ABSTRACT

Title of Document: MEASUREMENT OF CONTEMPORARY CARBON CONTENT OF BIS (2-ETHYLHEXYL) PHTHALATE IN MARKET BUTTER BY ACCELERATOR MASS SPECTROMETRY

Ting Tong, Doctor of Philosophy, 2014

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Bis (2-ethylhexyl) phthalate (DEHP) is a commonly used plasticizer and is thought to have potential for disrupting human endocrine function and inducing tumorigenesis. DEHP has been shown to be ubiquitous in food, especially fatty foods, such as milk, cheese, and butter. Consequently, the U.S. Food and Drug Administration (US-FDA) and the European Food Safety Authority (EFSA), have keen interests in determining whether or not the presence of this phthalate in food is the result of contamination with synthetic DEHP, made from petroleum derived feed stocks, or is in-fact, the result of natural processes. Herein, the fraction of contemporary carbon (i.e., naturally produced) in DEHP was determined for each of seven 1.1 kg samples of unsalted market butter by accelerator mass spectrometry (AMS) at the Lawrence Livermore National Laboratory, after isolation and purification methods optimized to provide ≈250 μg of the DEHP in butter containing

≈0.7 mg/kg DEHP at a total carbon purity of 92.5 ± 1.2 % to 97.3 ± 1.0 % (n=3, 1σ as determined by gas chromatography-electron impact-mass spectrometry (GC-EIMS). Method blanks contributed 0.52 ± 0.19 μg to 1.08 ± 0.08 μg (n=3, 1σ) carbon as DEHP in individual butter isolates, and median exogenous carbon contamination, including (1) contributions from post-HPLC handling (1.8 ± 9.1 μg to 22.2 ± 9.7 μg), (2) method derived carbonates (31.2 ± 7.2 μg), and (3) matrix-inherent carbonates (median of 120 μg carbon), was 50%. After correcting for these interferences, the mean fraction of contemporary DEHP in butter was determined to be 0.0220 ± 0.0497 (n=5, 1σ). At the 95 % confidence interval, 97.8 ± 9.9 % of the DEHP in butter was petrogenic. To our knowledge, this is the first report of the fraction of contemporary DEHP isolated from market butter in the U.S.

MEASUREMENT OF CONTEMPORARY CARBON CONTENT OF BIS (2-ETHYLHEXYL) PHTHALATE IN MARKET BUTTER BY ACCELERATOR MASS SPECTROMETRY

By

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Chapter 1 : Introduction and Background

1.1. DEHP Properties

Phthalate esters are commonly used in as (1) plasticizers in plastics, e.g., polyvinyl chloride (PVC), (2) viscosity control agents in ink and cosmetics, and (3) dispersants and emulsifying agents (Koo & Lee, 2004). One of the major phthalate esters produced for these purposes is bis (2-ethylhexyl) phthalate. The content of DEHP in polymer materials may vary but is typically ≈30% (w/w) (European Chemicals Bureau, 2008). DEHP is not covalently bonded to polymeric matrices and therefore it readily diffuses out from plastics and leaches into the environment. The annual production worldwide is 1 to 4 million metric tons (Pocar et al., 2012). Approximately 2% of the world's phthalates are released into the environment each year and part of this release is incorporated into the food chain (Huber, Grasl-Kraupp, & Schulte-Hermann, 1996).

DEHP has a low acute toxicity and can be metabolized quickly in humans: in fact, ≈ 47% of ingested DEHP is excreted via urine within two days. The major metabolites are mono (2-ethyl-5-hydroxyhexyl) phthalate (5OH-MEHP), mono (2-ethyl-5-oxohexyl) phthalate (5oxo-MEHP) and mono (2-ethylhexyl) phthalate (MEHP) (Koch, Bolt, & Angerer, 2004) (see Figure 1.1).

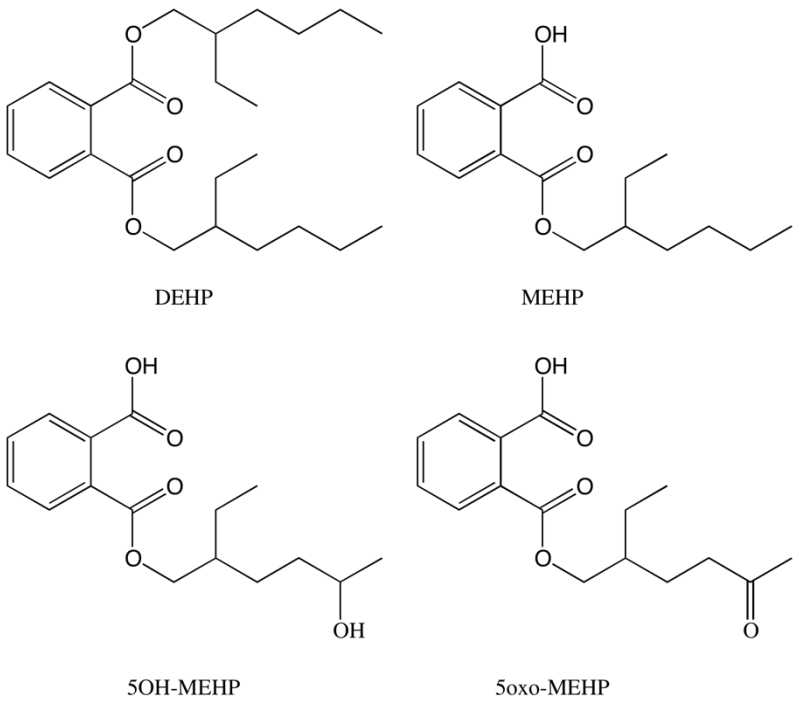


Figure 1.1 Structural formulae of DEHP, MEHP, 5OH-MEHP and 5oxo-MEHP

Long-term exposure to or overdose of DEHP may induce tumorigenesis (Ito et al., 2007), and male feminization (Lottrup et al., 2006) and/or infertility by endocrine function disruption (Hirosawa, Yano, Suzuki, & Sakamoto, 2006). Phthalate intoxication may occur by percutaneous absorption (Deisinger, Perry, & Guest, 1998), inhalation, and consumption. Koniecki *et al.* collected 252 personal care products in Canadian markets and detected phthalates in more than 50% of them (Koniecki, Wang, Moody, & Zhu, 2011). More recently, the U.S. Congress passed the *Consumer Product Safety Improvement Act of 2008*, which included a federal ban on phthalates in toys and children's products, to reduce the phthalate exposure of children.

DEHP is lipophilic and easily accumulated in lipids. There are various ways for lipophilic phthalates to migrate into food, especially oily and lipid-rich foods (i.e., fatty foods). For example, packing with plastics (Balafas, Shaw, & Whitfield, 1999) and using food additives (e.g., clouding agents) are known sources (Yen, Lin-Tan, & Lin, 2011). Such practices make DEHP contamination widespread. The main fatty food groups are meat and dairy products, including milk, cheese and butter. Cow's milk contains from 0.0085 to 0.17 mg/kg DEHP and reported levels in cheese vary from 0.041 to 1.23 mg/kg DEHP (Wormuth, Scheringer, Vollenweider, & Hungerbuhler, 2006). Nelson *et al.* (2013) recently reported an average DEHP concentration of 0.14 mg/kg in Stilton cheese (Nelson, Ondov, VanDerveer, & Buchholz, 2013). Butter, which is usually made from pasteurized fresh milk without fermentation, is consumed daily by a large fraction of the U.S. population (although, some butter is made from fermented cream with commercial starter culture bacteria, for instance, *Lactobacillus, Lactococcus, Leuconostoc and Streptococcus*) (Katla, Kruse, Johnsen, & Herikstad, 2001). Butter contains the highest mean (81.1% , w/w) level of lipids (listed in Table 1.1) of any dairy of the products (U.S. Department of Agriculture, 2013), and DEHP concentrations as large as 2.4 mg/kg have been reported (Sharman, Read, Castle, & Gilbert, 1994). The DEHP content of Giant® store brand unsalted butter used in my study was 0.7 mg/kg (Tong, unpublished data).

Table 1.1 Nutrient content in 100 g unsalted butter

Nutrients	***Content***
Energy, kcal	717
Water, g	17.94
Protein, g	0.85
Total Lipids, g	81.11
Saturated Fat, g	51.37
Monounsaturated Fat, g	21.02
Polyunsaturated Fat, g	3.04
Trans Fat, g	2.98
Cholesterol, mg	215
Total Carbohydrates, g	0.06
Ash, g	0.04
Vitamins	
Vitamin A, IU	2499
Vitamin E (alpha-tocopherol), mg	2.32
Folate, ug	3
Niacin, mg	0.04
Riboflavin, mg	0.03
Thiamin, mg	0.005
Vitamin B_6, mg	0.003
Vitamin D, IU	56
Pantothenic acid, mg	0.11
Vitamin B_{12}, ug	0.17
Vitamin K, ug	7
Minerals	
Calcium, mg	24
Iron, mg	0.02
Magnesium, mg	2
Phosphorous, mg	24
Potassium, mg	24
Sodium, mg	11
Zinc, mg	0.09
Selenium, ug	1
Unsaturated fatty acids	
Monounsaturated, g	21.021
16:1 Palmitoleic, g	0.961
18:1 Oleic, g	19.961
Polyunsaturated, g	3.043
18:2 Linoleic, g	2.728
18:3 Linolenic, g	0.315

Saturated fatty acids	
4:0 Butyric, g	3.226
6:0 Caproic, g	2.007
8:0 Caprylic, g	1.19
10:0 Capric, g	2.529
12:0 Lauric, g	2.587
14:0 Myristic, g	7.436
16:0 Palmitic, g	21.697
18:0 Stearic, g	9.999
Inorganic carbons	
Carbonates/bicarbonates, g [a]	0.024[b]

Source: USDA National Nutrient Database for Standard Reference, Release 20 (2007)
[a] Sodium carbonate (or bicarbonate) is a normal additive that is used in dairy products (Williams, 1887).
[b] unpublished data (Tong, 2013), measured with ion chromatography

1.2. Industrial Synthesis of DEHP

Most manufacturers synthesize DEHP from petrogenic phthalic anhydride and 2-ethyl-hexanol (European Chemicals Bureau, 2008). This involves a 2-step esterification as shown in: rapid alcoholysis of phthalic acids and reversible esterification from monoester to di-ester, which is the rate-determining step. Since anthropogenic DEHP is made from million-year-old fossil carbon, its isotope ratio of $^{14}C/^{12}C$ is below the detection limit of Accelerator Mass Spectrometry (AMS). For this reason it is regarded as being "^{14}C-dead" (see section 1.4).

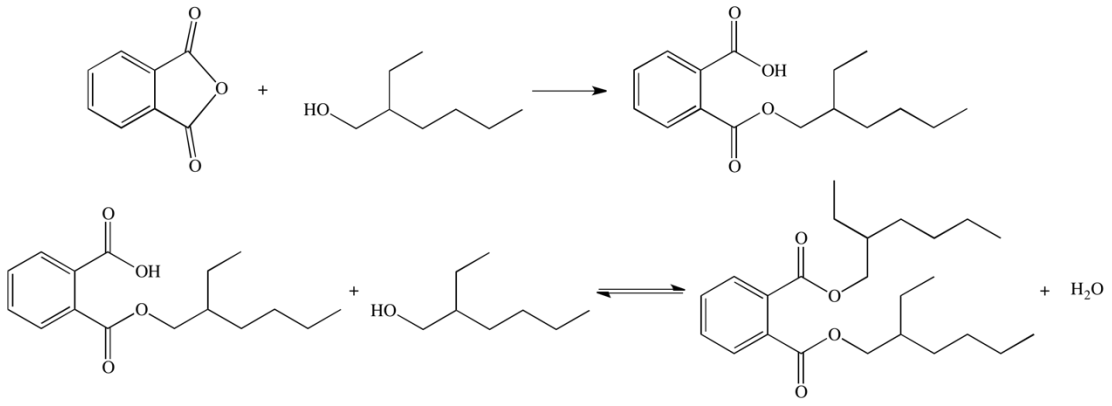


Figure 1.2 Industrial synthesis of DEHP from phthalic anhydride and 2-ethyl-hexanol by esterification

1.3. DEHP Occurrence in Various Organisms

Phthalate esters are found in many species of plants. The first discovery of phthalates in plants was reported by Japanese scientists. Hayashi *et al.* found several kinds of phthalates, including dimethyl phthalate, Di-n-butyl phthalate (DBP), Di-iso-butyl phthalate (DiBP), and DEHP in *Cryptotaenia Canadensis DC. Var. Jayonic Makino* ('mitsuba' in Japanese), a vegetable both cultivated and growing in wild areas all over Japan (Hayashi, Asakawa, Ishida, & Matsuura, 1967). Though these phthalates were identified with GC-MS and NMR, their concentrations were not provided. Uyeda identified DEHP in the filtrate of a culture of *Streptomyces* sp. strain No. A-1135 (Uyeda, Suzuki, & Shibata, 1990). They isolated 1.4 mg of an oily and colorless liquid from 1-L of culture filtrate after a 2-week cultivation, and identified it as DEHP with ^{13}C NMR and ^{1}H NMR. They also speculated that DEHP synthesis by this might have genetically evolved a natural synthesis route owing to DEHP interactions with some hydrophobic sites on cell membranes, presumed to be beneficial to this organism. It has been suggested that some molds might also synthesize DEHP. Specifically, Amade *et al.* (Amade, Mallea, & Bouaicha, 1994) reported that DEHP existed in filtrates of *Streptomyces* sp. cultures and that the producing organism was identified as *Penicillium olsonii.* But whether its presence in the filtrate truly resulted from natural synthesis by the *Penicillium olsonii* or by petrogenic DEHP contamination of the medium was not ascertained.

More recently, Chen (2004) found that a red alga, *Bangia atropurpurea*, from shallow coastal waters of Taiwan, synthesized DEHP *de novo* as evidenced by cultivating it in the laboratory with $NaH^{14}CO_3$ (Chen, 2004). Radioactive DEHP and DBP were produced afterwards. Additionally, in his control groups, different algae (*P. Angusta and P. Dentata*) were cultivated and only 6.35 ± 0.91 and 18.53 ± 0.18 mg/kg DEHP in dry filaments were detected compared to the experimental group (*Bangia atropurpurea*), in which the concentration was determined to be 34.74 ± 1.2 mg/kg.

Thus, aside from its anthropogenic sources, DEHP contamination of butter might occur owing to natural synthesis by organisms in forage, and possibly by fermentation microbes during dairy products production.

1.4. Radiocarbon

Carbon is a fundamental element of nature. Countless carbon skeletons contribute to the diversity of organic compounds. There are 15 known carbon isotopes, most of which are short-lived with half-lives of less than a second (see Table A 1.1) (Audia, Bersillonb, Blachotb, & Wapstrac, 2003). There are two naturally occurring stable carbon isotopes, ^{12}C and ^{13}C, with abundances of ≈99% and ≈1% respectively, and one long-lived radioisotope, ^{14}C, which accounts for ≈0.0000000001% of the carbon atoms in contemporary carbonaceous material in-equilibrium with the atmosphere (International Atomic Energy Agency (IAEA) and United Nations Educational Scientific and Cultural Organization, 2001).

^{14}C is formed by cosmic neutrons at altitudes between 9 and 15 km over high-geomagnetic areas at a rate of 1.54×10^{15} Bq/year (Svetlik et al., 2010).

$$\mathbf{^{1}_{0}n + {}^{14}_{7}N \rightarrow {}^{14}_{6}C + p} \quad (1.1)$$

^{14}C atoms in the upper atmosphere rapidly react with oxygen to form carbon monoxide which is subsequently oxidized into radiocarbon dioxide. $^{14}CO_2$ become distributed throughout the entire atmosphere below within weeks, and is subsequently incorporated into the biosphere by photosynthesis. Interchange between biomass and the atmospheric reservoir maintains the ^{14}C levels in living organisms. Once the exchange ceases, the isotope ratio of $^{14}C/^{12}C$ begins to decrease due to beta decay of ^{14}C, i.e.,

$$\mathbf{^{14}_{6}C \rightarrow {}^{14}_{7}N + {}^{0}_{-1}e + \overline{\nu_e}} \quad (1.2)$$

with a half-life of 5730 ± 40 years (Cambridge half-life, 1962).

Thus, the only difference between DEHP from different synthetic routes is its radiocarbon abundance. As discussed below, minute differences in the abundance of radiocarbon in individual compounds can be determined with great precision by Compound-Specific Isotope-Accelerator Mass Spectrometry (CSIA-AMS). These differences can be used to determine the relative amounts of DEHP that are synthesized from biogenic processes and petrochemicals, respectively.

CSIA-AMS has been applied to successfully measure the fraction of "modern carbon" (f_m) (see section 3.7.2), i.e., carbon derived from atmospheric reservoir, in dibutyl phthalate in algae (Namikoshi, Fujiwara, Nishikawa, & Ukai, 2006). By convention, the term "modern carbon" is defined as carbon having an isotope composition of biogenic carbon compounds synthesized in the year 1950 (Stuiver &

Polach, 1977). As described below, "modern carbon" is differentiated from contemporary carbon as the latter contains ≈5% less ^{14}C.

The difference of $^{14}C/^{12}C$ between the sample and the contemporary atmosphere reservoir can be used to estimate the age of organic materials because ^{14}C continuously decay to ^{14}N without replenishment.

The equation of radioactive decay is as follows:

$$\boldsymbol{N = N_0 e^{-\lambda t}} \tag{1.3}$$

$$\boldsymbol{t = \frac{1}{\lambda} ln\left(\frac{N_0}{N}\right) = \tau ln2 = T_{1/2}} \tag{1.4}$$

N_0 is the initial number of ^{14}C atoms and N is the current number of ^{14}C atoms. λ and τ are constants of the particular radioactive isotope. The Cambridge half-life of ^{14}C is 5730 ± 40 years, so τ=8267 year^{-1}. Consequently petroleum derived carbon, having been aged more than 250,000 years (43.6 half-lives), contains no detectable ^{14}C by AMS (Baumgardner, Humphreys, Snelling, & Austin, 2003).

Chapter 2 : Objective and Approach

As demonstrated above, DEHP in dairy products may come from both microbial metabolism and industrial contamination. According to Nelson (2013), the fraction of contemporary DEHP in Stilton cheese, 0.235 ± 0.073 (1σ), indicated that at least 75% of it was petrogenic (Nelson et al., 2013), despite the fact that it contains penicillium. Since most butter is not fermented while Stilton cheese is, lower abundances of ^{14}C in DEHP extracted from butter could be expected. Prior to 2010, no study of DEHP origins in butter or other dairy products consumed in the U.S. had been undertaken. Consequently, the U.S. Food and Drug Administration (US-FDA) sought to determine the origin of DEHP in fatty food and provided us with funding to optimize and apply CSIA-AMS methods to U.S. grocery store butter.

CSIA demands high-purity analytes that, in our case, had to be isolated from a complex organic matrix (81.1 % lipids and 1% proteins). A variety of refinements of the methods typically used for quantitative analytical determinations of phthalates in fatty foods, were required, not the least of which were to achieve a million-fold enrichment over the DEHP concentration in butter and scale up the methods to produce 250 μg quantities of highly-pure DEHP, and to do so without compromising the isolates with ubiquitous phthalate contamination. As described below, this was accomplished by liquid-liquid extraction, flash chromatography, and preparative scale high-performance-liquid chromatography (HPLC). Isotopic ratio measurements were accomplished at the Lawrence Livermore National Laboratory Center for Accelerator Mass Spectrometry (LLNL-CAMS). Since the principle route of human exposure to

DEHP relevant to the U.S. FDA is food intake, a well-developed method for quantitative determination of the fraction of petrogenic phthalate esters were needed, as was its application to a variety of fatty foods to support their mission to protect human health.

Chapter 3 : Laboratory and Computational Methods, and Preliminary Results

3.1. Preparation and DEHP Content Measurement

Before the work could be initiated, it was necessary to evaluate potential ^{14}C contamination and estimate the DEHP content in raw butter.

3.1.1. Swipe Tests

As suggested by LLNL, the laboratory preparing AMS samples must be free of ^{14}C contamination resulting from the use of radiocarbon-labeled materials that might have been used, most anywhere in the laboratory or even elsewhere in other laboratories in the same buildings accessed by researchers (Buchholz, Freeman, Haack, & Vogel, 2000).

To do so, glass fiber filters, wet with ethanol, were used to gently "swipe" approximately 2-3 cm^2 areas of various surface in each of the laboratories used in the project (see Table 3.1). The swiped filters and one blank filter (unused, an ethanol-wetted) were place in individual glass vials with PTFE-lined phenolic caps and sent to LLNL-CAMS.

The carbon in the filter matrix, as well as that picked up by swipes, was converted to graphite after spiking with 1.2 mg carbon in the form of tributyrin carrier to provide enough carbon for AMS measurement (Buchholz et al., 2000). The mean measured modern fraction (f_m) of the filters was ≈0.17. The suggested radiocarbon level on surfaces in the in sample preparation laboratory is 5-50 amol / mg C (see Table 3.2) (Buchholz et al., 2000). The measured fraction modern of filters are listed

in Table 3.1 and Figure 3.1. The condition of our lab was deemed "not serious" and the only action to be performed was "staying alert".

Table 3.1 Swipe test result in the sample preparation laboratory [a]

Location	***Fraction Modern (f_m)***	***Isotopic Ratio amol ^{14}C/mg C*** [b]
Blank	0.162 ± 0.010	13.5 ± 0.8
Door Handle	0.205 ± 0.009	17.1 ± 0.8
Computer Keyboard	0.178 ± 0.011	14.8 ± 0.9
Bench Top	0.176 ± 0.008	14.7 ± 0.7
Bench Top near Sink	0.181 ± 0.012	15.1 ± 1.0
Fume Hood	0.164 ± 0.011	13.7 ± 0.9
Balance	0.174 ± 0.012	14.5 ± 1.0
Window	0.153 ± 0.010	12.7 ± 0.8

[a] Swipe test was performed with Michael Nelson, in Room 3110, BLDG091, University of Maryland, College Park, on July, 2011
[b] atto mol=10^{-18} mol, the nature abundance of ^{14}C is 1×10^{-12}

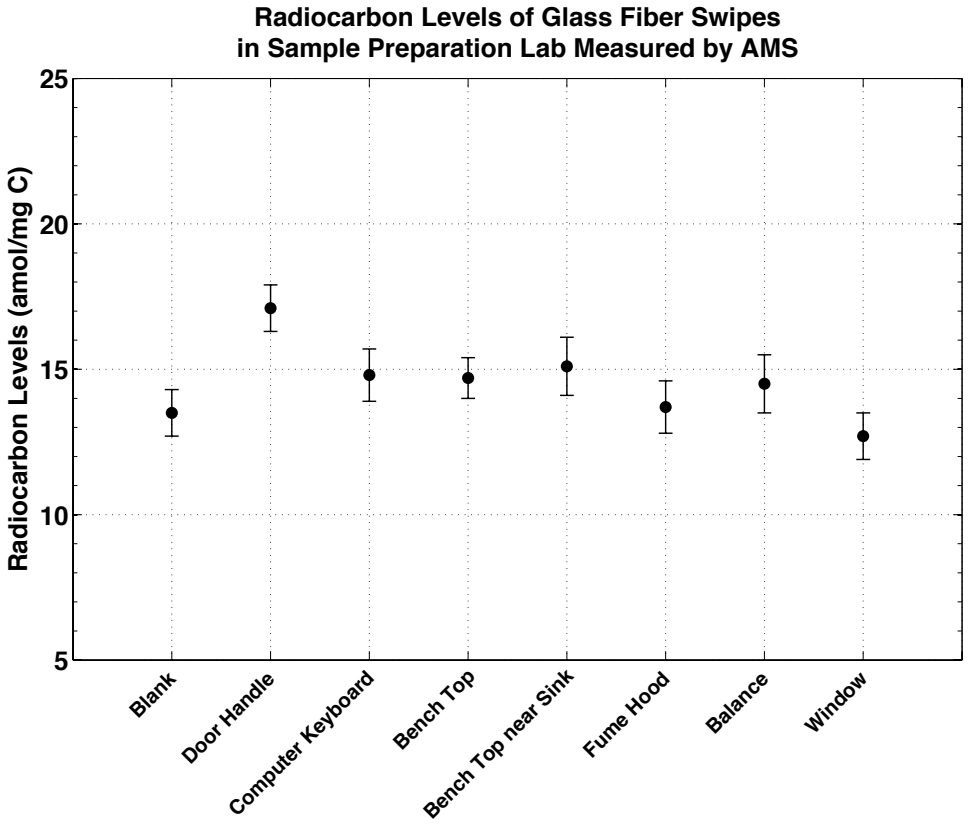


Figure 3.1 Radiocarbon (^{14}C) levels of glass fiber swipes measured by AMS

Table 3.2 The ^{14}C attention levels for swipe test (Buchholz, 2000)

amol 14C/mg C [a]	***fCi*** [b]	***Conclusion***	***Action***
5-50	0.3-3	Not Serious	Stay alert
50-100	3-6	May be dirty	Clean and re-swipe
>100	>6	Contaminated	Resurface

[a] amol = atto mol = 10^{-18} mol
[b] fCi = femto curie = 10^{-15} C

3.1.2. Butter Matrices

Giant® store brand unsalted butter (distributed by Foodhold USA, LLC, Landover, MD 20785) was selected for analysis in this study. Three batches of that butter were purchased at a local grocery store (Giant® #0334, 3521 East-West Highway, Hyattsville, MD 20782). The first batch, five pounds, purchased in December 2011, was used for screening and method development. The second 18-pound batch purchased in March 2011 was extracted to provide the first six samples for AMS, while a third 6-pound batch, purchased in November 2012, was extracted to produce the seventh sample.

As received, butter was packaged in 4-ounce sticks and wrapped in waxed paper, 4 sticks per paper box. Purchased butter in its original packing was wrapped with baked aluminum foil and stored in a freezer (-20 °C) for further treatment.

3.1.3. Measurement of DEHP Content in Butter

To meet the recommended ^{14}C measurement level at LLNL-CAMS (>50 μg carbon), DEHP content estimation in raw butter was perform prior to batch extractions.

Accordingly, 113.6 g butter plus 27.85 μg *d38*-DEHP (98 % pure, Cambridge Isotope Laboratories, Andover, MA, see Figure 3.2) as an internal standard was dissolved in 300 mL hexane (J.T.Baker®, 95% n-Hexane) and 30 mL acetone (Sigma-Aldrich® , ACS reagent, >99.5%) with gentle heat. The supernatant was then collected by gravity filtration. The resulting clear solution was extracted with 500 mL acetonitrile. Afterwards the acetonitrile layer was stored in a freezer (-20^{o}C) for 12 h to precipitate lipids. Acetonitrile was then removed and evaporated by rotary

evaporation and the resulting ≈0.7 g oily sample transferred to a newly prepared 25-mL column (10 g silica gel, 32 μm to 63 μm, Dynamic Adsorbents, Atlanta, GA) for further purification of the DEHP. This column was prepared by filling it with 25 mL 8% (v/v) acetone in hexane and then pouring in the silica gel. Prior to loading the butter sample, column conditioning was performed by rinsing with 25 mL of hexane. The sample was first eluted with 50 mL hexane to remove most lipids and non-polar matrix constituents. This was followed by elution with 50 mL 2% (v/v) acetone in hexane, while collecting the last 20 mL of eluate in 1-ml aliquots. DEHP in each aliquot was measured by a GC-EIMS (Shimadzu® QP2010S, Shimadzu® SHRXI-5MS with polysiloxane coated 30 m × 0.25 μm I.D. column, a temperature ramp of 15 °C/min starting at 90 °C, and He mobile phase flow rate 1.00 mL/min). Due to the large quantities of lipids and fatty acids, the split ratio was set to 200 to prevent the capillary from clogging. DEHP and *d38*-DEHP were detected only in the last 1-mL aliquot.

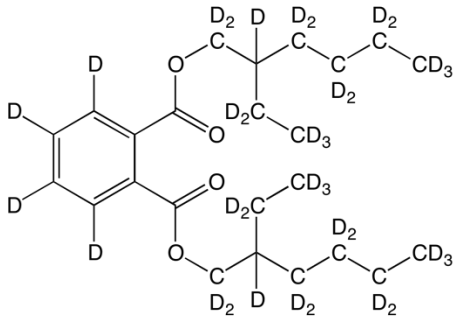


Figure 3.2 The structure of the fully deuterated DEHP (d38-DEHP)

In this preliminary work, only an estimation of the DEHP concentration was needed. This was obtained using the known concentration and response of the internal

standard and spectra collected in selected ion monitoring (SIM) mode. DEHP reliably produces three major fragmentation peaks in EIMS: m/z=149 (base peak), 167, and 279 (see Figure 3.3 and Figure 3.4). The fragmentation pattern of *d38*-DEHP is similar while its base peak is shifted to m/z=154 as expected from its structure (See Figure 3.5).

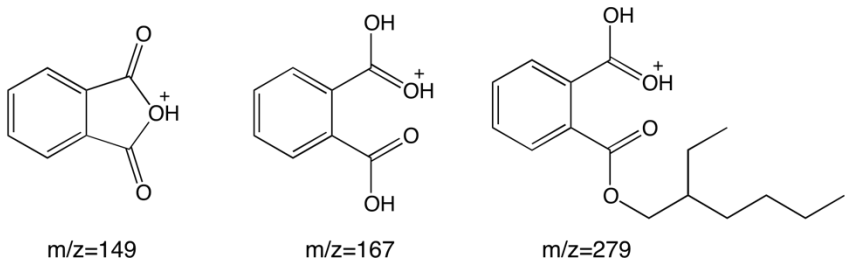


Figure 3.3 DEHP mass spectrometry fragment ions

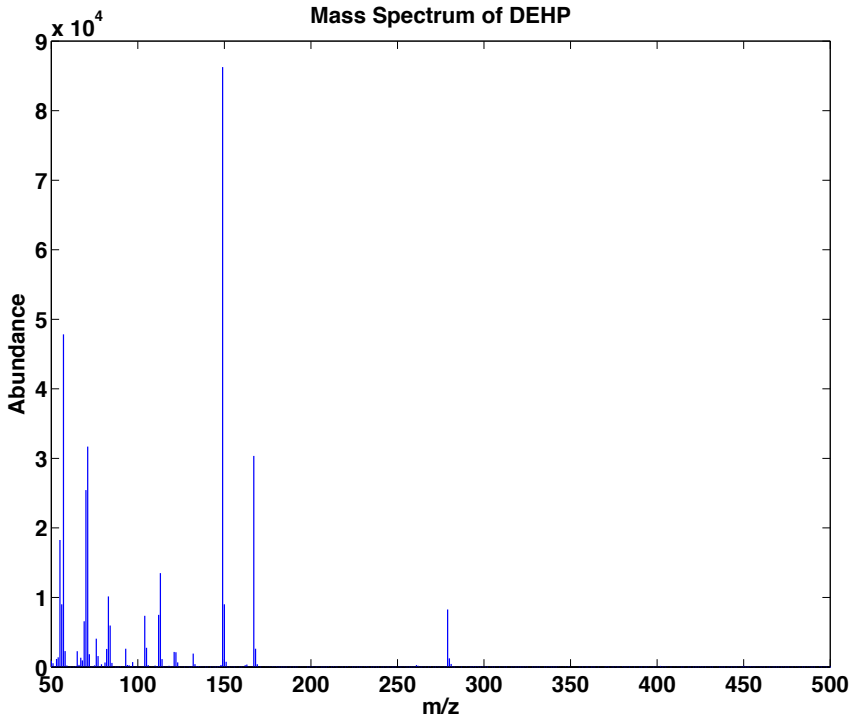


Figure 3.4 Electron-impact mass spectrum of a 93.96 mg/kg solution of DEHP in hexane (prepared with 99.8 ± 0.1 % pure DEHP, Supelco® Analytical, Bellefonte, PA)

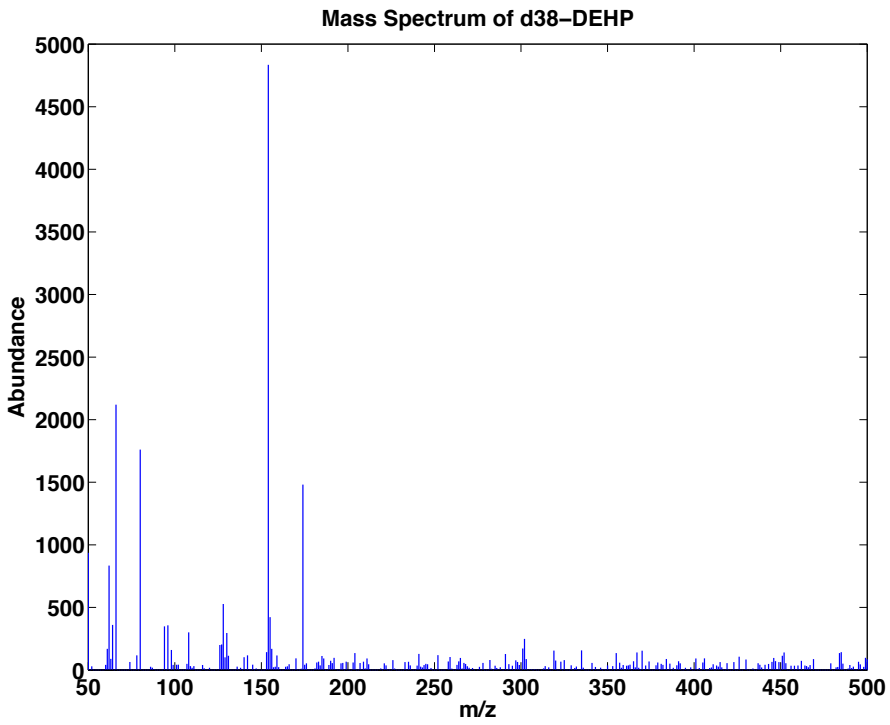


Figure 3.5 Electron-impact mass spectrum of a 5.56 mg/kg solution of d38-DEHP in hexane

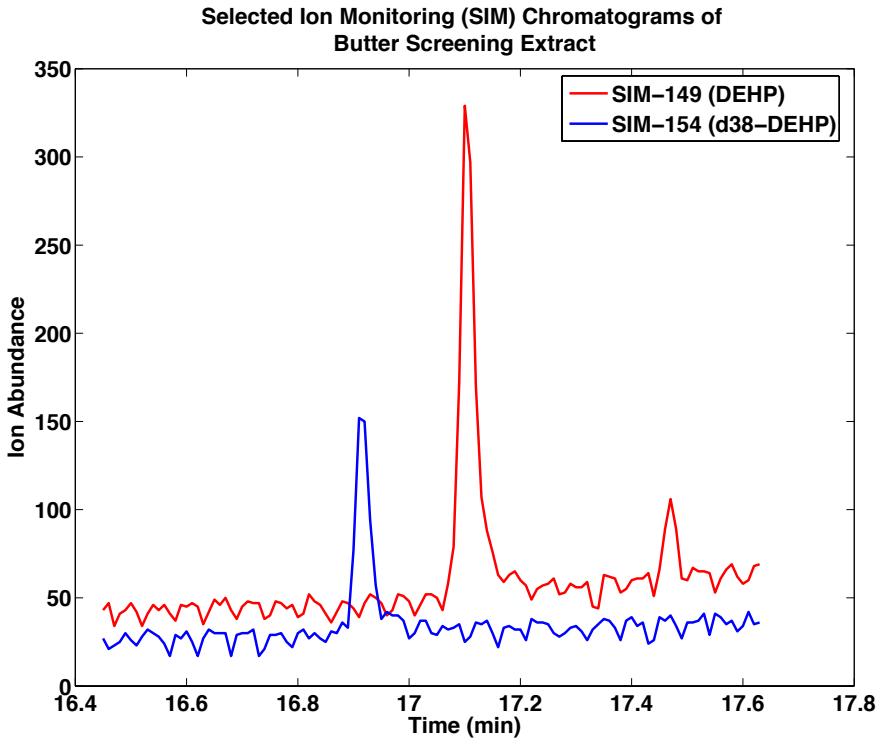


Figure 3.6 Selected ion monitoring (m/z=149, 154) chromatograms of butter extract

Since two different m/z channels were applied to measure DEHP and *d38*-DEHP, the DEHP content in butter was calculated by assuming the DEHP and *d38* DEHP have the same response factor to the instrument:

$$\boldsymbol{c_{DEHP}} = \frac{\boldsymbol{A_{DEHP}}}{\boldsymbol{A_{d38-DEHP}}} \cdot \boldsymbol{c_{d38-DEHP}} \tag{3.1}$$

where c is the content of analyte in butter in mg/kg and A is the peak area in the corresponding SIM chromatogram. The calculated DEHP content in butter was ≈0.73 mg/kg.

