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Automated Extraction and GC/MS Determination of Phthalates in Consumer Products

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ABSTRACT

The US Consumer Product Safety Commission's (CPSC) Test Method CPSC-CH-C1001-09.3 [1], is used by testing laboratories for the determination of phthalate content in children's toys and child care articles covered by the standard set forth in the Consumer Product Safety Improvement Act Section 108. The CPSC determined that an appropriate combination of methods of extraction and analysis is sufficient to determine the concentration of the six regulated phthalates in most consumer products. The general manual approach is to dissolve the sample completely in tetrahydrofuran, precipitate any PVC polymer with hexane, filter and then dilute the solution with cyclohexane, and analyze by Gas Chromatography-Mass Spectrometry (GC-MS).

A combined autosampler and sample preparation robot commonly used for sample introduction in GC or HPLC can be used to perform a wide variety of sample preparation techniques using a single instrument set-up and associated control software. Among the autosampler capabilities controlled by MAESTRO software are filtration and centrifugation, both of which can be used to clean up polymer extracts for further analysis. The autosampler can be configured as part of a GC or LC system or can be used independently as benchtop workstation.

In this work, we demonstrate automated extraction of phthalates in consumer products based on CPSC method CPSC-CH-C1001-09.3 directly combined with GC-MS analysis of the extract. The entire extraction and analysis process is streamlined and helps reduce or eliminate exposure of laboratory personnel to potentially hazardous materials.

INTRODUCTION

Most polymer materials contain uniformly distributed additives that are used to alter the chemical or physical properties. For example, plasticizers, such as phthalates, can be added to polymers to make the final product more pliable. However, since the plasticizers are not chemically bonded to the polymeric material, they could potentially migrate into food or water or be inadvertently ingested through human contact.

Some phthalates have been found to have undesired toxicological effects. For this reason, the US Congress has permanently banned three types of phthalates (DEHP, DBP, BBP) and also banned (on an interim basis) three additional types of phthalates (DINP, DIDP, DnOP) in any amount greater than 0.1 percent (computed for each phthalate, individually) in children's toys and certain child care articles.. In order to ensure compliance with governmental health and safety regulations, it is necessary to monitor products for these compounds.

The sample preparation of polymers being monitored for their respective additives, is an important part of the overall analysis. The manual extraction procedures employed are often the rate-determining step and involve the use of hazardous chemicals and solvents. Typically, liquid dissolution of the polymer is first performed in order to release the compounds of interest located within the sample. A solvent, in which the polymer is not soluble, is then normally added to precipitate the polymer and leave the analytes of interest in solution. Filtration of the final extract is then performed prior to analysis by either GC or HPLC.

This general procedure can be applied to a wide variety of polymers and plastics. In this paper we show that the manual procedure established for the extraction of phthalates from consumer products comprised of polyvinylchloride (PVC) is easily automated using the GERSTEL MultiPurpose Sampler (MPS). The entire process is conveniently controlled using the MAESTRO software.

EXPERIMENTAL

Materials. A standard containing bis(2-ethylhexyl)phthalate, dibutyl phthalate, di-n-octyl phthalate, diisodecyl phthalate, diisononyl phthalate, and benzyl butyl phthalate at 1 mg/mL in cyclohexane was purchased from AccuStandard (#APP-9-PHTH-MIX). All solvents used were reagent grade or better.

A certified reference material sample consisting of the phthalates listed within method CPSC-CH-C1001-09.3 in a polyethylene matrix (CRM-PE001) was purchased from SPEX CertiPrep. This standard consists of diisodecyl phthalate (DIDP) and diisononyl phthalate (DINP) at concentrations of 30 mg/g and bis(2-ethylhexyl)phthalate (DEHP), butylbenzyl phthalate (BBP), diethyl phthalate, dimethyl phthalate, di-n-butyl phthalate (DBP), and di-n-octyl phthalate (DnOP) at 3 mg/g.

An generic, no-name toy duck product for small children was purchased from a local market. Three unknown (CPSC-1, CPSC-2, CPSC-3), incurred polyvinyl chloride samples were donated by a local CPSC testing facility. All polyvinyl chloride samples extracted were first cut into small pieces no larger than 2 mm and then weighed into glass 10 mL screw top vials and then placed onto the appropriate autosampler tray.

PTFE syringe filters, 17 mm, 0.45 μm, (Varian #A4170) in the GERSTEL syringe filtration format, were placed onto the appropriate autosampler tray.

