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Rapid Screening for Phthalates in Food and Beverages Using Atmospheric Solids Analysis Probe (ASAP) with Xevo TQ MS

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Abstract

This Application note demonstrates screening for phthalates in food and beverages using a simple and rapid technique with minimal sample preparation and no chromatographic separation.

Benefits

- Qualitative screen for phthalates in food and beverages in less than two minutes, increasing sample throughput and lab efficiency.
- Minimal sample preparation necessary; eliminates the use of different extraction techniques for complex food matrices.
- Provides detection of phthalates at legislated control levels

Introduction

Phthalates (esters of phthalic acids) are additives that are widely used in plastics and other materials,

primarily to make them soft and flexible. They are used in industry as well as in medical and consumer products. Since phthalates are not chemically bound to plastics, they can be easily released into the environment. Thus, phthalates present in packaging materials may also be released into foods and beverages.

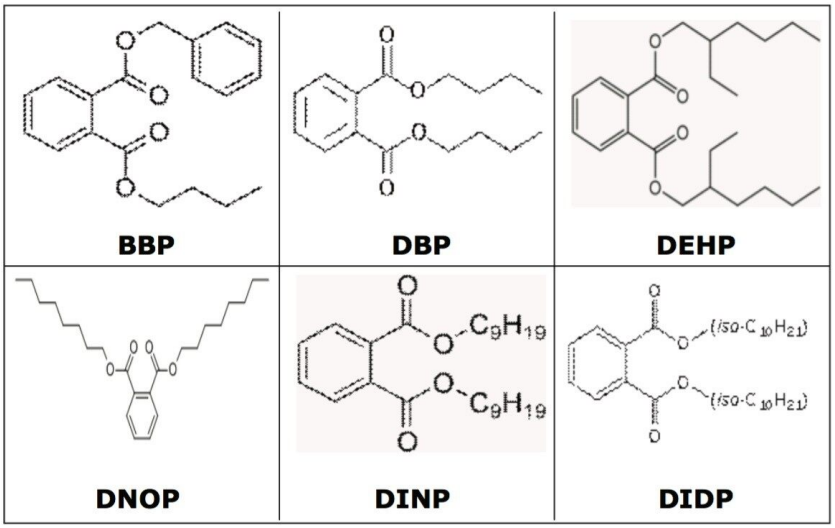

Figure 1. Chemical structures of the phthalates investigated.

In June 2011, a notification was sent out by the U.S. Food and Drug Administration (FDA) to manufacturers of food products and suppliers of food ingredients regarding the potential adulteration of emulsifiers with undeclared phthalate plasticizers; specifically di-2-ethylhexyl phthalate (DEHP).[1] In May 2011, the Taiwan Food and Drug Administration (TFDA) found DEHP in powdered probiotics, which was traced back to the clouding agent (emulsifier) supplier. This so-called clouding agent is a legal food additive that is commonly used in beverage, food, and dietary supplements. Clouding agents are generally made of acacia gum, emulsifier, palm oil, and various food additives. However, the supplier intentionally replaced the additives with DEHP in order to maximize profits.

Phthalates have long been considered as potential endocrine disrupters. Consumption of plasticizer-tainted food or beverage products increases the risk of reproductive abnormalities.[2] The regulations of Food Containers and Appliances (Taiwan) mandate that the maximum level of DEHP dissolved from plastic items must not exceed 1.5 ppm, and direct addition of DEHP to food is not permitted.

The U.S. FDA initiated a heightened surveillance program to screen suspect food products from Taiwan for DEHP and other plasticizers, such as butylbenzyl phthalate (BBP), di-n-butyl phthalate (DBP), di-n-octyl phthalate (DNOP), di-isononyl phthalate(DINP), and di-isodecyl phthalate (DIDP). Food safety regulators

require that all products found to be contaminated with phthalates must be recalled and removed from shelves immediately. Rigorous tests were carried out on various food and beverage products, including sport drinks, fruit juices, teas, fruit jams and jellies; food powders, and dietary supplement tablets.

This poses a major analytical challenge because the complexity of the food matrices requires the use of different extraction techniques. Thus the ability to rapidly screen for the presence of phthalates using a simple technique with minimal sample preparation and no chromatographic separation would be advantageous.

This application note describes a rapid screening method for phthalates in food and beverages using the Atmospheric Solids Analysis Probe (ASAP), coupled with Xevo TQ MS. The time required from sample preparation to analysis takes less than two minutes. This initial quick screening enables food testing labs to reduce the number of samples that require testing, allowing for faster turnaround times. Only those samples that show positive results can then be submitted for further confirmatory and quantitative analysis.