3.2. DEHP Batch Extraction and Enrichment

3.2.1. Crude Extraction of the Phthalate from Lipids

According to the computed DEHP content in raw butter above, at least ≈300 g of butter were needed to obtain ≈200 μg DEHP for AMS measurements (100 % recovery). However, the recovery was expected to be much lower, and in fact was later found to be ≈38% (see Table 3.5). Moreover, a portion of DEHP must be reserved for other measurements besides AMS, i.e., stable carbon isotope analysis. Thus ≈1.1 kg of butter (six sticks) was extracted for each designated sample (as shown in Table 3.3).

Along with the butter extracts, seven method blanks were prepared simultaneously (the 6^{th} and 7^{th} method blanks were prepared but not sent to LLNL for AMS. Only five method blanks were quantified). 570 μg of fully deuterated *d38*-DEHP were spiked into both butter mixtures and method blanks at the very beginning of the extraction and purification process to determine the yields and identify peaks in the HPLC chromatograms.

Table 3.3 The mass of butter and internal standard, d38-DEHP

Butter Sample ID	***Extraction Date***	***Butter Mass (g)[a]***	***Internal Standard d38-DEHP (µg)***
Butter1	3/14/2012	1137.1 ± 0.1	544.33 ± 0.05
Butter2	4/23/2012	1135.8 ± 0.1	565.42 ± 0.08
Butter3	5/14/2012	1139.0 ± 0.1	582.75 ± 0.07
Butter4	7/13/2012	1136.1 ± 0.1	594.64 ± 0.04
Butter5	8/22/2012	1133.1 ± 0.1	584.85 ± 0.03
Butter6	11/17/2012	1137.1 ± 0.2	578.26 ± 0.06
Butter7	11/28/2012	1126.0 ± 0.2	474.35 ± 0.04

[a] Uncertainty was calculated from standard deviation, n=3, 1 σ

For each sample, 1.1 kg butter was dissolved in 1 L hexane (J.T.Baker, 95% n-Hexane) with gentle heat (≈40 °C). The supernatant was gravity filtered to remove insoluble residue. The insoluble leftover was then extracted with 300 mL 17% (v/v) acetone in hexane for the second time. Filtrates were combined and reduced to 1.2 L with a rotary evaporator.

Figure 3.7 Butter extraction and method blank preparation

Acetonitrile (J.T.Baker, HPLC grade, 99.9%) was used to perform solvent partitioning. Each 400 mL hexane extract was mixed with 500 mL acetonitrile to enrich DEHP due to its higher solubility in acetonitrile compared to most coexisting non-polar components, i.e., lipids. Another 500 mL of acetonitrile was used to extract the same batch of hexane extract again. The acetonitrile/hexane partition coefficient (K_{ah}) of DEHP is 1.52 ± 0.12 (Kotowska, Garbowska, & Isidorov, 2006). Because DEHP is a nonelectrolyte and maintains molecular form in both hexane and acetonitrile, the following estimation is acceptable:

$$\boldsymbol{Distribution\ ratio\ (D) \approx K_{ah} = 1.52\ \pm\ 0.12} \qquad (3.2)$$

Hexane and acetonitrile are slightly miscible. To simplify the calculation, the volume of hexane is assumed to be invariant.

$$\boldsymbol{E = \left[\frac{D}{D+\frac{V_h}{V_{a1}}} + \left(1 - \frac{D}{D+\frac{V_h}{V_{a1}}}\right) \times \frac{D}{D+\frac{V_h}{V_{a2}}}\right] \times 100\%} \quad (3.3)$$

V_h was the volume of hexane and V_a was the volume of acetonitrile. The calculated recovery (E) of DEHP from the hexane extract is ≈88%.

In contrast, lipids or fatty acids have much lower K_{ah}. No exact partition coefficient was found for a butter fat mixture. A 20-carbon saturated fatty acid ethyl ester, whose K_{ah} is approximately 0.03 (Zhou, Chen, & Li, 2002) was used as a representative for the acetonitrile/hexane system at room temperature. The separation factor (SF) for DEHP and lipids is:

$$\boldsymbol{SF = \frac{D_{DEHP}}{D_{lipids}} \approx 50} \quad (3.4)$$

After partitioning, the resulting six 500 mL light-yellow acetonitrile extracts were combined, reduced to 1 L with rotary evaporation and then stored in a freezer (-20 °C) for 12 h. Lipids and proteins precipitated after cooling and were removed by gravity filtration. Solvent (a mixture of hexane and acetonitrile) was removed by rotary evaporation, and the residue was retrieved in 4 mL hexane for further purification by pressurized flash column chromatography.

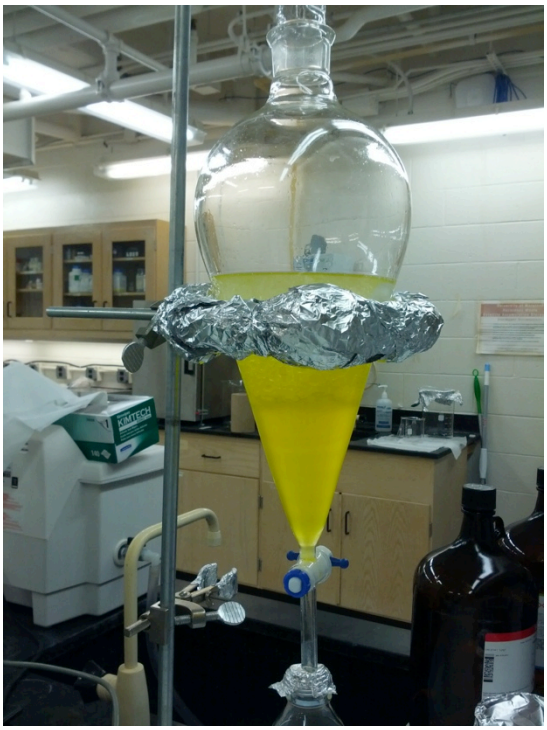


Figure 3.8 Liquid-liquid extraction of the butter extract in a separatory funnel

3.2.2. Flash Chromatography

A flow control system was installed, including a cylinder of compressed nitrogen, an organic carbon scrubber (CRS® model 300 hydrocarbon purifier), a stainless steel filter (Swagelok®, stainless steel in-line particulate filter, 0.5 micron pore size) and two 500-mL glass columns with PTFE stopcocks. Two stainless steel valves were mounted to control the gas flow and adjust the pressure (5-10 psi). All parts were connected with stainless steel hose or copper tube with Swagelok® fittings, which were sonicated and rinsed with acetone prior to installation.

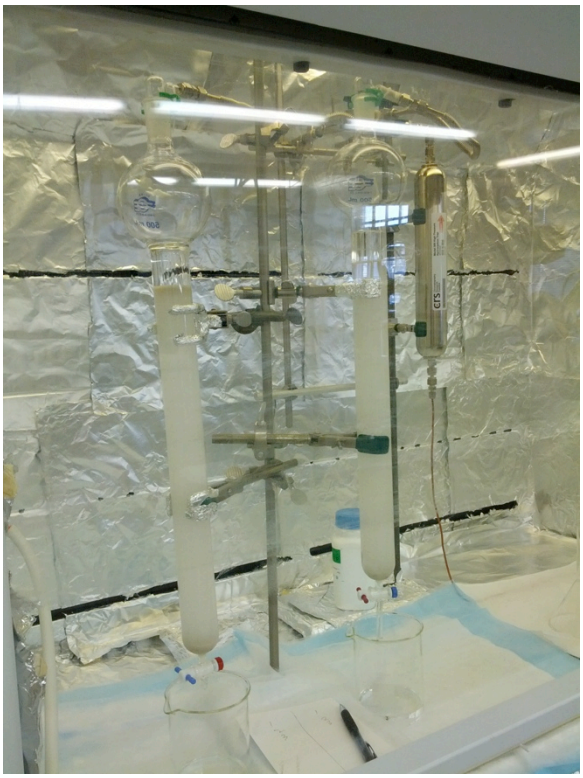


Figure 3.9 Columns with the flow control system

The flash columns were packed with 175 g silica gel individually. The columns were flushed with 500 mL of 5% (v/v) acetone in hexane to compact the silica gel. The gel was topped with a thin layer of baked sand to prevent silica gel from splashing when adding eluent. 400 mL of 33% (v/v) acetone in hexane and 1000 mL hexane were applied to the column to rinse and condition the stationary phase.

Each ≈1 mL of the post-liquid-partitioning sample was loaded to a newly packed flash column, and therefore four columns in total were needed to purify each butter extract. The first elution was performed with 200 mL of hexane to elute most of the nonpolar compounds and was followed by elution with 1500 mL of 1.6% (v/v) acetone in hexane to elute more polar compounds.

Eluates (50 mL per aliquot) were firstly monitored with thin layer chromatography (TLC) (Analtech Uniplate™ TLC plate, silica gel HLF scored 10×20 mm 250 micron w/UV254). The developing agent was 1:1 methanol/hexane (Jayakrishnan & Sunny, 1996). The developed plate was dipped into $KMnO_4$ solution (3 g $KMnO_4$, 20 g K_2CO_3, 5 mL 5% NaOH and 300 mL H_2O) and dried with a heating gun. A yellow dot with the same retardation factor (R_f) value as the standard DEHP demonstrated the existence of DEHP in that aliquot.

GC-MS was then used as a validation method. Each aliquot was qualitatively checked with a Shimadzu QP5000 GC-EIMS with a DB-5 column (Agilent® J&W, 30 m × 0.25 mm, 0.25 micron, (5%-phenyl)-methylpolysiloxane) DEHP Identification was based on selected ion monitoring (SIM) for DEHP (m/z=149) and *d38*-DEHP (m/z=154) (see Table A 2.5). The result showed that DEHP and *d38*-DEHP were usually eluted from the column between 1100 mL and 1500 mL 1.6% (v/v) acetone in hexane.

All DEHP-containing eluates were combined to yield a total of 1600 mL DEHP-containing solution. Solvent was removed subsequently with a rotary evaporator and the leftover was reconstituted in 1 mL of acetonitrile for preparative scale HPLC purification.

3.2.3. Preparative Scale High Performance Liquid Chromatography

3.2.3.1. Instrument Setup

Each Post-flash-chromatography sample was injected repeatedly into a Hewlett-Packard 1050 high performance liquid chromatography (HPLC) with a C18

column (Agilengt® Zorbax Eclipse, XDB-C18 15 cm × 9.4 mm-ID, 5 micron) for final purification. Gradient elution was applied starting with 90% acetonitrile and 10% water at 30 °C, and 4 mL/min. The mobile phase composition was continuously adjusted to a final composition of 95% acetonitrile and 5% water after 10 min at the same temperature and flow rate. The HP1050 was equipped with a diode array detector (DAD), which was set to 254 nm because DEHP has the highest absorbance at this wavelength (Orsi et al., 2006). *d38*-DEHP and DEHP were eluted out at 19 and 21 min, respectively, as shown in Figure 3.10. Based on peak initial and end times, d38-DEHP and DEHP eluates were collected manually at the mobile phase drain respectively in separate clean vials with PTFE lined phenolic caps. The total volume of the DEHP-containing eluates was ≈50 mL.

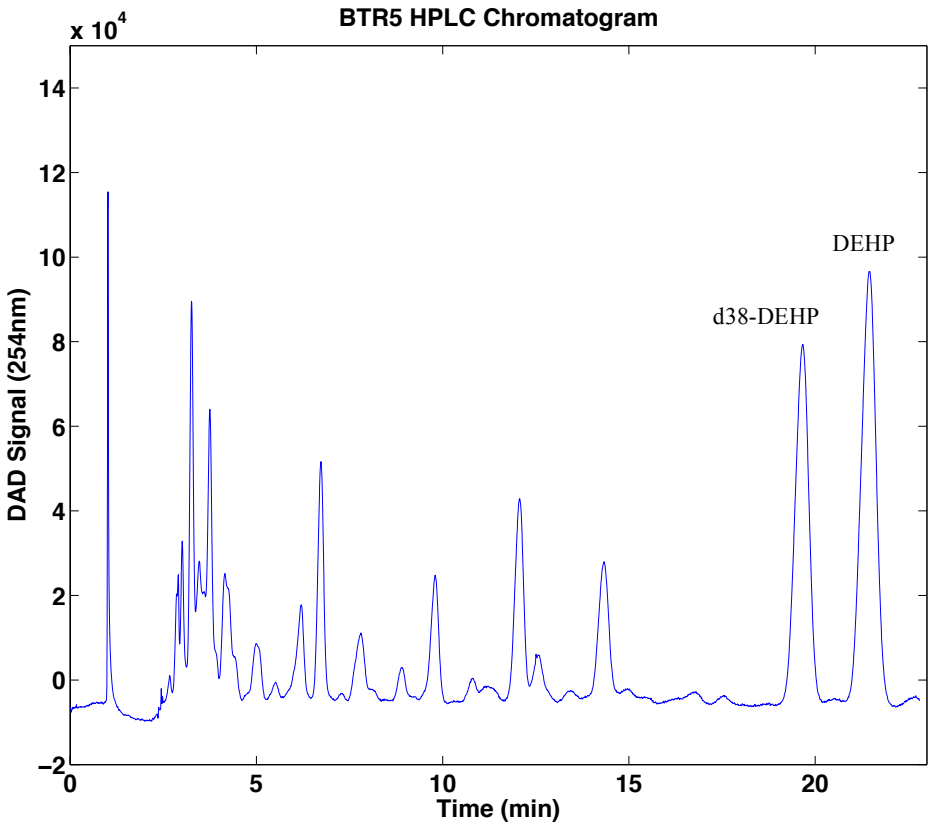


Figure 3.10 HPLC chromatogram of one injection of butter extract (BTR5), $t_{d38\text{-}DEHP}$=19 min, t_{DEHP}=22 min

3.2.3.2. Calibration

DEHP and *d38*-DEHP calibrants were prepared in advance (see Table A 2.14) and obtained calibration curves are shown in Figure 3.11 and Figure 3.12. The DEHP mass (µg) was calculated based on the concentration of the prepared Supelco® DEHP standard solution and the injected volume (see Table A 2.14 and Table A 2.15).

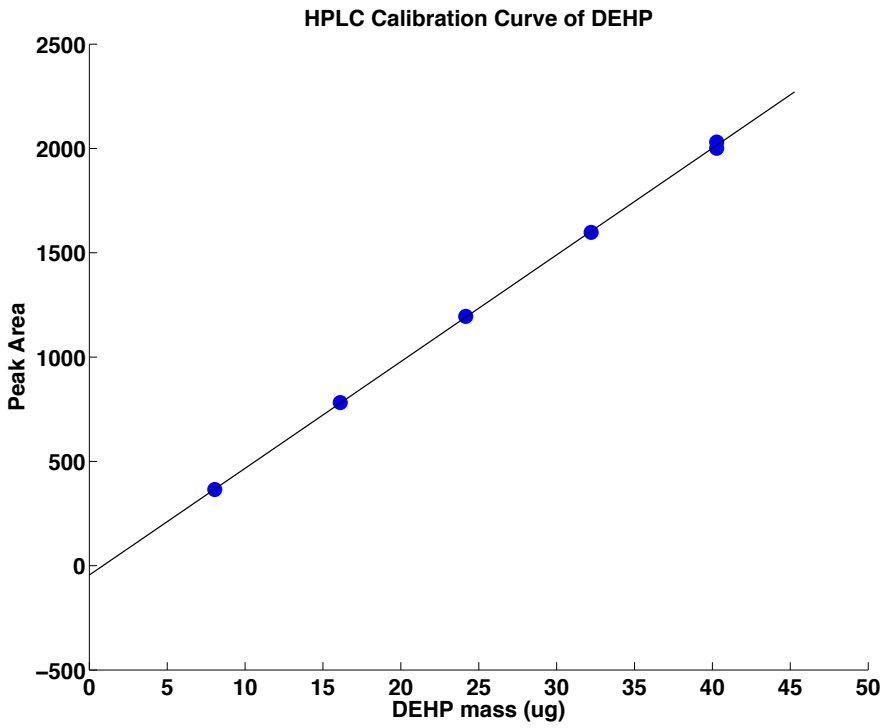


Figure 3.11 HPLC calibration curve of peak area with respect to DEHP mass, n=6, slope=51.13 ± 0.38, intercept=-44.44 ± 11.18, R^2=0.9998

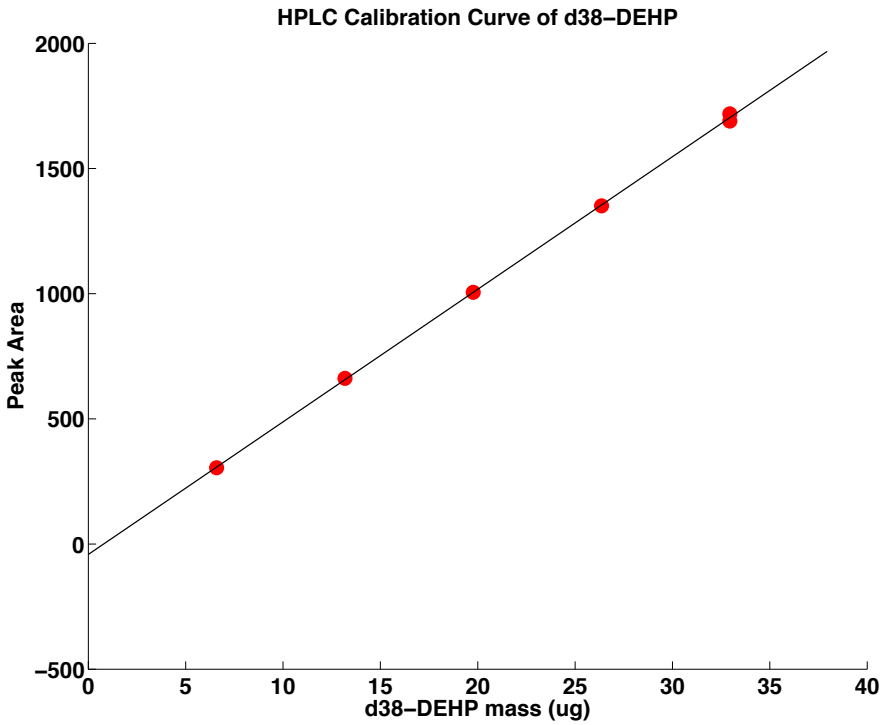


Figure 3.12 HPLC calibration curve of peak area with respect to d38-DEHP mass, n=6, slope=52.96 ± 0.44, intercept=-41.37 ± 10.70, R^2=0.9997

3.2.3.3. Resolution and Peak Contamination Assessment

Since *d38*-DEHP was eluted ahead of DEHP, there was a chance of contamination due to tailing of the internal standard. Resolution is the ability of a chromatograph to separate two adjacent peaks, and was calculated from peak width and retention time.

An approach to estimate the percentage of d38-DEHP contamination within the DEHP peak was based on two independent ideal Gaussian distributions. Peak areas were the integral of detector signal over peak elution time. The peak area was proportional to the analyte concentration (*W*).

$$W_i = f_i^{'} A_i \approx \frac{1}{slope_i} A_i \tag{3.5}$$

$$A_i = \int_{t_{is}}^{t_{ie}} \frac{dS}{dt} \tag{3.6}$$

$$n = \frac{f_1^{'} \cdot \int_{2s}^{2e} \frac{dS}{dt}}{f_1^{'} \cdot \int_{2s}^{2e} \frac{dS}{dt} + f_2^{'} \cdot A_2} \times 100\% \tag{3.7}$$

f is the detector-response correction factor for a specific analyte. S and n are the detector signal counts and the mass fraction of *d38*-DEHP in DEHP peak, respectively.

Table 3.4 Peak properties of standard DEHP (0.403 mg/mL) and d38-DEHP (0.329 mg/mL) for simulating peak contamination

Peak	*Compound*	*Start time (min)*	*End time (min)*	*Peak width (min)*	*Standard deviation σ*	*Retention time (min)*	*Peak Area*	*Correction Factor, f*
1	*d38*-DEHP	25.289	26.669	1.380	0.345	25.769	1005.244	0.0196
2	DEHP	26.845	28.472	1.627	0.407	27.364	1194.776	0.0189

Calculations showed that there was less than 0.1% (w/w) *d38*-DEHP in collected DEHP eluates. As a matter of fact, the GC-MS results demonstrated that the content of the internal standard in the DEHP eluate collected was, in each case, below the detection limit.

The resolution factor (R) is another measure of the separation between two compounds. $R \geq 1.5$ is considered to be a baseline separation while $1 \leq R < 1.5$ is moderate separation but acceptable for quantitative analysis (Rouessac & Rouessac, 2007). The resolution factor in this case can be calculated using the following equation (data listed in Table 3.4):

$$\boldsymbol{R = \frac{t_{R,DEHP} - t_{R,d38}}{(W_{b,DEHP} + W_{b,d38})/2} = 1.06} \quad (3.8)$$

where W_b is the peak width and t_R is the retention time of DEHP or *d38*-DEHP as indicated. While acceptable for analytical purposes, a value of 1.06 indicated that ≈2.3% of DEHP might be contaminated by *d38*-DEHP. However no *d38*-DEHP peak was detected with GC-EIMS afterwards and is presumed to be more accurate.

3.2.3.4. DEHP Contents in Butter and Recovery Computation

To calculate the concentration of DEHP in the butter samples that were processed, the DEHP/*d38*-DEHP ratio must be calculated first for each injection as follows:

$$\boldsymbol{\frac{m_{DEHP}}{m_{d38}} = \frac{slope_{d38}}{slope_{DEHP}} \cdot \left(\frac{A_{DEHP} - b_{DEHP}}{A_{d38} - b_{d38}}\right)} \quad (3.9)$$

where *m* and *A* are the mass of analyte and peak area in a single HPLC injection of a butter extract, *slope* and *b* are the slope and intercepts of the corresponding calibration curves. The content of DEHP (c_{DEHP}) in each raw butter sample was subsequently computed as follows:

$$\boldsymbol{c_{DEHP} = \frac{m_{d38,spiked}}{m_{butter}} \cdot \frac{slope_{d38}}{slope_{DEHP}} \cdot \frac{\sum_i^n \left(\frac{m_{DEHP,i}}{m_{d38,i}}\right)}{n}} \quad (3.10)$$

where *n* is the required number of injections to the HPLC column for each butter extract.

Table 3.5 DEHP contents in raw butter and recovery of isolations and purifications

Butter Sample ID	*Butter Mass (g)*	*Internal Standard d38-DEHP (µg)*	*Number of Injection*	*Average Mass Ratio*	*DEHP Content in Raw Butter (mg/kg)*	*Recovery (%)*
Butter1	1137.1 ± 0.1	544.33 ± 0.05	13	-	-	-
Butter2	1135.8 ± 0.1	565.42 ± 0.08	13	-	-	-
Butter3	1139.0 ± 0.1	582.75 ± 0.07	12	1.32 ± 0.04	0.67 ± 0.02	38.5 ± 0.1
Butter4	1136.1 ± 0.1	594.64 ± 0.04	10	1.32 ± 0.03	0.69 ± 0.01	36.9 ± 0.1
Butter5	1133.1 ± 0.1	584.85 ± 0.03	10	1.35 ± 0.01	0.69 ± 0.01	36.4 ± 0.1
Butter6	1137.1 ± 0.2	578.26 ± 0.06	15	1.43 ± 0.06	0.73 ± 0.03	34.3 ± 0.1
Butter7	1126.0 ± 0.2	474.35 ± 0.04	14	0.73 ± 0.02	0.31 ± 0.01	44.5 ± 0.2

The acetonitrile-water solvent in each post-HPLC DEHP-containing aliquot was removed by rotatory evaporation. The temperature of the water bath was increased to 70 °C to evaporate the water in the HPLC eluate. Hexane (3-4 mL) was added into the recovery flask to retrieve the DEHP. This was the last step in the purification process. Masses and purities of these samples for AMS were quantified and transferred to a 2-mL Agilent® vials with extraordinary caution and stored in a -20 °C freezer for further processing while the remaining sample masses were reserved for stable carbon isotope analysis.

The DEHP isolates from butter and method blanks were designated as BTR and BLK in the following measurements, including stable carbon isotope analysis, GC-EIMS and AMS.

3.3. Mass and Purity Assessments with GC-EIMS

3.3.1. AMS Sample Mass Quantification with GC-EIMS

The mass of DEHP was determined in each isolate by GC-EIMS (JEOL® JMS700 MStation, double focusing magnetic sector mass spectrometer, coupled with Agilent® 6890N GC system) with 1 μL injections, 1.00 mL/min column flow of helium, 15 °C/min temperature programming starting at 90 °C. DEHP was eluted at 15.8 min. The mass spectra were collected from m/z 50 to 500 at intervals of 1-s duration. Two series of standard DEHP solutions from petrogenic DEHP (99.8 ± 0.1 % pure, Supelco® Analytical, Bellefonte, PA) were prepared to make an analytical calibration curve for both butter extract samples and method blanks.

These samples were analyzed in two batches: (1) batch 1 included BTR1, BTR2, BLK1 and BLK2; batch 2 included BTR3 to BTR7 and BLK3 to BLK5. Calibration curves for batch 1 analysis were shown in Figure 3.13 and Figure 3.14. Those for batch 2 analysis are shown in Figure 3.15 and Figure 3.16. Because AMS measures only ^{14}C and ^{13}C atoms in samples provided for analysis, DEHP masses in all butter and blank samples were converted to carbon mass from its known molecular formula (see Table 3.6).

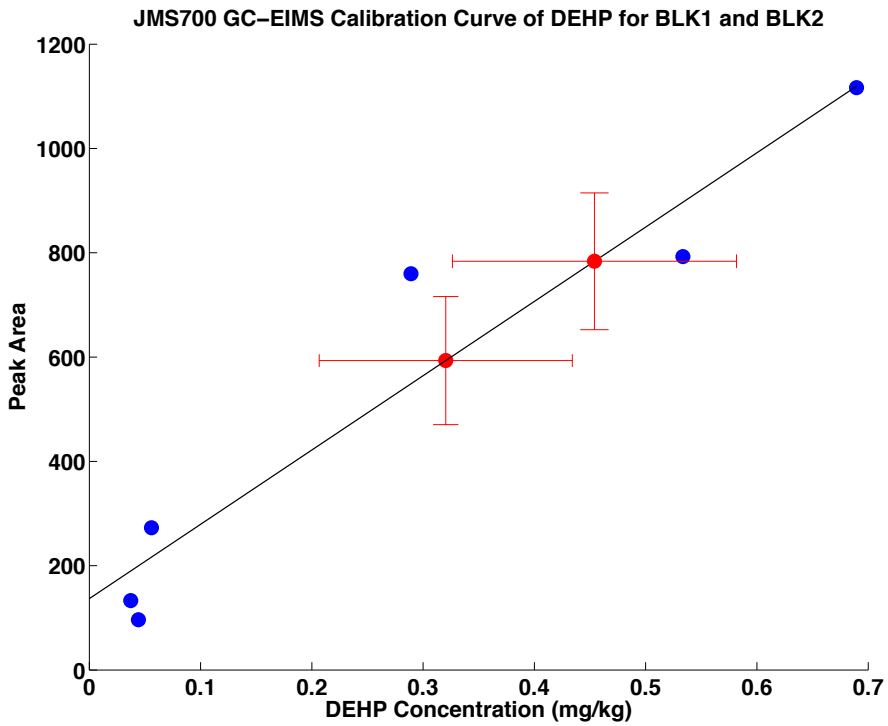


Figure 3.13 GC-EIMS calibration curve for BLK1 (0.32 ± 0.11 mg/kg) and BLK2 (0.45 ± 0.13 mg/kg), n=6, replicates=3, slope=1424.77 ± 213.73, intercept=136.86 ± 80.45, R2=0.9174

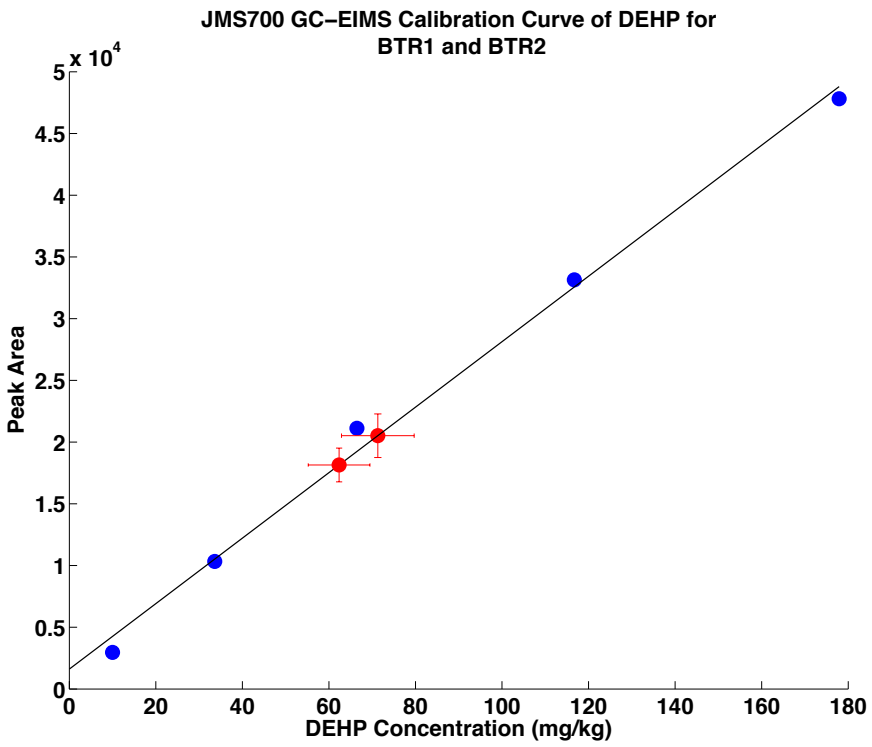


Figure 3.14 GC-EIMS calibration curve for BTR1 (71.30 ± 8.40 mg/kg) and BTR2 (62.35 ± 7.12 mg/kg), n=5, replicates=3, slope=265.18 ± 10.96, intercept=-1612.01 ± 1106.14, R^2=0.9949

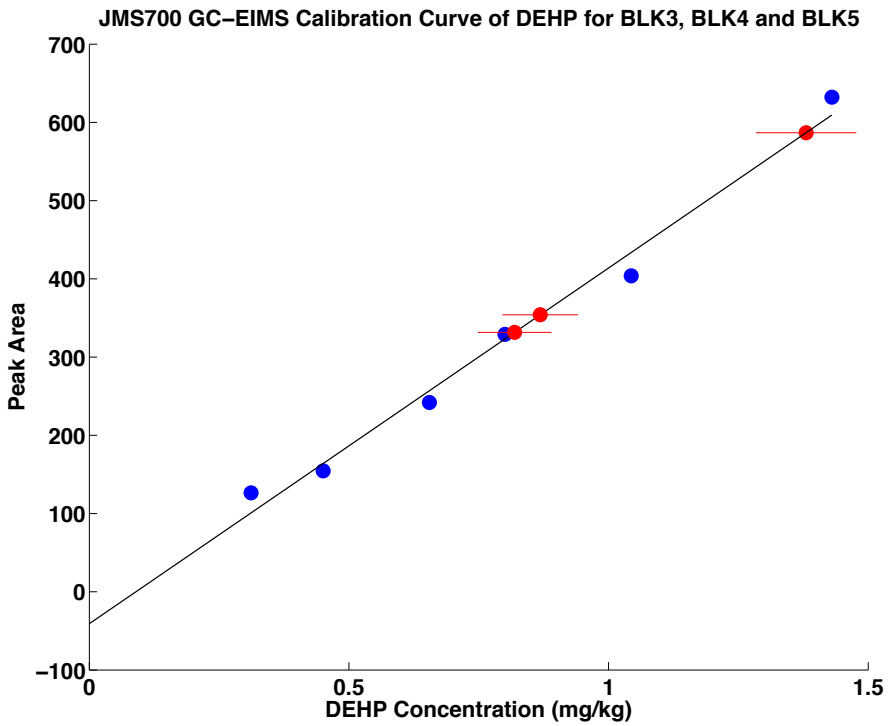


Figure 3.15 GC-EIMS calibration curve for BLK3 (1.38 ± 0.10 mg/kg), BLK4 (0.82 ± 0.07 mg/kg) and BLK5 (0.87 ± 0.07 mg/kg), n=6, replicates=1, slope=454.65 ± 26.83, intercept=-40.79 ± 23.28, R^2=0.9862

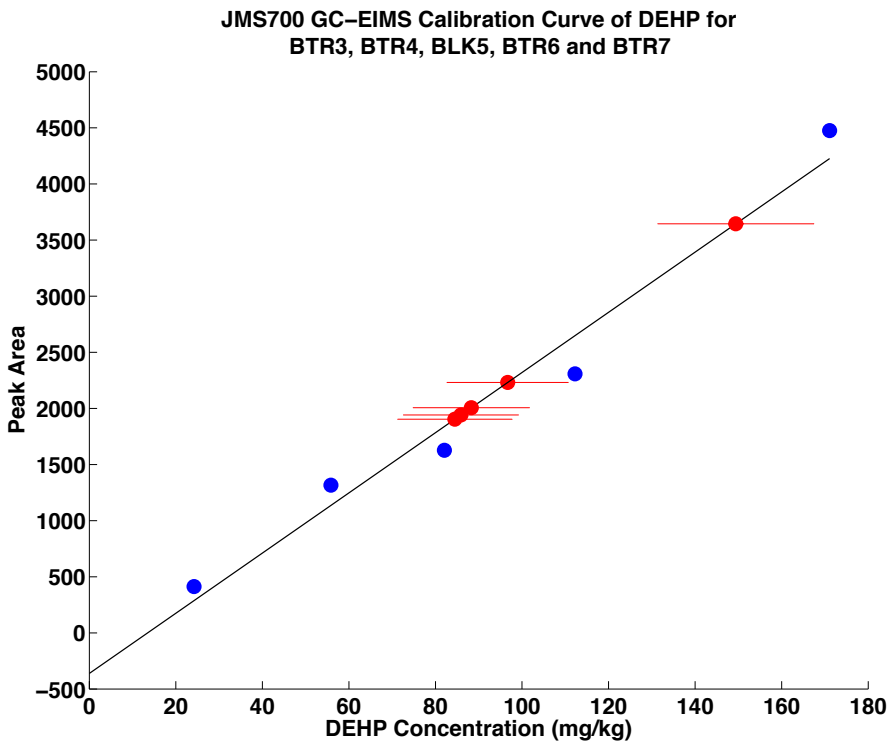


Figure 3.16 GC-EIMS calibration curve for BTR3 (96.68 ± 14.03 mg/kg), BTR4 (149.41 ± 18.05 mg/kg), BTR5 (84.48 ± 13.23 mg/kg), BTR6 (88.28 ± 13.47 mg/kg) and BTR7 (85.89 ± 13.32 mg/kg), n=5, replicates=1, slope=26.81 ± 2.67, intercept=360.90 ± 273.47, R^2=0.9710

3.3.2. ^{14}C-Labled and Petrogenic-DEHP-Spiked Method Blanks

The carbon mass of DEHP in the method blank samples were insufficient to provide enough counts for AMS, and therefore external DEHP was spiked into each sample. The total carbon mass is needed because, as later demonstrated, the method blanks contained carbon in forms other than DEHP. To remedy this situation, BLK1 and BLK2 were both split equally into two portions on a mass basis. One of the halves of each method blank was spiked with ≈40 µL dead DEHP solution (3292.9 ± 2.3 mg/kg) from the Supelco® standard, and the remaining half for each was spiked

with 110 μL of live DEHP solution (727.93 ± 1.73 mg/kg) in CH_2Cl_2, prepared with Bis (2-ethylhexyl-$^{2}H_{17}$) phthalate, [carbonyl-^{14}C]- (Moravek® Biochemicals Inc., 2000 dps/g), after dilution with "dead" DEHP. Prior to spiking, the activity of the ^{14}C-labeled solution obtained from Moravek® was verified by Liquid Scintillation Counting (LSC) using a volume of solution equivalent to 0.4843±0.0002 g of DEHP (See Table A 1.2). The spiked solution masses were measured with a Mettler Toledo® balance to permit accurate computation of the mass of DEHP.

