This study shows that headspace samples acquired on the new Centri® automated multi-mode sampling and concentration system for gas chromatography–mass spectrometry (GC–MS) can be used to screen food and beverages for trace-level additives. A breakfast cereal and a tea infusion were investigated, and the antioxidant BHT detected in both samples at the ng/g level, along with a range of aroma compounds.

Butylated hydroxytoluene (BHT, 3,5-di-*tert*-butyl-4-hydroxy-toluene) is one of a number of antioxidants added to foodstuffs to slow down the rate of oxidation processes that are a major factor in spoilage. It is also widely used as an antioxidant in cosmetics, pharmaceuticals and industrial oils. Although classified by the US Food and Drug Administration as 'GRAS' (generally recognised as safe), the use of BHT in food is the subject of some concern because of uncertainties over health risks, and this has led to a need for continued monitoring.

In this study we demonstrate the fully automated sampling and detection of BHT in two foodstuffs (a rice-based breakfast cereal and an infusion of black tea) using syringe headspace sampling with trap-based focusing on the new Centri automated multi-mode platform, in conjunction with GC–MS.

The headspace profiles (Figure 1) show detection of BHT in both samples, with the black tea infusion also displaying a large number of aroma compounds. These include hexanal (#3) and *trans*-hex-2-enal (#5) as major components, which contribute 'green/grassy' notes to tea, and both α-ionone (#29) and β-ionone (#30), which although minor components have a low odour threshold, with significant 'woody/floral' aromas.

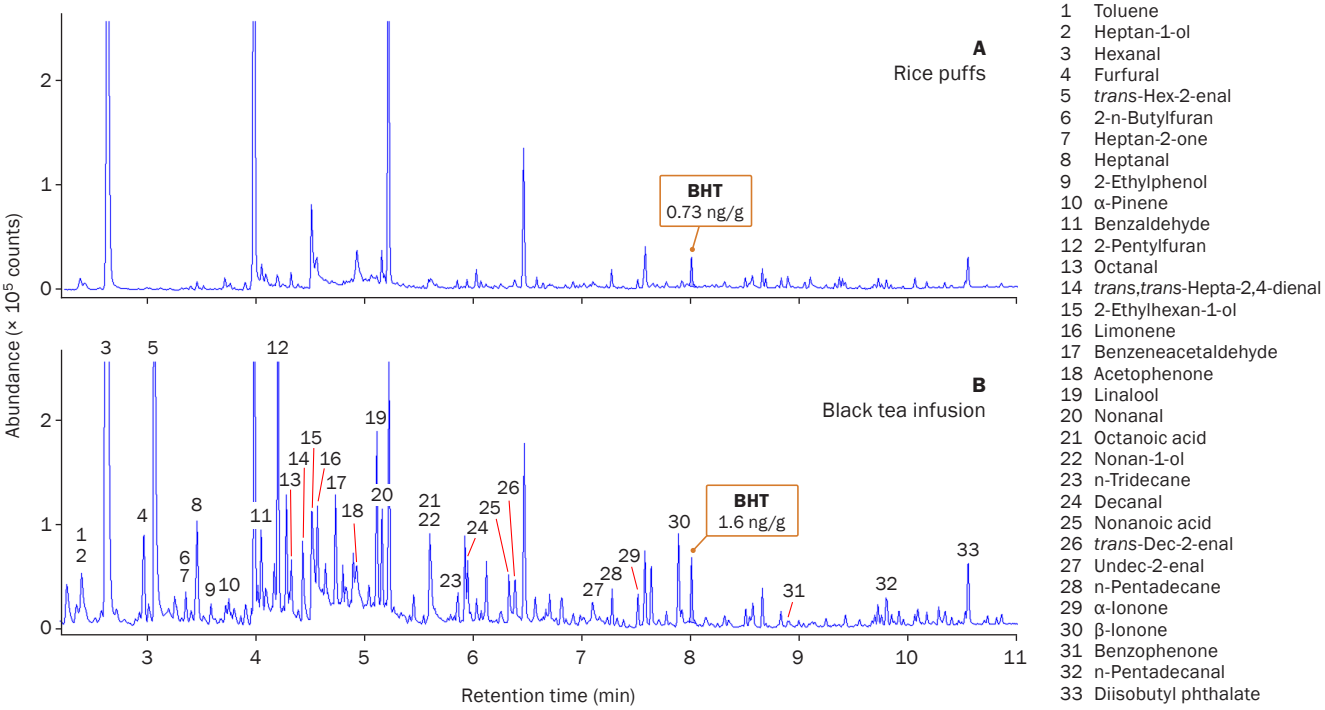

Figure 1: Headspace profiles of (**A**) rice puffs and (**B**) black tea infusion. BHT is indicated in both cases, and the black tea infusion shows a large number of aroma compounds.