Instrumentation. Automated extraction, clean-up, and introduction to the GC/MS system was performed using a MultiPurpose Sampler (MPS XL) in dual head configuration with a six position heated agitator, 2.5 mL ALEX syringe, and GERSTEL Syringe Filtration Option as shown in Figure 1. Analyses were performed using on a 7890 GC equipped with a 5975C Inert XL MSD with triple axis detector (Agilent Technologies), PTV inlet (CIS 4, GERSTEL). The MPS XL was fitted with a 10 μL liquid syringe for liquid introduction to the GC/MS.

Figure 1. GERSTEL MultiPurpose Sampler (MPS XL) with Syringe Filtration Option.

Analysis conditions.

PTV: baffled liner
split (20:1) or splitless
50°C; 12°C/s; 280°C (3 min)

Column: 30 m HP-5MS (Agilent)
$d_i = 0.25$ mm $d_f = 0.25$ μm

Pneumatics: He, constant flow = 1.0 mL

Oven: 50°C (1 min); 20°C/min;
310°C (5 min)

MSD: Full scan, 40-350 amu

SIM Parameters (Mass, Dwell):
Group 1: 5 min
(91, 10), (105, 10), (149, 10), (167, 10), (194, 10), (194, 10), (205, 10), (212, 10), (223, 10)
Group 2: 11.7 min
(91, 10), (149, 10), (167, 10), (206, 10), (279, 10)
Group 3: 13.7 min
(149, 10), (167, 10), (261, 10), (279, 10), (293, 10), (307, 10)

Standard preparation. From the stock standard, a set of standards was prepared for the low level calibration curve covering the range from 50-1000 ng/mL and a set of standards was prepared for the high level calibration covering the range from 5-100 μg/mL.

RESULTS AND DISCUSSION

The manual steps in the Test Method CPSC-CH-C1001-09.3 [1] include:

1. Weigh a 50 mg sample of polyvinyl chloride into a sealable glass vial.
2. Add 5 mL of THF to the sample.
3. Shake, stir, or mix the sample for at least 30 minutes to complete the dissolution. Sonication and/or gentle heating may be used to expedite dissolution. If the material is not completely dissolved, extend the mixing time for an additional 2 hours before proceeding.
4. Precipitate any PVC polymer with 10 mL of hexane for every 5 mL of THF used during dissolution.
5. Shake and allow at least 5 minutes for the polymer to settle.
6. Filter the THF/hexane solution through a 0.45 mm PTFE filter, collecting a few mL of filtered solution into a separate vial.
7. Combine 0.3 mL of the THF/hexane solution with 0.2 mL of internal standard (if used), and dilute to 1.5 mL using cyclohexane.
8. 1 μL is injected for GC/MS analysis.

As shown in Figure 2, the manual liquid-liquid extraction was easily translated into a MAESTRO Prep Sequence and was demonstrated to successfully prepare sample extracts for subsequent analysis by GC/MS.

We first determined that the solvents being used during the extraction were free of phthalates by taking an empty vial through the entire extraction procedure without adding a polymer sample. The resulting extract was then analyzed using the GC/MS method. No phthalates were detected from the extracted blank solvent sample.

