Greenpeace Research Laboratories Analytical Results 2017-03

Analysis of plastic toys from Russia, Kyrgyzstan, Armenia, Kazakhstan or Belarus for the presence of phthalate esters, metals and organic chemical contaminants

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Introduction

Sixteen samples of plastic toys were received from Greenpeace Russia for analysis at the Greenpeace Research Laboratories. These consisted of 4 samples which arrived on 7th November 2016, and 12 samples on the 3rd April 2017. According to documentation supplied, four samples were purchased in Russia in November 2016, and twelve samples were purchased in Russia, Kyrgyzstan, Armenia, Kazakhstan or Belarus in March 2017. Details of the samples received are provided in Table 1.

For each toy, sections of plastic cut from the toy (the main soft plastic material) were analysed quantitatively for a range of phthalate esters (also known as phthalates) and for metals/metalloids, and qualitatively for the presence of semi-volatile (solvent-extractable) organic compounds (in order to identify any other additives or contaminants that may be present).

In addition, for four of the samples (RU16001-04), metals/metalloids analysis was also performed separately on each coloured section of the toys to investigate the composition of different coloured coatings.

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Sample code	Description	Date of purchase	Plastic section analysed for phthalates
Russia			
RU16001	blue elephant with red ears	07.11.2016	composite of red & blue sections
RU16002	pink pig	07.11.2016	pink section
RU16003	yellow duck	07.11.2016	yellow section
RU16004	multi-coloured unicorn	07.11.2016	composite of unpainted & painted sections
RU17001	bear with girl	29.03.2017	dark brown plastic
RU17002	doll in clothing	29.03.2017	pink plastic
RU17003	peppa pig	29.03.2017	pink head section
RU17004	4 cubes (all same plastic)	29.03.2017	pink cube, unpainted
Kyrgyzstan			
RU17005	yellow angry bird	22.03.2017	yellow plastic
RU17006	ball, solid foam	22.03.2017	red coated foam
Armenia			
RU17007	pack of plastic vehicles	20.03.2017	orange plastic car
RU17008	frog	20.03.2017	white plastic with yellow/green coating
Kazakhstan			
RU17009	snake bath toy	25.03.2017	green plastic
RU17010	bear	25.03.2017	brown plastic
Belarus			
RU17011	6 hard plastic cubes with pictures	25.03.2017	plastic cube
RU17012	Isabella mermaid doll	25.03.2017	pink soft plastic of head

Table 1. Description of the toy samples purchased in Russia, Kyrgyzstan, Armenia, Kazakhstan or Belarus in 2016 and 2017

Materials and methods

All samples were wrapped in aluminium foil immediately after purchase without the removal of any packaging, and sent to the Greenpeace Research Laboratories at the University of Exeter in the UK. Subsections of flexible plastic were cut from each toy using tools and surfaces that had been rinsed with analytical grade acetone and then analytical grade pentane. One section from each toy was wrapped in solvent rinsed aluminium foil and these subsamples were then dispatched to independent accredited laboratories to carry out quantification for certain phthalates and one adipate. The remaining subsamples from each toy were analysed at the Greenpeace Research Laboratories for qualitative analysis of extractable organic chemicals, and for quantification of a range of metals and metalloids. A sample of the foil used to wrap the toys upon purchase was analysed for the presence of phthalates, and no phthalates were detectable.

For the qualitative organic chemical analysis, semi-volatile organic compounds were isolated from samples using Accelerated Solvent Extraction (ASE) with a mixture of pentane and acetone. Extracted compounds were subsequently identified as far as possible using gas chromatography/mass spectrometry (GC/MS) operated in both SCAN and SIM modes.

Metal and metalloid concentrations were determined for all samples by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) following acid digestion and using an appropriate certified reference

material in addition to intra-laboratory standards. More detailed descriptions of the sample preparation and analytical procedures are presented in the Appendix 1

Results and Discussion

The results for the samples are outlined in the following sections, divided into areas by the three types of chemical analysis. The concentrations of phthalates as reported by the independent accredited laboratory are given in Table 2, together with data from confirmatory qualitative analysis for the same phthalates as performed in our own laboratories, and the identities of any additional organic chemicals that could be identified in individual samples. Concentrations of metals and metalloids are reported in Table 3a and 3b. A full list of organic chemicals identified in each sample is provided in Appendix 2.

In some cases, the concentration of an analyte was below the limit of quantification for the analytical methods employed in this study. These are shown in the results tables as '<x' where x is the method quantification limit for the individual chemical.

Five samples contained very high concentrations of phthalates (RU16002, RU17007, RU17009, RU17010 and RU17012). For four of these samples, the predominant phthalate was DEHP. This included the sample that was bought in Russia, RU16002 (280000 mg/kg, 28% by mass), two samples bought in Kazakhstan, RU17009 (310000 mg/kg, 31% by mass) and RU17010 (320000 mg/kg, 32% by mass), and one sample bought in Belarus, RU17012 (260000 mg/kg, 26% by mass). For these four samples, DEHP made up over 99% of the total concentration of all quantified phthalates for each sample.

For the other sample, RU17007 bought in Armenia, the quantified phthalates were predominantly DiBP (190000 mg/kg, 19% by mass), and to a lesser extent DnBP (3060 mg/kg, 0.306% by mass), with these two compounds making up 98% and 2%, respectively, of the total concentration of all quantified phthalates in this sample.

Three of the samples with very high concentrations of DEHP (RU17009, 10, 12) also contained detectable concentrations of DnBP, in the range 26-506 mg/kg, and DiBP was also detected in one of these (RU17009) at 36 mg/kg.

Two additional samples also contained DEHP at reasonably high concentrations; RU17002, purchased in Russia (1280 mg/kg, 0.128% by mass), and RU17011, purchased in Belarus (443 mg/kg, 0.0443%).

In all other cases, the quantified phthalates were either not detected, or present at only trace concentrations.

In addition to the phthalates detected in the samples, the adipate DEHA was detected in 5 samples, with concentrations ranging from 4 to 692 mg/kg. The two samples with the highest concentrations of DEHA also contained a very high concentration of DEHP, though there was no clear correlation between the two in terms of absolute concentrations.

Country of purchase	Russia								Kyrgyzstan		Armenia		Kazakhstan		Belarus	
Sample code	RU16 001	RU16 002	RU16 003	RU16 004	RU17 001	RU17 002	RU17 003	RU17 004	RU17 005	RU17 006	RU17 007	RU17 008	RU17 009	RU17 010	RU17 011	RU17 012
PHTHALATES QUANTITATIVE ANALYSIS RESULTS																
DEHP	<1	280000	54	10	2	1280	5	3	7	6	<1	<1	310000	320000	443	260000
DnBP	4	<1	<1	<1	<1	4	2	<1	<1	24	3060	<1	218	506	<1	26
DiBP	<1	<1	<1	<1	<1	<1	2	<1	<1	6	190000	15	36	<1	1	<1
BBP	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
DINP	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
DIDP	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
DnOP	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
DnHP	-	-	-	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
DEP	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
DMP	<1	<1	<1	<1	<1	<1	1	<1	<1	<1	<1	<1	<1	<1	<1	<1
DEHA*	<1	692	<1	<1	<1	<1	<1	<1	<1	<1	<1	37	56	<1	6	4
ORGANOSCREEN QUALITATIVE ANALYSIS RESULTS																
Number of Compounds Isolated	7	18	7	7	18	15	33	25	36	18	65	12	34	13	35	15
Number of Compounds Identified to >90%	5	10	5	4	14	7	11	9	9	10	19	3	20	8	9	11
Percentage identified to > 90%	71	56	71	57	78	47	33	36	25	56	29	25	59	62	26	73
PLASTISICERS																
DEHP		√	√			√				√			√	√	√	√
DiBP										√	√	√	√	√	√	
DBP										√	√		√	√		
butyl 2-methylpropyl phthalate											√					
DiOP														√		
DEHA		√											√			
DEHT	√		√	√	√	√	√	√	√	√	√	√	√	√	√	√
2,2,4- Trimethyl-1,3-pentanediol diisobutyrate	√		√	√	√		√						√			
DINCH							√		√							

Table 2. Concentrations of individual phthalates (mg/kg) in each sample and list of organic compounds reliably identified during organoscreen GC/MS analysis. * DEHA is an adipate, not a phthalate. Phthalates and adipate analysed; di-(2-ethylhexyl) phthalate (DEHP), di-n-butyl phthalate (DnBP), di-iso-butyl phthalate (DIBP), butylbenzyl phthalate (BBP), di-iso-nonyl phthalate (DINP) and di-iso-decyl phthalate (DIDP), di-n-octyl phthalate (DNOP), di-n-hexyl phthalate (DnHP), diethyl phthalate (DEP), dimethyl phthalate (DMP), and di-(2-ethylhexyl) adipate (DEHA)

Country of purchase	Russia								Kyrgyzstan		Armenia		Kazakhstan		Belarus	
Sample code	RU16 001	RU16 002	RU16 003	RU16 004	RU17 001	RU17 002	RU17 003	RU17 004	RU17 005	RU17 006	RU17 007	RU17 008	RU17 009	RU17 010	RU17 011	RU17 012
FLAME RETARDANTS																
Phosphoric acid, 2-ethylhexyl diphenyl ester (Octicizer)					√											
Phosphorous acid, triphenyl ester											√					
OTHERS																
Long chain fatty acid esters					4	1	3	3	3	1	6		6			2
C9-c14 alcohols			√				2				2	1	1	1		
Linear aliphatic hydrocarbons	9				4	4	2	3	3		5		7	1	2	
Cyclic aliphatic hydrocarbons	2		1	2	2					1						
Phenol & derivatives					√			√		√	√					
1-Propene-1,2,3-tricarboxylic acid, tributyl ester							√		√							
2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-										√						
3-Octen-2-one										√						
Irganox 1076										√						
Benzenesulfonic acid, 4-methyl-, 2-ethylhexyl ester														√		
Benzene, 1,1'-(1,2-cyclobutanediyl)bis-															√	
Cyclobutane, 1,2-diphenyl-															√	
Naphthalene, 1,2,3,4-tetrahydro-1-phenyl-															√	

Table 2. continued; organic compounds reliably identified during organoscreen GC/MS analysis.