As described below, the results of ^{14}C measurements on these samples by AMS demonstrated that the method blanks, indeed, contained carbon in forms other than DEHP. As a result, additional work had to be done to determine its identity.

Table 3.6 Carbon mass of DEHP in AMS samples

Sample ID	*Carbon mass of DEHP from method blank (μg)*	*Carbon mass of DEHP from butter (μg)*	*Carbon Mass of dead DEHP spike (μg)*	*Carbon Mass of live DEHP spike (μg)*	*Total carbon mass of DEHP (μg)*
BLK1D	0.21 ± 0.07	-	52.00 ± 0.06	-	52.21 ± 0.09
BLK1L	0.28 ± 0.10	-	-	46.14 ± 0.11	46.42 ± 0.15
BLK2D	0.30 ± 0.09	-	65.63 ± 0.06	-	65.94 ± 0.10
BLK2L	0.35 ± 0.10	-	-	45.83 ± 0.11	46.81 ± 0.15
BLK3D	1.08 ± 0.08	-	77.93 ± 0.01	-	79.01 ± 0.08
BLK4D	0.73 ± 0.06	-	75.85 ± 0.01	-	76.58 ± 0.06
BLK5D	0.79 ± 0.07	-	77.58 ± 0.01	-	78.37 ± 0.07
BTR1	0.52 ± 0.19	123.87 ± 14.65	-	-	124.39 ± 14.65
BTR2	0.70 ± 0.20	113.16 ± 13.00	-	-	113.86 ± 13.00
BTR3	1.08 ± 0.08	76.77 ± 11.27	-	-	77.85 ± 11.27
BTR4	0.73 ± 0.06	104.16 ± 12.64	-	-	104.89 ± 12.64
BTR5	0.79 ± 0.07	70.04 ± 11.07	-	-	70.83 ± 11.07
BTR6	0.87 ± 0.19[a]	64.86 ± 10.03	-	-	65.73 ± 10.03
BTR7	0.87 ± 0.19[b]	65.89 ± 10.35	-	-	66.76 ± 10.35

[a,b] the carbon mass of DEHP from method blank for BTR6 and BTR7 were not measured, the value here was the average of BTR3, BTR4 and BTR5

3.3.3. Quantification of the Carbon Purities of DEHP isolates with GC-EIMS

The carbon purities of DEHP in butter isolate samples for AMS were determined by GC-EIMS. BTR1 and BTR2 were measured with a Shimadzu® JMS700 as described in Section 3.3.1, while BTR3 to BTR7 were measured with a Shimadzu® QP2010S (Shimadzu SHRXI-5MS column, 30 m × 0.25 μm I.D., polysiloxane coated) with 1 μL injection, 1.00 mL/min column flow of helium, temperature programmed at a rate of 15 °C/min from 90 °C to 300°C. DEHP was eluted at 17 min and m/z scanned from 50 to 500 at 0.3 scans s^{-1}. Standard DEHP

solutions prepared from petrogenic DEHP (99.8 ± 0.1 % pure, Supelco® Analytical, Bellefonte, PA) were used to calculate purities.

The purity (P_{TIC}) is often determined from the total ion chromatograph of an analyte from the ratio of the area of the peak at its retention time (as shown in equation 3.11), i.e., A_{DEHP} to the total area of all peaks,

$$\boldsymbol{P_{TIC} = \frac{A_{DEHP}}{\sum A_i}} \tag{3.11}$$

Figure 3.17 shows the total ion chromatogram (TIC) of seven butter isolates: BTR1 to BTR7 (GC column was changed after the first two samples were measured, and thus the retention time of DEHP varied). All peaks in each chromatogram were identified and listed in Appendix 3. The butter isolates contained as many as 21 compounds in addition to DEHP. In each case, co-eluted compounds were identified by similarity matching with NIST MS library spectra. As indicated in Table 3.7, BTR3 contained only two additional compounds, cholesterol and Z, E-2, 13-octadecadien-1-ol at minor concentrations. These two compounds were present in many of the samples but in every case, the area of each peak was <1%. However, in many of the isolates, most of the peaks identified were siloxanes, $(C_2H_6SiO)_x$, which were attributed to GC column bleeding owing to the high temperature required to elute DEHP.

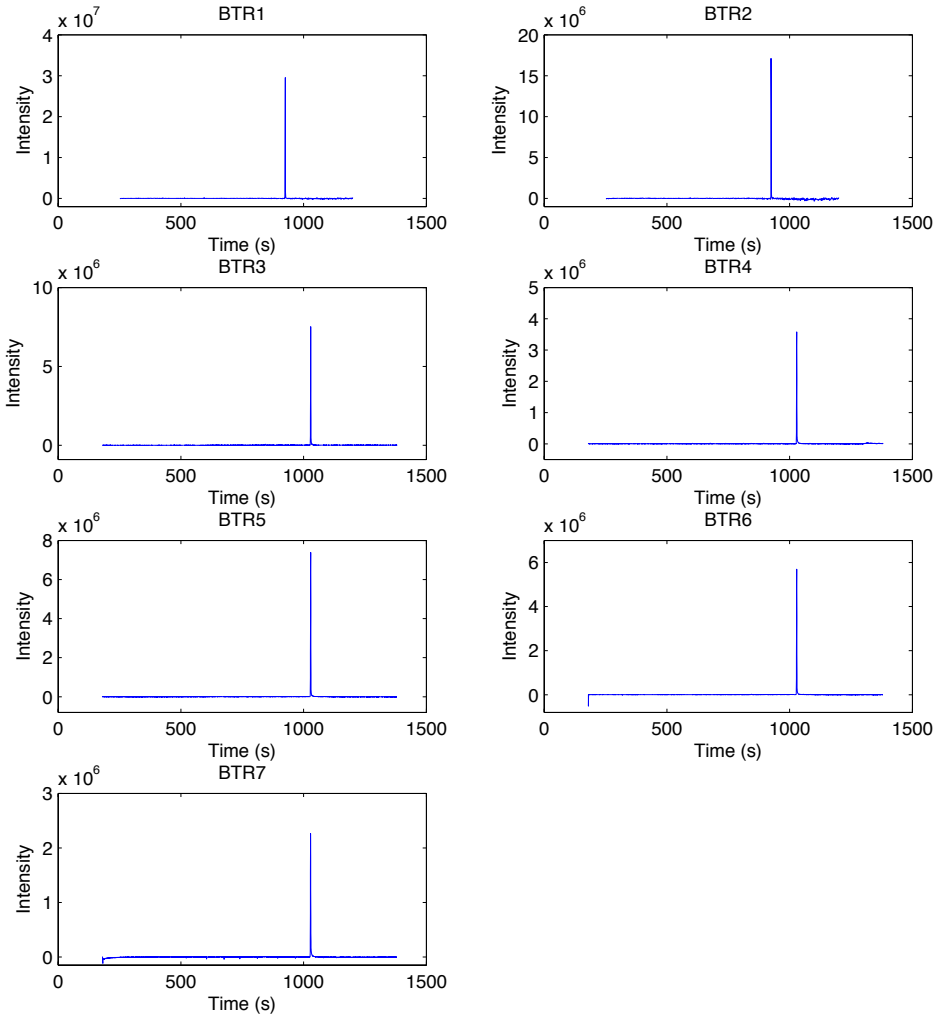


Figure 3.17 Total ion chromatograms of BTR1 to BTR7

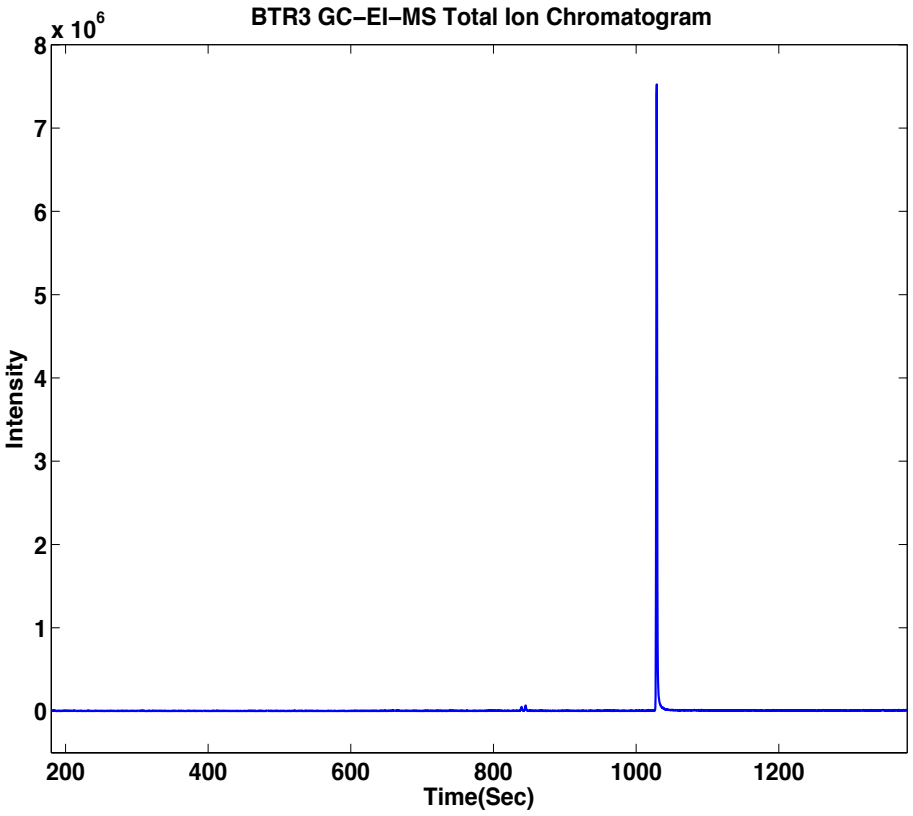


Figure 3.18 The total ion chromatogram of BTR3

Given the large number and high concentrations of compounds in the butter matrix there existed a distinct possibility that one or more of them might have been co-eluted at the same retention time as DEHP (Guo, Liang, Xu, Li, & Huang, 2004). Therefore, the m/z spectra in the TIC region containing the DEHP peak were subjected to multivariate deconvolution with spectra developed from the Supelco® DEHP standard using the same GC-EIMS instrument, to determine the net DEHP contribution. This was accomplished with a least squares deconvolution algorithm implemented in Matlab®, wherein the spectra of each scan of a standard DEHP sample were used to fit the corresponding scan of the DEHP peak (≈ 16 min) of each

isolate (see Appendix 3 for additional details). The residual counts were taken to belong to co-eluted compounds. Before deconvolution, the spectra of each isolate were corrected for background (solvent blank and column bleeding). Results for the deconvolution of the DEHP peak region of BTR3, the standard, and the residual were plotted in three in three dimensional figures (see Figure 3.19). The residual was calculated as follows:

$$\boldsymbol{R_{resid} = M_{sample} - R \cdot M_{std}} \tag{3.12}$$

where R_{resid} was the residual of deconvolution. M_{sample} was the MS signal of the isolated DEHP sample from butter in the elution region (50 scans before peak initial time and 50 scans after the peak end time respectively). M_{std} was the MS signal matrix for the corresponding standard DEHP. R was the deconvolution coefficient obtained for the least square fit. In some cases, negative residuals were obtained due to mismatches between the m/z calibration between the sample and standards. In those cases, a simplified approximation was applied: the channel containing a negative residual was added to the nearest channel with positive counts.

$$\boldsymbol{P_{inpeak} = 1 - \frac{\sum\sum R_{resid\_corr}}{\sum\sum M_{sample}}} \tag{3.13}$$

$$\boldsymbol{P_{corr} = P_{TIC} \times P_{inpeak}} \tag{3.14}$$

$$\boldsymbol{purity_C = \frac{P_{corr} \cdot r_{DEHP}}{P_{corr} \cdot P_{DEHP} + \sum P_i r_i}} \tag{3.15}$$

where P_{inpeak} was the ratio of DEHP within the peak, which was estimated by the residual signal after deconvolution. P_{TIC} was the DEHP ratio based on the peak areas in the total ion chromatogram. P_i and r_i were the co-eluted compounds and their carbon ratios respectively.

The deconvolution result demonstrated than there were no identifiable co-eluted compounds underneath the DEHP peak and owing the large number of siloxane compounds eluted from the GC column, the carbon content of each unidentified residual peak was calculated by assuming it represented siloxanes, $(C_2H_6SiO)_x$ (carbon ratio=0.3237) (see Appendix 3).

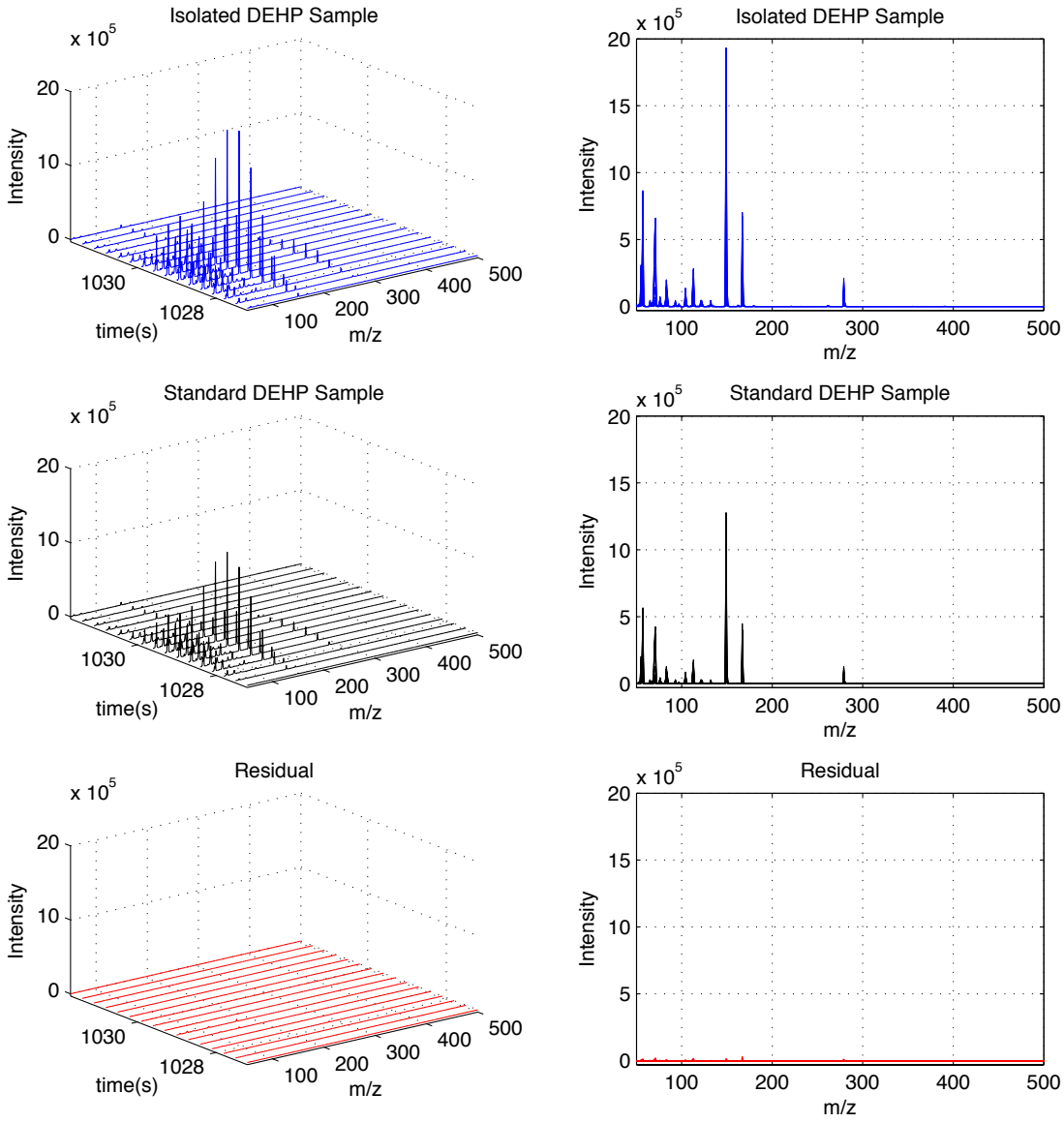


Figure 3.19 BTR3 deconvolution at peak region with standard Supelco® DEHP

Table 3.7 Example of co-eluted peak identification and purity calculation demonstration (BTR3)

Retention Time (min)	***Compound***	***Carbon Ratio***	***Peak Area***	***Purity by Peak Area (%)***	***Purity within DEHP Peak by Deconvolution (%)***	***Carbon Purity (%)***
13.985	Cholesterol	0.8394	84516	0.67		0.79
14.08	Z,E-2,13-Octadecadien-1-ol	0.8120	118219.2	0.94		1.06
17.15	DEHP peak		12400179	98.39		
	DEHP	0.7375			94.26 ± 3.46[b]	95.59 ± 1.80[b]
	Residual	0.3237[a]			5.74 ± 0.27[b]	2.56 ± 0.18[b]

[a] unidentified residual calculated as siloxane, $(C_2H_6SiO)_x$
[b] 1σ uncertainty, n=3

The resolved chromatogram is shown in Figure 3.20. At current magnitude, the resolved signal (black line) is close to the original signal (blue line). The integral residual (red line) is less than 10% of the integral original signal.

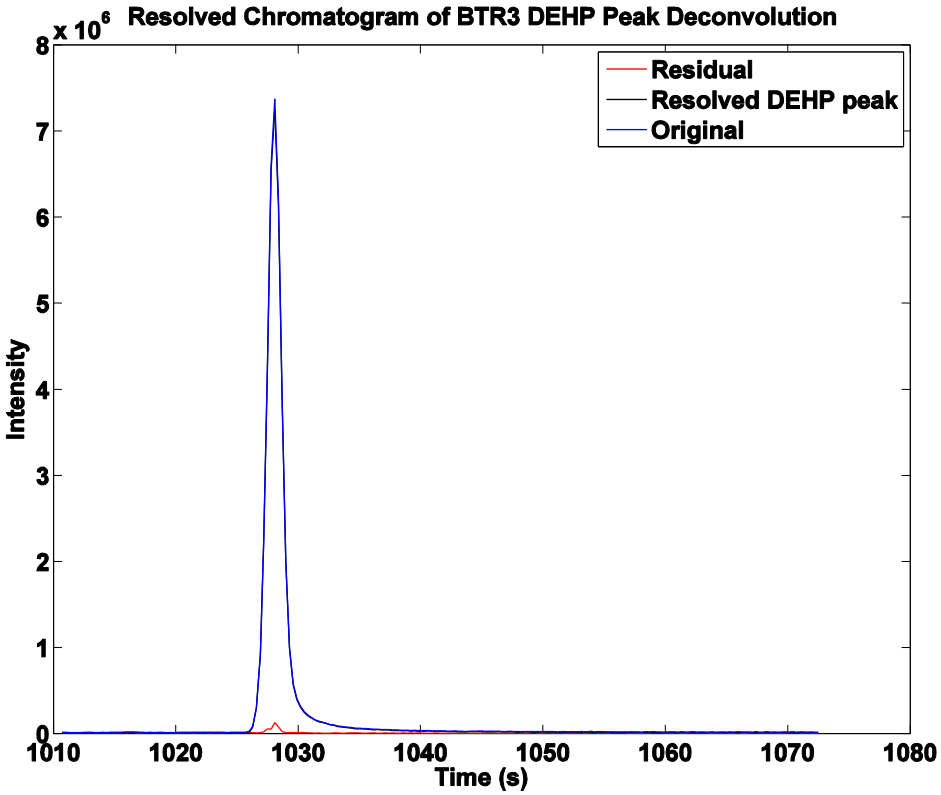


Figure 3.20 Resolved chromatogram of BTR3 DEHP peak deconvolution

Table 3.8 Carbon purity of each post-HPLC butter isolate

Sample ID	*DEHP peak area ratio in TIC (%)*	*Purity within DEHP Peak by Deconvolution (%)*	*DEHP Purity (%)*	*Carbon Purity (%)*	*Average of carbon purity and uncertainty (%)* [a]
BTR1	99.28	94.45	93.77	96.76	97.29 ± 1.03
	99.37	93.97	93.38	96.63	
	99.59	97.50	97.10	98.48	
BTR2	98.56	95.79	94.41	96.60	97.11 ± 0.47
	98.75	97.37	96.15	97.53	
	98.83	96.45	95.33	97.20	
BTR3	98.39	94.26	92.74	95.59	93.51 ± 1.80
	93.72	93.86	87.97	92.53	
	92.17	93.31	86.01	92.40	
BTR4	96.89	90.67	87.84	93.83	92.54 ± 1.15
	91.91	91.76	84.34	92.19	
	91.09	91.11	83.00	91.61	
BTR5	98.54	93.86	92.48	96.24	97.13 ± 0.77
	99.56	95.57	95.15	97.54	
	99.44	95.76	95.23	97.60	
BTR6	99.41	92.76	92.22	96.16	95.71 ± 1.85
	99.69	94.63	94.34	97.29	
	97.29	94.51	91.95	93.68	
BTR7	99.10	89.78	88.98	94.23	95.58 ± 1.17
	99.81	92.14	91.97	96.21	
	99.89	92.07	91.97	96.29	

[a] n=3,1σ

The total carbon mass measured with GC-EIMS (m_{GCMS}) was calculated from carbon mass of DEHP (m_{DEHP}) and carbon purity (see Table 4.1):

$$\boldsymbol{m_{GCMS} = \frac{m_{DEHP,total}}{Purity_C}} \tag{3.16}$$

$$\boldsymbol{m_{coe} = m_{GCMS} - m_{DEHP,total}} \tag{3.17}$$

3.4. Measurements of Carbonates with Ion Chromatography

The purity derived from GC-EIMS data did not reflect inorganic carbon impurities, e.g., carbonates, which are non-volatile electrolytes and as such are invisible to gas chromatography. As indicated in Table 1.1, carbonates are known components of butter and the possibility of carbonate migration through the purification process could not be excluded.

For water in the open air, the concentration of dissolved CO_2 can be calculated by Henry's Law.

$$\boldsymbol{c = pK_H} \tag{3.18}$$

p is the partial pressure of CO_2 in the atmosphere, K_H is the Henry's Law.

$$\boldsymbol{CO_{2(aq)} + H_2O \rightleftharpoons H^+ + HCO_3^-} \tag{3.19}$$

$$\boldsymbol{[HCO_3^-] = 1.84\times10^{-6}\ M}$$

$$\boldsymbol{pH = 5.71}$$

Carbonates and bicarbonates exist in aqueous solution (pH>4) (or micro particles as fine particles in organic solvents). The predominant species of polyprotic acid varies with the pH change. For carbonic acid, the ratios for the major species are as follows:

$$\boldsymbol{\alpha_{H_2CO_3} = \frac{[H^+]^2}{[H^+]^2+[H^+]K_{a1}+K_{a1}K_{a2}}} \tag{3.20}$$

$$\boldsymbol{\alpha_{HCO_3^-} = \frac{[H^+]K_{a1}}{[H^+]^2+[H^+]K_{a1}+K_{a1}K_{a2}}} \tag{3.21}$$

$$\boldsymbol{\alpha_{CO_3^{2-}} = \frac{K_{a1}K_{a2}}{[H^+]^2+[H^+]K_{a1}+K_{a1}K_{a2}}} \tag{3.22}$$

α is the fraction of each particular form of the total dissolved carbonates. With the α values, the ratios of carbonate species were plotted in Figure 3.21.

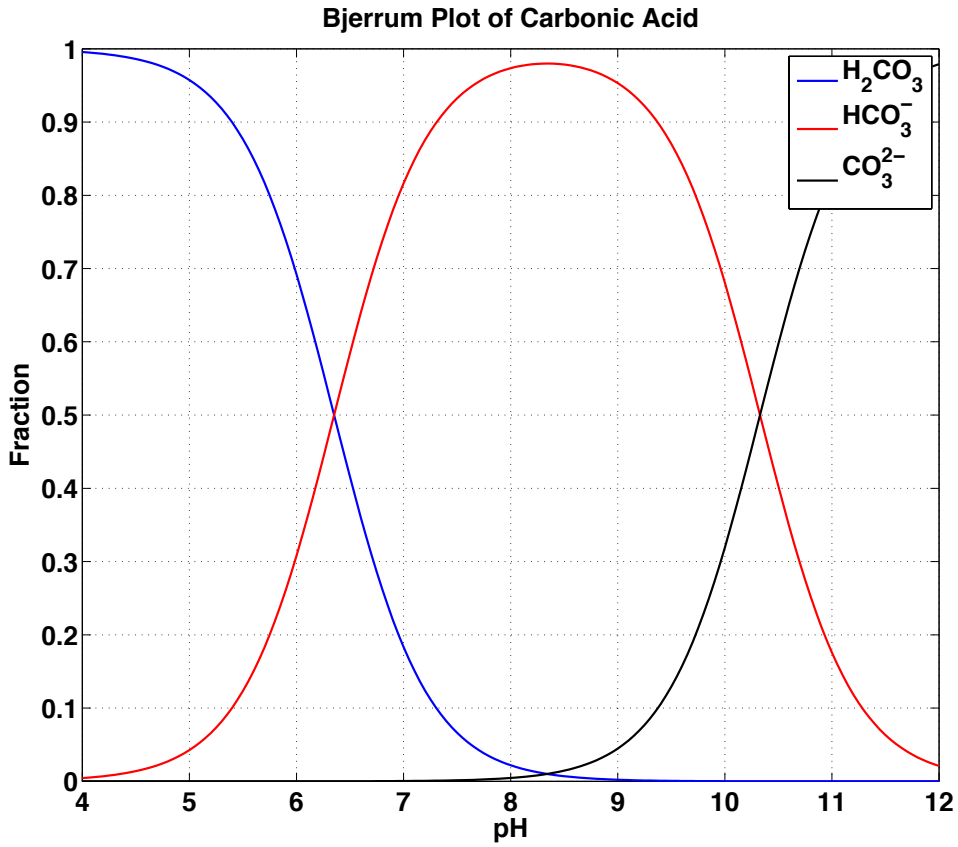


Figure 3.21 Bjerrum plot of carbonic acid and fraction of each species

According to the Bjerrum plot in Figure 3.21, both carbonate and bicarbonate ions existed in the system at pH=7.5, which was the pH value of the ion chromatography (IC). Indeed they were indistinguishable by IC under the conditions for measurement. In succeeding interpretations carbonates refer to both species unless otherwise specified.

3.4.1. Carbonate Content in Butter

To determine the content of carbonate ions in raw butter, 37.1 g of butter was dissolved in 50 mL hexane and extracted with 100 mL 4 mM Sodium 4-Hydroxybenzoate. The aqueous layer was kept in a freezer (-20 °C) for 12 h to solidify lipids. Afterwards, the filtrate collected after filtering through a 0.45 μm pore-diameter syringe filter was injected into an anion column (IonPac® AS14, 4 × 250 mm, P/N 46124) installed in a Dionex® DX120 (Thermo Scientific®, USA) ion chromatography system. The mobile phase was 4 mM Sodium 4-Hydroxybenzoate at pH 7.5, and the flow rate was set to 1.00 mL/min (pressure 1250 psi). An integrated conductivity detector was used to acquire the signal. The retention time of carbonate was 1.99 min (see Figure 3.22).

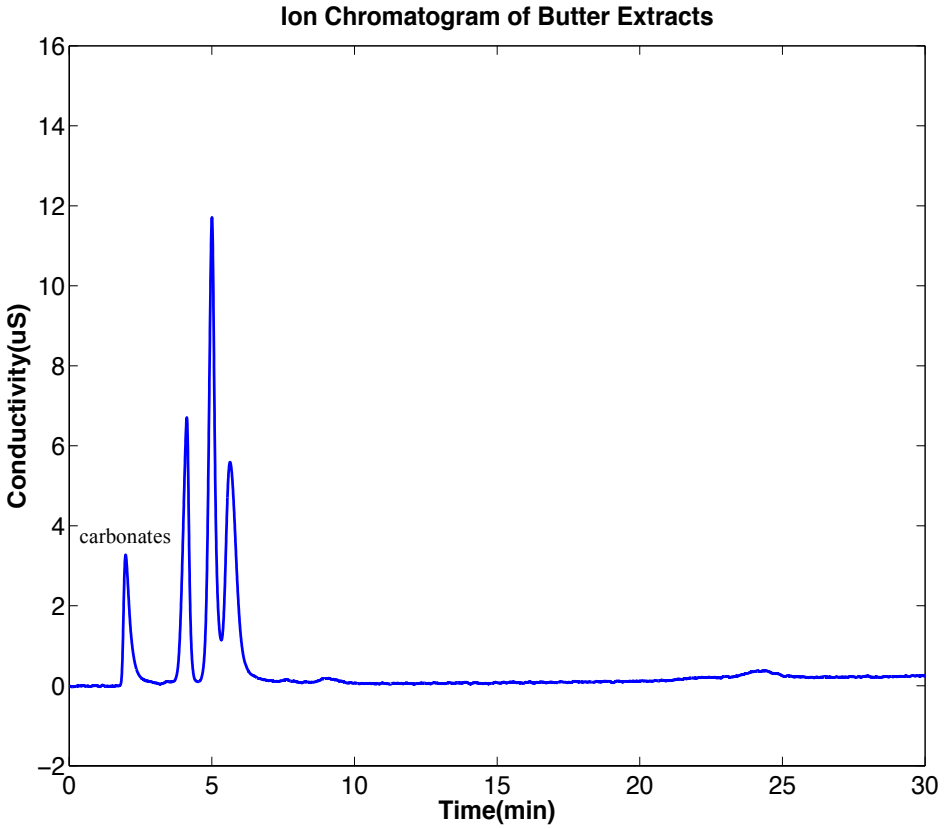


Figure 3.22 Ion chromatogram of a butter extract in 4mM sodium 4-hydroxybenzoate ($R_{carbonates}$=1.99 min)

The concentration of carbonates in the aqueous extract was calculated using a series of calibrants (see Table A 5.2): 0.0015 ± 0.0001 mol/L. The content of carbonates in raw butter was ≃242 ppm.