Experimental

ASAP analysis method

The ASAP analysis procedure is shown in Figure 2.

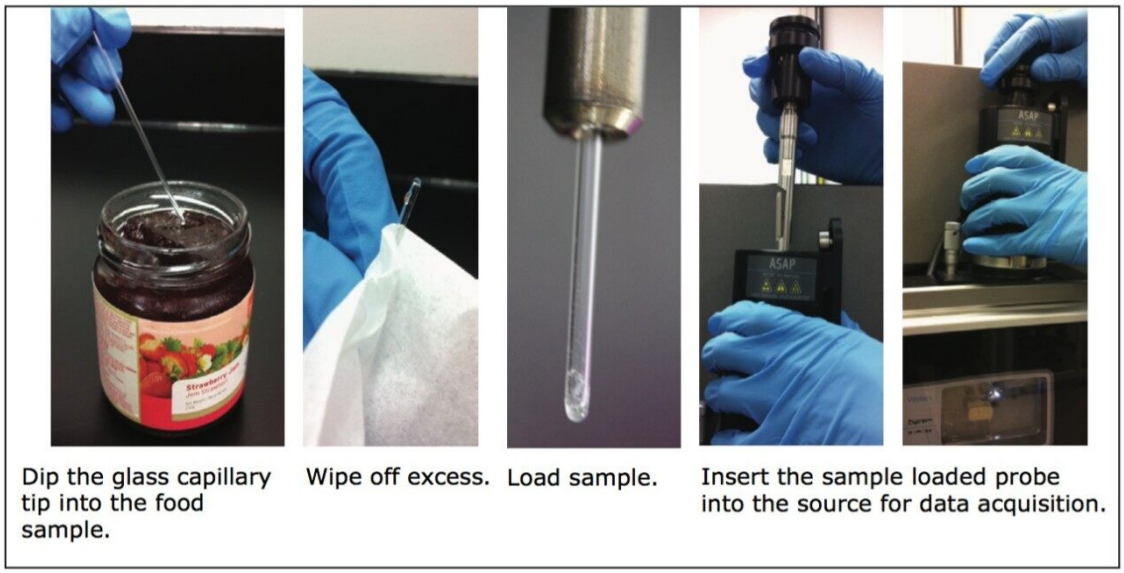

Figure 2. Sample preparation and loading for ASAP analysis.

MS conditions

Ionization mode:	ASAP positive
Corona current:	10µA
Cone voltage:	30 V
Source temp.:	150 °C
Desolvation gas:	800 L/hr
Acquisition time range:	0.3 to 1.5 min
Probe temp.:	100 °C (initial) to 450 °C

Sample preparation

The glass capillary was first dipped into the food sample, and any excess sample was wiped off with a lint-free tissue. The sampling method varies slightly depending on the matrix type, as shown in Table 1. The capillary was then attached onto the ASAP probe and loaded directly into source enclosure of the Xevo TQ

MS. The desolvation gas was rapidly heated to 450 °C, and MRM data were acquired using the MS tune page conditions specified on page 3. IntelliStart Software was used to automatically develop MRM acquisition methods for the six phthalate compounds targeted in this analysis, as described in Table 2. IntelliStart requires only the entry of basic compound information, and it automatically locates the precursor ion, and optimizes the cone voltages and collision energies.

Matrix type	Sample prep method	Examples
Solid	1) Grind sample into powder 2) Dip capillary into sample 3) Wipe off excess 4) Analyze	Health supplement tablets (whole-form), biscuits
Solid (powder)	1) Dip capillary into sample 2) Wipe off excess 3) Analyze	Milk powder, grounded spices
Liquid	1) Dip capillary into sample 2) Wipe off excess 3) Analyze	Syrup, fruit juice, milk
Gel-like	1) Dip capillary into sample 2) Wipe off excess 3) Analyze	Jams, creams

Table 1. Sampling method for various food matrices.