The certified reference material samples were taken through the manual extraction procedure steps and the analysis results compared to those obtained for the same certified reference material sample extracted automatically using the MAESTRO Prep Sequence. Figure 3 shows a comparison of the results obtained using manual and automated sample preparation. The chromatograms show that performing automated liquid-liquid extraction does not adversely affect the resulting analysis of the extract.
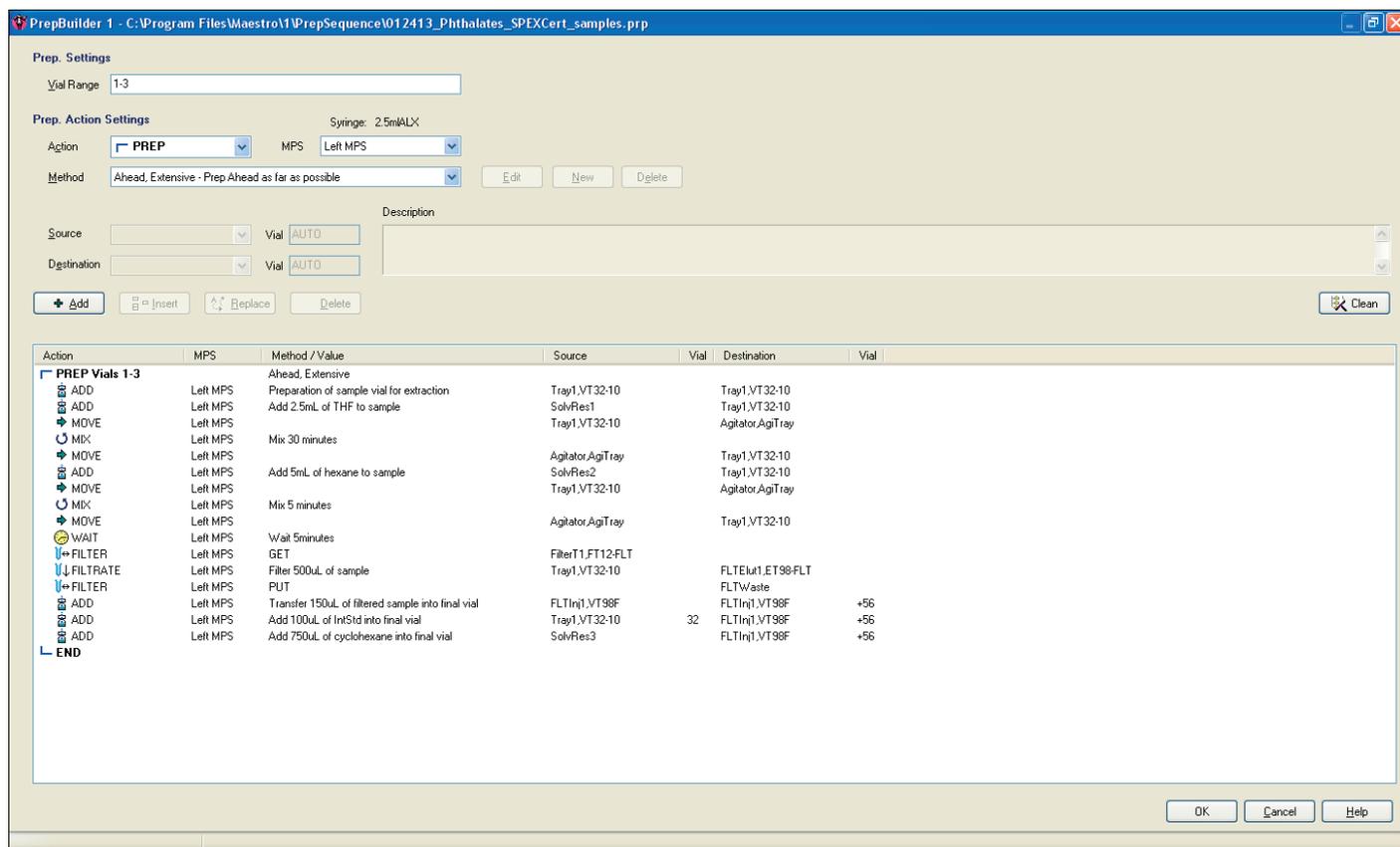
Figure 2. MAESTRO Prep Sequence for the automated liquid-liquid extraction procedure.
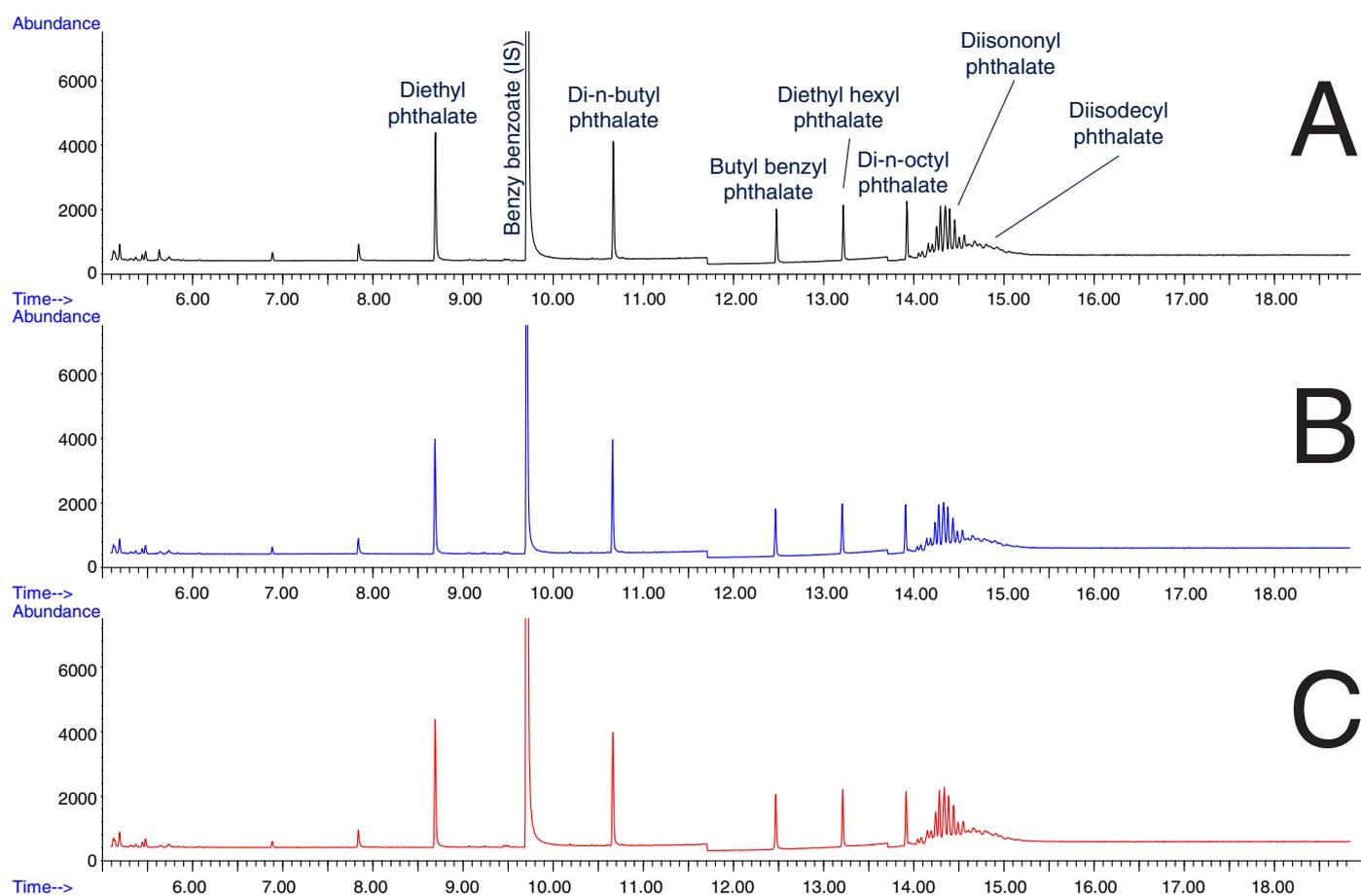

