# DIFFERENTIATING PHTHALATE ISOMERS WITH MULTI-PASS CYCLIC ION MOBILITY AND RAPID SCREENING IN COSMETIC AND PERSONAL CARE PRODUCTS

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## OVERVIEW

- **Ion mobility separation of C8 phthalate isomers was accomplished with the SELECT SERIES™ Cyclic™ IMS Mass Spectrometer.**
- **Direct analysis with the atmospheric solids analysis probe (ASAP™) allowed for the detection and identification of additives in consumer products.**
- **Additives were identified using accurate mass and CCS values.**

## INTRODUCTION

Phthalates (esters of phthalic acid) are a group of chemical additives that are used extensively in plastic manufacturing in a range of consumer and household products. Phthalates are also used as plasticizers, solubilizers, or denaturants in cosmetics and personal care products such as perfumes, nail polishes and hair spray.[1] Concern about the prevalence of this class of compounds and other additives in consumer and household products is rising. Many phthalates are classified as hazardous because of their effects on the reproductive system and they have an association with an increased risk of cancer.[2]

Direct analysis MS like the atmospheric solids analysis probe (ASAP) allow for rapid screening for phthalates and other additives in cosmetic and consumer products with little to no sample preparation. While phthalate detection can be accomplished in this rapid screen, identification of the different phthalate isomers requires an extra dimension of separation such as ion mobility. Phthalate isomers can be very similar structurally and a high resolving power in the ion mobility dimension is needed for a confident identification. The unique geometry of the Cyclic IMS allows for the scaling of the IMS dimension utilizing multi-pass acquisitions to get baseline resolution of the different phthalate isomers.

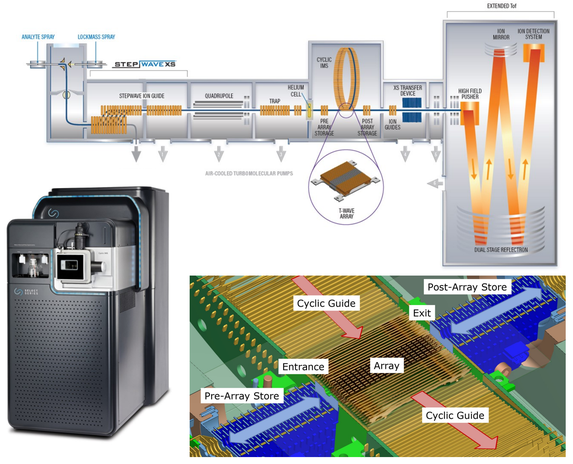


*Figure 1. (Top) Schematic of the SELECT SERIES Cyclic IMS Instrumentation. It contains three main regions: the trap region, the cyclic ion mobility device, and the transfer region. (Bottom) Zoom in of the cyclic ion mobility*

## ION MOBILITY SEPARATION OF PHTHALATE ISOMERS

Different C8 phthalate isomers (di-n-octyl phthalate, bis (2-ethylhexyl) phthalate, and dioctyl terephthalate) were analyzed with direct infusion and ESI$^+$ to test the ion mobility separation. Two ions were generated: the protonated species and the sodium adducts (figure 2).

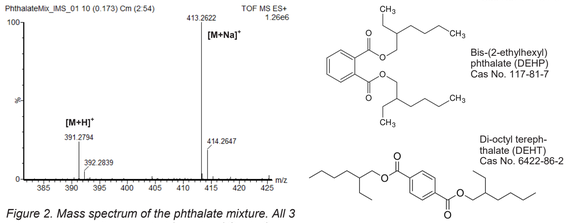





*Figure 2. Mass spectrum of the phthalate mixture. All 3 compounds have the chemical formula of $C_{24}H_{38}O_4$.*

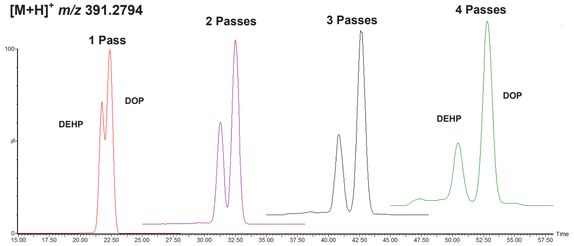


*Figure 3. Ion mobility traces showing separation of DEHP and DOP as [M+H]$^+$ ions with multiple passes in the Cyclic IMS.*

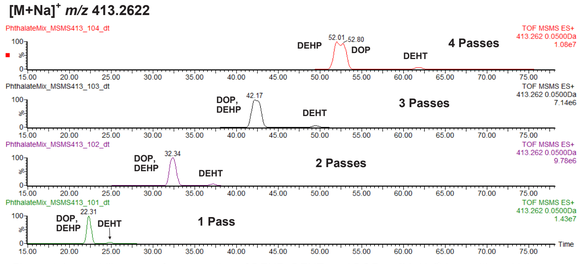


*Figure 4. Ion mobility traces for separation of DEHP, DEHT, and DOP as [M+Na]$^+$ ions with multiple passes in the Cyclic IMS.*

## ASAP ANALYSIS

Direct analysis MS with ASAP was used for rapid screening for additives in a variety of cosmetic and consumer products with little to no sample preparation. First, a glass capillary was dipped into the product and excess material was wiped off. The capillary was then loaded into the ASAP probe and the probe was placed into the source for data acquisition. With ASAP, ions are generated with thermal desorption using heated nitrogen and corona discharge for sample ionization.