Analyte	Precursor ion	Product ion	Cone voltage (V)	Collision energy (eV)
BBP	313.14	149	17	11
		205		7
		239		5
DBP	279.16	149	20	14
		205		17
*DEHP	391.28	149		20
		167	19	14
		279		9
*DNOP	391.28	149	18	12
		261		10
		121		40
DINP	419.31	149	15	26
		275		12
		293		13
DIDP	447.35	149	18	25
		289		9
		307		11

*Table 2. MRM parameters for phthalates. (*DEHP and DNOP are isomers).*

Results and Discussion

The list of six prohibited phthalates (DEHP, BBP, DBP, DNOP, DINP, and DIDP) was rapidly screened in food and beverages using the Atmospheric Solids Analysis Probe (ASAP) coupled with Xevo TQ MS. In this experiment, four food matrices were screened for the presence of phthalates: flavored syrup, fruit juice, jam, and dietary supplement tablets. In all cases, minimal sample preparation was required, as described in the Experimental section. No chromatographic separation is necessary for the analysis.

Figure 3 shows the TIC traces of six phthalates detected in fruit juice in comparison with the matrix blank.

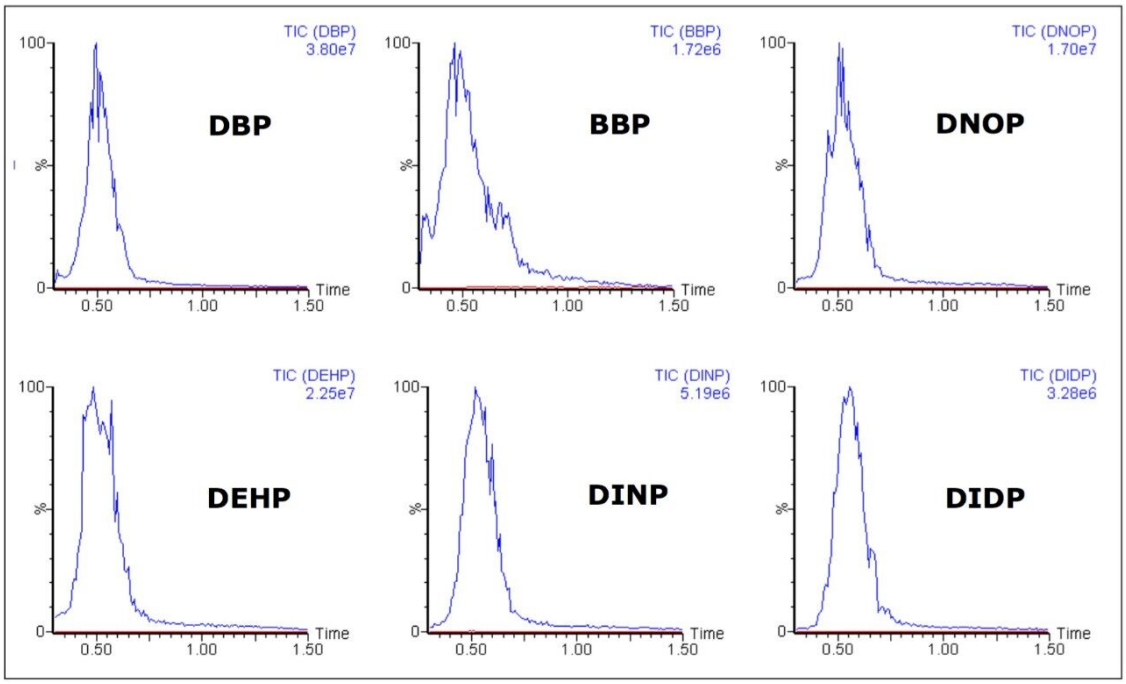

Figure 3. TIC traces of the six phthalates analyzed, spiked at 1 ppm (blue trace) versus blank (red trace) in fruit juice.

The phthalates were successfully detected at 1 ppm, which is below the levels stipulated by the Food Containers and Appliances (Taiwan). MS analysis was completed in less than 1.5 min, and the total time from sample preparation to analysis was achieved in less than 2 min.

Of particular interest among the six phthalates is DEHP, which was the plasticizer contaminant first found in the clouding agents in Taiwan. The results of detection of DEHP in various food matrices using ASAP/Xevo TQ MS are illustrated in Figure 4.