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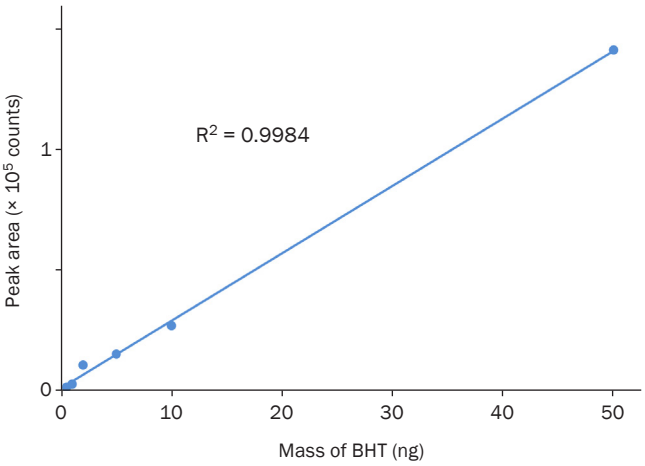

Figure 2: Six-point calibration of BHT from 1–50 ng, showing a high degree of linearity.

Quantitation for BHT was achieved on the basis of a six-point calibration curve from 1–50 ng (Figure 2), and indicated concentrations of 0.73 ng/g for the rice puffs, and 1.6 ng/g for the black tea infusion.

Two features of this analysis combine to allow sub-nanogram sensitivity for headspace sampling:

- The use of analyte re-focusing on the Centri focusing trap results in better GC–MS peak shape compared to headspace methods that do not use analyte focusing.
- The use of a very low 2:1 split ratio for the injection means that a large proportion of the sample is sent to the GC–MS. On many trap-based systems, the use of such a low ratio would result in poor peak shape, but this is avoided with Centri because of the optimised design and highly efficient backflush desorption of the focusing trap.

In conclusion, we have shown the ability of Centri to offer highly sensitive headspace–trap analysis of foods and beverages for improved detection of trace-level additives and aroma compounds. This capability is complemented by the other sampling modes available with Centri – HiSorb high-capacity sorptive extraction, thermal desorption and SPME – all of which can benefit from cryogen-free trapping for enhanced sensitivity. In addition, by allowing unattended sequential analysis of multiple sample types using different injection modes, Centri greatly improves efficiency for high-throughput laboratories.

Experimental

Sample:
Rice puffs: 1 g.
Black tea infusion: 1 g of dried leaves with 10 mL of water.

Headspace–trap:

Instrument:	Centri (Markes International)
Equilibration:	80°C for 30 min with agitation at 300 rpm
Injection volume:	1 mL of headspace
Cold trap:	'Material emissions' (part no. U-T12ME-2S)
Trap flow:	50 mL/min
Trap desorption:	40°C to 290°C (3 min)
Outlet split:	2 mL/min
Flow path:	180°C

Background to Centri®

Markes International's Centri system for GC–MS is the first platform to offer high-sensitivity unattended sampling and pre-concentration of VOCs and SVOCs in solid, liquid and gaseous samples.

Centri allows full automation of sampling using HiSorb™ high-capacity sorptive extraction, headspace, SPME, and tube-based thermal desorption. Leading robotics and analyte-trapping technologies are used to improve sample throughput and maximise sensitivity for a range of applications – including profiling of foods, beverages and fragranced products, environmental monitoring, clinical investigations and forensic analysis.

In addition, Centri allows samples from any injection mode to be split and re-collected onto clean sorbent tubes, avoiding the need to repeat lengthy sample extraction procedures and improving security for valuable samples, amongst many other benefits.

For more on Centri, visit www.markes.com.

GC:

Column:	HP-5ms™, 30 m × 0.25 mm × 0.25 µm
Column flow:	2 mL/min
Oven program:	35°C (5 min), 10°C/min to 150°C (1 min), 30°C/min to 280°C (5 min).
Inlet:	220°C
Aux heater:	280°C

Quadrupole MS:

Scan mode:	Rice puffs: m/z 35–300; Black tea infusion: m/z 45–350
Source:	Rice puffs: 250°C; Black tea infusion: 300°C
Transfer line:	290°C
BHT quantitation:	Quantifier m/z 205; Qualifier m/z 220

Software:
TargetView™ GC–MS software (Markes International) was used to selectively remove unwanted background noise and to deconvolve analyte peaks, improving the identification of lower-level analytes during subsequent automated comparison against a customised library generated from spectra in the NIST 2017 database.

Applications were performed under the stated analytical conditions. Operation under different conditions, or with incompatible sample matrices, may impact the performance shown.

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