In addition to the organic chemical additives specifically quantified in this study, a number of other organic compounds, whether present as deliberate additives or as unintentional contaminants, were identified through the application of qualitative forensic mass spectrometry. One chemical that was conspicuous in all but one of the 16 samples analysed was DEHT (diethylhexyl terephthalate), a plasticiser thought to present a far lower hazard profile than the phthalate esters listed above. DEHT has been assessed using the GreenScreen methodology as presenting a low hazard for most toxicity endpoints, but with remaining data gaps relating to neurotoxicity and respiratory sensitization (ToxServices 2012a). As part of a broader assessment of alternatives to phthalate esters, Bui *et al.* (2016) concluded that the risk to humans from exposure to DEHT is currently low, though do note that, as a result of its increasing use as an alternative to phthalates esters, exposures are expected to continue to increase over time.

Two other plasticiser chemicals were found in this study, 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (best known as the commercial product Kodaflex TXIB) in 6 of the samples, and DINCH (diisononyl cyclohexanedicarboxylate) in two samples. As is the case for DEHT, both of these compounds have been assessed as being of substantially lower hazard compared to the phthalate esters, though again there are some significant data gaps. The diisobutyrate derivative was initially quite widely used in Europe as a phthalate ester replacement in cushioned PVC flooring, though its high volatility, combined with an increasing focus in some countries on reducing vapour emissions in the indoor environment, led to a reduction in such uses more than 20 years ago (Wilson 1996). In the case of DINCH, a Risk Management Option Analysis conducted by the French authorities under the REACH Regulation in January 2016 concluded that toxicity and other hazards were low for this plasticiser (ECHA 2016). Some outstanding concerns remain based on effects seen on the thyroid in rodents, but these are not thought to be of relevance to most humans, the one exception being the exposure of premature babies to high levels of DINCH as a phthalate-replacement plasticiser in PVC tubing for medical applications. Other assessments have also concluded that DINCH presents a low risk to humans (Bui *et al.* 2016), though a separate GreenScreen assessment (ToxServices 2012b) flags moderate risk of skin irritation and moderate persistence, as well as identifying the outstanding uncertainties and concerns regarding endocrine disruption.

Among other chemicals identified were trace residues of two harmful organophosphorus compounds, namely 2-ethyhexyl diphenyl phosphate (‘Octicizer’) in sample RU17001 and triphenyl phosphite (phosphorous acid, triphenyl ester) in sample RU 17007. Both are harmful if swallowed and very toxic to aquatic life, and triphenyl phosphite can cause skin and eye irritation in mammals and may induce allergic reactions in sensitive individuals.

Many of the toys contained residues of a range of fatty acids, alcohols and hydrocarbons, possibly arising from their use as processing aids in the manufacture of the plastics, or as contaminants in other chemicals used in manufacture. One of the toys, RU 17006 from Kyrgyzstan, contained Irganox 1076, a compound used as a stabiliser in plastics and which is widely approved for use in food contact materials. However, the same toy sample also contained residues of 2,6-bis(1,1-dimethylethyl)-2,5,cyclohexadiene-1,4-dione, a known skin, eye and respiratory irritant.

In all cases, a number of other compounds were isolated during the forensic analysis but could not be

reliably identified and hence their hazards cannot be assessed. This was particularly the case with sample RU17011, from Belarus, in which three of the largest peaks for compounds extracted from the sample simply could not be identified, two of these showing indications of being unknown isomeric mixtures.

Metals and metalloids

The concentrations of metals and metalloids in the individual samples are presented in Table 3a and 3b. Table 3a presents the result for the four samples for which analysis was carried out separately on each coloured section of the toys, and Table 3b presents the result for the twelve samples for which analysis was carried out on a section of the main soft plastic material of the toy only.

Country of purchase	**Russia**												
Main plastic	blue plastic			pink plastic			yellow plastic			pink plastic			
Coating	none	red	pink	none	blue	brown	none	orange	white	none	purple	red	yellow
Sample code	**RU16001**			**RU16002**			**RU16003**			**RU16004**			
Metal/metalloid	**a**	**b**	**c**	**a**	**b**	**c**	**a**	**b**	**c**	**a**	**b**	**c**	**d**
Antimony (Sb)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Arsenic (As)	<0.05	<0.05	<0.05	<0.05	<0.05	0.07	<0.05	<0.05	<0.05	<0.05	0.05	<0.05	0.07
Barium (Ba)	0.52	0.92	0.58	0.17	0.45	0.28	0.41	6.1	1.89	2.11	2.62	2.80	2.20
Cadmium (Cd)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Calcium (Ca)	96	99	25	21	42	11	42	94	35	84	86	82	78
Chromium (Cr)	0.55	0.31	0.33	0.20	1.75	0.98	0.25	0.26	0.58	0.23	0.38	0.34	0.32
Cobalt (Co)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Copper (Cu)	9.0	8.7	2.9	0.3	46.4	0.9	0.4	1.6	1.2	1.4	1.7	2.6	2.7
Lead (Pb)	0.2	0.2	0.1	0.1	7.4	0.4	0.1	0.3	0.3	0.3	0.1	0.2	0.2
Magnesium (Mg)	153	160	47	88	106	38	64	134	59	153	151	144	145
Manganese (Mn)	0.2	0.2	0.1	0.1	0.1	0.4	0.1	0.2	0.2	0.1	0.2	0.4	0.2
Mercury (Hg)	0.6	0.5	2.6	0.9	1.0	1.8	0.4	0.5	2.5	1.1	0.6	1.5	1.8
Nickel (Ni)	0.1	0.2	0.4	0.1	0.1	0.3	0.2	0.1	0.3	0.4	0.2	3.9	0.3
Zinc (Zn)	391	377	122	247	274	98	196	340	168	394	383	368	366

Table 3a. Concentrations of metals/metalloids (mg/kg) in each coloured section of the toy

Country of purchase	Russia				Kyrgyzstan		Armenia		Kazakhstan		Belarus	
Metal/metalloid	RU17 001	RU17 002	RU17 003	RU17 004	RU17 005	RU17 006	RU17 007	RU17 008	RU17 009	RU17 010	RU17 011	RU17 012
Antimony (Sb)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.35	<0.01
Arsenic (As)	0.02	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.11	<0.02	0.08	<0.02	0.02
Barium (Ba)	<0.2	<0.2	<0.2	<0.2	<0.2	13.5	<0.2	<0.2	0.2	10.3	1.5	<0.2
Cadmium (Cd)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.07	0.05	0.04	0.01	<0.01
Calcium (Ca)	112	51	<1	6	19	353	4010	4600	97	7860	660	35
Chromium (Cr)	0.06	0.08	0.12	0.12	0.13	0.21	1.09	4.02	0.19	0.50	0.64	0.22
Cobalt (Co)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.03	0.03	<0.02	<0.02	0.36	<0.02
Copper (Cu)	0.5	<0.2	<0.2	0.3	<0.2	<0.2	0.4	0.3	1.1	0.6	0.7	<0.2
Lead (Pb)	0.43	0.08	<0.04	<0.04	<0.04	<0.04	0.31	1.06	0.15	0.24	0.16	0.11
Magnesium (Mg)	<0.6	119	<0.6	44	<0.6	25	133	11400	157	513	47	14
Manganese (Mn)	<0.06	<0.06	<0.06	0.13	<0.06	0.26	2.83	10.1	0.49	2.94	3.95	0.23
Mercury (Hg)	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Nickel (Ni)	0.04	<0.02	<0.02	<0.02	<0.02	0.05	0.05	0.53	0.03	0.20	0.13	0.07
Zinc (Zn)	403	263	9	100	122	<1	147	93	111	4	12	76

Table 3b. Concentrations of metals/metalloids (mg/kg) in the main soft plastic material of the toy

Though various metals/metalloids were present at quantifiable concentrations in the individual samples, none of the materials analysed contained any of the quantified metals/metalloids at notably high concentrations. Though not directly comparable, the metal/metalloid concentrations in the toy samples were compared to limits set for toys sold within the EU (EU 2009, EU 2012), see Table 4. For all samples, no metal/metalloid concentration was higher that the limit set under EU regulations, with concentrations generally considerably lower than the regulatory limit. For one sample (RU16002b; pink plastic with blue coating) the lead concentration was 55% of the EU limit, and for two other samples (RU16002c, blue plastic with pink coating & RU16003c, yellow plastic with white coating), the mercury concentration was 33-34% of the EU limit.

	RU16001-04 & RU17001-12		
Metal/metalloid	Highest value (mg/kg)	Fraction of EU limit (%)	EU limit (mg/kg)
Antimony (Sb)	0.35	1	45
Arsenic (As)	0.11	3	3.8
Barium (Ba)	13.5	1	1500
Cadmium (Cd)	0.07	6	1.3
Calcium (Ca)	7860	-	-
Chromium (Cr)	4.02	11	37.5
Cobalt (Co)	0.36	3	10.5
Copper (Cu)	46.4	7	622.5
Lead (Pb)	7.4	55	13.5
Magnesium (Mg)	11400	-	-
Manganese (Mn)	10.1	1	1200
Mercury (Hg)	2.6	34	7.5
Nickel (Ni)	3.9	5	75
Zinc (Zn)	403	11	3750

Table 4.Highest concentrations of metals/metalloids (mg/kg) across the 16 samples, compared with limits set under the EU Toys Directive (EU 2009, EU 2012)

Conclusions

For over a third of the samples (6 out of 16 samples), the concentration of phthalates would have resulted in their sale being illegal in many other countries where regulations exist on the presence of certain phthalates in toys, in which a maximum permissible concentration of 0.1% by mass has been set for each individual component material of the toys (for example within the EU under Directive 2005/84/EC (EU 2005)). For 4 of these samples (RU16002, RU17009, RU17010, RU17012), the concentrations of DEHP were in the range 26% – 32% by mass.