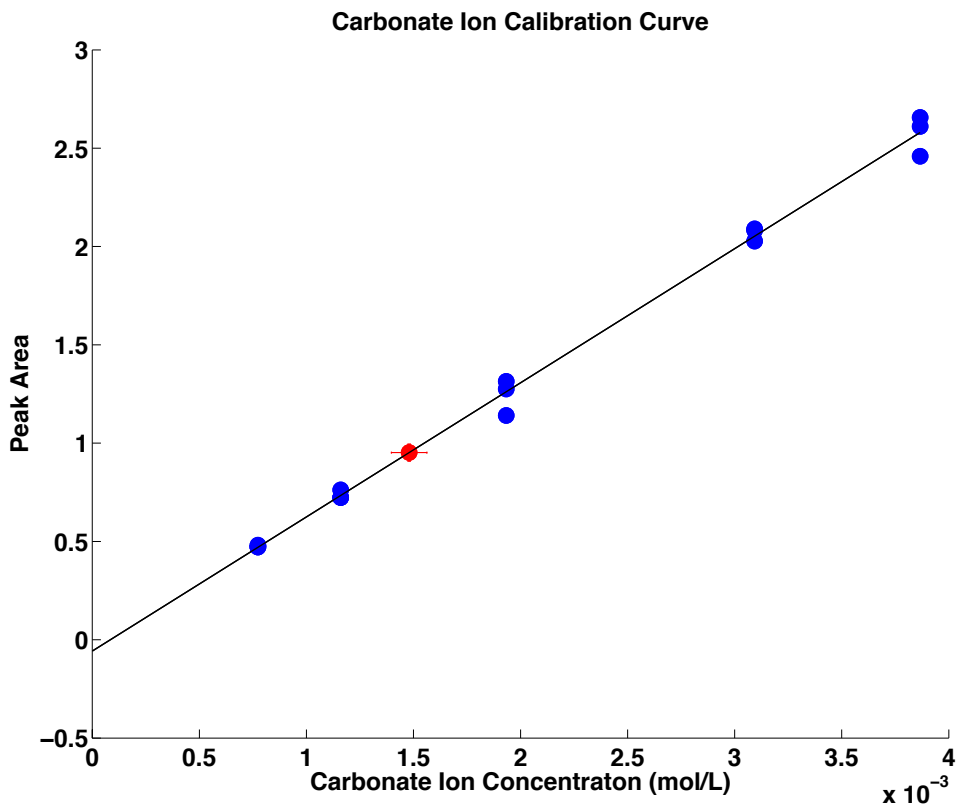


Figure 3.23 IC carbonates calibration curve for butter carbonates test (0.0015 ± 0.0001 M), n=5, replicates=3, slope=682.3 ± 12.8, intercept=-0.057 ± 0.031, R^2=0.9955

3.4.2. Method Derived Carbonates

Besides carbonates in butter, carbonates in solvent, in the silica gel, and/or in the apparatus may migrate into the final sample as well. Consequently a method blank sample was prepared with procedures identical to those described in sections 3.2.1-3.2.3. After the final purification step, the solvent of the post-HPLC eluate was removed by rotary evaporation and the residual was dissolved in 2 mL hexane. Next, 2 mL Milli-Q water was added to extract carbonates and a 25-µL portion of the

resulting aqueous solution was injected into the IC column and eluted with 4 mM sodium 4-hydrobenzoate. Negative signals were observed because the conductivity of the extracted aqueous layer was lower than the mobile phase. To make it easier to read, inverse conductivity was plotted (see Figure 3.24). Under most circumstance, the mobile phase would be used to extract the sample. However, 4-hydroxybenozic acid, the conjugate acid of 4-benzoate, is more soluble in hexane. Variation in their abundances would affect conductivity unpredictably. So Milli-Q water was used instead of the mobile phase to extract the sample. Moreover, note that we chose not to acidify the sample isolates with carbon-free acid to remove carbonates as this might have resulted phthalate hydrolysis at the same time, which would have reduced further the already trace amounts of DEHP.

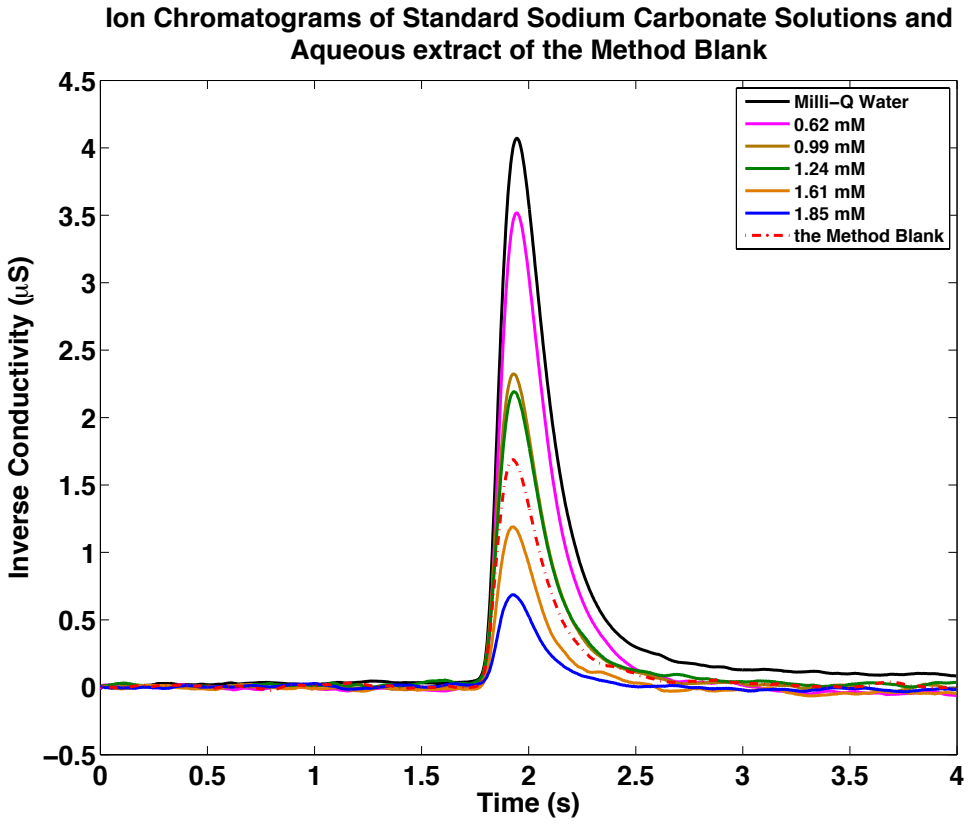


Figure 3.24 Ion chromatograms of standard sodium carbonate solutions and aqueous extract of the method blank

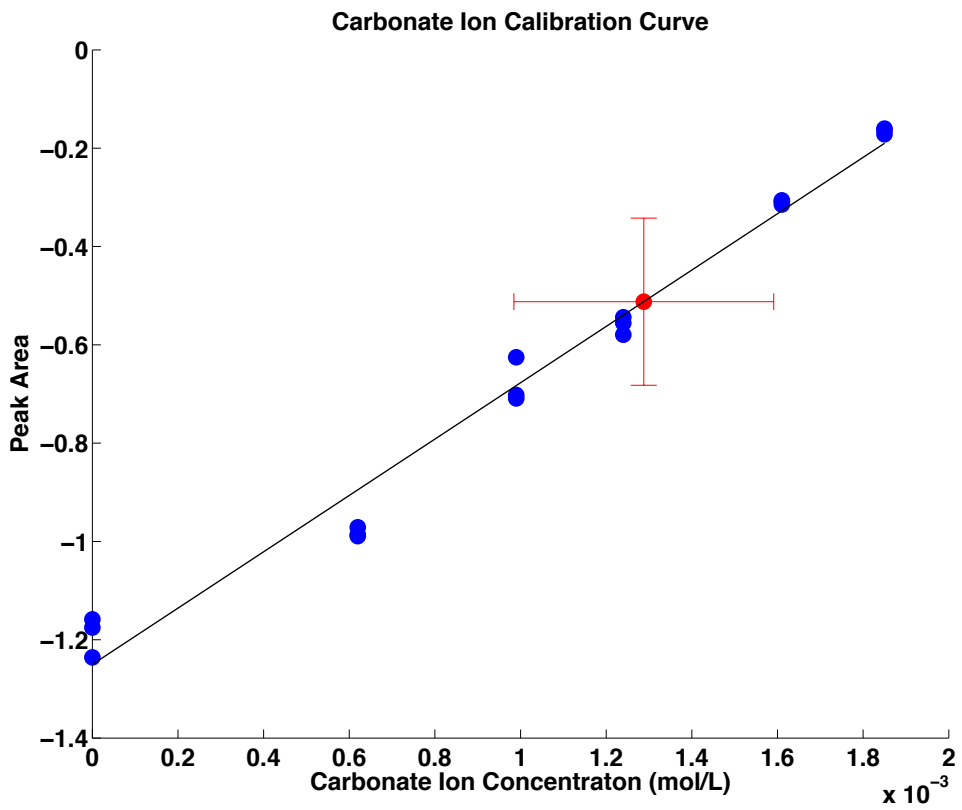


Figure 3.25 IC carbonates calibration curve for butter carbonates test (0.0013 ± 0.0003 M), n=6, replicates=3, slope=573.1 ± 20.6, intercept=-1.25 ± 0.03, R^2=0.9802

The retention times of carbonate and solvent were the same under the above-mentioned IC conditions. Using calibrants with various concentrations, the concentrations of carbonates in aqueous extracts of the method blanks, were determined to average 0.0013 ± 0.0003 M (see Table A 5.3). Converting the concentration into mass, we found that the method blank extraction procedures may induce 31.2 ± 7.2 µg extraneous carbon in the form of carbonate ions ($m_{exo,carbMtd}$).

3.5. AMS Sample Packing

Samples were sent to LLNL in two batches: the first batch included BLK1D, BLK1L, BLK2D, BLK2L, BTR1 and BTR2 plus two contemporary raw butter

samples. Each sample was dissolved in ≈200 μL dichloromethane and stored in a borosilicate vial (Wheaton® V-Vials Conical Bottom Vials, 1 mL) with a PTFE-lined phenolic cap. These vials were placed in a thermally-insulated packing box with dry ice and shipped to LLNL on June 2012.

The rest of the samples listed in Table 3.8 were shipped to LLNL in December of 2012 in quartz tubes (Glass Technologist Inc., 420 Afton Drive, Middletown, DE 19709, Quartz Tube, 1/4" O.D, 4 mm I.D, 6" Length, one flame sealed end) without solvent, and sealed with Swagelok® union fittings and glass rods (see Figure 3.26).

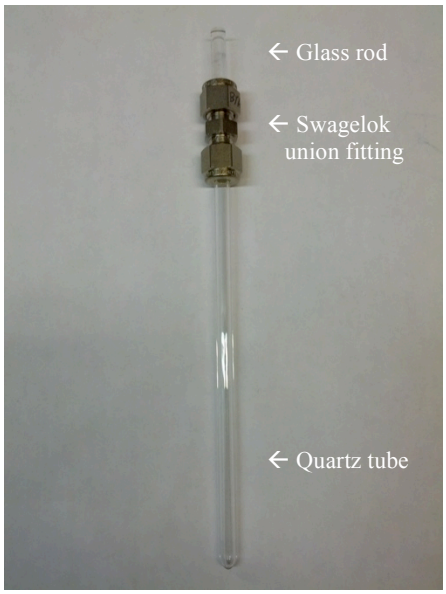


Figure 3.26 Quartz tube for AMS sample storage

3.6. Graphitization and ^{14}C Quantification by AMS

AMS has become the standard ^{14}C counting method for samples containing as little as tens of micrograms of carbon, i.e., the same magnitude as the mass of carbon isolated as DEHP in butter. AMS was successfully applied to measure the natural abundance of ^{14}C of dibutyl phthalate from marine algae by Namikoshi (Namikoshi et al., 2006). AMS can measure as low as 10^{-18} mole of radiocarbon with a precision of better than 10%. For this work, we collaborated with LLNL-CAMS, which was established to make AMS available to a wide variety of researchers.

Carbon-containing samples in quartz tubes for AMS were combusted to CO_2 and graphitized to elemental carbon, because the analysis must be performed on pure carbon targets to achieve the best sensitivity. To perform combustion and graphitization, analyte in each the tube was dried in advance with an oil-free pump

overnight to remove potential solvent residual. CuO was added to the quartz tube, and then the tube was sealed with an H_2/O_2 torch. The sealed quartz tube was then baked at 900 °C for 2 h to oxidize all carbon compounds to CO_2. Afterwards the tube was cracked and CO_2 was forced to pass a cold trap and cryogenically isolated from other byproducts of combustion, e.g., H_2O. The pressure of re-vaporized CO_2 was measured and converted to mass quantitatively afterwards. CO_2 then volumetrically passed through iron-catalyst-embedded tubes and was reduced to elemental carbon with H_2. To graphitize the sample thoroughly, CO_2 was heated at 500 °C for 3 h, and 550 °C for 4 h (Xu et al., 2007). A schematic diagram of LLNL's vacuum line is shown below:

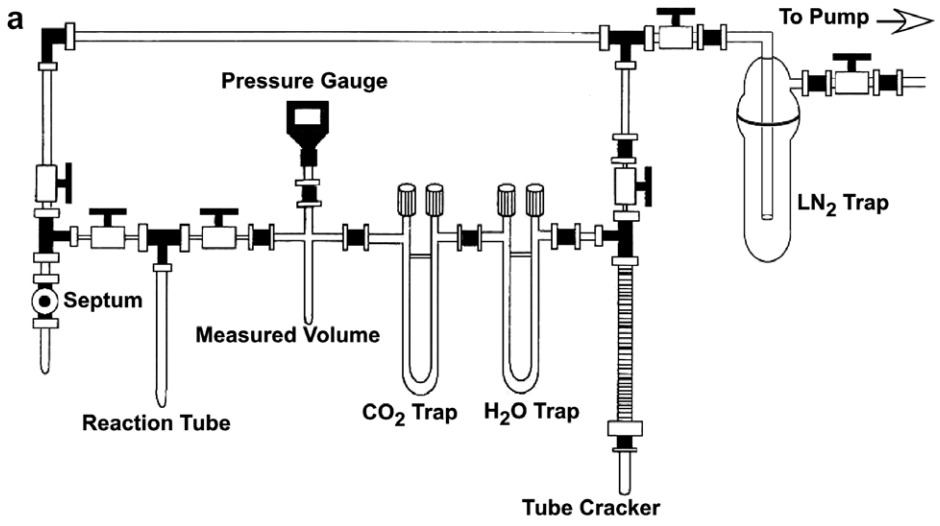


Figure 3.27 Schematic diagram of the vacuum line to extract CO_2 and measure pressure at LLNL-CAMS (Xu et al., 2007)

The graphitized sample pellet was bombarded with a Cs^+ beam to form negatively charged elemental ions and molecular ions, e.g., C^-, C^{2-}, C^{3-} and CH^-. The

primary interferential species for radiocarbon measurement, ^{14}N, was eliminated due to the instability of the negatively charged nitrogen ions ($^{14}N^-$ will not be produced at this stage) (McNichol, Jull, & Burr, 2006). Ion beam passed a low energy spectrometer at first to separate ^{12}C from ions with atomic/molecular mass 13 and 14. In general, ^{12}C ions are chopped into a smaller beam (usually 1% mass) and measured as the current created in Faraday Cups because the ion-count rates are too high for single ion counting. However, the ^{12}C data of the samples were measured at LLNL-CAMS. The rest of the ions were accelerated to gain at least 2.5 MeV energies in a tandem accelerator and pass through a molecular stripper (McNichol et al., 2006). Molecular ions were destroyed accordingly by collisions with the atoms in the stripper, where they also lose one or more electrons. ^{13}C ions were measured in another Faraday Cup after the stripper. Finally, ^{14}C ions were counted by either a solid surface-barrier detector or a gas ionization detector. AMS counted ^{14}C as individual nuclei rather than deriving the amount of ^{14}C from measurements of activity.

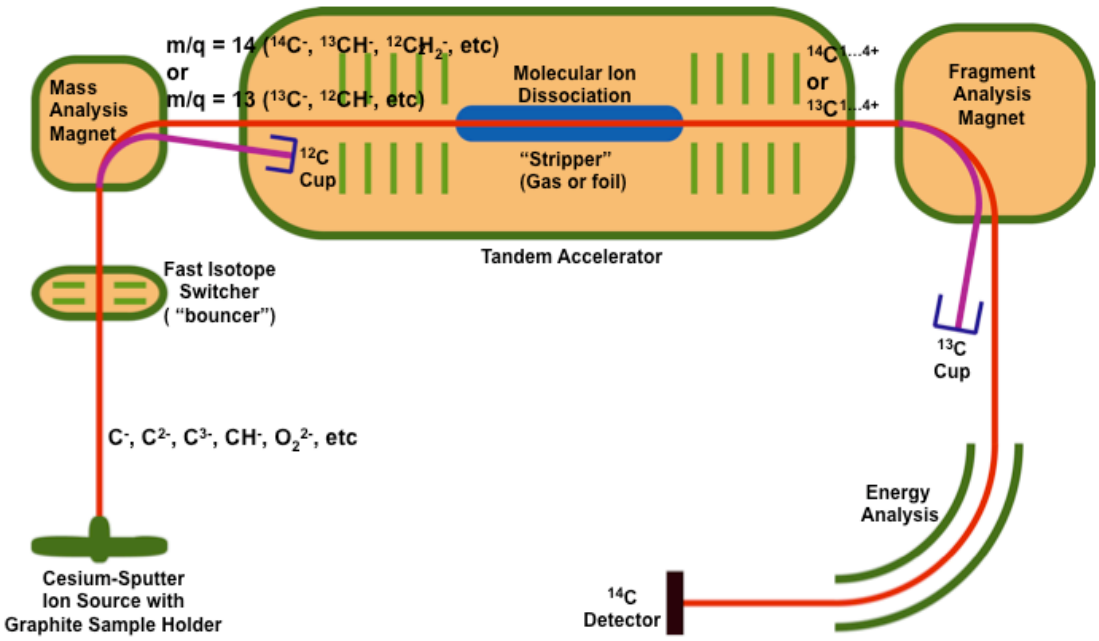


Figure 3.28 Schematic diagram of AMS (from LLNL, https://bioams.llnl.gov/technique.php)

The $^{14}C/^{13}C$ ratio was then applied to fraction modern (f_m) and fraction of contemporary (f_c).

3.7. Fraction Modern (f_m) and Fraction of contemporary (f_c) Calculation

To determine either f_m or f_c of the samples, several concepts and standards have to be introduced first.

3.7.1. Standards for Measurement

The first standard is Pee Dee Belemnite (PDB), the established standard based on a cretaceous marine fossil, *Belemnitella Americana*, in North Carolina (Stuiver & Polach, 1977), whose isotopic ratio $^{13}C/^{12}C$ is 0.0112372 (Slater, Preston, & Weaver, 2001). After PDB was used up, Vienna Pee Dee Belemnite (VPDB) was selected as

the substitute, which is supposed to be identical to PDB. VPDB was set as a standard to correct isotopic fractionation during sample preparation, including biological processes. Isotopic fractionation occurs in all living organisms due to the difference in the rates of absorption and metabolism of carbon dioxide molecules of differing molar mass. For example, the photosynthesis pathway, plants favor lighter carbon isotopes rather than heavier ones, resulting in lower activities in the plants than observed in the atmosphere. The degree of fractionation is defined as the relative difference of the $^{13}C/^{12}C$ ratio in sample to that of VPDB, usually presented in a unit of per mil (‰). Since the mass difference between ^{14}C and ^{12}C is twice that between ^{13}C and ^{12}C, the depletion of ^{14}C is calculated as twice the $\delta^{13}C$ value for each sample.

$$\boldsymbol{R = \frac{^{13}C}{^{12}C}} \tag{3.23}$$

$$\boldsymbol{\delta^{13}C = \left(\frac{R_{sample}}{R_{PDB}} - 1\right) \times 1000}\ ‰ \tag{3.24}$$

R is the carbon isotopic ratio, R_{PDB}=0.0112372 (Slater et al., 2001).

$\delta^{13}C$ measurements determined with an Isoprime® elemental analyzer because no ^{12}C data is provided by LLNL: A small portion of each isolate was prepared for carbon isotope ratio measurement in the Stable Isotope Laboratory, Department of Geology, University of Maryland. Approximately 100-µL aliquots of each post-HPLC sample was removed from its Agilent vial and transferred to a tin capsule (Valencia, CA, 3.5×5 mm) for $\delta^{13}C$ measurement. The mass was obtained on a Mettler Toledo® UMT2 Ultra-microscale balance until the hexane solvent evaporated as indicated by achieving a constant weight. The stable carbon ratio was independent of the mass as long as it was above limit of quantification (LOQ>5 µg, peak height

between 1-12 nA). Tin capsules were folded with acetone rinsed forceps and stored in a sample holder till measurements were made. Seven raw butter samples (CTP) were prepared between each DEHP isolate, and submitted for analysis.

The Isoprime® elemental analyzer isotope ratio mass spectrometer (EA-IRMS) is equipped with a multi-collector and a continuous flow (CF) sample preparation system, coupled with a high temperature combustion oven (1040 °C). Ten measurements were made on a urea sample of known $\delta^{13}C$ fractionation for use as instrumental calibration references. The calibrated $\delta^{13}C$ values of samples are listed in Table 3.9.

Table 3.9 Isotopic ratios ($\delta^{13}C$ VPDB) of contemporary butter and DEHP isolates

Date	*Sample ID*	*Description*	*$\delta^{13}C$*	*Standard Deviation (1σ)*
9/6/2012	CTP1	Raw Butter	-21.08	
9/6/2012	CTP2	Raw Butter	-21.31	
				0.16
12/20/2012	CTP3	Raw Butter	-21.04	
12/20/2012	CTP4	Raw Butter	-21.09	
12/20/2012	CTP5	Raw Butter	-21.20	
12/20/2012	CTP6	Raw Butter	-21.13	
12/20/2012	CTP7	Raw Butter	-20.90	
				0.11
9/6/2012	BTR1	DEHP isolated from butter	-31.23	
9/6/2012	BTR2	DEHP isolated from butter	-30.85	
				0.27
12/20/2012	BTR3	DEHP isolated from butter	-24.59	
12/20/2012	BTR4	DEHP isolated from butter	-27.74	
12/20/2012	BTR5	DEHP isolated from butter	-27.73	
12/20/2012	BTR6	DEHP isolated from butter	-25.23	
12/20/2012	BTR7	DEHP isolated from butter	-23.42	
				1.93

The second standard represents carbon harvested in the "modern" year. The radiocarbon modern year is defined as 1950 AD. To avoid fossil fuels combustion interference during the industrial revolution, the "modern" activity is the ^{14}C activity of virtual "wood" in 1950 AD, which was actually extrapolated from 1890 AD tree-rings whose $\delta^{13}C$= -25‰ wrt VPDB (Stuiver & Polach, 1977). By definition, the specific of activity "modern" is 226.0 ± 1.1 Becquerel per kilogram of carbon (see Table 3.10) (Roussel-Debet, Gontier, Siclet, & Fournier, 2006).

The third standard (e.g., HOxII) is that used to calibrate either LSC or AMS instruments and calculate normalized sample activities, i.e., fraction modern. The international agreed modern carbon standard for the radiocarbon measurements is HOxI (SRM 4990B), which was oxalic acid created by the National Bureau of Standards (NBS) in 1955 AD (one batch, 1000 lb.). The modern activity is scaled to 95% of the measured activity (^{14}C counts) with $\delta^{13}C$=-19 ‰ wrt VPDB because HOxI incorporated the "bomb" carbon that was spiked in to the atmosphere as a result of nuclear weapon tests. Due to the limited quantity of the first standard, the first oxalic acid HOxI is no longer available. Hence a second standard, HOxII, was prepared by National Institute of Standards and Technology (NIST) from French beat harvests in the 1970s. The desired activity was scaled to 0.7459 of the measured activity and normalized to $\delta^{13}C$=-25 ‰ wrt VPDB and is in precise agreement with HOxI.

3.7.2. Calculating Fraction Modern (f_m) from Isotopic Ratio Measurements

Fraction modern can be calculated from both activity and carbon isotopic ratios. Given the fact that activities was only measured for the live standard but not butter isolates, the derivation of fraction modern from activity is listed in Appendix 1 for further reference.

AMS counts ^{14}C particles directly instead of activity. Accordingly, McNichol *et al.* summarized the method of fraction modern calculation from raw AMS data as follows (McNichol et al., 2006).

$$\boldsymbol{f_{m,14/12}} = \frac{\boldsymbol{R_{normSample,14/12}}}{\boldsymbol{R_{modern,14/12}}} \tag{3.25}$$

$$f_{m,14/13} = \frac{R_{normSample,14/13}}{R_{modern,14/13}} \tag{3.26}$$

R is the isotopic ratio, either $^{14}C/^{12}C$ or $^{14}C/^{13}C$. $R_{normSample}$ and R_{modern} are the normalized isotopic ratios of sample and standard, corrected from isotopic fractionation as described above.

$$\begin{aligned}\left(R_{14C/12C}\right)_{modern} &= 0.95\left(R_{14C/12C}\right)_{HOxI} = 0.95 \cdot \left(R_{14C/12C}\right)_{HOxI,measured} \cdot \left(\frac{1000-19}{1000+\delta^{13}C_{HOxI}}\right)^2 \\ &= 0.7459\left(R_{14C/12C}\right)_{HOxII} = 0.7459 \cdot \left(R_{14C/12C}\right)_{HOxII,measured} \cdot \left(\frac{1000-25}{1000+\delta^{13}C_{HOxII}}\right)^2\end{aligned} \tag{3.27}$$

$$\begin{aligned}\left(R_{14C/13C}\right)_{modern} &= 0.95\left(R_{14C/13C}\right)_{HOxI} = 0.95 \cdot \left(R_{14C/13C}\right)_{HOxI,measured} \cdot \left(\frac{1000-19}{1000+\delta^{13}C_{HOxI}}\right) \\ &= 0.7459\left(R_{14C/13C}\right)_{HOxII} = 0.7459 \cdot \left(R_{14C/13C}\right)_{HOxII,measured} \cdot \left(\frac{1000-25}{1000+\delta^{13}C_{HOxII}}\right)\end{aligned} \tag{3.28}$$

For the sample isotopic ratio, the machine background must first be subtracted from the measured value before normalization. As defined above, the $\delta^{13}C$ of sample is normalized to -25 ‰ with regard to PDB regardless of its composition (Donahue, linick, & Jull, 1990).

$$\left(R_{14C/12C}\right)_{normSample} = \left(R_{14C/12C}\right)_{measured} \cdot \left(\frac{1000-25}{1000+\delta^{13}C_S}\right)^2 \tag{3.29}$$

$$\left(R_{14C/13C}\right)_{normSample} = \left(R_{14C/13C}\right)_{measured} \cdot \left(\frac{1000-25}{1000+\delta^{13}C_S}\right) \tag{3.30}$$

According to the definition, the fraction modern is a nonnegative value ($f_m \geq 0$).

A variety of units have been used to present ^{14}C value. In order to compare data readily, a table of equivalent concentrations of ^{14}C in various units is listed as follows (Burlingame, 2007).

Table 3.10 Equivalent concentrations of ^{14}C units (Burlinggame, 2007)

^{14}C value	***Unit***
1.0	modern
1.176×10^{-12}	atm/atm C
1.176	pmol/mol C
13.56	dpm/g C
226.0	μBq/mg C
6.108	fCi/mg C
97.89	amol/mg C

3.7.3. Fraction Contemporary and Fraction Petrogenic

The abundance of ^{14}C in the atmosphere continuously fluctuated since 1950, the year designated as "modern", owing to both negative and positive factors. Nuclear weapon tests spiked in a huge amount of radioactive carbon to the atmosphere (1.64% relative share of the globe inventory) (Svetlik et al., 2010). Meanwhile, increasing fossil fuels combustion dilutes the abundance of ^{14}C. So the contemporaneous carbon activity (or isotopic) cannot just be derived from the "modern" activity by applying the correction for ^{14}C half-life. In this project, we aimed to apportion the source of DEHP in butter produced in the actual year of measurement, so it was necessary to adjust the result from conventional fraction modern (based on the "modern" year) to the contemporary year, i.e., fraction of contemporary (f_c) as expressed by Reddy (Reddy et al., 2002),

$$f_c = \frac{f_{m,DEHP}}{f_{m,atm}} \tag{3.31}$$

where $f_{m,atm}$ is the value measured for a contemporary sample of atmospheric carbon. However, such a sample would produce a "super-modern" value of fraction modern (f_m>1).

Since $f_{m,atm}$ varies with location and time, a new specific standard was defined in this project: i.e., raw butter. As a contemporary dairy product wherein the major constituents are ,by far, fats and proteins made from contemporary living animals, its activity (with isotopic fractionation correction) represents the current natural activity of the organisms appropriate to our study, including any fluctuations that occurred relative to the atmosphere (Pearson, 2000) (Nelson et al., 2013).

$$\boldsymbol{f_{m,atm} = f_{m,butterNorm}} \tag{3.32}$$

$$\boldsymbol{f_c = \frac{f_{m,DEHP}}{f_{m,butter}}\left(\frac{1000+2\delta^{13}C_{DEHP}}{1000+2\delta^{13}C_{butter}}\right)} \tag{3.33}$$

Fraction petrogenic represents the ratio of anthropogenically derived DEHP in the isolated DEHP from butter, i.e.,

$$\boldsymbol{f_p = 1 - f_c} \tag{3.34}$$

Chapter 4 : Results and Data Interpretation

For spiked blank samples, the total carbon mass of DEHP includes mass introduced by contamination derived from solvents, surface of the glassware used in processing, atmospheric deposition, and any other source acting during processing (m_{mtd}) and the corresponding spike (m_{spike})

$$\boldsymbol{m_{DEHP,total} = m_{mtd} + m_{spike}} \quad (4.1)$$

For butter isolate samples, the carbon mass of DEHP measured with GC-EIMS ($m_{DEHP,total}$) included the one from raw butter (m_{actual}) and the one introduced during sample purification due the ubiquity of DEHP, which was from method blank sample (m_{mtd}).

$$\boldsymbol{m_{DEHP,total} = m_{mtd} + m_{actual}} \quad (4.2)$$

4.1 Carbon Mass Measured Manometrically at LLNL

Carbon mass of each sample was determined manometrically at LLNL.

Unfortunately, the first batch, BTR1 and BTR2, leaked during shipment. What remained in BTR1 to be analyzed was below detection limit of AMS and there was only ≈40% BTR2 solution left, and so these samples were not processed by LLNL. For the second batch of samples prepared for AMS, the manometrically determined carbon mass (measured at LLNL) was twice as much as mass measured with GC-EIMS. The difference was termed as exogenous carbon (m_{GCMS} as shown in equation 3.16).

$$\boldsymbol{m_{exo} = m_{LLNL} - m_{GCMS}} \quad (4.3)$$

Exogenous carbon was determined for each sample and the results were listed in Table 4.1.

Table 4.1 Mass difference between sample carbon mass measured gravitationally in College Park and total carbon mass measured manometrically at LLNL

Sample ID	m_{actual} **(μg)**	m_{mtd} **(μg)**	$m_{DEHP,total}$ **(μg)**[a]	m_{coe} **(μg)**	m_{GCMS} **(μg)**	m_{LLNL}**(μg)**[b]	m_{exo} **(μg)**
BTR1	123.87 ± 14.65	0.52 ± 0.19	124.39 ± 14.65	3.33 ± 0.40	127.72 ± 15.1	-[c]	-
BTR2	113.16 ± 13.00	0.70 ± 0.20	113.86 ± 13.00	3.39 ± 0.39	117.25 ± 13.4	44 ± 2	-73.25 ± 13.18
BTR3	76.77 ± 11.27	1.08 ± 0.08	77.85 ± 11.27	5.41 ± 0.80	83.26 ± 12.16	247 ± 12	163.74 ± 16.72
BTR4	104.16 ± 12.64	0.73 ± 0.06	104.89 ± 12.64	8.45 ± 1.03	113.34 ± 13.73	200 ± 10	86.66 ± 16.12
BTR5	70.04 ± 11.07	0.79 ± 0.07	70.83 ± 11.07	2.10 ± 0.33	72.93 ± 11.41	143 ± 7	70.07 ± 13.18
BTR6	64.86 ± 10.03	0.87 ± 0.19	65.73 ± 10.03	2.95 ± 0.46	68.68 ± 10.56	221 ± 11	152.32 ± 14.92
BTR7	65.89 ± 10.35	0.87 ± 0.19	66.76 ± 10.35	3.09 ± 0.48	69.85 ± 10.86	990 ± 50	920.15 ± 50.57

[a] Carbon mass as DEHP in each butter extract sample, which was determined by Shimadzu QP2010 GC-EIMS with an analytical calibration curve, gravimetrically-prepared from standard Supelco DEHP. 1σ uncertainty, n=3.
[b] Carbon mass determined by CO_2 pressure-volume manometry after combustion at LLNL; relative uncertainty reported as ≈5%.
[c] Sample spilled during shipment. No data was acquired.