Figure 3. Stacked view of chromatograms resulting from automated 50 mg preparation (A), automated 25 mg preparation (B), and manual 25 mg preparation (C).

To increase total throughput of the system and avoid excessive use of harmful chemicals, we scaled all amounts of sample and solvents by a factor of 0.5. Also shown in Figure 3, is a comparison of chromatograms of 25 mg and 50 mg of the certified reference material taken through the extraction procedure using automation. The chromatograms show that decreasing the amount of the sample and solvents by 50 %, does not adversely affect the analysis results for the phthalates.

The duck and CPSC samples were run through the automated extraction procedure. The extracts were analyzed by GC/MS using split (20:1) and splitless introduction. The MS was run in SIM/Scan mode. The low level calibration curve was run in splitless mode, the high level calibration curve in split mode. Target analytes were identified based on retention time and mass spectra. The calibration curves were used to quantify the amount of each analyte found in the samples.

Sample CPSC-2 was run in triplicate to assess the precision of the overall analysis. The results are shown in Table 1. Samples CPSC-1 and 2 were found to contain all six target analytes. The replicates for sample CPSC-2 showed good precision with values ranging from 1.9-5.5 % RSD. Sample CPSC-3 shows high levels of DEHP.

Table 1. Weight percent phthalates found in samples using automated extraction.