For the other 2 samples (RU17002 & RU17007), the concentrations of a commonly regulated phthalate were 0.128% and 0.306%, respectively, just above the 0.1% by mass limit set in many countries. One of these sample (RU17007), however, contained 19% by mass of another closely related phthalate, DiBP. Although DiBP is not included in regulations in those countries that specifically address the presence of phthalates in toys, it is commonly recognised to be a hazardous chemical with similar level of concern to other phthalates that are. For example, within the EU DiBP is listed as a Substance of Very High Concern (SVHC) along with the very closely related DnBP and other phthalates that are included in regulations specific to toys (eg EU 2005).

Given the small number of samples purchased in each country, these results clearly cannot be taken to be more broadly representative of additive levels in toys sold in the countries covered in this study. The study does, however, indicate that at least some toys sold in these countries in 2016 and 2017 contain phthalates at concentrations which would make their sale illegal in those countries and regions in which relevant legislation designed to protect consumer health already exists. For 5 of the 16 samples, the concentration of a single phthalate in the plastic of the toy was in the range 19% to 32% by mass, values which are 190-320 times the 0.1% by mass limit commonly set for certain phthalates in other countries (e.g. EU 2005).

Many of the toys analysed in this study contained a number of different plastic materials. In many cases, the toy contained rigid plastic and/or non-plastic materials. Any legislation addressing the presence of phthalates in toys in Russia, Kyrgyzstan, Armenia, Kazakhstan or Belarus needs to set a maximum permissible concentration by mass for each homogenous material, as is generally the case for existing regulations in other countries (eg EU 2005), and not a concentration limit for the toy as a whole. A limit on a whole toy basis would permit the sale of a toy which included a material containing a regulated phthalate at a concentration above the regulatory limit as long as the concentration averaged for the whole toy was below the limit. This would fail to offer the necessary protection that any such regulation would aim to achieve.

For more information please contact:

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Appendix 1: Details of methodologies

Analysis for phthalate esters

10 individual phthalate esters, and one adipate ester (DEHA), were quantifies in a section of flexible plastic from each of the toys at an external accredited laboratory. A separate section of the same material was used for the extractable organic chemical screening analysis and for the metals quantification.

Analysis for extractable organic compounds

Preparation

Approximately 0.5 g of each toy sample was cut into small pieces using pre-cleaned scissors and extracted employing an Accelerated Solvent Extraction (ASE) technique, using a Dionex ASE-350, with pentane as a solvent, and at a temperature of 100^{o}C. Extracts were adjusted to 40 ml with pentane and an aliquote of 100ul was transferred into an autosampler vial containing a glass insert prior to GC/MS analysis. Following the initial analysis, only one sample, RU17006, was further concentrated to 1ml and re-analysed for organic compounds. The rest of the samples have not been concentrated and re-analysed due to the presence of some compounds (e.g., phthalates) at very high abundances in the original 40 ml extract, which could result in the system overload and contamination. Hence, it could be the case that some of the extracted compounds, which were present at trace levels in 40 ml extract, were not detected.

Analysis of semi-volatile organic chemicals

For the total organic compounds screening, samples were analysed using an Agilent 7890B GC with Restek Rxi-17Sil column (30m, 0.25mm ID, 0.25 µm film thickness) linked to an Agilent 5977A MSD operated in EI mode and interfaced with an Agilent Enhanced Chem Station data system. The GC oven temperature program employed was as follows: an initial temperature of 40^{0}C, raised to 260^{0}C at 10^{0}C/min, then to 295^{0}C at 50^{0}C/min (held for 15 min), and finally to 320^{0}C at 50^{0}C/min (held for 12 min). The carrier gas was helium, supplied at 1 ml/min. Identification of compounds was carried out by matching spectra against both the Wiley 10N11 and Pesticides Libraries, using expert judgment as necessary in order to avoid misidentifications. Additionally, both the spectra and retention times of compounds isolated from the samples were matched against those obtained during GC-MS analysis of standard mixtures containing a range of chlorinated benzenes, phenols and pesticides, polychlorinated biphenyls (PCBs), phthalates, polycyclic aromatic hydrocarbons (PAHs) and aliphatic hydrocarbons.

Quality control

A number of extraction and solvent blanks were also analysed to ensure the detection of any possible contamination resulting from sample handling in the laboratory. Any background contaminants detected in blanks are subtracted from the chromatograms obtained for the samples before mass spectra are interpreted.

Analysis for metals / metalloids

Preparation

A representative portion of each sample was cut into small pieces approximately $2mm^3$. Approximately 0.55 g of cut up sample was digested with 0.5 ml concentrated hydrochloric acid and 5 ml concentrated nitric acid, firstly overnight at room temperature, then using microwave-assisted digestion with a CEM MARS Xpress system, with a temperature ramp to 110°C over 30 minutes followed by holding at 110°C for a further 15 minutes. After allowing to cool to room temperature, excess pressure was released from each vessel, which were then resealed and underwent a second digestion with a temperature ramp to 210°C over 30 minutes followed by holding at 210°C for a further 15 minutes. Following cooling, the digest was filtered and made up to 25 ml with deionised water. For analysis, each digest solution was diluted 1:4 in deionised water, and the diluted solution used for analysis.

Analysis

Prepared sample digests were analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using an Agilent 7900 Spectrometer utilizing a collision cell with helium as the collision gas to minimize polyatomic interferences. Multi-element standards, matrix matched to the samples, at concentrations of 1, 10, 100 and 1000 μg/l respectively, other than for mercury (1, 2, 5, 20 μg/l respectively) were used for instrument calibration. Analysis employed in-line addition of an internal standard mix at 100 μg/l (Scandium, Germanium, Yttrium, Indium and Terbium).

Quality control

With each batch of samples, two sample were prepared for ICP analysis in duplicate and analysed to verify method reproducibility. In addition, a blank sample was prepared and digested using the same procedure. A certified reference material (CRM) sample was also prepared in an identical manner; EC681k, low density polyethylene, certified by the Institute for Reference Materials and Measurements (IRMM). All control samples were prepared in an identical manor to the samples.

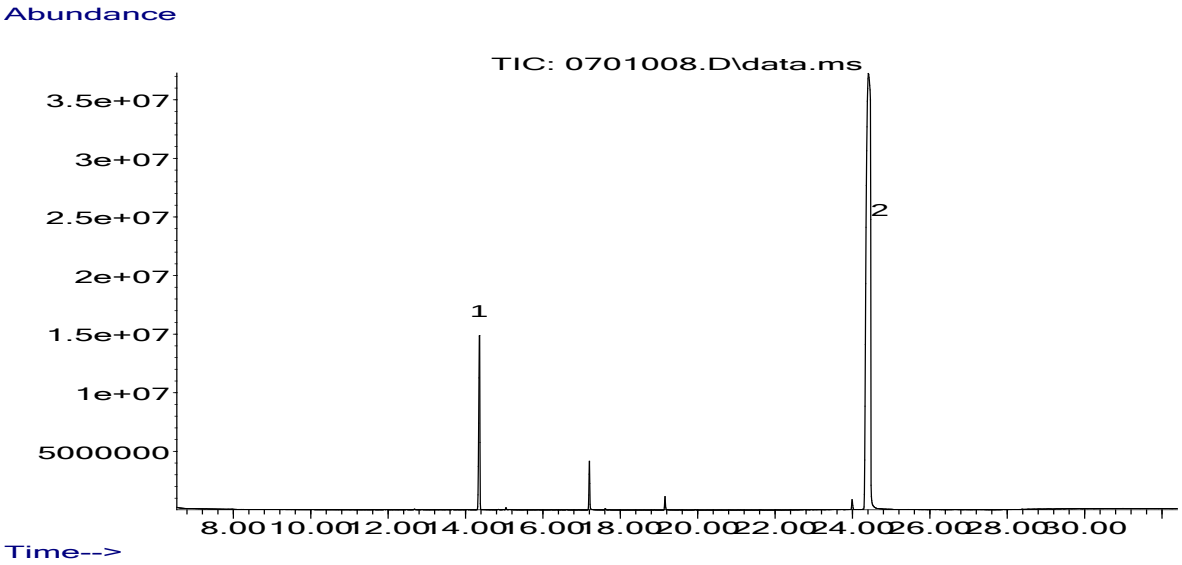
Calibration of the ICP-MS was validated by the use of quality control standards at 80 μg/l and 800 μg/l (4 μg/l and 16 μg/l for mercury) prepared in an identical manner but from different reagent stocks to the instrument calibration standards.

Further details of the methods employed can be provided on request.

Appendix 2: Detailed organic chemical analytical screening data

Detailed screening data arising from GC-MS analysis of each of the samples are presented below. These data list those semi-volatile organic compounds identified following solvent extraction. Only those substances identified to greater than 90% quality match (following verification by expert interpretation) are listed here.