4.2 Fraction Modern Measured with AMS

Values of fraction modern (f_m) determined in solvent-free isolates that were analyzed by LLNL, were listed in

Table 4.2: Seven DEHP samples isolated from butter, seven spiked method blank samples, two Supelco® DEHP, three "dead" DEHP standards and three "live" DEHP standards.

Table 4.2 Fraction modern ($f_{m,measured}$) measured at LLNL CAMS

Sample ID	***Description***	***Measured Fraction Modern by LLNL ($f_{m,measured}$)[a]***
BTR1	DEHP isolated from butter	-
BTR2	DEHP isolated from butter	0.0682 ± 0.0101
BTR3	DEHP isolated from butter	0.6484 ± 0.0032
BTR4	DEHP isolated from butter	0.2960 ± 0.0021
BTR5	DEHP isolated from butter	0.3045 ± 0.0025
BTR6	DEHP isolated from butter	0.6670 ± 0.0027
BTR7	DEHP isolated from butter	0.9414 ± 0.0034
BLK1D	Method blank with dead spike	0.0479 ± 0.0045
BLK1L	Method blank with live spike	0.6945 ± 0.0038
BLK2D	Method blank with dead spike	0.1249 ± 0.0043
BLK2L	Method blank with live spike	0.7132 ± 0.0058
BLK3D	Method blank with dead spike	0.4075 ± 0.0030
BLK4D	Method blank with dead spike	0.4260 ± 0.0027
BLK5D	Method blank with dead spike	0.3918 ± 0.0027
STD1	Supelco® DEHP (98.8%)	0.0018 ± 0.0042
STD2	Supelco® DEHP (98.8%)	0.0000 ± 0.0044
DS1	Dead DEHP standard solution	0.0110 ± 0.0053
DS2	Dead DEHP standard solution	0.0076 ± 0.0053
DS3	Dead DEHP standard solution	0.0085 ± 0.0053
LS1	Live DEHP standard solution	0.8473 ± 0.0064
LS2	Live DEHP standard solution	0.8154 ± 0.0064
LS3	Live DEHP standard solution	0.8021 ± 0.0077
CTP1	Contemporary butter	1.0545 ± 0.0041
CTP2	Contemporary butter	1.0576 ± 0.0037

[a] two-sigma limits

4.3 Exploration of Possible Exogenous Carbon Sources

The measured fraction modern of each AMS sample is a weighted arithmetic mean of all components (i.e., a mass balance method) (McNichol et al., 2006).

$$f_{m,measured} = \frac{\sum m_i \cdot f_{m,i}}{\sum m_i} \quad (4.4)$$

As indicated in Table 4.1 the DEHP samples from butter isolation (except BTR1 and BTR2) contained more than 70 μg of exogenous carbon. Thus the measured fraction modern does not reflect the true value of f_m of DEHP isolated from butter. As a result, the mass of modern carbon (m_{MC}) from the method blank ($m_{MC,mtd}$), the co-eluted compounds ($m_{MC,coe}$) and exogenous components ($m_{MC,exo}$) had to be subtracted from the total modern carbon mass of sample.

By definition, m_{MC} is the product of the sample mass and its measured modern fraction, i.e.,

$$m_{MC} = m \cdot f_m \quad (4.5)$$

The actual mass of modern carbon from the DEHP in the sample ($m_{MC,actual}$) is:

$$m_{MC,actual} = m_{MC,measured} - m_{MC,mtd} - m_{MC,coe} - m_{MC,exo} \quad (4.6)$$

and its actual f_m ($f_{m,actual}$) is:

$$f_{m,actual} = \frac{m_{MC,actual}}{m_{actual}} \quad (4.7)$$

In the above equations, the modern carbon mass of the method blank ($m_{MC,mtd}$) is calculated from the corresponding total carbon mass (m_{mtd}) and fraction modern ($f_{m,mtd}$). Due to the ubiquity of PVC material and other plastic products, the fraction modern of method blank DEHP was assumed to be identical to that of the petrogenic

Supelco® standards, which is 0.0009 ± 0.0013. The modern carbon mass of each co-eluted blank ($m_{MC,coe}$) was calculated from its total co-eluted carbon mass (m_{coe}) and the fraction modern ($f_{m,coe}$) of the co-eluted compounds. Most co-eluted compounds were organic compounds from butter, e.g., cholesterol and Z,E-2,13-Octadecadien-1-ol, and therefore its fraction modern was assumed to be the same as that determined for raw butter, which was 1.0561 ± 0.0022.

The carbon mass of exogenous carbon (m_{exo}) in each sample was calculated from the mass difference between those determined from GC-EIMS and those reported by LLNL (see Table 4.1). The sources of exogenous carbon were identified and the corresponding fraction modern for each type of exogenous carbon ($f_{m,exo,i}$) were computed or measured as described in the following sections, and the fraction modern of DEHP isolated from butter ($f_{m,actual}$) was calculated accordingly.

Exploration of exogenous carbon was focused on contamination occurring during the post-HPLC handling ($m_{exo,postHPLC}$), including packing, shipping and graphitization and inorganic carbonates.

4.3.1 Post-HPLC Exogenous Carbon

The fraction modern of post-HPLC exogenous carbon was calculated from the three dead standard samples, which were diluted from Supelco® DEHP in hexane without any chromatographic separation.

Table 4.3 Mass and fraction modern of the post-HPLC exogenous carbon

Sample ID	$m_{DEHP,total}$ (μg)[a]	m_{LLNL} (μg)	m_{exo} (μg)[b]	$f_{m,measured}$[c]	$f_{m,exo,postHPLC}$[d]
DS1	47.30 ± 0.04	78 ± 2	30.7 ± 2.0	0.0110 ± 0.0053	0.0266 ± 0.0071
DS2	47.95 ± 0.04	81 ± 2	33.0 ± 2.0	0.0076 ± 0.0053	0.0173 ± 0.0100
DS3	47.73 ± 0.04	83 ± 2	35.27 ± 2.0	0.0085 ± 0.0053	0.0188 ± 0.0085

[a] n=3, 1 σ

[b] calculated from error propagation, 1 σ

As a result, the fraction modern of post-HPLC exogenous carbon ($f_{m,exo,postHPLC}$) was 0.0209 ± 0.0050, which was "^{14}C-dead" petrogenic contaminant.

4.3.2 Carbonates from Raw Butter

The carbon mass of exogenous carbon as carbonates from butter ($m_{exo,carbBtr}$) was calculated accordingly for each sample:

$$\boldsymbol{m_{exo,carbBtr} = m_{exo} - m_{exo,postHPLC} - m_{exo,carbMtd}} \quad (4.8)$$

Carbonates generated during butter manufacturing were mainly contemporary, and therefore the fraction modern ($f_{m,exo,carbBtr}$) was 1.0561 ± 0.0022.

4.3.3 Method-derived Carbonates

The mass of method-derived carbonates was calculated in Section 3.4.2, which was 31.2 ± 7.2 μg. The fraction modern of the method derived carbonates ($f_{m,exo,carbMtd}$) was calculated from the spiked blanks with mass balance method to eliminate the interference of carbonates from experimental matrices.

$$\boldsymbol{f_{m,exo,carbMtd} = \frac{f_{m,measured} \cdot m_{LLNL} - f_{m,DEHP,total} \cdot m_{DEHP,total} - f_{m,exo,postHPLC} \cdot m_{exo,postHPLC}}{m_{exo,carbMtd}}} \quad (4.9)$$

Table 4.4 Fraction modern of method derived carbonates

Sample ID	$f_{m,measured}$	$m_{DEHP,total}$ ***(μg)***[a]	m_{LLNL} ***(μg)***	$m_{exo,postHPLC}$ ***(μg)***[b]	$m_{exo,carbMtd}$ ***(μg)***[c]	$f_{m,exo,carbMtd}$[d]
BLK1D	0.0479 ± 0.0045	52.21 ± 0.09	88 ± 4	22.94 ± 5.31	12.8 ± 3.0	0.2871 ± 0.0893
BLK1L	0.6945 ± 0.0038	46.42 ± 0.15	109 ± 5	48.71 ± 6.32	18.4 ± 4.2	0.6254 ± 0.2105
BLK2D	0.1249 ± 0.0043	65.94 ± 0.10	94 ± 5	9.71 ± 6.33	13.9 ± 3.2	2.6520 ± 0.7475
BLK2L	0.7132 ± 0.0058	46.81 ± 0.15	62 ± 3	-2.14 ± 5.06[a]	17.3 ± 4.0	0.3514 ± 0.1946

[a] n=3, 1σ
[b,c,d] Calculated from error propagation, 1σ
[e] This is a calculated value. Mass should be a non-zero value

The Dixon's Q test was applied to reject potential outlier.

$$\boldsymbol{Q = \frac{2.6520-0.6254}{2.6520-0.2871} = 0.8659 > 0.829\ (Q_{95\%,n=4})} \tag{4.10}$$

Accordingly, $f_{m,exo,carbMtd}$ of BLK2D could be eliminated at the 95% confidence level. The fraction modern of method-derived carbonates was 0.4213 ± 0.1797.

4.4 Determination of $f_{m,actual}$

As the composition of exogenous carbon had been resolved, fraction modern of DEHP isolated from butter ($f_{m,actual}$) can be calculated from the measured value eventually.

$$\boldsymbol{m_{exo} = m_{exo,postHPLC} + m_{exo,carbMtd} + m_{exo,carbBtr}} \tag{4.11}$$

$$\boldsymbol{f_{m,exo} = \frac{f_{m,exo,postHPLC} \cdot m_{exo,postHPLC} + f_{m,exo,carbMtd} \cdot m_{exo,carbMtd} + f_{m,exo,carbBtr} \cdot m_{exo,carbBtr}}{m_{exo}}} \tag{4.12}$$

The method blank as DEHP, the co-eluted blank and the exogenous carbon were added up to the total blank:

$$\boldsymbol{m_{totalBlank} = m_{mtd} + m_{coe} + m_{exo}} \tag{4.13}$$

$$f_{m,totalBlank} = \frac{f_{m,mtd} \cdot m_{exo,mtd} + f_{m,coe} \cdot m_{coe} + f_{m,exo} \cdot m_{exo}}{m_{totalBlank}} \quad (4.14)$$

$$m_{actual} = m_{LLNL} - m_{totalBlank} \quad (4.15)$$

$$f_{m,actual} = \frac{f_{m,measured} \cdot m_{LLNL} - f_{m,totalBlank} \cdot m_{totalBlank}}{m_{actual}} \quad (4.16)$$

The fraction of contemporary can be calculated as follows (Nelson et al., 2013):

$$F_{iso} = \frac{1 - 2 \cdot \frac{\delta^{13}C_{VPDB_{isolate}}}{1000}}{1 - 2 \cdot \frac{\delta^{13}C_{VPDB_{butter}}}{1000}} \quad (4.17)$$

$$f_c = \frac{f_{m,actual}}{f_{m,btr}} \cdot F_{iso} \quad (4.18)$$

F_{iso} was the isotopic fractionation correction coefficient.

Table 4.5 Mass and fraction modern (f_m) of components of the total carbon blanks for BTR3-BTR7

Sample ID	$m_{exo,carbBtr}$ ***(μg)***[a]	$m_{exo,postHPLC}$ ***(μg)***	$f_{m,\ exo}$	$m_{totalBlank}$ ***(μg)***	$f_{m,totalBlank}$	$f_{m,actual}$	f_c[d]
BTR3	130.75±20.87	1.79±9.12	0.9366±0.1655	170.23±17.10	0.9222±0.2041	0.0413±0.5069	0.0394±0.4832
BTR4	33.24±20.84	22.22±9.70	0.5863±0.2803	95.84±17.02	0.6014±0.2856	0.0150±0.2819	0.0143±0.2688
BTR5	18.44±18.09	20.43±9.70	0.5016±0.2973	72.96±13.39	0.4833±0.3066	0.1182±0.3342	0.1134±0.3205
BTR6	119.33±19.19	1.79±9.12[b]	0.9276±0.1635	156.14±15.26	0.9115±0.2016	0.0784±0.5419	0.0748±0.5171
BTR7	867.63±52.10	21.33±1.27[c]	1.0129±0.0823	924.11±51.17	1.0098±0.1137	-0.0176±1.9168	-0.0168±1.8230

[a] The fraction modern of carbonates in butter was assumed to be equal to fraction modern as raw butter, which is 1.0561 ± 0.0022

[b] BLK6 and BLK7 were not sent to LLNL, so we assume that the post HPLC exogenous carbon of BTR6 is same as BTR3 due to similar fraction modern and mass of exogenous carbon

[c] The post HPLC exogenous carbon of BTR7 is the average value as that of BTR5 and BTR6, uncertainty is the standard deviation.

[d] Unrounded data from error propagation, reported to 4 decimal places, 1σ .

Chapter 5 : Uncertainty Analysis and Monte Carlo Simulation

5.1 Uncertainty Analysis

The uncertainty of $f_{m,actual}$ in Table 4.5 was calculated by error propagation using the total differential method. However, this method overestimates the overall uncertainty when degrees of freedom are correlated. As a result, Monte Carlo simulation, a computerized mathematical technique to mimic repeated sampling actions, was implemented in Matlab® programs to compute fraction of contemporary of DEHP extracted and its uncertainty for each sample. One set of data was imported to the program as inputs for each AMS sample of butter extract. Each data set included the carbon mass of DEHP in the sample, masses and fraction modern of blanks and $\delta^{13}C$ of isolates. Additional input parameters are listed in Table 5.1. A uniformly distributed pseudo-random perturbation matrix was generated by the program and applied to the uncertainty of each variable to simulate tens of thousands of replicates. Each of the variables was perturbed independently.

The larger the perturbation matrix size is, the more accurate the estimation of fraction of contemporary would be. Ten to one million perturbations were tested with the program and the results showed that fractions contemporary tended to be stable after 1000 perturbations. For this reason the choice of 50,000 perturbations was judged to be more than adequate.

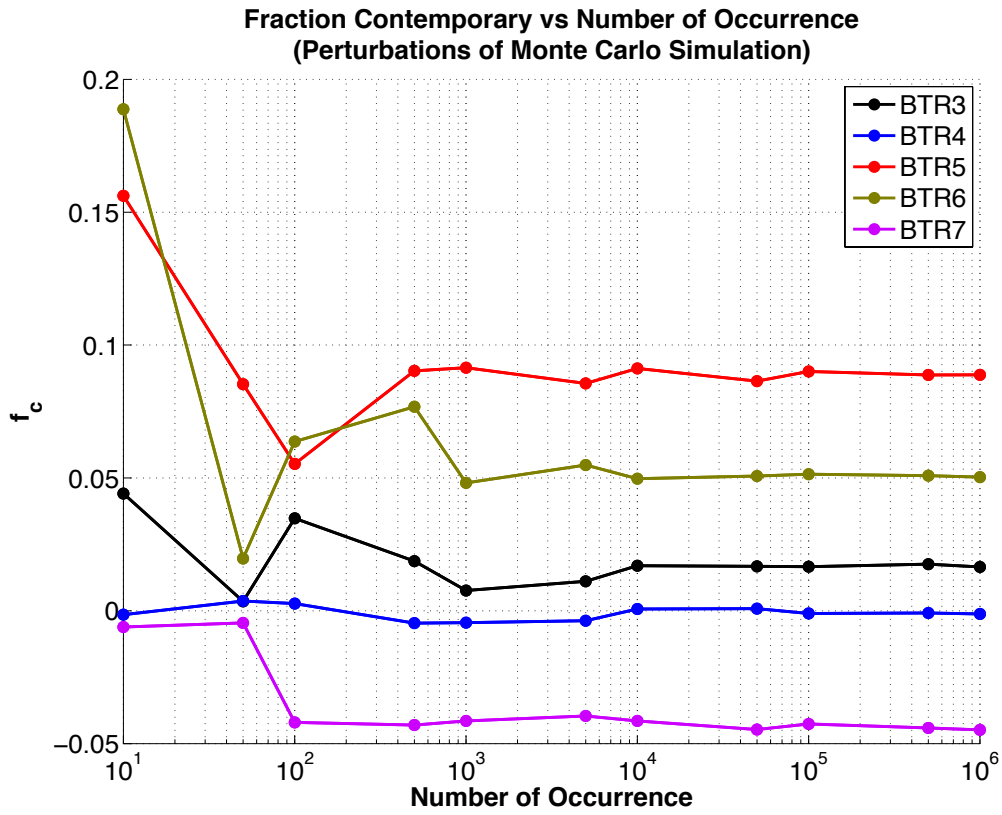


Figure 5.1 Fraction of contemporary of DEHP isolated from butter vs. number of perturbed data sets

5.2 Monte Carlo Simulation (n=50,000)

Each data set of BTR3 to BTR7 was perturbed to heuristically calculate uncertainties and explore their probability distributions.

Table 5.1 Example of input parameters for Monte Carlo simulation (BTR4)

Parameters	***BTR4***
$m_{DEHP,total}$	104.89 ± 12.64
m_{mtd}	0.73 ± 0.06
$f_{m,mtd}$	0.0009 ± 0.0013
$f_{m,coe}$	1.0561 ± 0.00219
$purity_C$	0.9254 ± 0.0115
$f_{m,measured}$	0.296 ± 0.0021
$f_{m,btr}$	1.0561 ± 0.00219
$\delta^{13}C_{sam}$	-24.74 ± 1.93
$\delta^{13}C_{btr}$	-21.11 ± 0.13
m_{LLNL}	200 ± 10
$m_{exo,carbMtd}$	31.2 ± 7.2
$f_{m,exo,carbMtd}$	0.4213 ± 0.1797
$m_{exo,postHPLC}$	22.22 ± 9.70
$f_{m,exo,postHPLC}$	0.0209 ± 0.0050
$f_{m,exo,carbBtr}$	1.0561 ± 0.0022

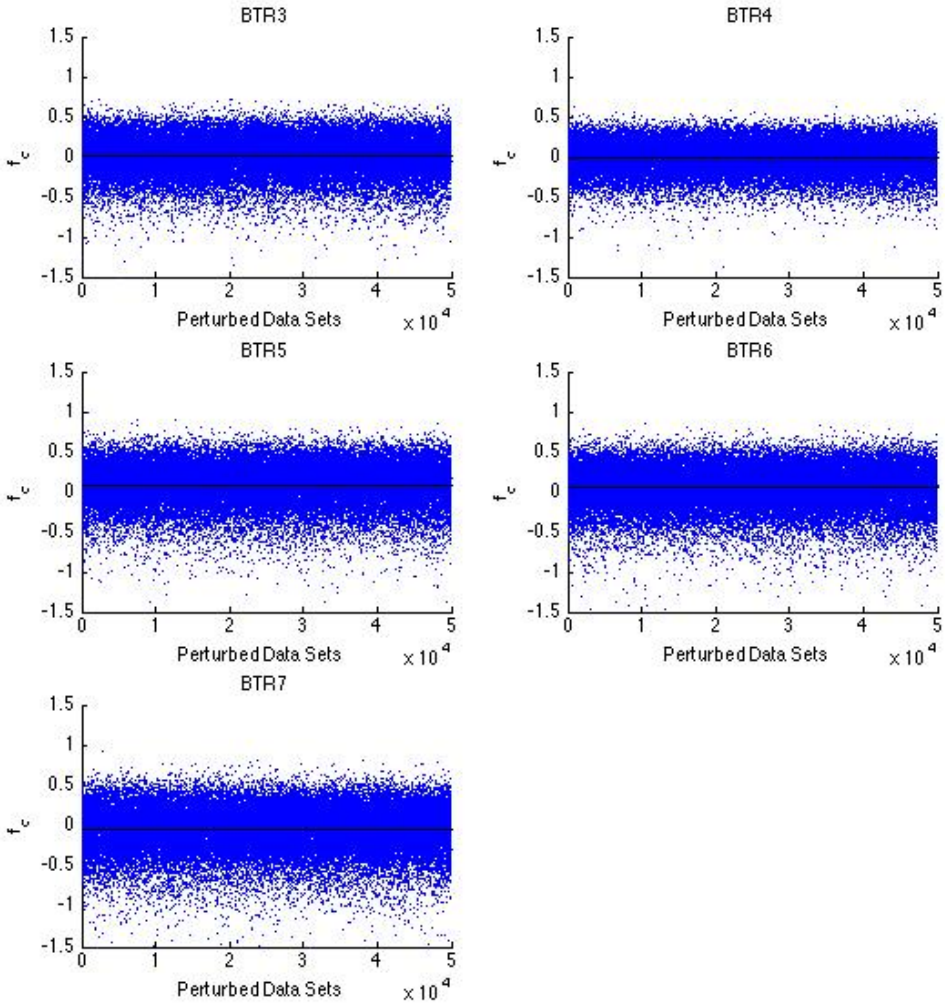


Figure 5.2 Fraction of contemporary versus number of perturbed data sets (n_{max}=50,000)

The probability distribution for each sample is was shown in Figure 5.2. The f_c of computer simulated replicates randomly varied near 0 with more scattered distribution in the negative region (either f_m or f_c should be a non-negative value.). Therefore the statistical distributions of fraction modern are constructed by counting the occurrences of f_c between -1.5 and 1.5. The binning interval is 0.05.

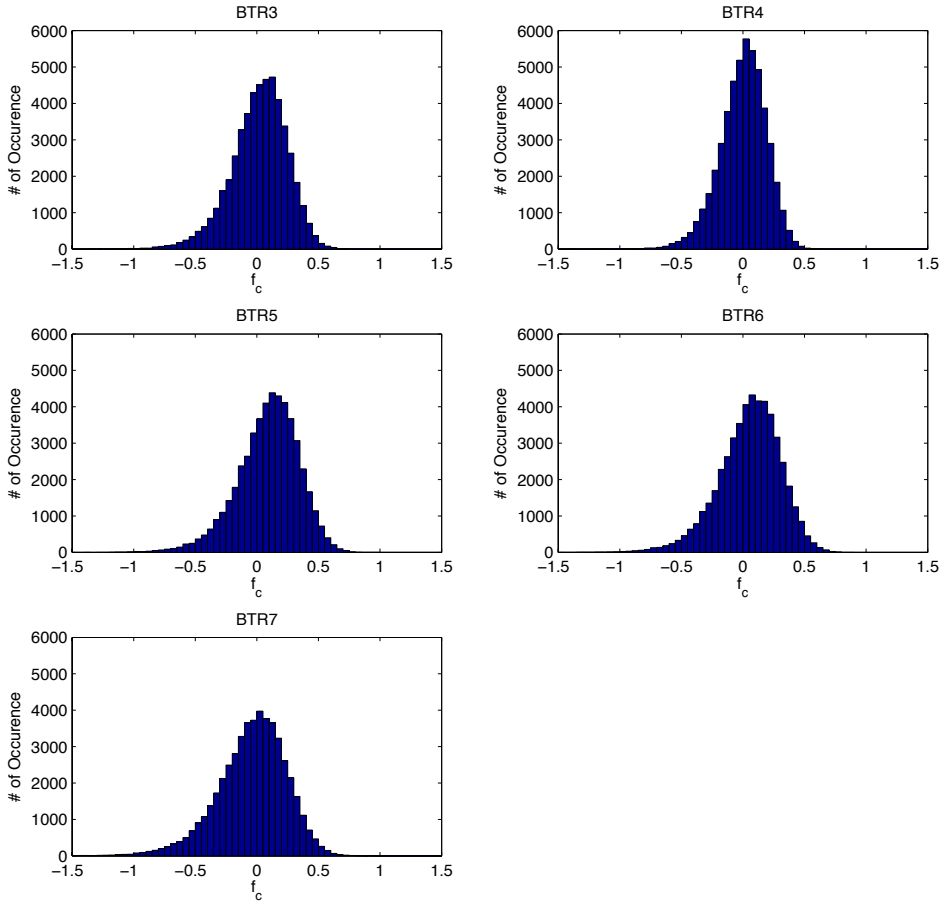


Figure 5.3 Histograms of fc distribution of 5 DEHP isolates from butter

The computed f_c of each DEHP was the mean of 50,000 computerized replicates and the uncertainties were the standard deviation (1σ).

The final fraction of contemporary and fraction modern of each DEHP isolated from butter extracts are listed in Table 5.2. Normalized fraction of contemporary probability distributions were presented Figure 5.4

Table 5.2 Fraction modern and fraction of contemporary (f_c) of DEHP isolated from butter by Monte Carlo Simulation

Sample ID	$\delta^{13}C$	$f_{m,actual}$	f_c [a]	f_p [b]
BTR3	-24.59 ± 1.93	0.0175 ± 0.2403	0.0167 ± 0.2290	0.9833 ± 0.2290
BTR4	-27.74 ± 1.93	0.0008 ± 0.1965	0.0008 ± 0.1874	0.9992 ± 0.1874
BTR5	-27.73 ± 1.93	0.0901 ± 0.2618	0.0864 ± 0.2511	0.9136 ± 0.2511
BTR6	-25.23 ± 1.93	0.0531 ± 0.2629	0.0507 ± 0.2509	0.9493 ± 0.2509
BTR7	-23.42 ± 1.93	-0.0470 ± 0.2937	-0.0447 ± 0.2794	1.0447 ± 0.2794
Mean (n=5, 1σ)	-25.74 ± 1.93	0.0229 ± 0.0520	0.0220 ± 0.0497	0.9780 ± 0.0497

[a,b] unrounded, computed data

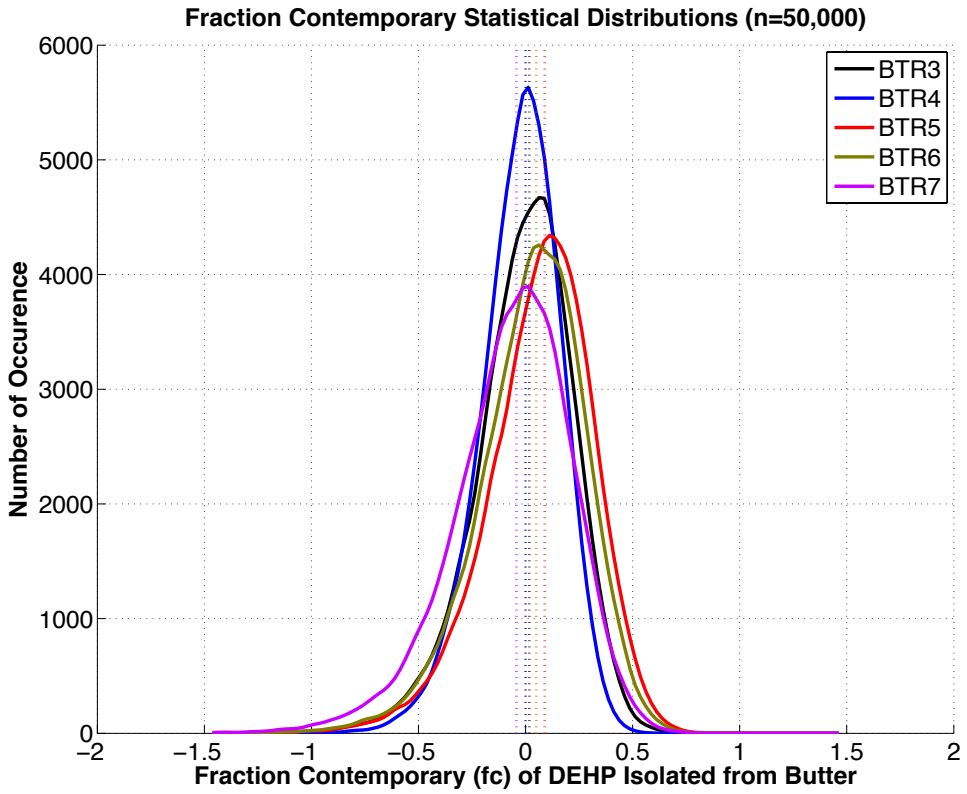


Figure 5.4 Statistical distribution of Fraction of contemporary (f_c) of DEHP in Butter.

Chapter 6 : Conclusion

The existence of DEHP in method blanks strongly proved the ubiquity of DEHP in the environment. The method of micro-scale compound specific isotope analysis in a fatty food matrix, butter, was optimized. Compared to the fraction of contemporary carbon in DEHP isolated from Stilton cheese, the f_c of the DEHP in butter is relatively lower, possibly owing to the lack of fermentation and possibly molds injection. The results demonstrate that the fraction petrogenic (f_p) of the isolated DEHP from butter, 97.80 ± 4.97 %, is of petrogenic possibly from butter production and packing. Thus at the 95% confidence level, no less than 88% of the DEHP in butter is of petrogenic origin.

It is noteworthy that BTR7 contained 920.15 ± 50.57 μg exogenous carbon while the other isolated DEHP samples only contained only 70-160 μg. It is possible that contamination came from some contemporaneous compounds with the same level of ^{14}C as the contemporary butter standard. If BTR7 is eliminated, the mean value of f_c would be 0.0346 ± 0.0380 and f_p would be 0.9614 ± 0.0380 (n=4, 1σ). However, compared to f_p 0.9780 ± 0.0497 (n=5, 1σ), the relative difference is only 1.70%.

Despite the finding that more than 70 μg of exogenous carbon existed in each DEHP isolates from butter, the fraction of contemporary carbon could be determined with a sufficient degree of accuracy to be useful to agencies responsible for monitoring and regulating the food supply system. Nevertheless, future work should

be undertaken to reduce the amounts of exogenous carbon observed in the current method.

In the future, this compound specific radiocarbon analysis method should be applied to more dairy products and lipids-rich food, including fatty meats, to determine the concentrations and origin(s) of phthalates in the U.S. diet.

Appendices

Appendix 1 : Background Data

1. Carbon Isotopes

15 known carbon isotopes with their half-life and decay modes are listed in the following table.

Table A 1.1 Half-life and decay modes of carbon isotopes

Nuclides	***Half-life***	***Decay Mode***	***Decay Daughter***
^{8}C	2.0×10^{-21} s	2p	^{6}Be
^{9}C	0.126 s	β^+; β^+, p; β^+,α	^{9}B(60%); ^{8}Be(23%); ^{5}Li(17%)
^{10}C	19.290 s	β^+	^{10}B
^{11}C	20.39 min	β^+	^{11}B
^{12}C	Stable	-	-
^{13}C	Stable	-	-
^{14}C	5730 years	β^-	^{14}N
^{15}C	2.449 s	β^-	^{15}N
^{16}C	0.747 s	β^-, n; β^-	^{15}N(97.9%); ^{16}N (2.1%)
^{17}C	0.193 s	β^-; β^-, n	^{17}N(71.6%); ^{16}N (28.4%)
^{18}C	0.092 s	β^-; β^-, n	^{18}N(68.5%); ^{16}N (31.5%)
^{19}C	0.0462 s	β^-, n; β^-; β^-, 2n	^{18}N(47%); ^{19}N (46%); ^{17}N(7%);
^{20}C	0.016 s	β^-, n; β^-	^{19}N (72.0%); ^{20}N(28.0%);
^{21}C	$<3\times10^{-8}$ s	n	^{20}C
^{22}C	0.0062 s	β^-	^{22}N

2. Liquid Scintillation Counting (LSC)

Beta counting is a method of measuring radioactive activity by detecting beta particles emitted from the decaying ^{14}C atoms. One beta counting technology is liquid scintillation counting. The energy of beta particles is converted into photons with two steps: first, aromatic solvent molecules with π electrons absorb the energy of beta particles and transfer the energy to scintillators (the π cloud of the aromatic ring absorbs the energy). Second, the excited scintillator molecules return to the ground state by photon emission. The intensity of the emitted photons is measured with a photomultiplier circuit that outputs voltage pulses that are proportional to the number of decays.

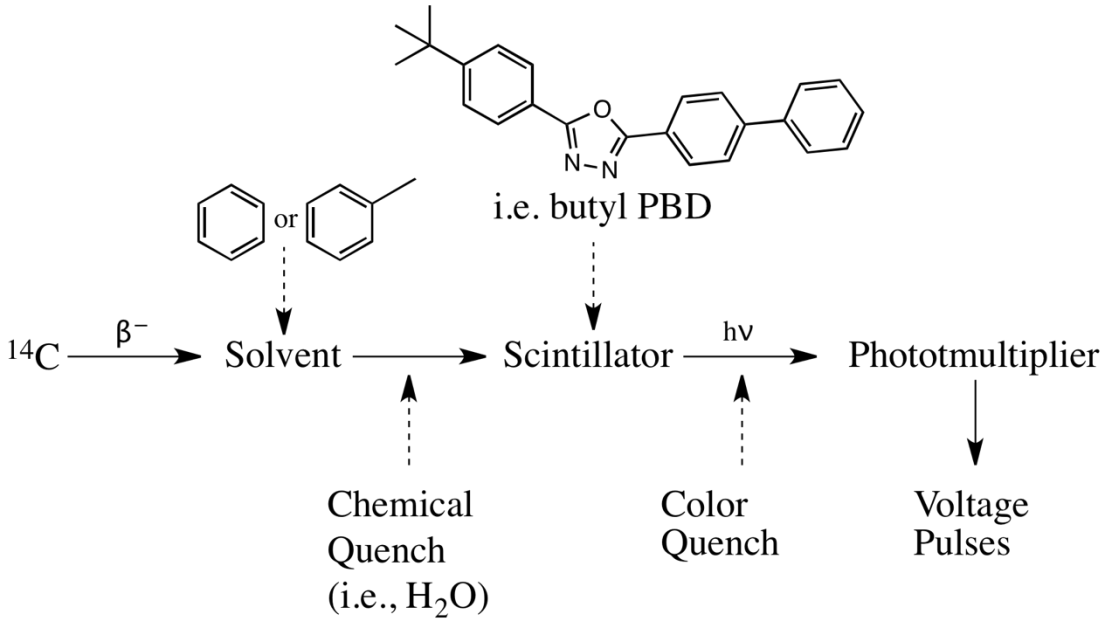


Figure A 1.1 Schematic Diagram of Liquid Scintillation Counting of ^{14}C

The counting efficiency is calculated as the ratio of counts per minute (CPM) to the actual decays per minute (DPM).

$$\boldsymbol{Counting\ Efficiency} = \frac{\boldsymbol{CPM}}{\boldsymbol{DPM}} \times \mathbf{100}\% \qquad \text{(A 1.1)}$$

The difference between CPM and DPM is due to chemical quenching, which involves energy loss when it is transferred from beta particles to the solvent molecules and scintillators (for instance, water in solvent is a typical quencher), and color quenching, which involves the intensity reduction of photons captured by the photomultiplier due to color interference (Ross, Noakes, & Spoulding, 1991).