Analyte*	DBP % w/w	BBP % w/w	DEHP % w/w	DnOP % w/w	DINP % w/w	DIDP % w/w	Total % w/w
CPSC-2 R1	0.642	0.360	0.252	0.630	0.710	0.304	2.90
CPSC-2 R2	0.586	0.336	0.226	0.575	0.642	0.299	2.66
CPSC-2 R3	0.607	0.342	0.235	0.599	0.664	0.293	2.74
Ave	0.612	0.346	0.238	0.601	0.672	0.299	2.77
%RSD	4.6	3.6	5.5	4.5	5.1	1.9	4.3
Duck	0.025	0.014	0.186		0.065		0.29
CPSC-1	0.121	0.124	0.206	0.111	0.138	0.150	0.85
CPSC-3	0.147	0.010	19.2				19.4

*DBP = dibutyl phthalate; BBP = benzyl butyl phthalate; DEHP = di-(2-ethylhexyl) phthalate; DnOP = di-n-octyl phthalate; DINP = 2diisononyl phthalate; DIDP = diisodecyl phthalate.

Figure 4 shows an example full scan chromatogram for the duck sample. The chromatogram shows the advantage of running in SIM/Scan mode as several other non-targeted plasticizers are seen in the chromatogram. These include diethyl phthalate, acetyl tri-n-butyl citrate, and diisononyl adipate.
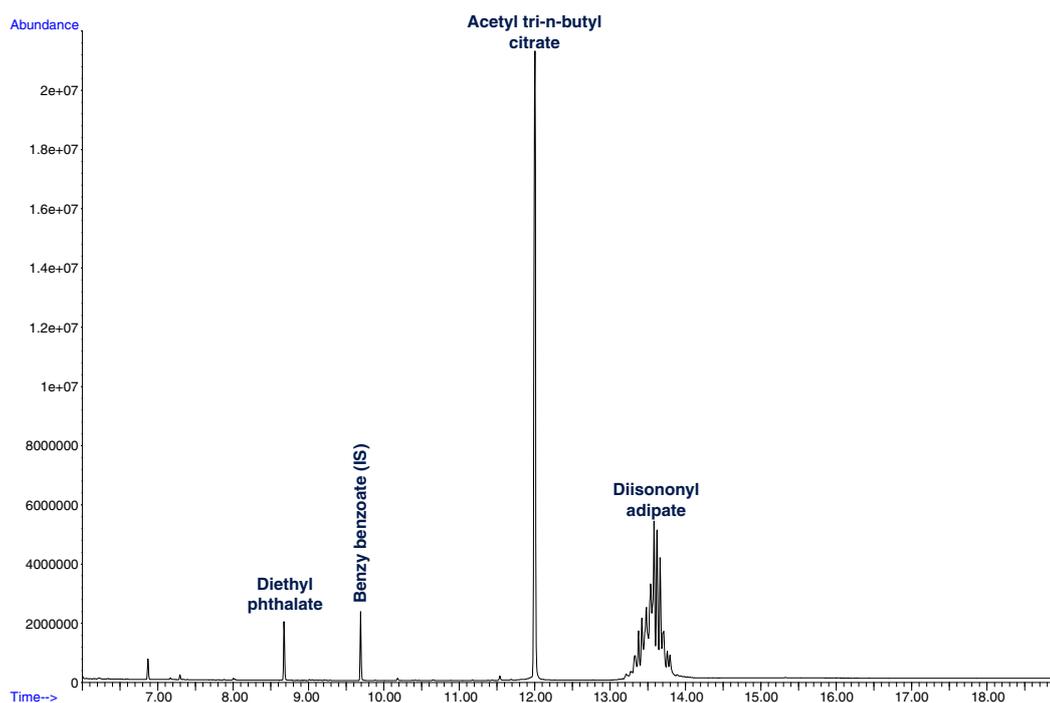
Figure 4. Full scan chromatogram for toy duck sample.