RU16001

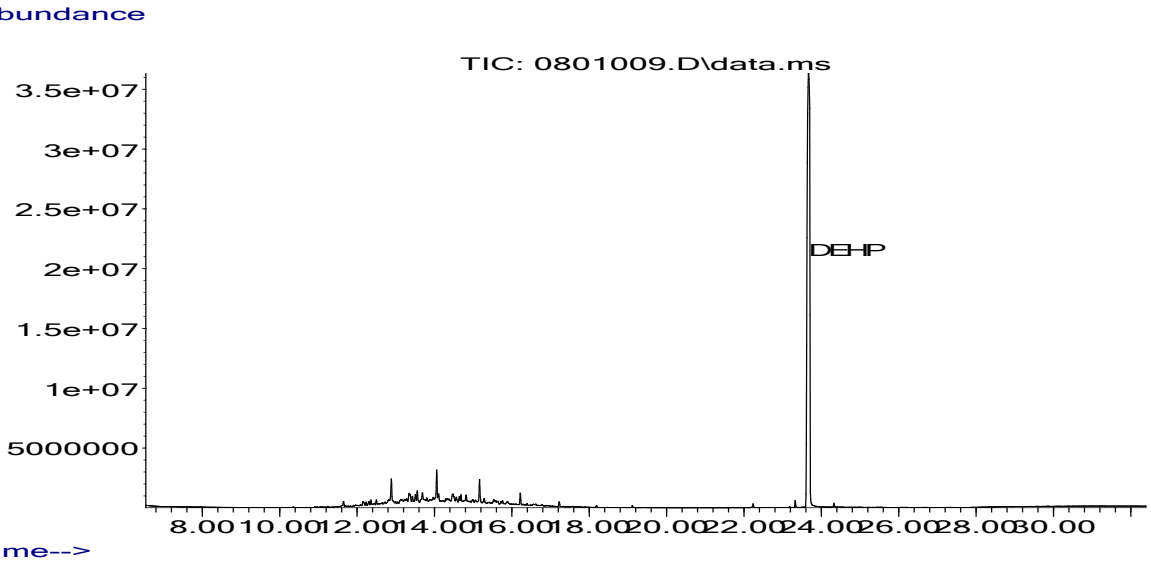


Number of compounds isolated: **7**

Compounds identified to better than 90%:

CAS#	**Name**
006422-86-2	1,4-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHT)
000112-88-9	1-Octadecene
006846-50-0	2-Methyl-propanoic acid, 2,2-dimethyl-1-(1-methylethyl)-1,3-propanediyl ester **1**
000295-65-8	Cyclohexadecane
000295-17-0	Cyclotetradecane

RU16002

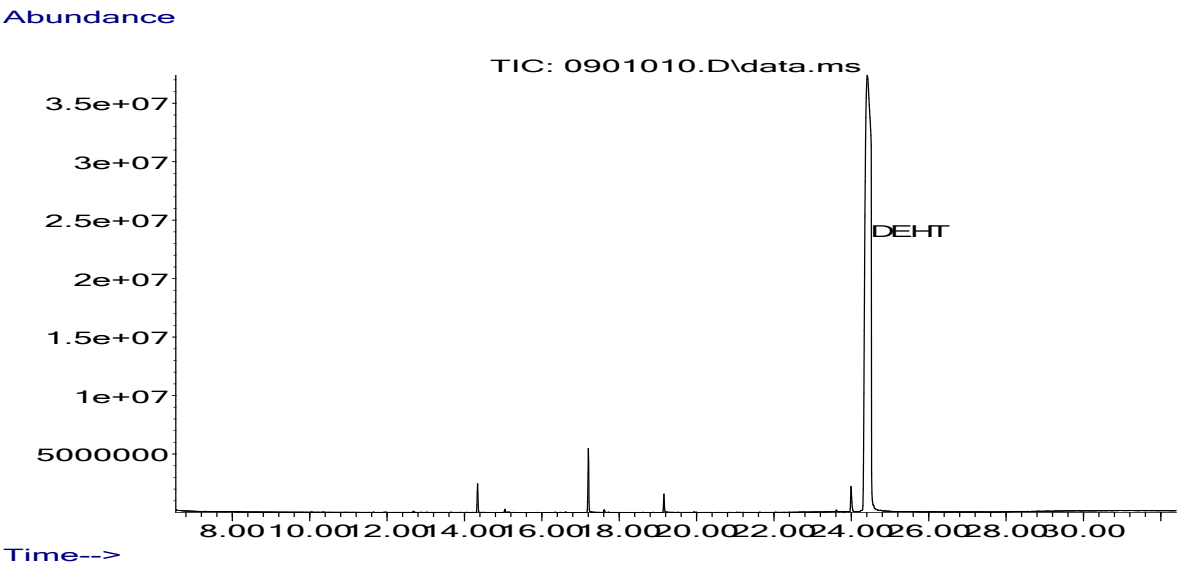


Number of compounds isolated: 18

Compounds identified to better than 90%:

CAS#	**Name**
000103-23-1	Adipic acid, bis(2-ethylhexyl) ester (DEHA)
000117-81-7	1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHP)
000629-78-7	Heptadecane
026429-11-8	Heptadecane, 4-methyl-
000544-76-3	Hexadecane
006418-43-5	Hexadecane, 3-methyl-
000629-92-5	Nonadecane
000593-45-3	Octadecane
000629-62-9	Pentadecane
001560-93-6	Pentadecane, 2-methyl-

RU16003

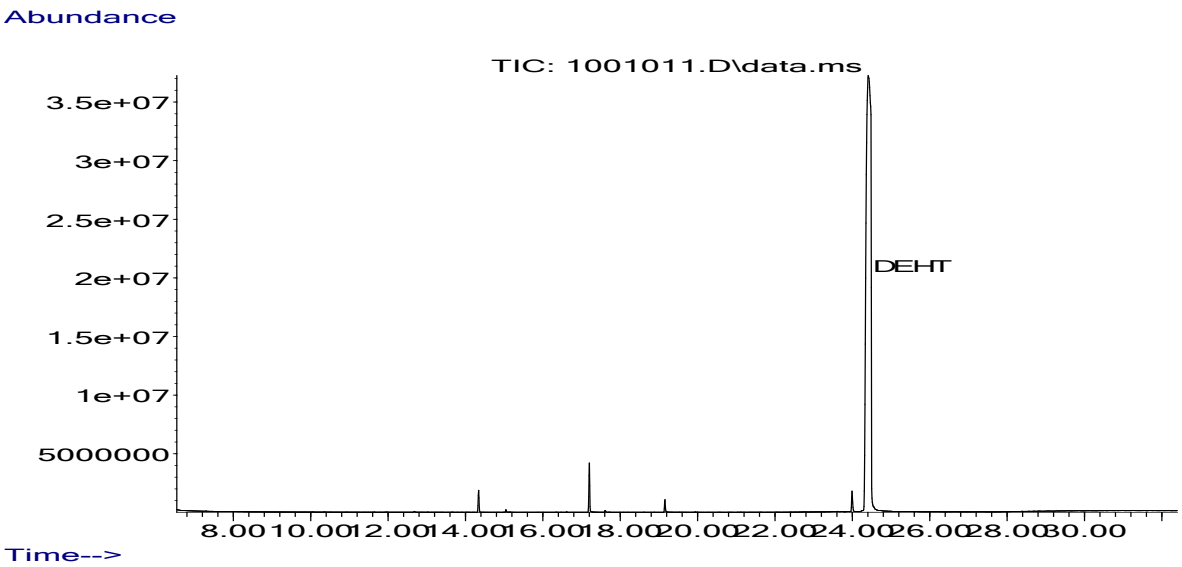


Number of compounds isolated: 7

Compounds identified to better than 90%:

CAS#	**Name**
000117-81-7	1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHP)
006422-86-2	1,4-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHT)
001454-84-8	1-Nonadecanol
006846-50-0	2-Methyl-propanoic acid, 2,2-dimethyl-1-(1-methylethyl)-1,3-propanediyl ester
000295-65-8	Cyclohexadecane

RU16004

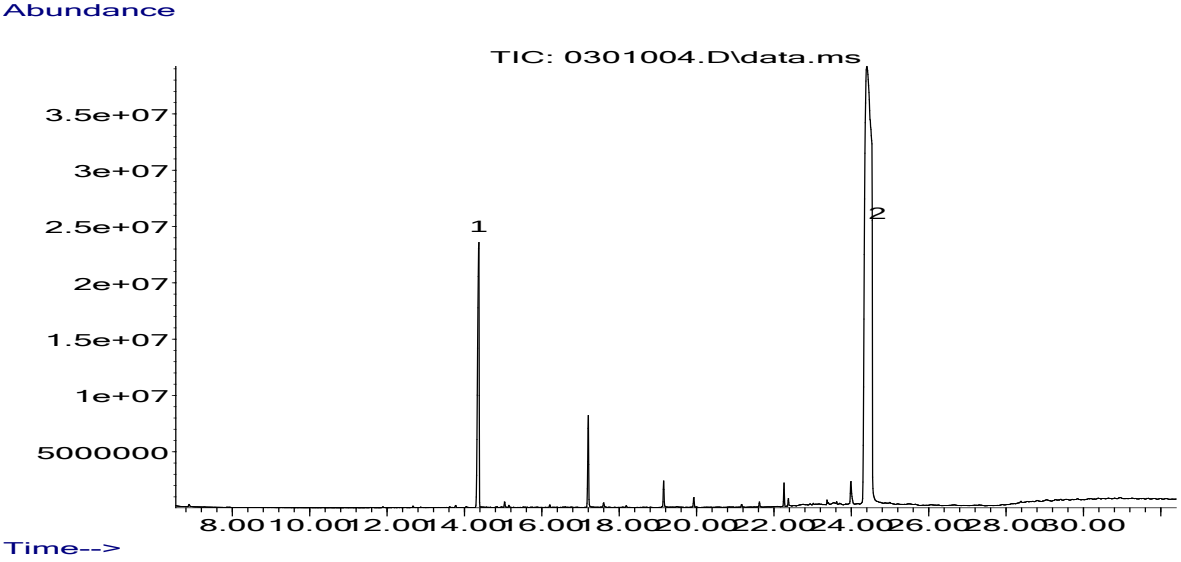


Number of compounds isolated: 7

Compounds identified to better than 90%:

CAS#	**Name**
006422-86-2	1,4-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHT)
006846-50-0	2-Methyl-propanoic acid, 2,2-dimethyl-1-(1-methylethyl)-1,3-propanediyl ester
000294-62-2	Cyclododecane
000295-65-8	Cyclohexadecane

RU17001

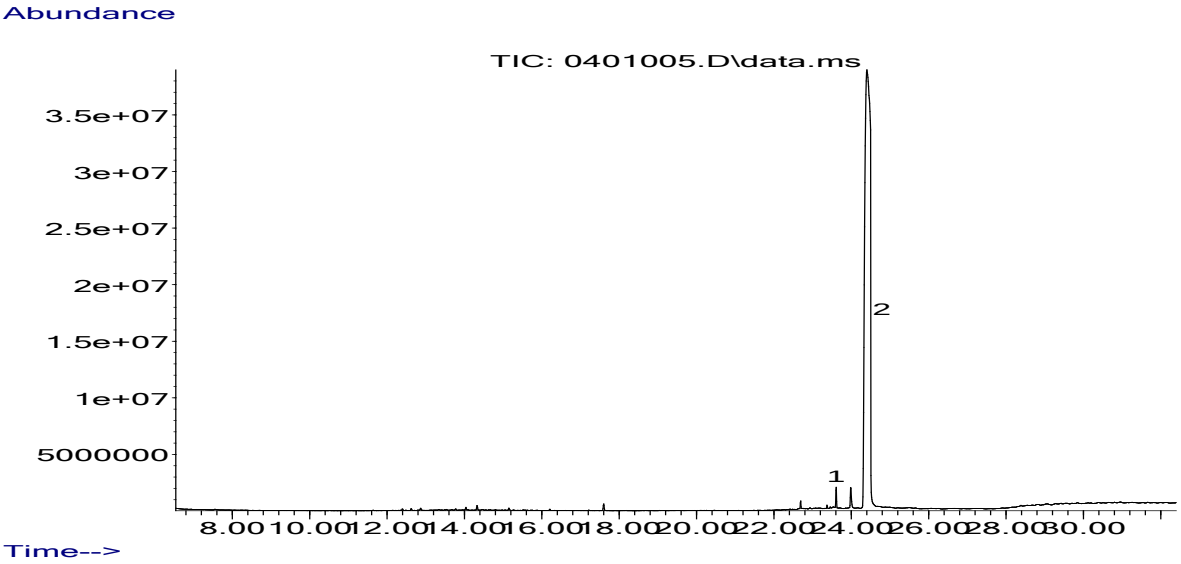


Number of compounds isolated: 18

Compounds identified to better than 90%:

CAS#	Name	
006422-86-2	1,4-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHT)	**2**
007425-14-1	2-Ethylhexyl 2-ethylhexanoate	
006846-50-0	2-Methyl-propanoic acid, 2,2-dimethyl-1-(1-methylethyl)-1,3-propanediyl ester	**1**
007206-21-5	5-Octadecene	
000294-62-2	Cyclododecane	
000295-65-8	Cyclohexadecane	
000629-94-7	Heneicosane	
000111-06-8	Hexadecanoic acid, butyl ester	
000112-39-0	Hexadecanoic acid, methyl ester	
000629-92-5	Nonadecane	
000593-45-3	Octadecane	
000123-95-5	Octadecanoic acid, butyl ester	
000108-95-2	Phenol	
001241-94-7	Phosphoric acid, 2-ethylhexyl diphenyl ester (Octicizer)	

RU17002

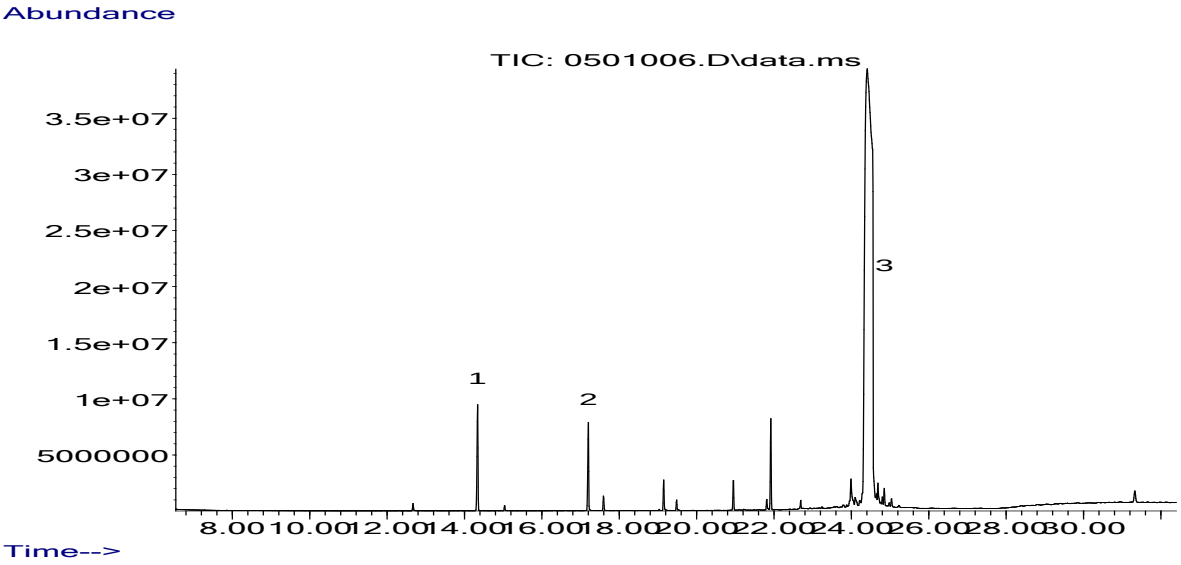


Number of compounds isolated: 15

Compounds identified to better than 90%:

CAS#	**Name**	
000117-81-7	1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHP)	1
006422-86-2	1,4-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHT)	**2**
000629-78-7	Heptadecane	
000544-76-3	Hexadecane	
000112-39-0	Hexadecanoic acid, methyl ester	
000629-92-5	Nonadecane	
000593-45-3	Octadecane	

RU17003

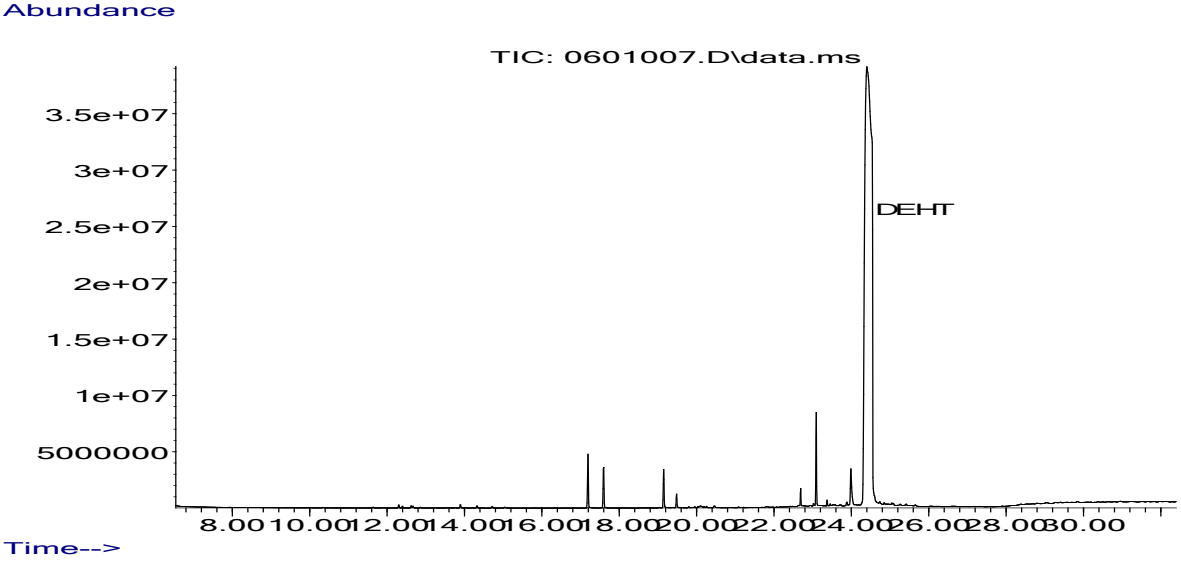


Number of compounds isolated: 33

Compounds identified to better than 90%:

CAS#	Name	
166412-78-8	1,2-Cyclohexanedicarboxylic acid, diisononyl ester (DINCH), 19 isomers	
006422-86-2	1,4-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHT)	**3**
000112-53-8	1-Dodecanol	
001454-84-8	1-Nonadecanol	
007568-58-3	1-Propene-1,2,3-tricarboxylic acid, tributyl ester	
001120-36-1	1-Tetradecene	
006846-50-0	2-Methyl-propanoic acid, 2,2-dimethyl-1-(1-methylethyl)-1,3-propanediyl ester	**1**
035953-54-9	2-Tetradecene, (e)-	**2**
000112-39-0	Hexadecanoic acid, methyl ester	
000112-61-8	Octadecanoic acid, methyl ester	
002566-91-8	Oxiraneoctanoic acid, 3-octyl-, methyl ester, cis-	