Though liquid scintillation counting is a well-developed technology, the sample size (≈ 1g carbon) limits its application to measure the activity of ^{14}C in DEHP isolated from butter at the magnitude to approximately 10^{-4} g (Krajcar Bronić, Horvatinčić, Barešić, & Obelić, 2009). For this reason, LSC was only used to measure the activity of live DEHP standards (727.93 mg/kg DEHP in CH_2Cl_2, prepared with Bis (2-ethylhexyl-$^{2}H_{17}$) phthalate, [carbonyl-^{14}C]-, Moravek® Biochemicals Inc., 2000 dps/g, and diluted with dead DEHP) that were applied for live spike.

Table A 1.2 LSC Measurements of 0.4843±0.0002 g Live DEHP standard

Cycle	*ID*	*CPM*	*2σ (%)*	*DPM*	*tSIEa*	*Efficiency (%)*	*Background Corrected DPM*	*Activity (dpm / g C)*
1	B[b]	25.7370	5.09	27.2766	587.46	94.36		
	S[c]	29.7144	4.74	31.9339	447.88	93.05		
							4.66±2.05	13.03±5.75
2	B	25.5147	5.11	27.0427	586.46	94.35		
	S	27.9167	4.89	29.9933	450.25	93.08		
							2.95±2.02	8.26±5.64
3	B	23.3833	5.34	24.7926	580.88	94.32		
	S	27.1324	4.96	29.1618	447.11	93.04		
							4.37±1.96	12.22±5.49
4	B	22.8021	5.41	24.1752	581.55	94.32		
	S	26.3052	5.03	28.2749	446.46	93.03		
							4.10±1.93	11.47±5.41
5	B	22.2353	5.48	23.5713	583.53	94.33		
	S	26.4970	5.02	28.4767	447.73	93.05		
							4.91±1.93	13.72±5.39
6	B	23.1076	5.37	24.4997	581.16	94.32		
	S	26.6609	5.00	28.6589	445.99	93.03		
							4.16±1.95	11.64±5.44

[a] Transformed External Standard Spectrum, which was used to measure sample quenching.
[b] Background
[c] Sample

3. Calculation of Fraction Modern (f_m) from Activity

The convention for reporting activities relative to HOxI as the standard to calculate the activities is as follows:

$$A_{ON} = 0.95A_{HOxI} \cdot \left[1 - \frac{2\left(19+\delta^{13}C_{HOxI}\right)}{1000}\right] \quad \text{(A 1.2)}$$

A_{ON} is the normalized activity of HOxI. If HOxII is used, the equation alters to:

$$A_{ON} = 0.7459A_{HOxII} \cdot \left[1 - \frac{2\left(25+\delta^{13}C_{HOxII}\right)}{1000}\right] \quad \text{(A 1.3)}$$

The absolute international standard activity (A_{abs}) is defined as the standard activity on the year of measurement, to correct the radioactive decay of standard from 1950.

$$A_{abs} = A_{ON} \cdot e^{\lambda(year-1950)} \quad \text{(A 1.4)}$$

$\delta^{13}C$ of the analyte is normalized to -25 ‰ with respect to PDB by definition regardless of its composition (Stuiver & Polach, 1977). Fraction modern (f_m) (Equation 2.14) and Percent Modern (pM) (Equation 2.15) were established at the 8th International Conference of Radiocarbon Dating.

$$A_{SN} = A_S \cdot \left[1 - \frac{2\left(25+\delta^{13}C_S\right)}{1000}\right] \quad \text{(A 1.5)}$$

$$f_m = \frac{A_{SN}}{A_{ON}} \quad \text{(A 1.6)}$$

$$pM = \frac{A_{SN}}{A_{abs}} \times 100\% \quad \text{(A 1.7)}$$

A_{SN} is the normalized activity of the analyte while A_S is the measured activity.

Appendix 2 : Extraction and Chromatography Data

1. Sample and Internal Standard Masses

Table A 2.1 Butter sample mass

Sample ID	*Butter sticks mass (g)*	*Waxed paper mass (g)*	*Butter mass (g)*
	1154.3	16.6	
BTR1	1154.2	16.6	
	1154.3	16.6	
Mean	1154.3	16.6	1137.7
Standard deviation (1σ)	0.1	0	0.1
	1150.3	14.6	
BTR2	1150.5	14.6	
	1150.4	14.6	
Mean	1150.4	14.6	1135.8
Standard deviation (1σ)	0.1	0	0.1
	1156.0	17.1	
BTR3	1156.0	17.0	
	1156.1	17.0	
Mean	1156.0	17.0	1139.0
Standard deviation (1σ)	0.1	0.1	0.1
	1151.7	15.7	
BTR4	1151.9	15.8	
	1151.9	15.7	
Mean	1151.8	15.7	1136.1
Standard deviation (1σ)	0.1	0.1	0.1
	1148.5	15.4	
BTR5	1148.6	15.4	
	1148.5	15.5	
Mean	1148.5	15.4	1133.1
Standard deviation (1σ)	0.1	0.1	0.1
	1151.5	14.3	
BTR6	1151.7	14.5	
	1151.6	14.6	
Mean	1151.6	14.5	1137.1
Standard deviation (1σ)	0.1	0.2	0.2
	1139.4	13.4	
BTR7	1139.7	13.6	
	1139.6	13.7	
Mean	1139.6	13.6	1126.0
Standard deviation (1σ)	0.2	0.2	0.2

Internal Standard: *d38*-DEHP (2541 mg/kg in Acetonitrile).

Table A 2.2 Mass of internal standards (d38-DEHP) spiked in butter samples

Sample ID	***Mass of vial (g)***	***Mass of vial plus I.S. solution (g)***	***Mass of empty vial after spiking (g)***	***Mass of I.S. Solution (g)***	***I.S. mass (μg)***
	2.51264	2.73275	2.51851		
BTR1	2.5127	2.73273	2.51853		
	2.51274	2.73276	2.51854		
Mean	2.51269	2.73275	2.51853	0.21422	544.33
Standard deviation (1σ)	0.00005	0.00002	0.00002	0.00002	0.05
	2.52942	2.75360	2.53112		
BTR2	2.52939	2.75364	2.53110		
	2.52940	2.75366	2.53112		
Mean	2.52940	2.75363	2.53111	0.22252	565.42
Standard deviation (1σ)	0.00002	0.00003	0.00001	0.00003	0.08
	2.52548	2.75530	2.52594		
BTR3	2.52551	2.75532	2.52597		
	2.52549	2.75528	2.52597		
Mean	2.52549	2.75530	2.52596	0.22934	582.75
Standard deviation (1σ)	0.00002	0.00002	0.00002	0.00003	0.07
	2.51453	2.75166	2.51765		
BTR4	2.51452	2.75167	2.51766		
	2.51451	2.75169	2.51765		
Mean	2.51452	2.75167	2.51765	0.23402	594.64
Standard deviation (1σ)	0.00001	0.00002	0.00001	0.00002	0.04
	2.50930	2.74045	2.51028		
BTR5	2.50931	2.74046	2.51030		
	2.50931	2.74046	2.51030		
Mean	2.50931	2.74046	2.51029	0.23016	584.85
Standard deviation (1σ)	0.00001	0.00001	0.00001	0.00001	0.03
	2.52833	2.75733	2.52975		
BTR6	2.52836	2.75734	2.52977		
	2.52835	2.75736	2.52979		
Mean	2.52835	2.75734	2.52977	0.22757	578.26
Standard deviation (1σ)	0.00002	0.00002	0.00002	0.00003	0.06
	2.50922	2.69777	2.51111		
BTR7	2.50923	2.69778	2.51110		
	2.50922	2.69779	2.51109		
Mean	2.50922	2.69778	2.51110	0.18668	474.35
Standard deviation (1σ)	0.00001	0.00001	0.00001	0.00001	0.04

Table A 2.3 Mass of internal standards (d38-DEHP) spiked in method blank samples

Sample ID	*Mass of vial (g)*	*Mass of vial plus I.S. solution (g)*	*Mass of empty vial after spiking (g)*	*Mass of I.S. Solution (g)*	*I.S. mass (μg)*
	2.48945	2.67990	2.49042		
BLK1	2.48947	2.67991	2.49043		
	2.48946	2.67994	2.49045		
Mean	2.48946	2.67992	2.49043	0.18948	481.48
Standard deviation (1σ)	0.00001	0.00002	0.00002	0.00003	0.07
	2.53446	2.74727	2.53570		
BLK2	2.53444	2.74729	2.53574		
	2.53445	2.74730	2.53576		
Mean	2.53445	2.74729	2.53573	0.21155	537.56
Standard deviation (1σ)	0.00001	0.00002	0.00003	0.00003	0.09
	2.51789	2.74042	2.51906		
BLK3	2.35179	2.74040	2.51909		
	2.35179	2.74041	2.51912		
Mean	2.40716	2.74041	2.51909	0.22132	562.37
Standard deviation (1σ)	0.09590	0.00001	0.00003	0.00003	0.08
	2.49413	2.70464	2.49830		
BLK4	2.49412	2.70463	2.49829		
	2.49413	2.70462	2.49829		
Mean	2.49413	2.70463	2.49829	0.20634	524.30
Standard deviation (1σ)	0.00001	0.00001	0.00001	0.00001	0.03
	2.52721	2.75485	2.52772		
BLK5	2.52720	2.75484	2.52775		
	2.52719	2.75484	2.52774		
Mean	2.52720	2.75484	2.52774	0.22711	577.08
Standard deviation (1σ)	0.00001	0.00001	0.00002	0.00002	0.04
	2.53460	2.76130	2.53932		
BLK6	2.53459	2.76125	2.53931		
	2.53461	2.76127	2.53930		
Mean	2.53460	2.76127	2.53931	0.22196	564.01
Standard deviation (1σ)	0.00001	0.00003	0.00001	0.00003	0.07
	2.52297	2.72711	2.52364		
BLK7	2.52299	2.72712	2.52366		
	2.52298	2.72711	2.52365		
Mean	2.52298	2.72711	2.52365	0.20346	517.00
Standard deviation (1σ)	0.00001	0.00001	0.00001	0.00001	0.03

2. Liquid-Liquid Extraction

Table A 2.4 Liquid –Liquid extraction data

Sample ID	*Number of paper filtrations*	*1st extraction w/ hexane (mL)*	*2nd extraction w/ 16.7% acetone in hexane (mL)*	*Final vol. of oily sample (mL)*	*Sample vol. for L-L extraction (mL)*	*Extraction subunit*	*ACN Vol. for each extraction (mL)*	*Number of ACN extraction for each subunit*	*Final ACN Sample Vol. (mL)*
BTR1	8	1000	300	1200	400	3	500	2	1000
BLK1	8	500	150	400	400	1	500	2	500
BTR2	8	1000	300	1200	400	3	500	2	1000
BLK2	8	1000	300	1200	400	3	500	2	1000
BTR3	8	1000	300	1200	400	3	500	2	1000
BLK3	8	1000	300	1200	400	3	500	2	1000
BTR4	8	1000	300	1200	400	3	500	2	1000
BLK4	8	1000	300	1200	400	3	500	2	1000
BTR5	8	1000	300	1200	400	3	500	2	1000
BLK5	8	1000	300	1200	400	3	500	2	1000
BTR6	8	1000	300	1200	400	3	500	2	1000
BLK6	8	1000	300	1200	400	3	500	2	1000
BTR7	8	1000	300	1200	400	3	500	2	1000
BLK7	8	1000	300	1200	400	3	500	2	1000

3. Flash Chromatography

Each post liquid-liquid extraction butter isolate was split to four 3-mL subunits and loaded to 4 newly packed silica columns respectively (except BLK1, which was split to 2 subunit). Columns were packed with 175 g silica gel and 500 mL 5% (v/v) acetone in hexane. The mobile phase (eluent) was changed as follows:

- 400 mL 33% (v/v) acetone in hexane
- 1000 mL hexane
- Load butter isolates or method blanks
- 200 mL hexane
- 1500 mL 1.6% (v/v) acetone in hexane

Once switched to 1.6% (v/v) acetone in hexane, eluates were collected in baked glassware for GC-MS measurement. So the volumes of eluates in the following table denote the volume of 1.6% (v/v) acetone in hexane used to elute DEHP.

Table A 2.5 Eluate fractions volumes of flash chromatography (mL) [a]

Sample ID (subunit)	*GCMS Instrument*	*#1*	*#2*	*#3*	*#4*	*#5*	*#6*	*#7*	*#8*	*#9*	*#10*
		1000-1030	1030-1060	1060-1090	**1090-1120**	**1120-1150**	**1150-1180**	**1180-1210**	**1210-1240**	**1240-1270**	1270-1300
BTR1-1	Shimadzu® QP2010S						**#11**	**#12**	**#13**	**#14**	**#15**
							1300-1330	1330-1360	1360-1390	1420-1450	1450-1480
BTR1-2	Shimadzu® QP2010S	900-950	950-1000	**1000-1050**	**1050-1100**	**1100-1150**	**1150-1200**	**1200-1250**	1250-1300	1350-1400	1400-1500
BTR1-3	Shimadzu® QP5000	900-950	950-1000	1000-1050	**1050-1100**	**1100-1150**	**1150-1200**	**1200-1250**	**1250-1300**	**1350-1400**	1400-1500
BTR1-4	Shimadzu® QP5000	**900-950**	**950-1000**	**1000-1050**	**1050-1100**	**1100-1150**	**1150-1200**	1200-1250	1250-1300	1350-1400	1400-1500
BLK1-1	Shimadzu® QP2010S	900-950	950-1000	**1000-1050**	**1050-1100**	**1100-1150**	**1150-1200**	**1200-1250**	1250-1300	1350-1400	1400-1500
BLK1-2	Shimadzu® QP5000	900-950	950-1000	1000-1050	**1050-1100**	**1100-1150**	**1150-1200**	**1200-1250**	**1250-1300**	**1350-1400**	1400-1500
BTR2-1	Shimadzu® QP5000	1100-1150	**1150-1200**	**1200-1250**	**1250-1300**	**1300-1350**	1350-1400	1400-1450	1450-1500		
BTR2-2	Shimadzu® QP5000	1100-1150	1150-1200	**1200-1250**	**1250-1300**	**1300-1350**	**1350-1400**	1400-1450	1450-1500		
BTR2-3	Shimadzu® QP5000	1100-1150	1150-1200	**1200-1250**	**1250-1300**	**1300-1350**	**1350-1400**	1400-1450	1450-1500		
BTR2-4	Shimadzu® QP5000	1100-1150	1150-1200	1200-1250	**1250-1300**	**1300-1350**	**1350-1400**	**1400-1450**	1450-1500		
BLK2-1	Shimadzu® QP5000	1100-1150	1150-1200	1200-1250	1250-1300	**1300-1350**	**1350-1400**	**1400-1450**	**1450-1500**		
BLK2-2	Shimadzu® QP5000	1100-1150	1150-1200	1200-1250	**1250-1300**	**1300-1350**	**1350-1400**	**1400-1450**	1450-1500		
BLK2-3	Shimadzu® QP5000	1100-1150	**1150-1200**	**1200-1250**	**1250-1300**	**1300-1350**	1350-1400	1400-1450	1450-1500		
BLK2-4	Shimadzu® QP5000	1100-1150	1150-1200	**1200-1250**	**1250-1300**	**1300-1350**	**1350-1400**	1400-1450	1450-1500		

[a] Bold fractions contain *d38*-DEHP

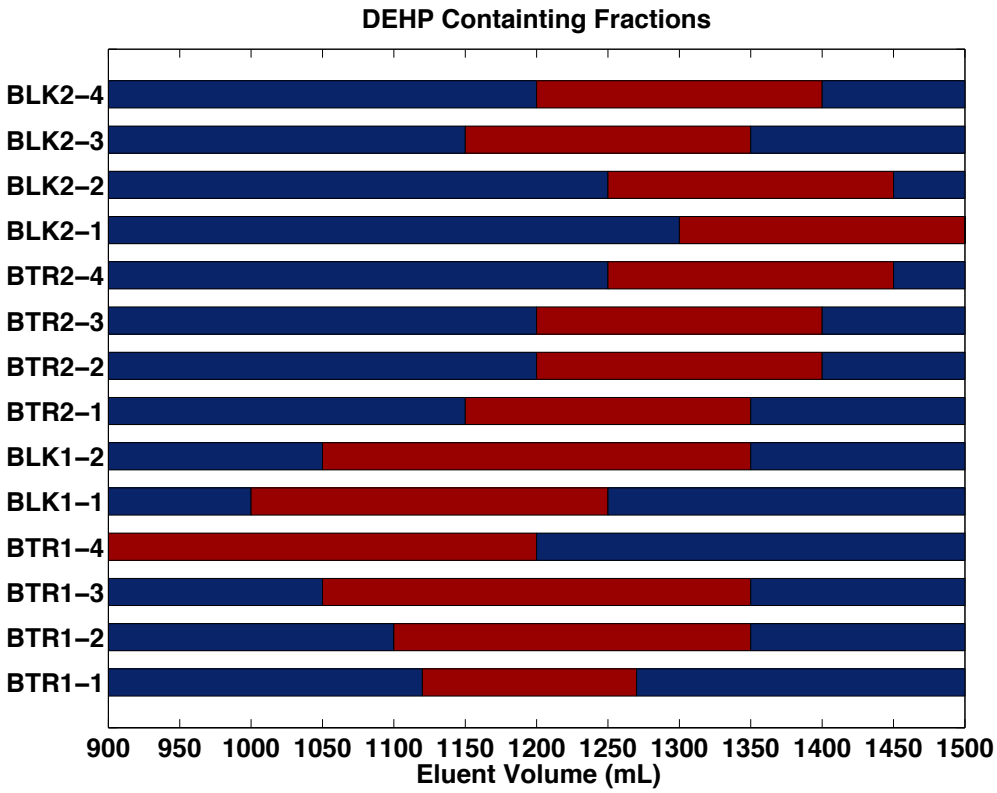


Figure A 2.1 DEHP containing fraction of flash chromatography eluate for BTR1, BTR2, BLK1 and BLK2

4. Shimadzu® QP5000 GC-EIMS Calibration

- Shimadzu® QP5000 Calibration with standard DEHP and *d38*-DEHP solutions μ
- *d38*-DEHP stock solution (I.S.): 2541 mg/kg in Acetonitrile

Table A 2.6 d38-DEHP standard solutions for Shimadzu® QP5000 GC-EIMS calibration

Sample ID	***Vol. of I.S. solution (μ g)***	***Mass of vial (g)***	***Mass of vial plus I.S. solution (g)***	***Total Mass after dilution w. hexane (g)***	***[d38-DEHP](mg/kg)***	***Peak Area***
		2.50847	2.51643	3.58869		
CALD38V1.D01	10	2.50852	2.51641	3.58870		
		2.50846	2.51643	3.58868		
Mean		2.50848	2.51642	3.58869	18.68	128463
Standard deviation (1σ)		0.00003	0.00001	0.00001		
		2.51937	2.53447	3.66136		
CALD38V2.D01	20	2.51943	2.53448	3.66134		
		2.51944	2.53450	3.66139		
Mean		2.51941	2.53448	3.66136	33.53	305917
Standard deviation (1σ)		0.00004	0.00002	0.00003		
		2.51849	2.54165	3.67063		
CALD38V3.D01	30	2.51848	2.54167	3.67065		
		2.51849	2.54168	3.67067		
Mean		2.51849	2.54167	3.67065	51.12	416562
Standard deviation (1σ)		0.00001	0.00002	0.00002		
		2.52359	2.55466	3.68442		
CALD38V4.D02	40	2.52362	2.55466	3.68441		
		2.52363	2.55470	3.68440		
Mean		2.52361	2.55467	3.68441	67.99	639830
Standard deviation (1σ)		0.00002	0.00002	0.00001		
		2.50847	2.51643	3.58869		
CALD38V5.D01	50	2.50852	2.51641	3.58870		
		2.50846	2.51643	3.58868		
Mean		2.50848	2.51642	3.58869	77.13	743135
Standard deviation (1σ)		0.00001	0.00002	0.00001		

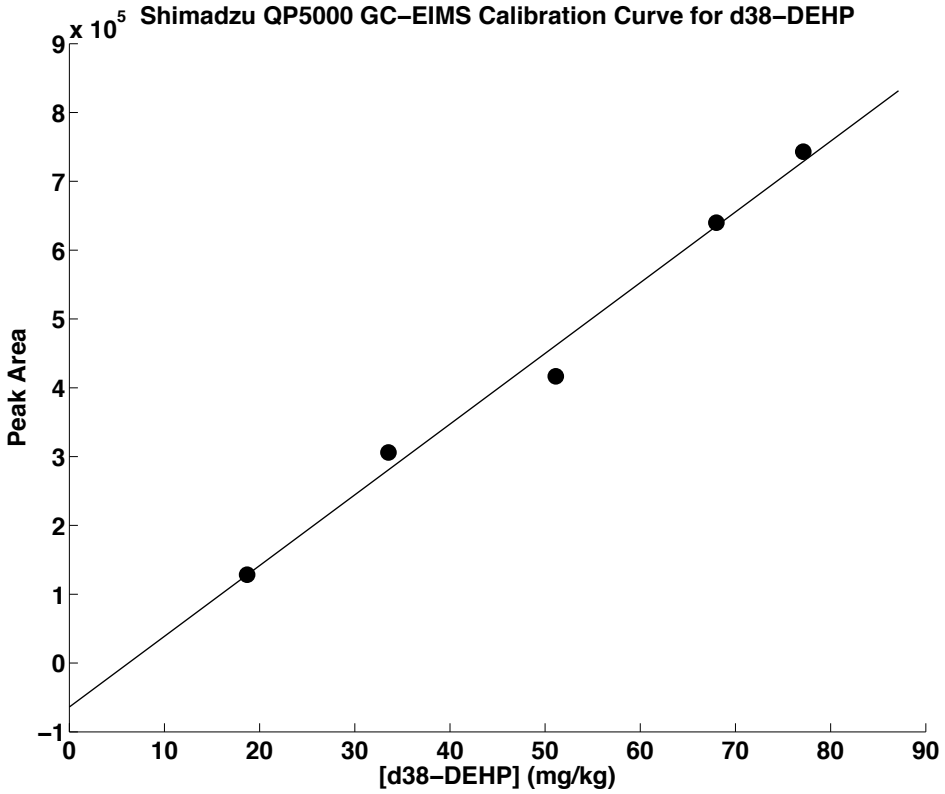


Figure A 2.2 Shimadzu QP5000 GC-EIMS Calibration Curve for d38-DEHP, n=5, replicates=1, slope=10277.8 ± 644.7, intercept=-63921.3 ± 34908.7, R^2=0.9883.

- DEHP stock solution: 3919 mg/kg in Acetonitrile

Table A 2.7 DEHP standard solutions for Shimadzu® QP5000 GC-EIMS calibration

Sample ID	*Vol. of DEHP solution (μ g)*	*Mass of vial (g)*	*Mass of vial plus DEHP solution (g)*	*Total Mass after dilution w. hexane (g)*	*[DEHP] (mg/kg)*	*Peak Area*
		2.51882	2.52233	3.65523		
CALDEHP1.D01	5	2.51882	2.52235	3.65523		
		2.51883	2.52237	3.65521		
Mean		2.51882	2.52235	3.65522	12.16	50443
Standard deviation (1σ)		0.00001	0.00002	0.00001		
		2.52730	2.53543	3.73083		
CALDEHP2.D01	10	2.52732	2.53548	3.73082		
		2.52731	2.53547	3.73085		
Mean		2.52731	2.53546	3.73083	26.54	106443
Standard deviation (1σ)		0.00001	0.00003	0.00002		
		2.49069	2.50597	3.61115		
CALDEHP3.D01	20	2.49070	2.50596	3.61115		
		2.49067	2.50596	3.61115		
Mean		2.49069	2.50596	3.61115	53.43	355353
Standard deviation (1σ)		0.00002	0.00001	0.00000		
		2.55238	2.57548	3.67195		
CALDEHP4.D02	30	2.55239	2.57548	3.67192		
		2.55235	2.57551	3.67197		
Mean		2.55237	2.57549	3.67195	80.92	650430
Standard deviation (1σ)		0.00002	0.00002	0.00003		
		2.51770	2.54806	3.64058		
CALDEHP5.D01	40	2.51773	2.54805	3.64055		
		2.51772	2.54809	3.64059		
Mean		2.51772	2.54807	3.64057	105.93	814501
Standard deviation (1σ)		0.00002	0.00002	0.00002		
		2.51037	2.54987	3.57593		
CALDEHP5.D01	50	2.51036	2.54989	3.57591		
		2.51038	2.54987	3.57592		
Mean		2.51037	2.54988	3.57592	145.30	1204219
Standard deviation (1σ)		0.00001	0.00002	0.00001		

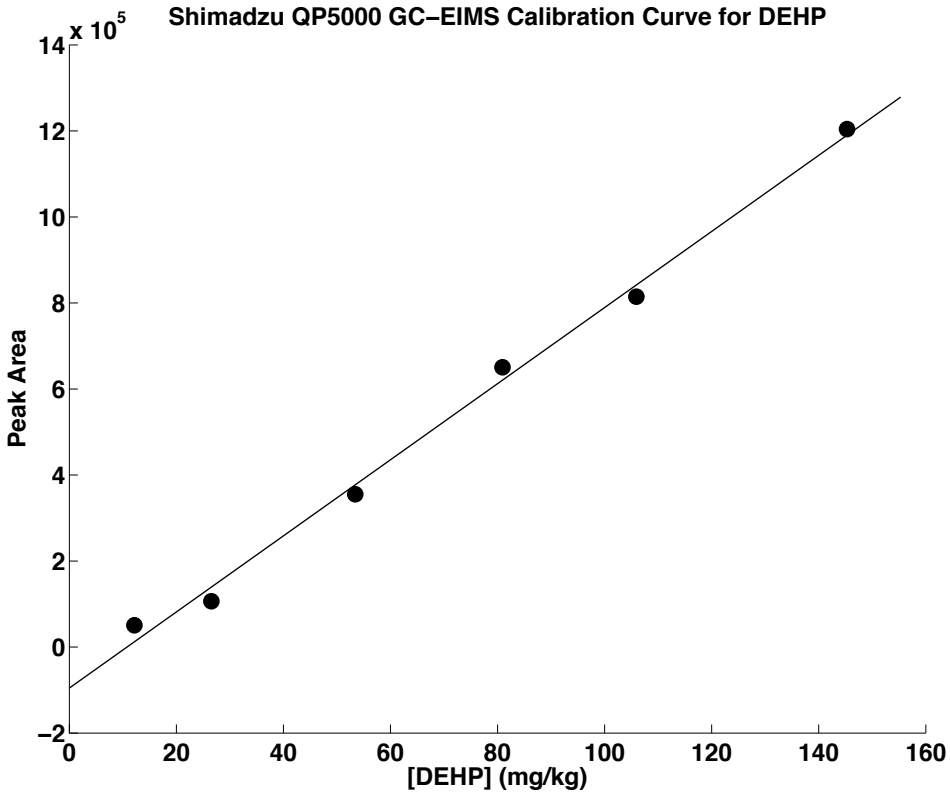


Figure A 2.3 Shimadzu QP5000 GC-EIMS Calibration Curve for DEHP, n=6, replicates=1, slope=8846.6 ± 311.0, intercept=-95343.5 ± 26206.0, R^2=0.9951.

The DEHP containing fractions of each subunit were combined and reduced to 2 mL hexane solution. These post-FC sample were measured with Shimadzu® QP5000 to estimate DEHP content in raw butter and method recoveries.

Table A 2.8 DEHP and d38-DEHP contents of four BTR2 subunits (post-FC) samples.

Sample ID	*File*	*d38-DEHP peak area*	*DEHP peak area*	*[d38-DEHP] (mg/kg)*	*[DEHP] (mg/kg)*	*[DEHP] in raw butter (mg/kg)*
	FCBTR2.D05	608817	919578			
BTR2-SUB1	FCBTR2.D06	599103	928107			
	FCBTR2.D07	605452	944924			
Mean		604457	930870	65.0	116.0	0.88
Standard deviation (1σ)		4933	12897	5.3	5.2	0.13
	FCBTR427.D01	330103	613019			
BTR2-SUB2	FCBTR427.D02	324001	605065			
	FCBTR427.D03	347296	633798			
Mean		333800	617294	38.7	80.6	1.04
Standard deviation (1σ)		12080	14836	4.3	4.4	0.25
	FCBTR429.D01	190521	419694			
	FCBTR429.D02	155577	379411			
BTR2-SUB3	FCBTR429.D03	174770	349878			
	FCBTR429.D04	165748	329952			
	FCBTR429.D05	165257	336606			
	FCBTR429.D06	165023	319017			
Mean		169483	355760	22.7	51.0	1.11
Standard deviation (1σ)		11964	37589	3.9	5.5	0.23
	FCBTR430.D01	89642	218793			
	FCBTR430.D02	107948	246773			
BTR2-SUB4	FCBTR430.D03	106764	221573			
	FCBTR430.D04	97760	211879			
	FCBTR430.D05	102749	219257			
	FCBTR430.D06	107882	221439			
Mean		102124	223286	16.2	36.0	1.11
Standard deviation (1σ)		7264	12038	3.6	3.5	0.27

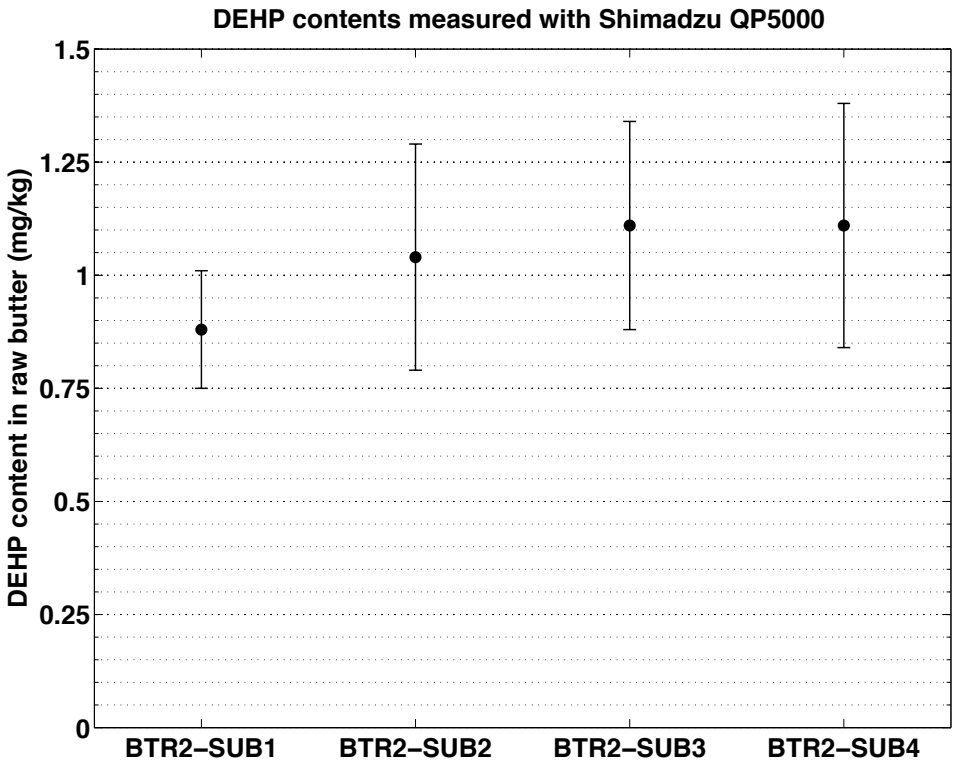


Figure A 2.4 DEHP content in raw butter, computed from four post-FC subunits of BTR2.

The estimated recovery of BTR2 at this stage was ≈37.8% (the mass of each post-FC subunit is ≈1.5 g and the mass of spiked I.S. for BTR2 was 565.42 μg).

5. HPLC Calibration

BTR1, BLK1, BTR2 and BLK2 were measured with an assembled HPLC system: Dionex® P580 pump, Agilent® Zorbax Eclipse XDB-C18 column (15 cm × 9.4 mm-ID, 5 micron) and Spectroflow 757 Absorbance Detector (254 nm). Mobile phase was 90 % Acetonitrile and 10 % water and switched to 95 % Acetonitrile and 5% water. Pressure was ≈1500 psi.