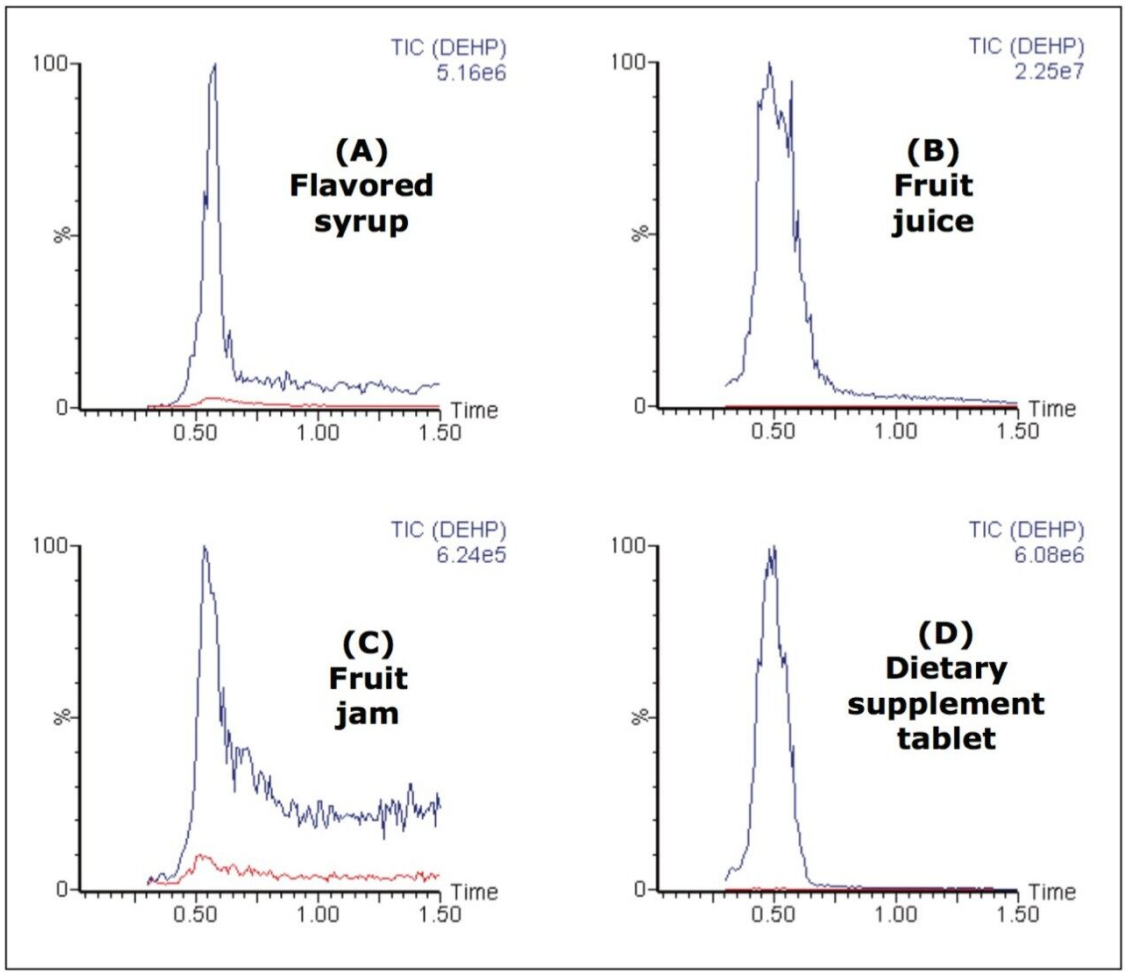

Figure 4. TIC traces of DEHP spiked at 1 mg/kg (blue) versus blank (red) in flavoured syrup (A), fruit juice (B), fruit jam (C), and dietary supplement tablets (D).

These results demonstrate the potential of using ASAP for quick screening of DEHP and other prohibited phthalates in food regulatory and contract testing labs that require fast turnaround analysis times.

As a new capillary is used for every sample, the chances of sample carry-over are greatly reduced. This would also minimize the number of false positives in the screening of these food products.

Conclusion

In this application note, we have described how the Atmospheric Solids Analysis Probe (ASAP) combined

with Xevo TQ MS, provide qualitative screening for phthalates in food and beverages. This solution provides a rapid preliminary screening method for phthalates, where potentially contaminated samples will be further analyzed and quantified by GC-MS and LC-MS methods.

The interchangeable source design on the Xevo TQ MS provides an added advantage by allowing rapid change over from the ASAP Probe to an ESI source for LC-MS analysis of suspected positive samples. The ability to quickly and reliably screen for phthalates in a variety of food and beverage matrices greatly improves lab productivity and efficiency. With reduced gas and solvent usage, the environmental impact is also minimized.

References

1. U.S. Food and Drug Administration. Food News, Notification to Industry,22 June 2011. http://www.fda.gov/Food/ResourcesForYou/FoodIndustry/ucm260291.htm
2. Agency for Toxic Substances and Disease Registry. http://www.atsdr.cdc.gov/

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