RU17004

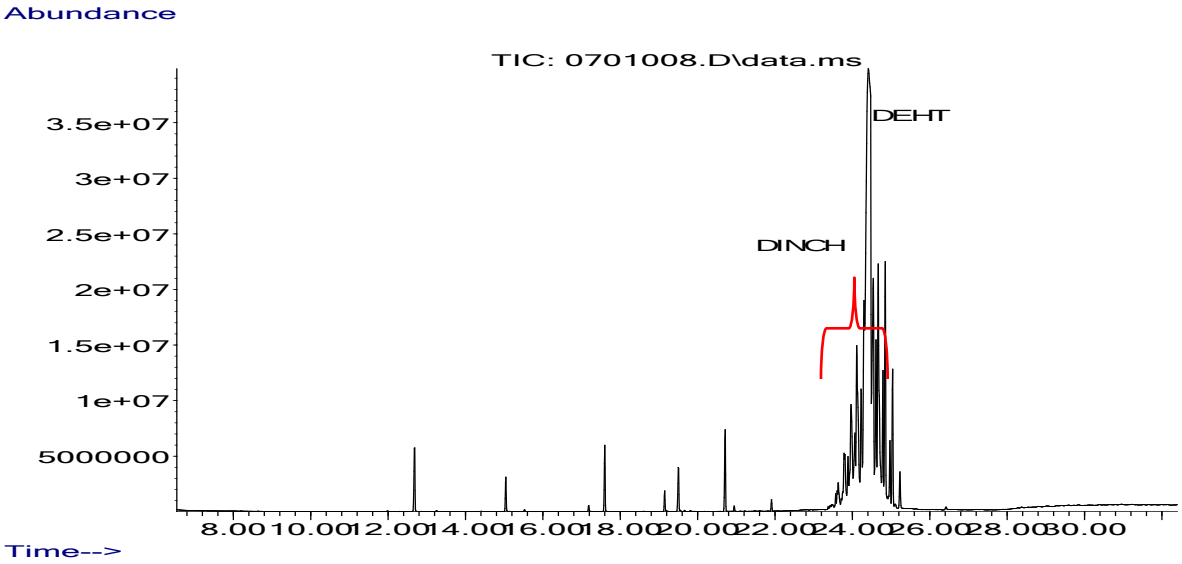


Number of compounds isolated: 25

Compounds identified to better than 90%:

CAS#	**Name**
006422-86-2	1,4-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHT)
000112-41-4	1-Dodecene
000629-73-2	1-Hexadecene
000112-88-9	1-Octadecene
000111-82-0	Dodecanoic acid, methyl ester
000544-76-3	Hexadecane
000112-39-0	Hexadecanoic acid, methyl ester
000112-61-8	Methyl stearate
005875-45-6	Phenol, 2,5-bis(1,1-dimethylethyl)-

RU17005

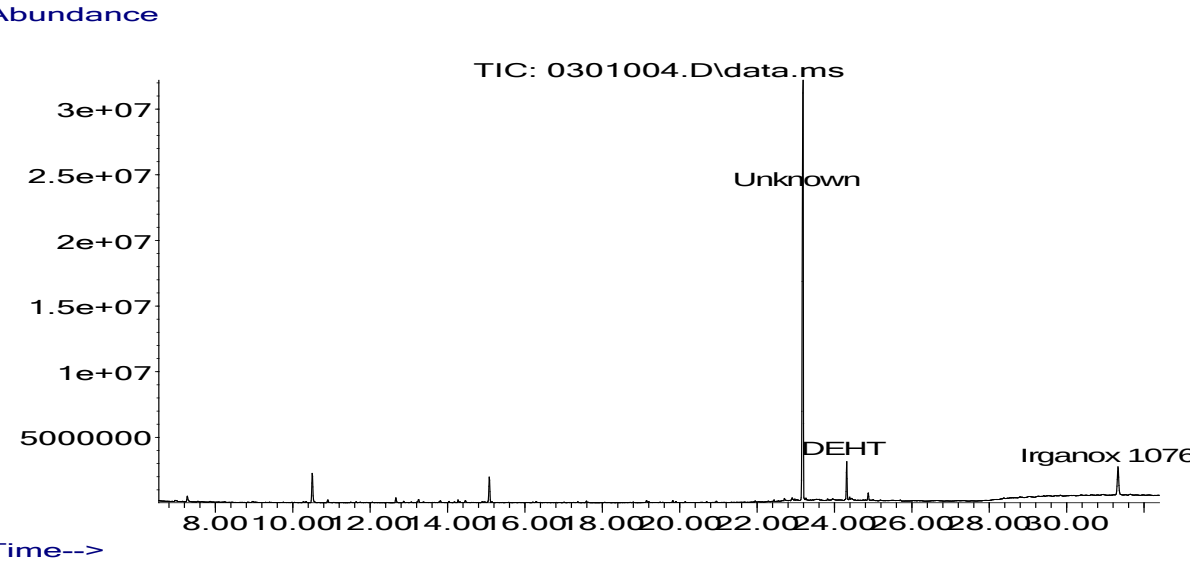


Number of compounds isolated: **36**

Compounds identified to better than 90%:

CAS#	**Name**
166412-78-8	1,2-Cyclohexanedicarboxylic acid, diisononyl ester (DINCH), 18 isomers
006422-86-2	1,4-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHT)
007568-58-3	1-Propene-1,2,3-tricarboxylic acid, tributyl ester
000872-05-9	1-Decene
001120-36-1	1-Tetradecene
035953-54-9	2-Tetradecene, (e)-
002462-84-2	9-Octadecenoic acid, methyl ester
000112-39-0	Hexadecanoic acid, methyl ester
000124-10-7	Myristic acid, methyl ester

RU17006

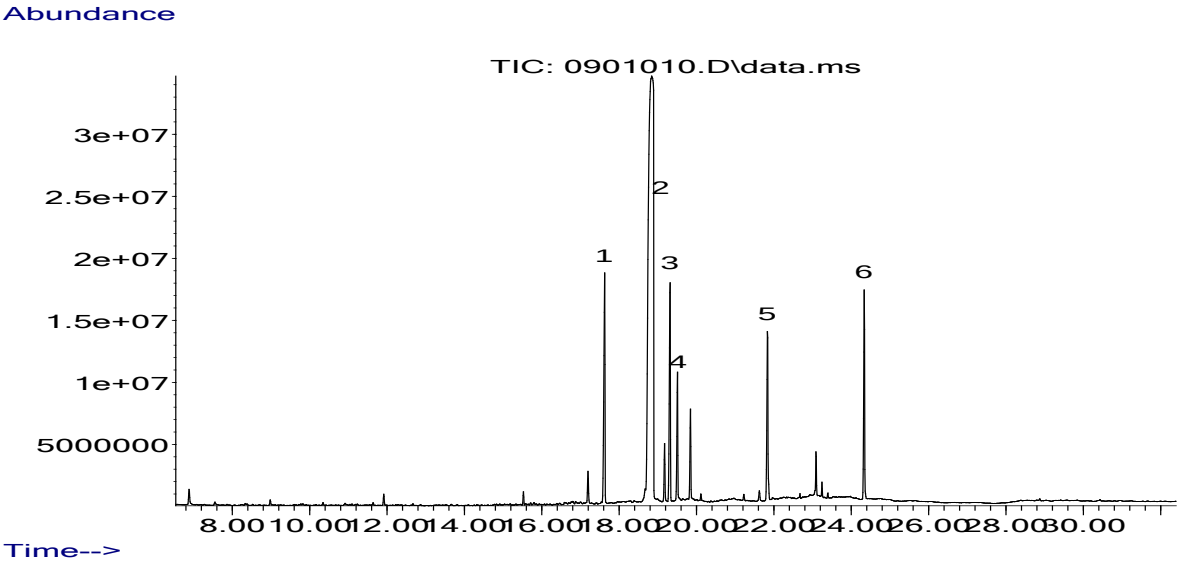


Number of compounds isolated: 18

Compounds identified to better than 90%:

CAS#	**Name**
000117-81-7	1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHP)
000084-69-5	1,2-Benzenedicarboxylic acid, diisobutyl ester (DiBP)
000084-74-2	1,2-Benzenedicarboxylic acid, dibutyl ester (DBP)
006422-86-2	1,4-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHT)
000719-22-2	2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-
001669-44-9	3-Octen-2-one
002082-79-3	Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, octadecyl ester (Irganox 1076)
000295-65-8	Cyclohexadecane
000112-39-0	Hexadecanoic acid, methyl ester
000128-37-0	Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-

RU17007

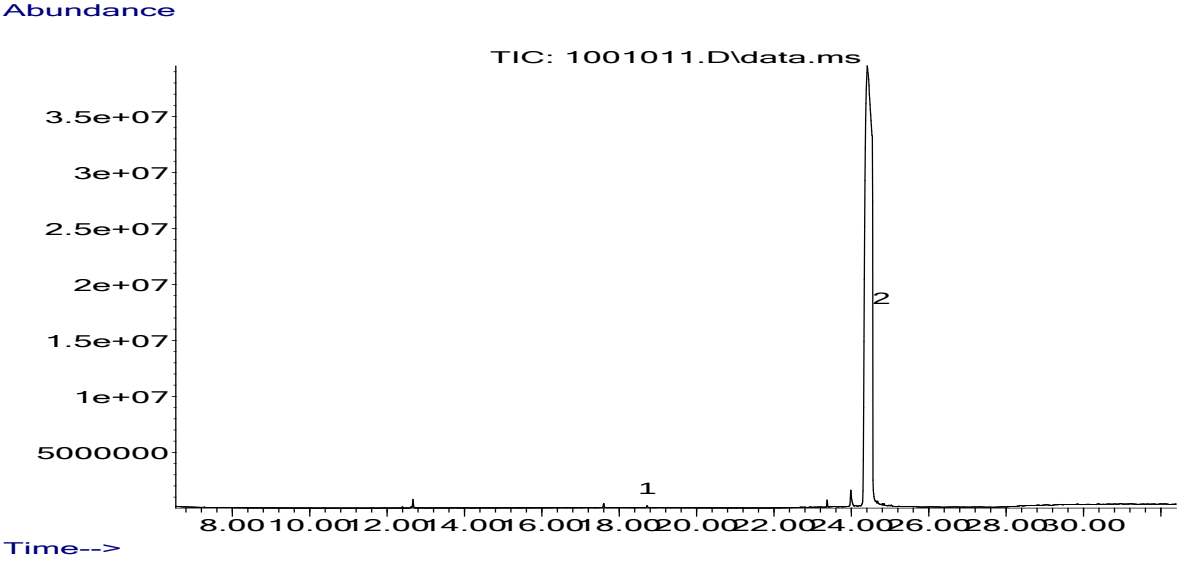


Number of compounds isolated: 65

Compounds identified to better than 90%:

CAS#	Name	
000084-69-5	1,2-Benzenedicarboxylic acid, diisobutyl ester (DiBP)	**2**
017851-53-5	1,2-Benzenedicarboxylic acid, butyl 2-methylpropyl ester	**3**
006422-86-2	1,4-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHT)	**6**
000112-53-8	1-Dodecanol	
000112-88-9	1-Octadecene	
000112-72-1	1-Tetradecanol	
000084-74-2	Dibutyl phthalate	
000929-77-1	Docosanoic acid, methyl ester	
000112-40-3	Dodecane	
001120-28-1	Eicosanoic acid, methyl ester	
000112-39-0	Hexadecanoic acid, methyl ester	**1**
000124-10-7	Myristic acid, methyl ester	
000112-61-8	Octadecanoic acid, methyl ester	**4**
006084-76-0	Oxiraneoctanoic acid, 3-octyl-, methyl ester	**5**
000629-62-9	Pentadecane	
000108-95-2	Phenol	
000101-02-0	Phosphorous acid, triphenyl ester	
000629-59-4	Tetradecane	
000629-50-5	Tridecane	

RU17008

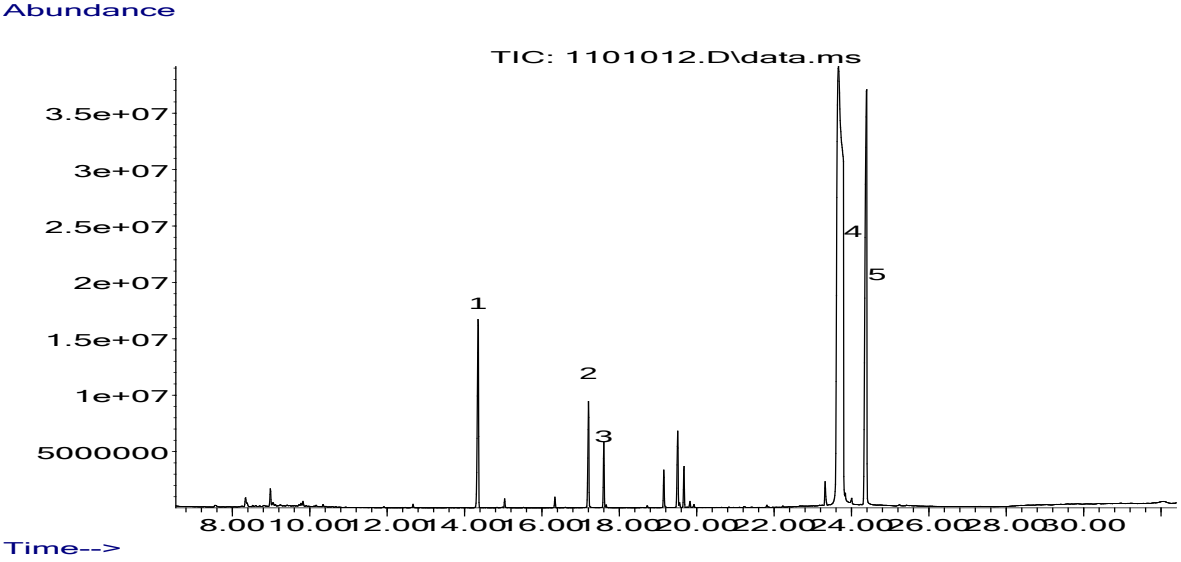


Number of compounds isolated: 12

Compounds identified to better than 90%:

CAS#	**Name**	
000084-69-5	1,2-Benzenedicarboxylic acid, diisobutyl ester (DiBP)	**1**
006422-86-2	1,4-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHT)	**2**
000112-53-8	1-Dodecanol	

RU17009

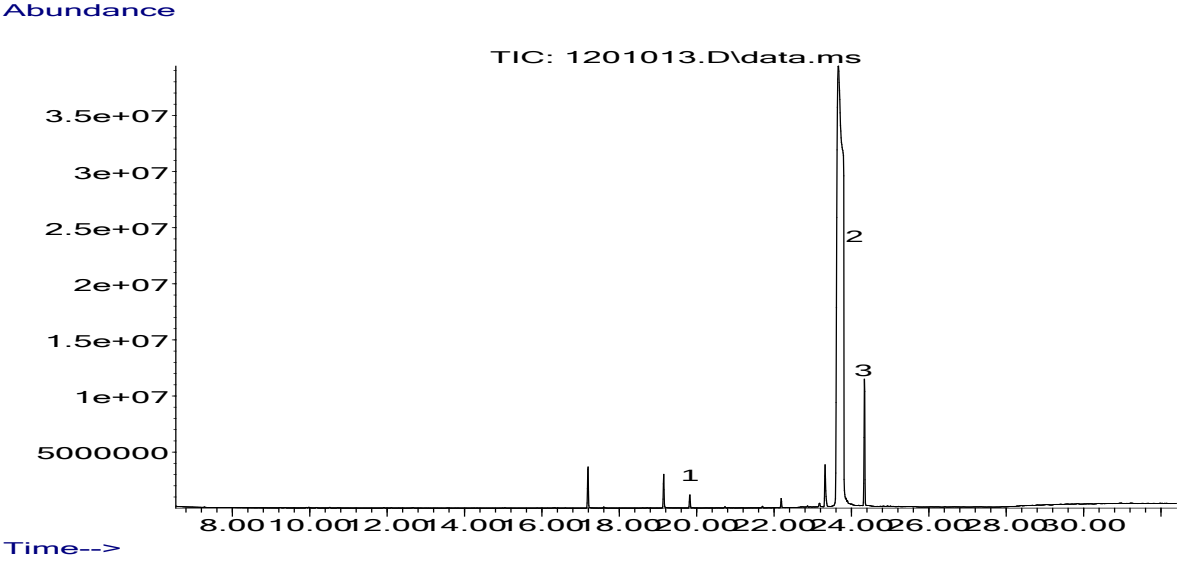


Number of compounds isolated: 34

Compounds identified to better than 90%:

CAS#	Name	
000084-69-5	1,2-Benzenedicarboxylic acid, diisobutyl ester (DiBP)	
000084-74-2	1,2-Benzenedicarboxylic acid, dibutyl ester (DBP)	
000117-81-7	1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHP)	**4**
006422-86-2	1,4-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHT)	**5**
000112-53-8	1-Dodecanol	
000112-88-9	1-Octadecene	
001120-36-1	1-Tetradecene	
006846-50-0	2-Methyl-propanoic acid, 2,2-dimethyl-1-(1-methylethyl)-1,3-propanediyl ester	**1**
035953-54-9	2-Tetradecene, (E)-	**2**
000301-00-8	9,12,15-Octadecatrienoic acid, methyl ester	
002566-97-4	9,12-Octadecadienoic acid, methyl ester	
001120-25-8	9-Hexadecenoic acid, methyl ester, (Z)-	**3**
001937-62-8	9-Octadecenoic acid, methyl ester, (E)-	
000103-23-1	Adipic acid, bis(2-ethylhexyl) ester (DEHA)	
000112-40-3	Dodecane	
003891-98-3	Dodecane, 2,6,10-trimethyl-	
000112-39-0	Hexadecanoic acid, methyl ester	
002566-91-8	Oxiraneoctanoic acid, 3-octyl-, methyl ester	
000629-59-4	Tetradecane	
000629-50-5	Tridecane	

RU17010

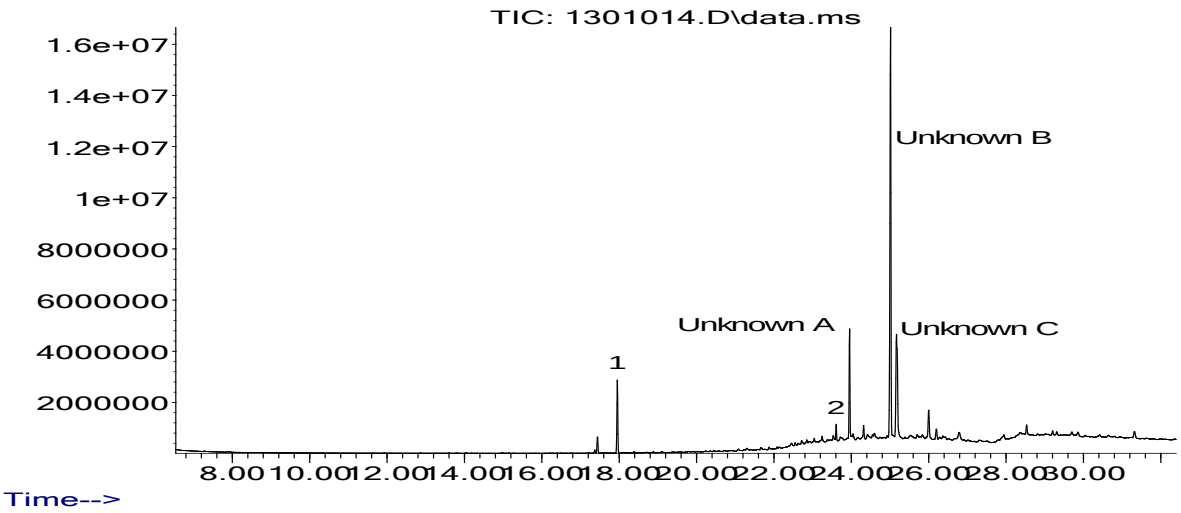


Number of compounds isolated: 13

Compounds identified to better than 90%:

CAS#	**Name**	
000117-81-7	1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHP)	**2**
000084-74-2	1,2-Benzenedicarboxylic acid, dibutyl ester (DBP)	1
000084-69-5	1,2-Benzenedicarboxylic acid, diisobutyl ester (DiBP)	
000131-20-4	1,2-Benzenedicarboxylic acid, diisooctyl ester (DiOP)	
006422-86-2	1,4-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHT)	**3**
035953-54-9	2-Tetradecene, (E)-	
078016-72-5	Benzenesulfonic acid, 4-methyl-, 2-ethylhexyl ester	
001454-84-8	Nonadecanol-1	

RU17011



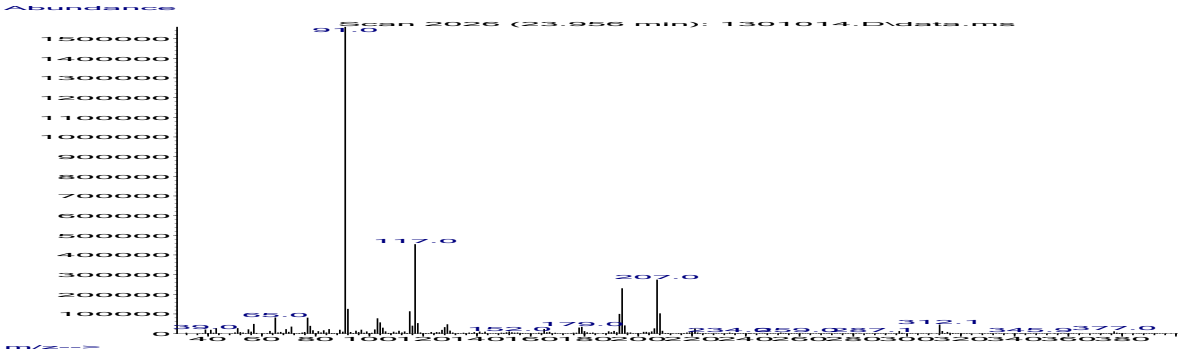
Number of compounds isolated: 35

Compounds identified to better than 90%:

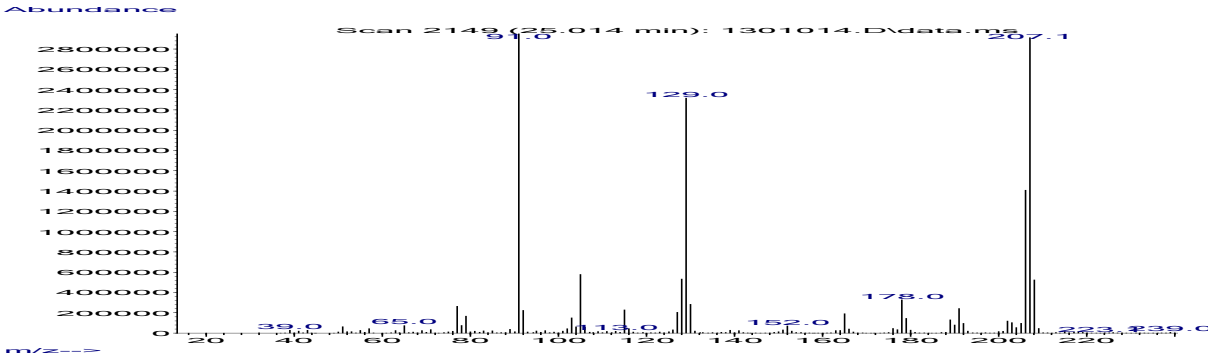
CAS#	**Name**	
000117-81-7	1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHP)	**2**
000084-69-5	1,2-Benzenedicarboxylic acid, diisobutyl ester (DiBP)	
006422-86-2	1,4-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHT)	
004757-69-1	1H-Indole, 2-methyl-3-phenyl-	
020071-09-4	Benzene, 1,1'-(1,2-cyclobutanediyl)bis-	**1**
003018-21-1	Cyclobutane, 1,2-diphenyl-	
000638-36-8	Hexadecane, 2,6,10,14-tetramethyl-	
003018-20-0	Naphthalene, 1,2,3,4-tetrahydro-1-phenyl-	
000630-02-4	Octacosane	

Note: chromatogram contained three abundant peaks of compounds that could not be reliably identified. Their GC/MS fragmentation is presented below. Unknowns B & C showed fragmentation typical for isomeric compounds.

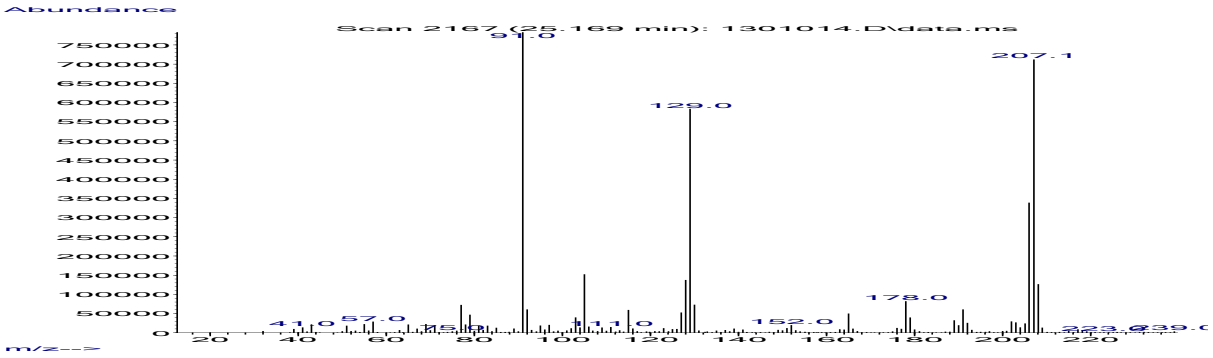
Unknown A



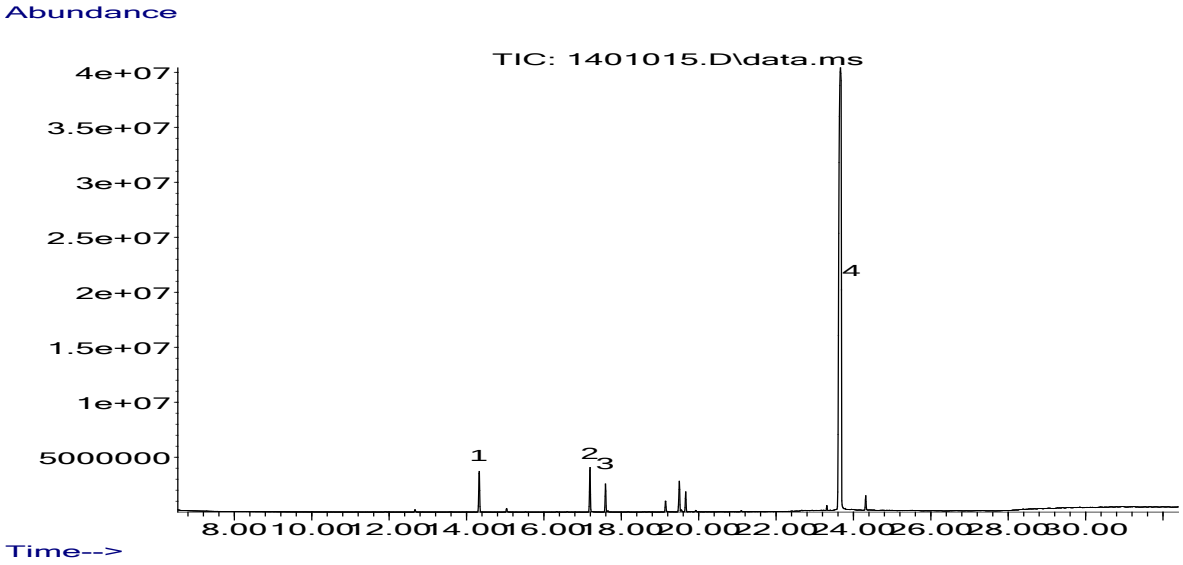
Unknown B



Unknown C



RU17012



Number of compounds isolated: 15

Compounds identified to better than 90%:

CAS#	Name	
000117-81-7	1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHP)	**4**
006422-86-2	1,4-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHT)	
000872-05-9	1-Decene	
000112-41-4	1-Dodecene	
000629-73-2	1-Hexadecene	**2**
052380-33-3	11-Octadecenoic acid, methyl ester	
006846-50-0	2-Methyl-propanoic acid, 2,2-dimethyl-1-(1-methylethyl)-1,3-propanediyl ester	**1**
035953-54-9	2-Tetradecene, (E)-	
000112-63-0	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	
000112-62-9	9-Octadecenoic acid (Z)-, methyl ester	
000112-39-0	Hexadecanoic acid, methyl ester	**3**