- DEHP standard solution: 80.0 µg/mL in Acetonitrile

Table A 2.9 HPLC (with Dionex P580 pump) calibration with DEHP

Sample ID	***Vol. of standard solution (µg)***	***Pressure (bar)***	***DEHP Initial Time***	***DEHP End Time***	***Retention Time***	***Peak Area***
cal2274a	50	60	0:33:16	0:34:00	0:33:35	13770
cal2274b	50	56	0:32:28	0:33:18	0:32:50	18710
cal2274c	50	58	0:31:40	0:32:27	0:32:04	16940
c2276a	75	57	0:31:46	0:32:44	0:32:10	24370
c2276b	75	55	0:31:43	0:32:28	0:32:07	24480
c2276c	75	56	0:31:47	0:32:41	0:32:07	24450
cal2278a	100	58	0:31:34	0:32:28	0:31:59	30700
cal2278b	100	47	0:31:38	0:32:31	0:32:02	30200
cal2278c	100	50	0:31:38	0:32:30	0:32:02	31740
c22710a	125	52	0:31:50	0:32:45	0:32:13	40740
c22710b	125	53	0:31:42	0:32:36	0:32:06	39390
c22710c	125	53	0:31:27	0:32:23	0:31:55	41280
c22712a	150	56	0:31:39	0:32:37	0:32:06	47290
c22712b	150	56	0:32:14	0:33:10	0:32:37	45630
c22712c	150	56	0:32:22	0:33:28	0:32:50	47930

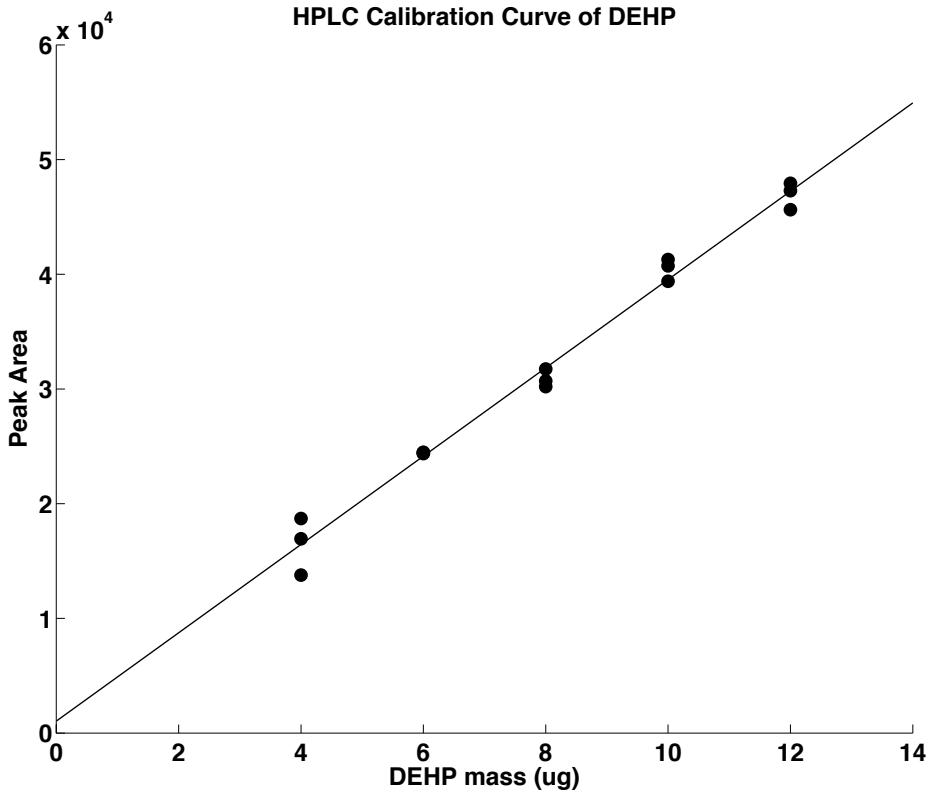


Figure A 2.5 HPLC (with Dionex P580 pump) calibration curve for DEHP, n=5, replicates=3, slope=3849.5 ± 125.0, intercept=1045.3 ± 1060.3, R^2=0.9865.

Table A 2.10 BTR1 HPLC peak properties

Sample ID	*File Name*	*Inj. Vol. (µL)*	*Pressure (bar)*	*D38 Initial Time*	*D38 End Time*	*D38 Ret. Time*	*D38 Peak Area*	*DEHP Initial Time*	*DEHP End Time*	*DEHP Ret. Time*	*DEHP Peak Area*	*Peak Interval*
BTR1	btr101	100	58	0:30:30	0:31:28	0:30:57	33470	0:32:41	0:33:41	0:33:06	83310	0:01:13
BTR1	btr102	120	61	0:30:05	0:30:49	0:30:24	35530	0:31:55	0:32:54	0:32:18	105900	0:01:06
BTR1	btr103	120	60	0:29:56	0:30:42	0:30:16	36490	0:31:56	0:32:57	0:32:20	103600	0:01:14
BTR1	btr104	120	60	0:30:00	0:30:48	0:30:22	37850	0:32:05	0:33:06	0:32:29	104800	0:01:17
BTR1	btr105	120	61	0:29:54	0:30:56	0:30:22	42330	0:32:02	0:33:03	0:32:27	100500	0:01:06
BTR1	btr106	120	58	0:29:44	0:30:44	0:30:11	40440	0:31:50	0:32:53	0:32:16	102400	0:01:06
BTR1	btr107	120	61	0:29:43	0:30:39	0:30:07	42200	0:31:45	0:32:49	0:32:11	104200	0:01:06
BTR1	btr108	120	61	0:30:43	0:31:39	0:31:06	38980	0:32:49	0:33:51	0:33:14	104900	0:01:10
BTR1	btr109	120	58	0:29:34	0:30:21	0:29:54	36660	0:31:34	0:32:35	0:31:59	102600	0:01:13
BTR1	btr110	120	62	0:29:25	0:30:15	0:29:47	38630	0:31:24	0:32:24	0:31:48	103700	0:01:09
BTR1	btr111	120	62	0:29:24	0:30:17	0:29:50	40450	0:31:26	0:32:27	0:31:50	103900	0:01:09
BTR1	btr112	125	55	0:29:06	0:29:55	0:29:28	36240	0:31:03	0:32:05	0:31:27	108800	0:01:08
BTR1	btr113	80	60	0:28:53	0:29:37	0:29:10	21940	0:30:45	0:31:36	0:31:07	56470	0:01:08

Table A 2.11 BLK1 HPLC peak properties and DEHP containing portion collection

Sample ID	*File Name*	*Inj. Vol. (µL)*	*Pressure (bar)*	*D38 Initial Time*	*D38 End Time*	*D38 Ret. Time*	*D38 Peak Area*	*DEHP Initial Time*	*DEHP End Time*	*DEHP Ret. Time*	*DEHP Peak Area*	*Peak Interval*
BLK1	blk101	120	58	0:28:24	0:29:19	0:28:46	103500	0:30:30	0:31:30	-	-	0:01:11
BLK1	blk102	80	59	0:27:55	0:28:45	0:28:15	70280	0:29:53	0:30:53	-	-	0:01:08
BLK1	blk103	100	56	0:27:47	0:28:41	0:28:09	87140	0:29:56	0:30:56	-	-	0:01:15
BLK1	blk104	100	57	0:27:25	0:28:26	0:27:55	88240	0:29:39	0:30:39	-	-	0:01:13
BLK1	blk105	100	56	0:27:34	0:28:25	0:27:54	87100	0:29:37	0:30:37	-	-	0:01:12
BLK1	blk106	100	55	0:27:16	0:28:09	0:27:38	89890	0:29:20	0:30:20	-	-	0:01:11
BLK1	blk107	100	56	0:27:17	0:28:07	0:27:37	88400	0:29:21	0:30:21	-	-	0:01:14
BLK1	blk108	100	57	0:27:18	0:28:07	0:27:38	89390	0:29:19	0:30:19	-	-	0:01:12
BLK1	blk109	100	57	0:26:58	0:27:49	0:27:19	90380	0:29:01	0:30:01	-	-	0:01:12
BLK1	blk110	100	52	0:28:39	0:29:32	0:29:01	84180	0:30:41	0:31:41	-	-	0:01:09
BLK1	blk111	120	59	0:28:28	0:29:23	0:28:49	107500	0:30:38	0:31:38	-	-	0:01:15
BLK1	blk112	150	56	0:28:03	0:29:00	0:28:25	133200	0:30:11	0:31:11	-	-	0:01:11
BLK1	blk113	165	58	0:27:40	0:28:35	0:28:01	144800	0:29:52	0:30:52	-	-	0:01:17

Table A 2.12 BTR2 HPLC peak properties

Sample ID	*File Name*	*Inj. Vol. (µL)*	*Pressure (bar)*	*D38 Initial Time*	*D38 End Time*	*D38 Ret. Time*	*D38 Peak Area*	*DEHP Initial Time*	*DEHP End Time*	*DEHP Ret. Time*	*DEHP Peak Area*	*Peak Interval*
BTR2	btr201	130	58	0:30:35	0:31:25	0:30:56	61550	0:32:38	0:33:40	0:33:06	86880	0:01:13
BTR2	btr202	120	63	0:29:54	0:30:45	0:30:16	57110	0:31:58	0:32:56	0:32:23	79830	0:01:13
BTR2	btr203	120	63	0:29:43	0:30:34	0:30:06	57430	0:31:46	0:32:43	0:32:11	77190	0:01:12
BTR2	btr204	130	65	0:29:33	0:30:29	0:29:57	61890	0:31:45	0:32:47	0:32:11	86800	0:01:16
BTR2	btr205	130	58	0:30:35	0:31:28	0:30:58	62930	0:32:44	0:33:43	0:33:09	84200	0:01:16
BTR2	btr206	130	62	0:30:14	0:31:07	0:30:38	58170	0:32:21	0:33:20	0:32:46	83220	0:01:14
BTR2	btr207	130	61	0:30:03	0:30:55	0:30:26	59430	0:32:09	0:33:08	0:32:33	84510	0:01:14
BTR2	btr208	130	62	0:29:43	0:30:35	0:30:05	62840	0:31:47	0:32:45	0:32:12	85980	0:01:12
BTR2	btr209	130	61	0:29:46	0:30:37	0:30:08	59870	0:31:49	0:32:47	0:32:13	82940	0:01:12
BTR2	btr210	130	62	0:29:45	0:30:40	0:30:08	65540	0:31:49	0:32:48	0:32:14	85770	0:01:09
BTR2	btr211	130	59	0:29:47	0:30:40	0:30:09	58690	0:31:50	0:32:47	0:32:14	75790	0:01:10
BTR2	btr212	160	61	0:30:07	0:31:02	0:30:30	72740	0:32:13	0:33:15	0:32:28	101500	0:01:11
BTR2	btr213	150	61	0:30:24	0:31:20	0:30:48	71720	0:32:33	0:33:37	0:33:00	101200	0:01:13

Table A 2.13 BLK2 HPLC peak properties and DEHP containing portion collection

Sample ID	*File Name*	*Inj. Vol. (µL)*	*Pressure (bar)*	*D38 Initial Time*	*D38 End Time*	*D38 Ret. Time*	*D38 Peak Area*	*DEHP Initial Time*	*DEHP End Time*	*DEHP Ret. Time*	*DEHP Peak Area*	*Peak Interval*
BLK2	blk201	120	60	0:29:09	0:30:04	0:29:31	99840	0:31:15	0:32:15	-	-	0:01:11
BLK2	blk202	130	60	0:28:07	0:29:05	0:28:30	113900	0:30:10	0:31:10	-	-	0:01:05
BLK2	blk203	130	57	0:28:29	0:29:25	0:28:52	112000	0:30:32	0:31:32	-	-	0:01:07
BLK2	blk204	130	56	0:28:13	0:29:09	0:28:35	111700	0:30:17	0:31:17	-	-	0:01:08
BLK2	blk205	130	54	0:27:59	0:28:57	0:28:22	115600	0:30:04	0:31:04	-	-	0:01:07
BLK2	blk206	130	54	0:28:20	0:29:16	0:28:42	114500	0:30:26	0:31:26	-	-	0:01:10
BLK2	blk207	130	54	0:28:22	0:29:19	0:28:45	110400	0:30:25	0:31:25	-	-	0:01:06
BLK2	blk208	130	54	0:28:12	0:29:10	0:28:34	115000	0:30:18	0:31:18	-	-	0:01:08
BLK2	blk209	130	53	0:28:07	0:29:03	0:28:29	111900	0:30:13	0:31:13	-	-	0:01:10
BLK2	blk210	130	54	0:27:59	0:28:56	0:28:21	111400	0:30:04	0:31:04	-	-	0:01:08
BLK2	blk211	130	54	0:28:04	0:29:03	0:28:27	116000	0:30:13	0:31:13	-	-	0:01:10
BLK2	blk212	130	54	0:27:47	0:28:43	0:28:09	113500	0:29:52	0:30:52	-	-	0:01:09
BLK2	blk213	130	54	0:27:30	0:28:21	0:27:51	75050	0:29:31	0:30:31	-	-	0:01:10

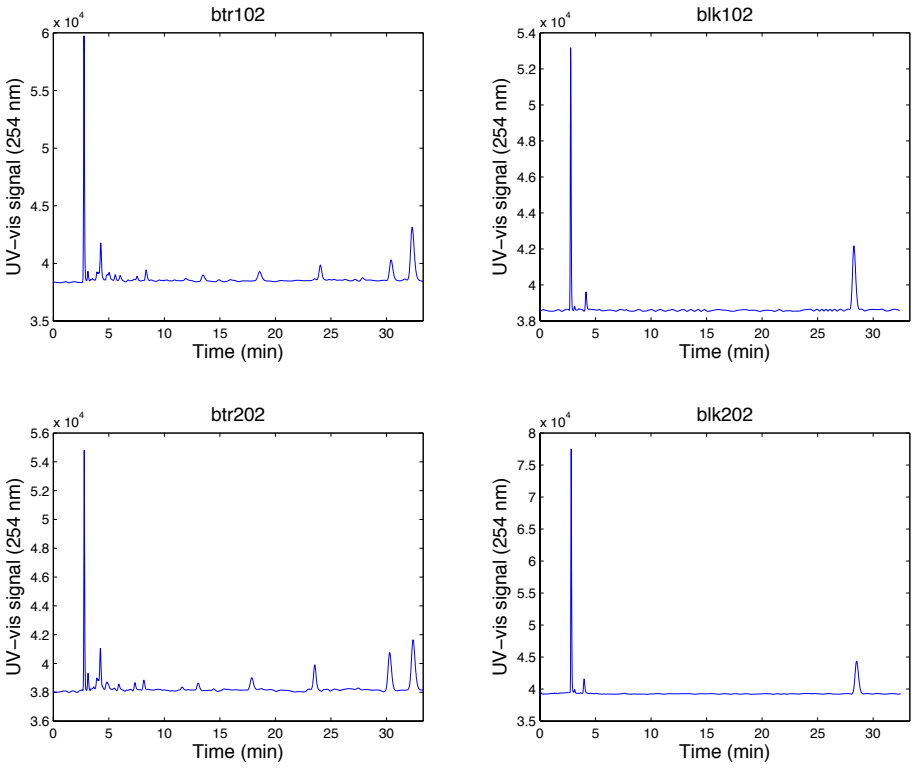


Figure A 2.6 HPLC chromatograms of btr102, blk102, btr202 and blk 202, t_R(d38-DEHP) ≈ 30 min, t_R(DEHP) ≈ 32 min.

BTR3, BLK3, BTR4, BLK4, BTR5, BLK5, BTR6 and BTR7 were measured with Hewlett-Packard 1050 HPLC system, Agilent® Zorbax Eclipse XDB-C18 column (15 cm × 9.4 mm-ID, 5 micron) and DAD (254 nm). Mobile phase was 90 % Acetonitrile and 10 % water and increased to 95 % Acetonitrile and 5% water gradually. The column temperature was set to 30 °C.

HPLC calibration standards were prepared from DEHP (3919 mg/kg) and *d38*-DEHP (2541 mg/kg) stock solutions and diluted with acetonitrile (ACN).

Table A 2.14 Hewlett-Packard 1050 HPLC calibration standards

Sample ID	***Empty vial mass (g)***	***w/. DEHP stock (g)***	***w/. D38 stock (g)***	***Total mass in ACN (g)***	***[DEHP] (µg/kg)***	***[d38-DEHP] (µg/kg)***
	2.54184	2.58896	2.64945	3.87428		
HPLCSTD1112	2.54188	2.58897	2.64946	3.87429		
	2.54183	2.58895	2.64945	3.87426		
Mean	2.54185	2.58896	2.64945	3.87428	138.59	115.36
Standard deviation (1σ)	0.00003	0.00001	0.00001	0.00002	0.08	0.02
	2.51381	2.63388	2.78536	3.43218		
HPLCSTD1126	2.51379	2.63387	2.78537	3.43219		
	2.5138	2.63387	2.78535	3.43220		
Mean	2.5138	2.63387	2.78536	3.43219	512.38	419.13
Standard deviation (1σ)	0.00001	0.00001	0.00001	0.00001	0.05	0.03

Table A 2.15 HP 1050 HPLC calibration

Sample	*File*	*Inj. Vol (µL)*	*Temp. (C)*	*Pressure (bar)*	*D38 Ret. Time (min)*	*D38 Ini. Time*	*D38 End Time*	*D38 Peak Area*	*DEHP Ret. Time*	*DEHP Ini. Time*	*DEHP End Time*	*DEHP Peak Area*	*Resolution*
HPLCSTD1112	TT0002	20	30	135	18.486	18.139	18.995	76.118	19.965	18.995	20.689	94.762	1.160
HPLCSTD1112	TT0003	40	30	136	18.460	17.950	19.103	176.567	19.896	19.343	20.616	209.915	1.184
HPLCSTD1112	TT0004	60	30	139	18.429	17.875	18.955	278.116	19.879	19.302	20.775	338.335	1.136
HPLCSTD1112	TT0005	80	30	135	18.154	17.559	18.865	396.723	19.610	18.865	20.312	461.196	1.058
HPLCSTD1112	TT0009	100	30	140	19.305	18.755	20.089	476.305	20.904	20.182	21.672	566.188	1.132
HPLCSTD1112	TT0010	100	30	130	17.572	16.952	18.352	473.608	18.837	18.352	19.645	563.126	0.939
HPLCSTD1126	TT0012	20	23	139	25.822	25.294	26.454	304.662	27.408	26.634	28.244	365.284	1.145
HPLCSTD1126	TT0013	100	23	140	25.878	25.095	26.895	1718.331	27.457	26.928	28.325	2030.888	0.988
HPLCSTD1126	TT0014	40	23	127	25.778	25.071	26.585	661.663	27.357	26.585	28.355	781.745	0.962
HPLCSTD1126	TT0015	60	23	127	25.769	25.289	26.669	1005.244	27.364	26.845	28.472	1194.776	1.061
HPLCSTD1126	TT0016	80	23	139	26.188	25.627	27.187	1350.826	27.982	27.417	29.284	1597.740	1.047
HPLCSTD1126	TT0017	100	23	134	20.258	19.607	21.327	1689.718	22.006	21.427	23.377	2001.002	0.953

Table A 2.16 HP 1050 HPLC peak properties of BTR3

Sample	*File*	*Inj. Vol (µL)*	*Temp. (C)*	*Pressure (bar)*	*D38 Ret. Time (min)*	*D38 Ini. Time*	*D38 End Time*	*D38 Peak Area*	*DEHP Ret. Time*	*DEHP Ini. Time*	*DEHP End Time*	*DEHP Peak Area*	*Resolution*
BTR3	TT0047	100	35	138	16.242	15.847	16.830	1027.953	17.415	16.830	18.270	1331.646	0.968
BTR3	TT0048	100	35	135	15.749	15.152	16.293	1009.805	16.950	16.293	17.725	1295.886	0.934
BTR3	TT0049	100	35	131	16.222	15.782	16.785	998.091	17.447	16.785	18.099	1286.087	1.057
BTR3	TT0050	100	35	129	16.475	15.890	17.250	1003.381	17.729	17.350	18.556	1299.148	0.977
BTR3	TT0051	100	35	179	15.847	15.423	16.530	977.458	16.968	16.530	17.460	1253.966	1.101
BTR3	TT0052	100	35	159	16.110	14.961	16.775	1077.520	17.206	16.775	17.711	1258.044	0.797
BTR3	TT0053	100	35	135	15.698	15.192	16.372	979.330	16.789	16.372	17.315	1254.466	1.028
BTR3	TT0054	100	35	130	16.175	15.676	16.930	970.522	17.501	16.983	18.396	1252.423	0.994
BTR3	TT0055	100	35	123	16.408	15.700	16.968	963.269	17.670	16.968	18.586	1243.055	0.875
BTR3	TT0056	100	35	123	15.741	15.230	16.377	943.504	16.844	16.377	17.404	1206.623	1.015
BTR3	TT0057	100	35	124	16.249	15.768	16.686	904.983	17.378	16.686	18.181	1206.533	0.936
BTR3	TT0058	80	35	125	15.907	15.461	16.341	523.359	17.037	16.562	17.568	672.534	1.198

Table A 2.17 HP 1050 HPLC peak properties of BTR4

Sample	*File*	*Inj. Vol (µL)*	*Temp. (C)*	*Pressure (bar)*	*D38 Ret. Time (min)*	*D38 Ini. Time*	*D38 End Time*	*D38 Peak Area*	*DEHP Ret. Time*	*DEHP Ini. Time*	*DEHP End Time*	*DEHP Peak Area*	*Resolution*
BTR4	TT0059	100	35	130	16.500	15.493	17.004	1256.570	17.768	17.004	18.596	1636.111	0.817
BTR4	TT0060	100	35	123	16.062	14.924	16.684	1248.000	17.189	16.684	17.657	1550.718	0.825
BTR4	TT0061	100	35	130	16.079	15.490	16.586	1113.627	17.278	16.586	17.796	1391.255	1.040
BTR4	TT0062	100	23	130	18.257	17.330	18.983	1096.670	19.976	18.983	20.783	1444.505	0.996
BTR4	TT0063	100	23	131	19.587	18.722	20.098	1123.639	21.346	20.765	21.938	1416.908	1.380
BTR4	TT0064	100	23	132	19.422	18.009	19.995	1101.223	21.118	19.995	21.822	1429.798	0.890
BTR4	TT0065	100	23	130	19.763	18.846	20.278	1066.430	21.453	20.278	22.072	1381.986	1.048
BTR4	TT0066	100	23	130	19.511	18.220	20.074	1096.046	21.211	20.074	21.860	1422.483	0.934
BTR4	TT0067	100	23	129	19.391	18.152	19.992	1081.931	21.071	19.992	21.792	1393.988	0.923
BTR4	TT0068	100	23	131	19.397	18.129	20.435	1033.620	21.093	20.435	21.742	1303.669	0.939

Table A 2.18 HP 1050 HPLC peak properties of BTR5

Sample	*File*	*Inj. Vol (µL)*	*Temp. (C)*	*Pressure (bar)*	*D38 Ret. Time (min)*	*D38 Ini. Time*	*D38 End Time*	*D38 Peak Area*	*DEHP Ret. Time*	*DEHP Ini. Time*	*DEHP End Time*	*DEHP Peak Area*	*Resolution*
BTR5	TT0069	100	23	130	18.904	18.181	19.421	1066.112	20.412	19.421	21.004	1412.223	1.068
BTR5	TT0070	100	23	130	19.667	18.847	20.194	1042.888	21.457	20.754	22.167	1363.633	1.297
BTR5	TT0071	100	23	131	19.168	18.063	19.730	1038.323	20.872	20.236	21.636	1351.940	1.111
BTR5	TT0072	100	23	130	18.690	18.045	19.205	1039.082	20.167	19.205	20.831	1366.036	1.060
BTR5	TT0073	100	23	130	10.204	9.869	10.622	1024.443	11.020	10.622	11.645	1318.544	0.919
BTR5	TT0074	100	23	130	19.519	18.821	20.079	971.524	21.245	20.079	21.901	1278.411	1.121
BTR5	TT0075	100	23	130	18.723	18.004	19.263	951.673	20.239	19.684	20.857	1241.265	1.247
BTR5	TT0076	100	23	131	18.775	17.726	19.380	944.476	20.302	19.714	20.954	1232.507	1.055
BTR5	TT0077	100	23	130	18.729	18.089	19.235	932.723	20.219	19.235	20.849	1228.962	1.080
BTR5	TT0078	100	23	130	19.782	19.140	20.287	906.722	21.495	20.287	22.180	1197.858	1.127
BTR5	TT009	100	23	130	19.646	18.301	20.155	887.354	21.271	20.155	22.061	1162.466	0.864

Table A 2.19 HP 1050 HPLC peak properties of BTR6

Sample	*File*	*Inj. Vol (µL)*	*Temp. (C)*	*Pressure (bar)*	*D38 Ret. Time (min)*	*D38 Ini. Time*	*D38 End Time*	*D38 Peak Area*	*DEHP Ret. Time*	*DEHP Ini. Time*	*DEHP End Time*	*DEHP Peak Area*	*Resolution*
BTR6	TT0018	100	23	138	19.080	17.887	19.700	609.139	20.587	20.145	21.327	773.620	1.006
BTR6	TT0019	100	23	139	18.657	18.244	19.210	98.352	20.129	19.657	20.850	147.740	1.364
BTR6	TT0020	100	23	140	19.876	19.100	20.335	795.612	21.556	21.055	22.220	1024.756	1.400
BTR6	TT0021	100	23	135	19.083	18.284	19.924	821.788	20.724	19.924	21.537	1202.978	1.009
BTR6	TT0022	100	23	136	20.089	19.637	20.674	764.581	21.809	21.287	22.607	1014.512	1.459
BTR6	TT0023	100	23	140	20.004	18.862	20.609	776.928	21.762	20.609	22.475	1114.628	0.973
BTR6	TT0024	100	23	130	17.141	16.553	17.900	757.040	18.772	18.098	19.367	990.958	1.247
BTR6	TT0025	100	23	129	19.370	18.791	20.031	751.477	21.069	20.471	21.911	1084.708	1.268
BTR6	TT0026	100	23	130	18.778	18.302	19.316	738.307	20.254	19.715	21.155	1056.370	1.203
BTR6	TT0027	100	23	131	19.350	18.605	19.979	746.209	21.055	20.405	21.952	1073.807	1.167
BTR6	TT0028	100	23	130	19.280	18.192	19.925	729.707	20.991	20.379	21.939	1038.484	1.039
BTR6	TT0029	100	23	130	19.382	18.670	19.950	714.546	21.070	20.324	21.857	1020.850	1.200
BTR6	TT0030	100	23	131	19.523	18.980	20.180	696.598	21.243	20.180	21.980	999.217	1.147
BTR6	TT0031	100	23	130	18.794	17.635	19.635	696.784	20.284	19.635	21.075	976.980	0.866
BTR6	TT0032	80	23	130	18.363	17.685	19.032	191.847	19.837	19.152	20.605	288.173	1.053

Table A 2.20 HP 1050 HPLC peak properties of BTR7

Sample	*File*	*Inj. Vol (µL)*	*Temp. (C)*	*Pressure (bar)*	*D38 Ret. Time (min)*	*D38 Ini. Time*	*D38 End Time*	*D38 Peak Area*	*DEHP Ret. Time*	*DEHP Ini. Time*	*DEHP End Time*	*DEHP Peak Area*	*Resolution*
BTR7	TT0033	100	23	139	19.082	17.874	19.630	1182.281	20.731	20.194	21.340	839.797	1.136
BTR7	TT0034	100	23	138	17.736	16.830	18.390	981.066	19.151	18.390	19.990	674.763	0.896
BTR7	TT0035	100	23	130	17.638	16.674	18.310	869.744	19.048	18.310	19.737	596.210	0.921
BTR7	TT0036	100	23	130	17.566	17.008	18.212	448.704	18.975	18.212	19.848	297.558	0.992
BTR7	TT0037	100	23	131	18.126	17.366	18.713	831.408	19.538	18.713	20.460	578.922	0.913
BTR7	TT0038	100	23	130	18.786	17.890	19.423	825.777	20.334	19.423	21.316	570.179	0.904
BTR7	TT0039	100	23	142	18.770	17.911	19.498	780.151	20.345	19.781	20.858	502.249	1.182
BTR7	TT0040	100	23	133	18.192	17.248	18.888	703.829	19.753	18.888	20.328	480.550	1.014
BTR7	TT0041	100	23	134	18.082	17.610	18.658	436.688	19.609	18.658	20.116	304.956	1.219
BTR7	TT0042	100	23	150	18.672	18.062	19.244	778.724	20.211	19.244	21.009	537.215	1.044
BTR7	TT0043	100	23	135	18.289	17.339	18.819	766.076	19.914	19.179	20.192	514.961	1.304
BTR7	TT0044	100	23	157	18.340	17.383	18.886	750.442	19.919	19.423	20.434	504.170	1.256
BTR7	TT0045	100	23	135	18.191	17.311	18.711	650.617	19.746	19.165	20.338	436.277	1.209
BTR7	TT0046	100	23	137	18.309	17.702	18.832	597.106	19.871	19.329	20.449	403.465	1.388

Table A 2.21 HP 1050 HPLC peak properties of BLK3

Sample	*File*	*Inj. Vol (µL)*	*Temp. (C)*	*Pressure (bar)*	*D38 Ret. Time (min)*	*D38 Ini. Time*	*D38 End Time*	*D38 Peak Area*	*DEHP Ret. Time*	*DEHP Ini. Time*	*DEHP End Time*	*DEHP Peak Area*	*Resol ution*
BLK3	TT0080	100	23	131	20.190	19.625	20.700	1857.856	-	21.300	22.300	-	-
BLK3	TT0081	100	23	130	19.014	18.448	19.600	1846.357	-	20.200	21.200	-	-
BLK3	TT0082	100	23	137	19.635	19.026	20.200	1787.867	-	20.800	21.800	-	-
BLK3	TT0083	100	23	135	20.063	19.499	20.600	1752.076	-	21.200	22.200	-	-
BLK3	TT0084	100	23	142	20.007	19.384	20.700	1588.728	-	21.300	22.300	-	-
BLK3	TT0085	100	23	142	20.385	19.783	21.100	1572.479	-	21.700	22.700	-	-
BLK3	TT0086	100	23	137	20.421	19.731	21.100	1539.215	-	21.700	22.700	-	-
BLK3	TT0087	100	23	135	20.358	19.732	21.000	1530.990	-	21.600	22.600	-	-
BLK3	TT0088	100	23	136	20.300	19.610	20.900	1525.203	-	21.500	22.500	-	-
BLK3	TT0089	100	23	139	20.173	19.561	20.800	1503.722	-	21.400	22.400	-	-

Table A 2.22 HP 1050 HPLC peak properties of BLK4

Sample	*File*	*Inj. Vol (µL)*	*Temp. (C)*	*Pressure (bar)*	*D38 Ret. Time (min)*	*D38 Ini. Time*	*D38 End Time*	*D38 Peak Area*	*DEHP Ret. Time*	*DEHP Ini. Time*	*DEHP End Time*	*DEHP Peak Area*	*Resolution*
BLK4	TT0090	100	23	139	19.321	18.657	20.800	1696.188	-	20.400	21.400	-	-
BLK4	TT0091	100	23	134	19.328	19.681	19.900	1670.200	-	20.500	21.500	-	-
BLK4	TT0092	100	23	130	19.424	18.749	19.900	1683.984	-	20.500	21.500	-	-
BLK4	TT0093	100	23	130	19.234	18.595	19.800	1654.985	-	20.400	21.400	-	-
BLK4	TT0094	100	23	140	19.297	18.730	19.900	1591.156	-	20.500	21.500	-	-
BLK4	TT0095	100	23	140	19.328	18.634	19.900	1635.743	-	20.500	21.500	-	-
BLK4	TT0096	100	23	133	19.012	17.860	19.600	1617.296	-	20.200	21.200	-	-
BLK4	TT0097	100	23	134	19.331	18.442	19.900	1599.020	-	20.500	21.500	-	-
BLK4	TT0098	100	23	133	19.567	18.960	20.100	1558.567	-	20.700	21.700	-	-
BLK4	TT0099	100	23	134	19.250	18.628	19.800	1471.643	-	20.400	21.400	-	-

Table A 2.23 HP 1050 HPLC peak properties of BLK5

Sample	*File*	*Inj. Vol (µL)*	*Temp. (C)*	*Pressure (bar)*	*D38 Ret. Time (min)*	*D38 Ini. Time*	*D38 End Time*	*D38 Peak Area*	*DEHP Ret. Time*	*DEHP Ini. Time*	*DEHP End Time*	*DEHP Peak Area*	*Resolution*
BLK5	TT0100	100	23	139	19.257	18.962	20.100	2077.897		20.700	21.700	-	-
BLK5	TT0101	100	23	135	19.733	19.061	20.300	2042.664		20.900	21.900	-	-
BLK5	TT0102	100	23	132	19.463	18.910	20.100	2057.859		20.700	21.700	-	-
BLK5	TT0103	100	23	139	20.001	19.256	20.600	2045.465		21.200	22.200	-	-
BLK5	TT0104	100	23	133	20.166	19.458	20.800	2026.207		21.400	22.400	-	-
BLK5	TT0105	100	23	134	20.099	19.390	20.800	1984.979		21.400	22.400	-	-
BLK5	TT0106	100	23	133	20.105	19.479	20.700	1963.502		21.300	22.300	-	-
BLK5	TT0107	100	23	134	20.101	19.189	20.700	1943.225		21.300	22.300	-	-
BLK5	TT0108	100	23	133	19.475	18.795	20.100	1893.747		20.700	21.700	-	-
BLK5	TT0109	100	23	133	20.050	19.425	20.700	1816.160		20.300	21.300	-	-

Appendix 3 : Mass measurements and Purity Assessments with GC-EIMS

1. Shimadzu JMS-700 GC-MS calibration

BLK1 and BLK2 were measured in June 2012 while BLK3, BLK4 and BLK5 were measured in December 2012. Therefore two sets of standard solutions were

Sample ID	*DEHP stock used*	*Empty vial mass (g)*	*Mass of vial w/. DEHP stock (g)*	*Mass of DEHP stock added (g)*	*Empty Vol. flask mass (g)*	*Total mass in ACN (g)*	*[DEHP] (µg/kg)*
		2.46792	2.48639		15.80199	21.41398	
JMS700STK1	Supelco® neat DEHP	2.46792	2.48641		15.80197	21.41397	
		2.46793	2.48641		15.80197	21.41396	
Mean		2.46792	2.48640	0.01848	15.80198	21.41397	3293.95
Standard deviation (1σ)		0.00001	0.00001	0.00001	0.00001	0.00001	2.30
		2.52042	2.52990			3.81931	
JMS700STK2	JMS700STK1	2.52044	2.52988			3.81932	
		2.52044	2.52988			3.81931	
Mean		2.52043	2.52989	0.00945		3.81931	23.97
Standard deviation (1σ)		0.00001	0.00001	0.00002		0.00001	0.04
		2.52453	2.55772			3.73293	
JMS700STK3	JMS700STK1	2.52453	2.55770			3.73293	
		2.52454	2.55770			3.73292	
Mean		2.52453	2.55771	0.00671		3.73293	17.98
Standard deviation (1σ)		0.00001	0.00001	0.00001		0.00001	0.02
		2.52453	2.55772			3.73293	
JMS700STK4	JMS700STK1	2.52453	2.55770			3.73293	
		2.52454	2.55770			3.73292	
Mean		2.52453	2.55771	0.03317		3.73293	90.40
Standard deviation (1σ)		0.00001	0.00001	0.00001		0.00001	0.04

prepared for calibrations (splitless, detector voltage 1.000 kV).