**ASAP Parameters:**
Corona current: 3 µA
Cone Voltage: 20V
Desolvation Gas Flow: 600 L/h
Cone Gas Flow: 50 L/h
Temperature Ramp: 50-500 °C
Source Temperature: 100 °C
MS Analyzer Mode: V Mode

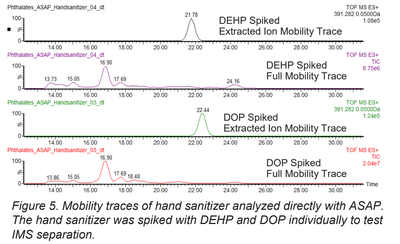


*Figure 5. Mobility traces of hand sanitizer analyzed directly with ASAP. The hand sanitizer was spiked with DEHP and DOP individually to test IMS separation.*

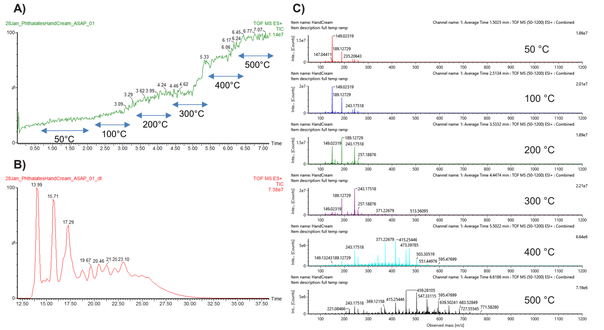


*Figure 6. Example data for the ASAP analysis of a hand cream. A) Total ion chromatogram across the temperature ramp. B) Ion mobility trace for all ions detected. C) Mass spectra generated at different temperatures.*

## ASAP ANALYSIS RESULTS

ASAP experiments were performed with six different commercial products. The data was processed with UNIFI™ Scientific Information System to generate a set of components that were uniquely defined by *m/z*, drift-time and retention time. The detected components were then searched against an experimentally derived database for extractables and leachables for compound identification.[3]

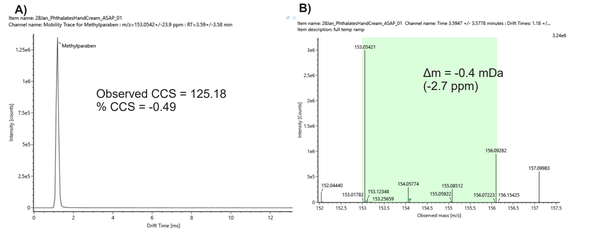


*Figure 7. A) Extracted drift trace for the ion identified as methylparaben in a hand cream sample. B) Mass spectrum for the ion identified as methylparaben at the observed drift time.*

*Table 1. Table of additives detected in cosmetic and consumer products. Criteria for identification was mass error <5 ppm and CCS %Delta <3% from the Waters Extractables and Leachables HRMS library.[3]*

| Compound Name | Hand Sanitizer | Hand Cream | Nail Polish | Mascara | Lip Gloss | Concealer |
|---|---|---|---|---|---|---|
| Erucamide | + | + | | | | + |
| Methylparaben | | + | | | | |
| Oxybenzone | | + | | + | + | ++ |
| Triphenyl phosphate | | | ++ | | | |
| Irgafos 168 phosphate | | | | | | + |
| Octadecanamide | + | | | + | | + |
| 4-tert-Octylphenol | + | | | + | | |
| 2-Aminobiphenyl* | + | | | + | + | |
| Phthalic anhydride | + | ++ | + | + | + | + |
| 2,4-dihydroxy-benzophenone | | | + | | | |

*2-Aminobiphenyl could not be distinguished from 4-Aminobiphenyl

## CONCLUSIONS

- **Ion mobility separation of C8 phthalate isomers was accomplished with multiple passes in the cyclic IMS.**
- **The flexibility of the SELECT SERIES Cyclic IMS ion source allows for direct MS analysis of samples with little to no sample preparation with ASAP.**
- **Additives were matched with entries in a HRMS library based on accurate mass and CCS values.**

**References**

1. Goh, E. and Gay, M. Rapid Screening for Phthalates in Food and Beverages using Atmospheric Solids Analysis Probe (ASAP) with Xevo TQ MS. Waters Application Note 720004066EN 2011.
2. Cooper, J. High Throughput Analysis of Phthalates and Parabens in Cosmetics and Personal Care Products Using UPLC with Mass Detection and Empower 3 Software. Waters Application Note 720005521EN 2015.
3. Cooper, J., Sanig, R, Barkinowitz, G., and Cabovska, B. Screening Workflow Using Ion Mobility-Mass Spectrometry for the Analysis of Extractables and Leachables. Waters Application Note 720006868EN 2020.

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