Figure 5A shows a full scan chromatogram for sample CPSC-2. Figure 5B shows extracted ion chromatograms of the SIM data. The target analytes are identified in the SIM chromatogram. The full scan chromatogram shows the presence of another compound, diisononyl cyclohexane-1,2-dicarboxylate
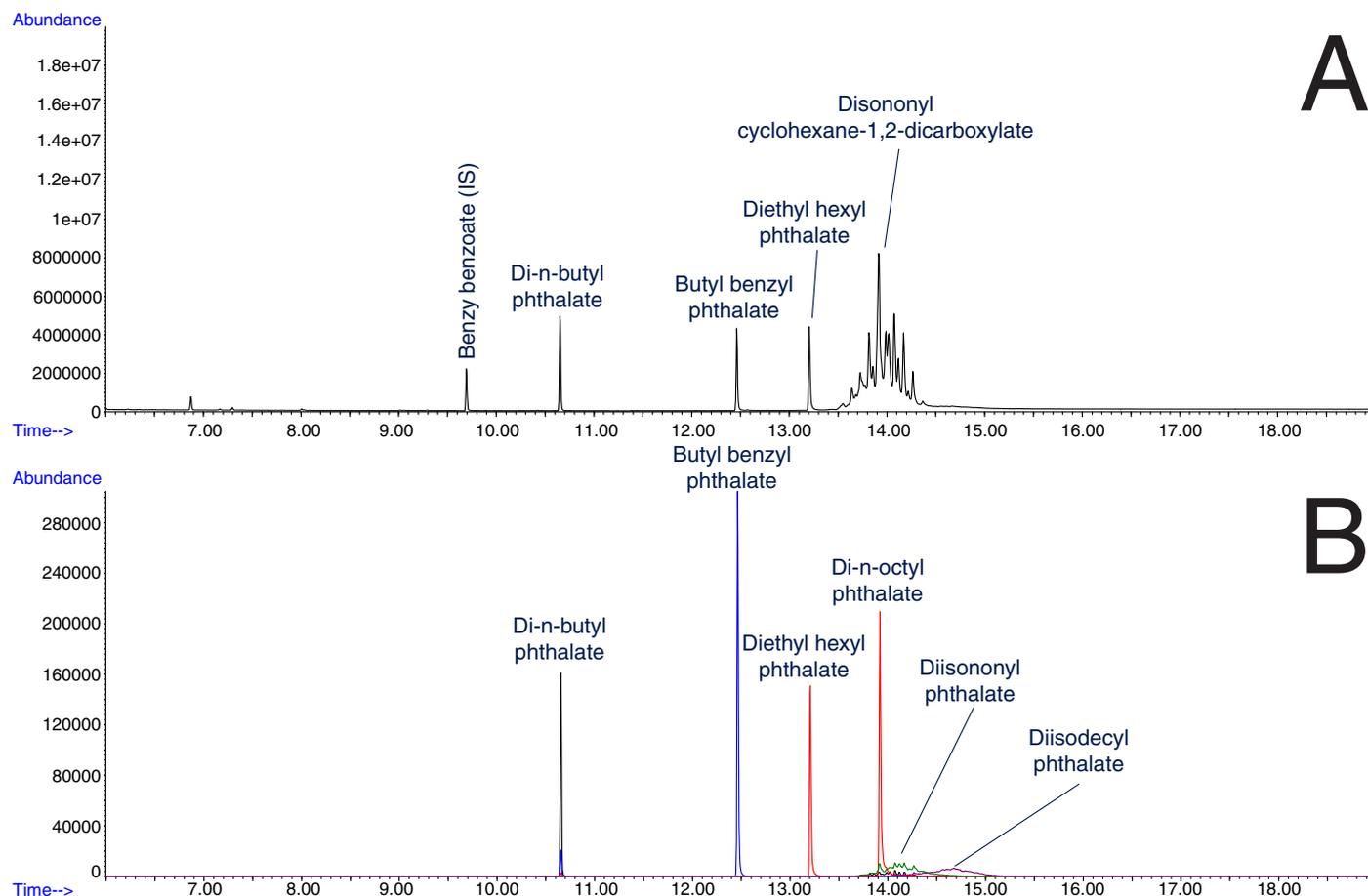
Figure 5. Full scan chromatogram (A) and extracted ion chromatograms (B) for sample CPSC-2.

CONCLUSIONS

As a result of this study, we were able to show:

- A manual liquid-liquid extraction procedure could be transferred to the dual head GERSTEL MultiPurpose Sampler (MPS XL) and fully automated..
- Certified reference material and incurred samples were found to give appropriate results when extracted and analyzed using the automated method.
- The automated liquid extraction GC/MS method proved to be precise with RSDs ranging of 1.9-5.5 % for all phthalates being monitored.
- Phthalates that must be monitored in children's toys and child care articles using Test Method CPSC-CH-C1001-09.3 can be determined in relevant samples using the automated extraction and GC/MS analysis method.

REFERENCES

[1] United States Consumer Product Safety Commission, Test Method: CPSC-CH-C1001-09.3 Standard Operating Procedure for Determination of Phthalates, April 1st, 2010.

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