Table A 3.1 DEHP stock solutions preparation for BLK1 and BLK2

Table A 3.2 Standard solutions of JMS700 GC-EIMS calibration for BLK1 and BLK2

Sample ID	*Stock solution*	*Mass of vial (g)*	*Mass of vial plus DEHP solution (g)*	*Total Mass after dilution w. CH_2Cl_2 (g)*	*[DEHP] (mg/kg)*	*Peak Area*
		2.51612	2.52133	5.03026		
JMS700BK12-1	JMS700STK3	2.51612	2.52134	5.03023		
		2.51613	2.52134	5.03022		
Mean		2.51612	2.52134	5.03024	0.0373	133.06
Standard deviation (1σ)		0.00001	0.00001	0.00002	0.0001	
		2.53325	2.53867	4.73775		
JMS700BK12-2	JMS700STK3	2.53327	2.53866	4.73774		
		2.53327	2.53868	4.73776		
Mean		2.53326	2.53867	4.73775	0.0441	96.41
Standard deviation (1σ)		0.00001	0.00001	0.00001	0.0001	
		2.49432	2.49944	4.68995		
JMS700BK12-3	JMS700STK2	2.49434	2.49945	4.68996		
		2.49433	2.49946	4.68996		
Mean		2.49433	2.49945	4.68996	0.0560	272.63
Standard deviation (1σ)		0.00001	0.00001	0.00001	0.0002	
		2.52156	2.55602	4.66508		
JMS700BK12-4	JMS700STK3	2.52157	2.55603	4.66506		
		2.52156	2.55605	4.66506		
Mean		2.52156	2.55603	4.66507	0.2891	759.79
Standard deviation (1σ)		0.00001	0.00002	0.00001	0.0004	
		2.51159	2.56392	4.86229		
JMS700BK12-5	JMS700STK2	2.51160	2.56392	4.86228		
		2.51161	2.56393	4.86228		
Mean		2.51160	2.56392	4.86228	0.5335	792.78
Standard deviation (1σ)		0.00001	0.00001	0.00001	0.0009	
		2.48171	2.49693	4.47720		
JMS700BK12-6	JMS700STK4	2.48172	2.49693	4.47719		
		2.48171	2.49694	4.47721		
Mean		2.48171	2.49693	4.47720	0.6895	1116.5
Standard deviation (1σ)		0.00001	0.00001	0.00001	0.0005	

Table A 3.3 DEHP stock solutions preparation for BLK3, BLK4 and BLK5

Sample ID	*DEHP stock used*	*Empty vial mass (g)*	*Mass of vial w/. DEHP stock (g)*	*Mass of DEHP stock added (g)*	*Empty Vol. flask mass (g)*	*Total mass in hexane (g)*	*[DEHP] (µg/kg)*
		2.53506	2.53886		15.84304	22.54339	
JMS700STKA	Supelco® neat DEHP	2.53507	2.53887		15.84303	22.54338	
		2.53505	2.53885		15.84302	22.54337	
Mean		2.53506	2.53886	0.00380	15.84303	22.54338	567.1
Standard deviation (1σ)		0.00001	0.00001	0.00001	0.00001	0.00001	2.1
		2.53388	2.53905		15.99359	21.87950	
JMS700STKB	Supelco® neat DEHP	2.53389	2.53904		15.99358	21.87961	
		2.53390	2.53906		15.99359	21.87959	
Mean		2.53389	2.53905	0.00516	15.99359	21.87957	876.7
Standard deviation (1σ)		0.00001	0.00001	0.00001	0.00001	0.00006	2.4
		2.52304	2.63003			3.52694	
JMS700STKA1	JMS700STKA	2.52305	2.63002			3.52693	
		2.52305	2.63004			3.52693	
Mean		2.52305	2.63003	0.10698		3.52693	60.44
Standard deviation (1σ)		0.00001	0.00001	0.00001		0.00001	0.23
		2.52867	2.59775			3.63728	
JMS700STKB1	JMS700STKB	2.52868	2.59776			3.63725	
		2.52869	2.59775			3.63723	
Mean		2.52868	2.59775	0.06907		3.63725	54.62
Standard deviation (1σ)		0.00001	0.00001	0.00001		0.00003	0.15
		2.52844	2.62434			3.63468	
JMS700STKB1-1	JMS700STKB1	2.52845	2.62435			3.63470	
		2.52844	2.62436			3.63468	
Mean		2.52844	2.62435	0.09591		3.63469	4.74
Standard deviation (1σ)		0.00001	0.00001	0.00001		0.00001	0.01

Table A 3.4 Standard solutions of JMS700 GC-EIMS calibration for BLK3, BLK4 and BLK5

Sample ID	*Stock solution*	*Mass of vial (g)*	*Mass of vial plus DEHP solution (g)*	*Total Mass after dilution w. hexane (g)*	*[DEHP] (mg/kg)*	*Peak Area*
		2.50465	2.52978	3.56686		
JMS700BK345-1	JMS700STKA1	2.50464	2.52977	3.56687		
		2.50465	2.52979	3.56687		
Mean		2.50465	2.52978	3.56687	1.4301	632.18
Standard deviation (1σ)		0.00001	0.00001	0.00001	0.0055	
		2.51941	2.66548	3.19000		
JMS700BK345-2	JMS700BK345-1	2.51940	2.66549	3.19001		
		2.51940	2.66547	3.19002		
Mean		2.51940	2.66548	3.19001	0.3115	126.43
Standard deviation (1σ)		0.00001	0.00001	0.00001	0.0012	
		2.54036	2.63490	3.53447		
JMS700BK345-3	JMS700STKB1-1	2.54038	2.63491	3.53446		
		2.54039	2.63490	3.53445		
Mean		2.54038	2.63490	3.53446	0.4507	154.64
Standard deviation (1σ)		0.00002	0.00001	0.00001	0.0010	
		2.53609	2.54846	3.67704		
JMS700BK345-4	JMS700STKA1	2.53610	2.54846	3.67702		
		2.53609	2.54845	3.67702		
Mean		2.53609	2.54846	3.67703	0.6549	241.98
Standard deviation (1σ)		0.00001	0.00001	0.00001	0.0025	
		2.51576	2.71273	3.68091		
JMS700BK345-5	JMS700STKB1-1	2.51577	2.71273	3.68090		
		2.51575	2.71275	3.68089		
Mean		2.51576	2.71274	3.68090	0.8013	329.04
Standard deviation (1σ)		0.00001	0.00001	0.00001	0.0017	
		2.53642	2.79203	3.69609		
JMS700BK345-6	JMS700STKB1-1	2.53643	2.79201	3.69613		
		2.53643	2.79199	3.69611		
Mean		2.53643	2.79201	3.69611	1.0447	403.79
Standard deviation (1σ)		0.00001	0.00002	0.00002	0.0022	

BTR1 and BTR2 were measured in June 2012 while BTR3, BTR4 and BTR5 were measured in December 2012. Therefore two sets of standard solutions were prepared for calibrations (splitless, 0.800 kV).

Table A 3.5 Standard solutions of JMS700 GC-EIMS calibration for BTR1 and BTR2

Sample ID	***Stock solution***	***Mass of vial (g)***	***Mass of vial plus DEHP solution (g)***	***Total Mass after dilution w. hexane (g)***	***[DEHP] (mg/kg)***	***Peak Area***
		2.52337	2.53024	4.78156		
JMS700BR12-1	JMS700STK1	2.52339	2.53023	4.7815		
		2.52338	2.53024	4.78155		
Mean		2.52338	2.53024	4.78154	10.00	2967.97
Standard deviation (1σ)		0.00001	0.00001	0.00003	0.02	
		2.49955	2.51971	4.47544		
JMS700BR12-2	JMS700STK1	2.49954	2.51972	4.47542		
		2.49956	2.51973	4.47543		
Mean		2.49955	2.51972	4.47543	33.61	10333.28
Standard deviation (1σ)		0.00001	0.00001	0.00001	0.03	
		2.54637	2.5929	4.85169		
JMS700BR12-3	JMS700STK1	2.54636	2.59289	4.85167		
		2.54637	2.59288	4.8517		
Mean		2.54637	2.59289	4.85169	66.45	21117.98
Standard deviation (1σ)		0.00001	0.00001	0.00002	0.05	
		2.51567	2.58909	4.58698		
JMS700BR12-4	JMS700STK1	2.51568	2.58908	4.58697		
		2.51568	2.58909	4.58696		
Mean		2.51568	2.58909	4.58697	116.71	33140.78
Standard deviation (1σ)		0.00001	0.00001	0.00001	0.08	
		2.52758	2.64258	4.65625		
JMS700BR12-5	JMS700STK1	2.52757	2.64259	4.65624		
		2.52758	2.64259	4.65626		
Mean		2.52758	2.64259	4.65625	177.91	47818.02
Standard deviation (1σ)		0.00001	0.00001	0.00001	0.12	

Table A 3.6 DEHP stock solutions preparation for BTR3, BTR4 and BTR5

Sample ID	*DEHP stock used*	*Empty vial mass (g)*	*Mass of vial w/. DEHP stock (g)*	*Mass of DEHP stock added (g)*	*Empty Vol. flask mass (g)*	*Total mass in hexane (g)*	*[DEHP] (µg/kg)*
		2.5132	2.54874		15.53459	22.51043	
JMS700STKC	Supelco® neat DEHP	2.51319	2.54876		15.53458	22.5104	
		2.51321	2.54877		15.53454	22.51028	
Mean		2.51320	2.54876	0.03556	15.53457	22.51037	5097.15
Standard deviation (1σ)		2.5132	2.54874		15.53459	22.51043	2.62
		2.52431	2.59269			3.62826	
JMS700STKC2	JMS700STKC	2.52432	2.5927			3.62827	
		2.52434	2.59271			3.62825	
Mean		2.52432	2.59270	0.06838		3.62826	315.71
Standard deviation (1σ)		0.00002	0.00001	0.00002		0.00001	0.18

Table A 3.7 Standard solutions of JMS700 GC-EIMS calibration for BTR3, BTR4, BTR5, BTR6 and BTR7

Sample ID	*Stock solution*	*Mass of vial (g)*	*Mass of vial plus DEHP solution (g)*	*Total Mass after dilution w. hexane (g)*	*[DEHP] (mg/kg)*	*Peak Area*
		2.52569	2.59682	3.45317		
JMS700BR37-1	JMS700STKC2	2.5257	2.59681	3.45318		
		2.52569	2.5968	3.45318		
Mean		2.52569	2.59681	3.45318	24.21	412.56
Standard deviation (1σ)		0.00001	0.00001	0.00001	0.01	
		2.53106	2.70801	3.53128		
JMS700BR37-2	JMS700STKC2	2.53107	2.708	3.5313		
		2.53105	2.70798	3.53128		
Mean		2.53106	2.70800	3.53129	55.85	1315.97
Standard deviation (1σ)		0.00001	0.00002	0.00001	0.03	
		2.51622	2.76802	3.48482		
JMS700BR37-3	JMS700STKC2	2.51621	2.76801	3.48475		
		2.51623	2.76801	3.48477		
Mean		2.51622	2.76801	3.48478	82.07	1627.09
Standard deviation (1σ)		0.00001	0.00001	0.00004	0.05	
		2.52351	2.89631	3.57204		
JMS700BR37-4	JMS700STKC2	2.52352	2.89629	3.57205		
		2.52353	2.89628	3.57204		
Mean		2.52352	2.89629	3.57204	112.24	2308.35
Standard deviation (1σ)		0.00001	0.00002	0.00001	0.06	
		2.54667	2.58123	3.57686		
JMS700BR37-5	JMS700STKC	2.54668	2.58126	3.57688		
		2.54669	2.58128	3.57688		
Mean		2.54668	2.58126	3.57687	171.08	4475.2
Standard deviation (1σ)		0.00001	0.00003	0.00001	0.16	

2. GC-EIMS Chromatogram Peak Identification and Integration

Carbon purities of samples were calculated based on peak areas and deconvolution. BTR1 and BTR2 were measured with Shimadzu® JMS700 GC-EIMS. To identify these tiny peaks, two-step measurement method was used: first, the sample was injected with splitless mode (detector voltage 1.000 kV), while the ion intensity for the DEHP peak was too high and the peak was "chopped off" due to detector saturation. Second, the sample was injected again with split mode (split ratio=20, detector voltage 1.000 kV) to get completed DEHP peak while the impurity peaks were invisible. To compute the purity by peak areas, a substitutive equation was used:

$$\boldsymbol{P_{TIC}} = \frac{\mathbf{20}\cdot\boldsymbol{A_{DEHP}}}{\mathbf{20}\cdot\boldsymbol{A_{DEHP}}+\sum \boldsymbol{A_{inpurities}}} \qquad \text{(A 3.1)}$$

BTR3, BTR4, BTR5, BTR6 and BTR7 were measured with Shimadzu® QP2010S, which was able to detect and show complete peaks for both DEHP and impurities.

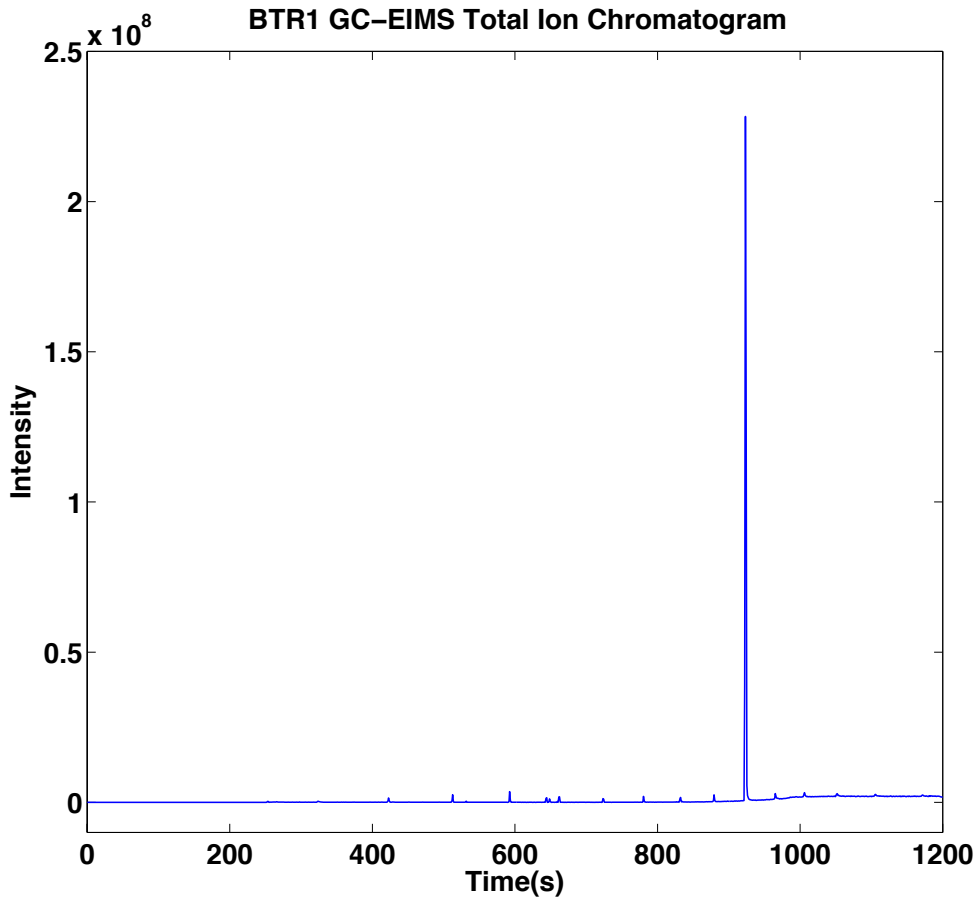
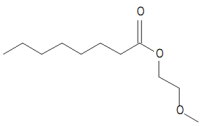
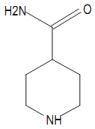
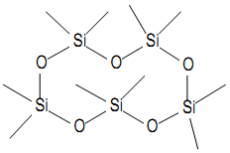
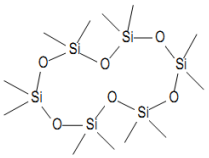
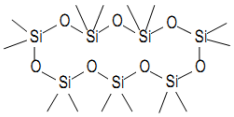
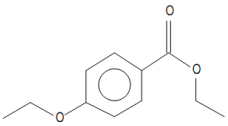
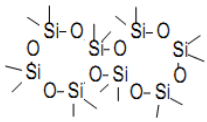
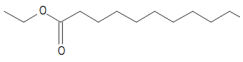
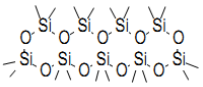
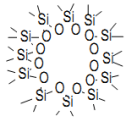
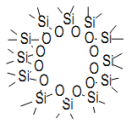
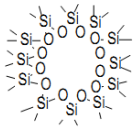
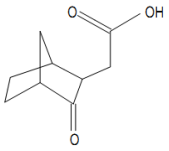
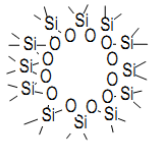
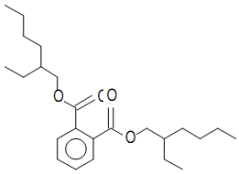
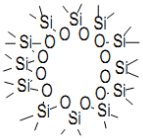
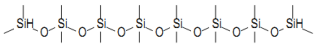
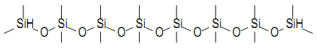
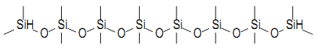
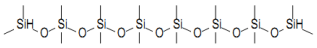
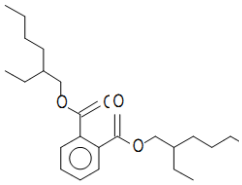
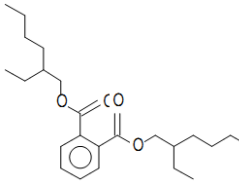
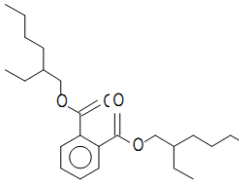


Figure A 3.1 BTR1 GC-EIMS total ion chromatogram

Table A 3.8 BTR1 Shimadzu® JMS700 GC-EIMS TIC peak identification

#	t_R (min)	Peak Width	Spec. #	Compound	Formula	Mol. Mass	C mass ratio	Structure	Peak Area	%
1	4.232	253-256	255	Octanoic acid, 2-methoxyethyl ester	$C_{11}H_{22}O_3$	202	0.6535		571424.004	0.053
2	4.432	265-269	267	4-Piperidinecarboxamide	$C_6H_{12}N_2O$	128	0.5625		151482.8655	0.014
3	5.398		325	Cyclopentasiloxane, decamethyl-	$C_{10}H_{30}O_5Si_5$	370				
4	7.046		424	Cyclohexasiloxane, dodecamethyl-	$C_{12}H_{36}O_6Si_6$	444				
5	8.545		514	Cycloheptasiloxane, tetradecamethyl-	$C_{14}H_{42}O_7Si_7$	518				
6	8.844	531-534	532	Benzoic acid, 4-ethoxy-, ethyl ester	$C_{11}H_{14}O_3$	194	0.6804		375999.624	0.035
7	9.877		594	Cyclooctasiloxane, hexadecamethyl-	$C_{16}H_{48}O_8Si_8$	592				
8	10.726	644-647	645	1,22-Docosanediol	$C_{22}H_{46}O_2$	342	0.7719		2794256.946	0.260
9	10.809	649-652	650	Tetradecanoic acid, ethyl ester	$C_{16}H_{32}O_2$	256	0.7500		1509452.037	0.140
10	10.992	660-662	661	Compound name:14-Heptadecenal	$C_{17}H_{32}O$	252	0.8095		271029.699	0.025

11	11.026		663	Cyclononasiloxane, octadecamethyl-	$C_{18}H_{54}O_9Si_9$	666				
12	12.075		726	Tetracosamethyl-cyclododecasiloxane	$C_{24}H_{72}O_{12}Si_{12}$	888				
13	13.007		782	Tetracosamethyl-cyclododecasiloxane	$C_{24}H_{72}O_{12}Si_{12}$	888				
14	13.856		833	Tetracosamethyl-cyclododecasiloxane	$C_{24}H_{72}O_{12}Si_{12}$	888				
15	13.906	835-838	836	Bicyclo[2.2.1]heptane-2-acetic acid, 3-oxo-, (r1,cis-3,cis-4)-	$C_9H_{12}O_3$	168	0.6428		241955.802	0.023
16	14.655		881	Tetracosamethyl-cyclododecasiloxane	$C_{24}H_{72}O_{12}Si_{12}$	888				
17	15.371	923-935	924	Bis(2-ethylhexyl) phthalate	$C_{24}H_{38}O_4$	390				
18	16.087		967	Tetracosamethyl-cyclododecasiloxane	$C_{24}H_{72}O_{12}Si_{12}$	888				
19	16.770		1008	1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl-	$C_{16}H_{50}O_7Si_8$	578				
20	17.519		1053	1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl-	$C_{16}H_{50}O_7Si_8$	578				
21	18.418		1107	1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl-	$C_{16}H_{50}O_7Si_8$	578				

22	19.517		1173	1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl-	$C_{16}H_{50}O_7Si_8$	578	
		925-932		Bis(2-ethylhexyl) phthalate	$C_{24}H_{38}O_4$	390	 40734799.425
		923-931		Bis(2-ethylhexyl) phthalate	$C_{24}H_{38}O_4$	390	 46941301.71
		924-933		Bis(2-ethylhexyl) phthalate	$C_{24}H_{38}O_4$	390	 72684157.086

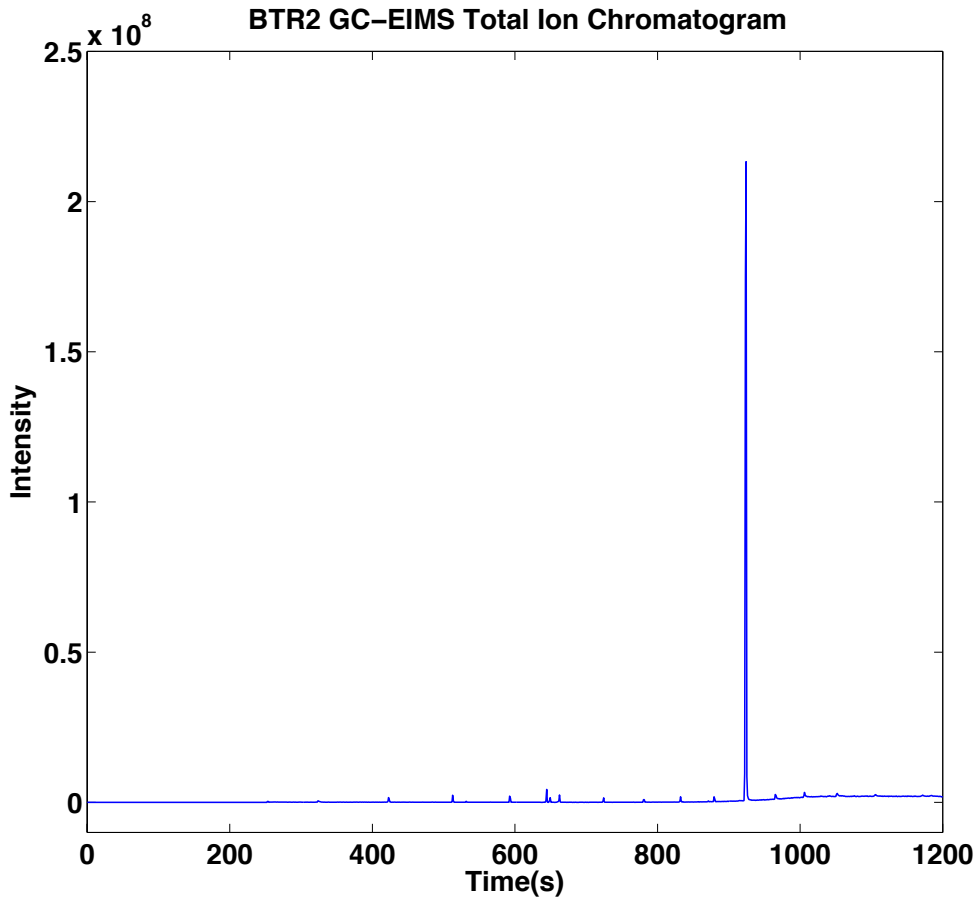
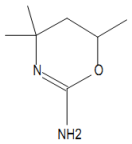
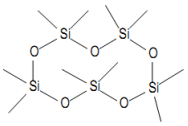
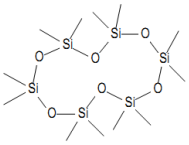
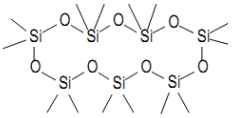
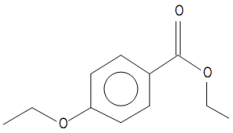
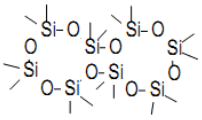
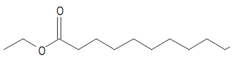
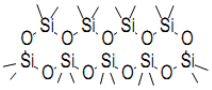
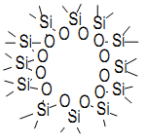
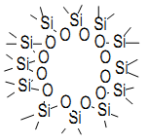
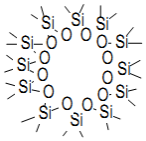
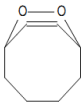
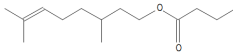
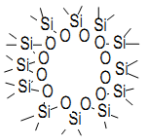
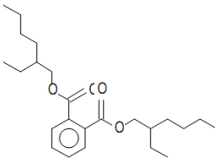
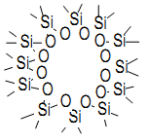
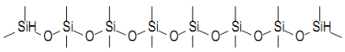
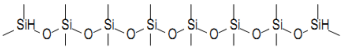
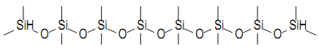


Figure A 3.2 BTR2 GC-EIMS total ion chromatogram

Table A 3.9 BTR2 Shimadzu® JMS700 GC-EIMS TIC peak identification

#	t_R (min)	Peak Width	Spec. #	Compound	Formula	Mol. Mass	C mass ratio	Structure	Peak Area	%
1	4.216	253-256	254	2-Amino-5,6-dihydro-4,4,6-trimethyl-4H-1,3-oxazine	$C_7H_{14}N_2O$	142	0.5915		589053.357	0.089
2	5.398		325	Cyclopentasiloxane, decamethyl-	$C_{10}H_{30}O_5Si_5$	370				
3	7.046		424	Cyclohexasiloxane, dodecamethyl-	$C_{12}H_{36}O_6Si_6$	444				
4	8.545		514	Cycloheptasiloxane, tetradecamethyl-	$C_{14}H_{42}O_7Si_7$	518				
5	8.861	532-535	533	Benzoic acid, 4-ethoxy-, ethyl ester	$C_{11}H_{14}O_3$	194	0.6804		384455.16	0.058
6	9.877		594	Cyclooctasiloxane, hexadecamethyl-	$C_{16}H_{48}O_8Si_8$	592				
7	10.743	644-647	646	Heptadecanal	$C_{17}H_{34}O$	254	0.8031		4772384.838	0.721
8	10.809	649-652	650	Tetradecanoic acid, ethyl ester	$C_{16}H_{32}O_2$	256	0.7500		2116373.508	0.320
9	10.992	660-662	661	3-Dodecen-1-ol, (Z)-	$C_{12}H_{24}O$	184	0.7826		53015.931	0.008
10	11.042		664	Cyclononasiloxane, octadecamethyl-	$C_{18}H_{54}O_9Si_9$	666				
11	12.075		726	Tetracosamethyl-cyclododecasiloxane	$C_{24}H_{72}O_{12}Si_{12}$	888				

12	13.024		783	Tetracosamethyl-cyclododecasiloxane	$C_{24}H_{72}O_{12}Si_{12}$	888				
13	13.873		834	Tetracosamethyl-cyclododecasiloxane	$C_{24}H_{72}O_{12}Si_{12}$	888				
14	13.923	836-838	837	7,8-Dioxabicyclo[4.2.2]dec-9-ene	$C_8H_{12}O_2$	140	0.6857		147973.878	0.022
15	14.522	871-874	873	Citronellyl butyrate	$C_{14}H_{26}O_2$	226	0.7434		395011.593	0.060
16	14.655		881	Tetracosamethyl-cyclododecasiloxane	$C_{24}H_{72}O_{12}Si_{12}$	888				
17	15.371	922-934	924	Bis(2-ethylhexyl) phthalate	$C_{24}H_{38}O_4$	390	0.7385			
18	16.087		967	Tetracosamethyl-cyclododecasiloxane	$C_{24}H_{72}O_{12}Si_{12}$	888				
19	16.770		1008	Octasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl-	$C_{16}H_{50}O_7Si_8$	578				
20	17.536		1054	Octasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl-	$C_{16}H_{50}O_7Si_8$	578				
21	18.418		1107	Octasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl-	$C_{16}H_{50}O_7Si_8$	578				

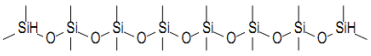
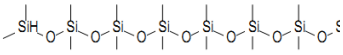
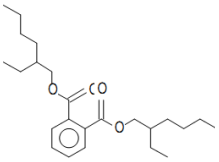
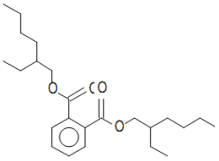
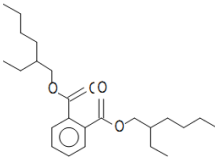
22	19.534		1174	Octasiloxane, 1,1,3,3,5,5,7,7,9,9, 11,11,13,13,15,15-hexadecamethyl-	$C_{16}H_{50}O_7Si_8$	578		
23	19.734		1186	Octasiloxane, 1,1,3,3,5,5,7,7,9,9, 11,11,13,13,15,15-hexadecamethyl-	$C_{16}H_{50}O_7Si_8$	578		
Trial (1)		924-931		Bis(2-ethylhexyl) phthalate	$C_{24}H_{38}O_4$	390		2885234 1.777
Trial (2)		923-930		Bis(2-ethylhexyl) phthalate	$C_{24}H_{38}O_4$	390		3331888 7.76
Trial (3)		924-931		Bis(2-ethylhexyl) phthalate	$C_{24}H_{38}O_4$	390		3586040 2.701

Table A 3.10 BTR3 Shimadzu® QP2010S GC-EIMS peak identification, deconvolution and carbon purity calculation (Trial 1)

t_R (min)	BTR3 co-eluted compounds	Carbon ratio	Peak area	Peak ratio (%)	Adjusted Peak ratio by carbon	Carbon Purity (normalized peak ratio by carbon) (%)
3.125	Hydroperoxide, 1-methylhexyl	0.6364				
5.315	n/a					
7.110	Cyclohexasiloxane, dodecamethyl	0.3243				
8.695	3-Butoxy-1,1,1,7,7,7-hexamethyl-3,5,5-tris(trimethylsiloxy)tetrasiloxane	0.3864				
10.080	Cyclooctasiloxane,hexadecamethyl	0.3243				
11.265	n/a					
12.335	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322				
13.525	n/a					
13.985	Cholesterol	0.8394	84516	0.67	0.56	0.79
14.080	Z,E-2,13-Octadecadien-1-ol	0.8120	118219.2	0.93	0.76	1.06
14.910	Cyclononasiloxane, octadecamethyl	0.3243				
15.995	n/a					
16.100	Heptasiloxane,hexadecamethyl	0.3609				
16.955	n/a					
17.150	DEHP peak	0.7375	12400179	98.39		
18.035	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322				
18.900	Heptasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecamethyl	0.3333				
19.875	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322				
21.025	n/a (counted as siloxane)	0.3237				
22.435	n/a					
	Purity within DEHP peak by deconvolution			94.26		
	DEHP	0.7374		92.74	68.38	**95.59**
	Residual with DEHP peak by deconvolution calculated as siloxane C_2H_6SiO	0.3237		5.65	1.83	2.55

Table A 3.11 BTR3 Shimadzu® QP2010S GC-EIMS peak identification, deconvolution and carbon purity calculation (Trial 2)

t_R (min)	BTR3 co-eluted compounds	Carbon ratio	Peak area	Peak ratio (%)	Adjusted Peak ratio by carbon	Carbon Purity (normalized peak ratio by carbon) (%)
3.125	Hydroperoxide, 1-methylhexyl	0.6364				
5.315	n/a					
7.110	Cyclohexasiloxane, dodecamethyl	0.3243				
8.695	3-Butoxy-1,1,1,7,7,7-hexamethyl-3,5,5-tris(trimethylsiloxy)tetrasiloxane	0.3864	25767.45	0.20	0.59	0.84
10.080	Cyclooctasiloxane,hexadecamethyl	0.3243				
11.265	n/a					
12.335	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322				
13.525	n/a					
13.985	Cholesterol	0.8394	82881	0.65	0.55	0.78
14.080	Z,E-2,13-Octadecadien-1-ol	0.8120	110352.45	0.87	0.71	1.01
14.910	Cyclononasiloxane, octadecamethyl	0.3243				
15.995	n/a					
16.100	Heptasiloxane,hexadecamethyl	0.3609	60607.35	0.48	0.17	0.25
16.955	n/a					
17.150	DEHP peak	0.7375	11876830.5	93.72		
18.035	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322	138959.85	1.10	0.36	0.52
18.900	Heptasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecamethyl	0.3333	168064.05	1.33	0.44	0.63
19.875	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322	138089.4	1.09	0.36	0.52
21.025	n/a (counted as siloxane)	0.3237	71219.1	0.56	0.18	0.26
22.435	n/a					
	Purity within DEHP peak by deconvolution			93.86		
	DEHP	0.7374		87.96	64.87	**92.54**
	Residual with DEHP peak by deconvolution calculated as siloxane C_2H_6SiO	0.3237		5.75	1.86	2.66

Table A 3.12 BTR3 Shimadzu® QP2010S GC-EIMS peak identification, deconvolution and carbon purity calculation (Trial 3)

t_R (min)	BTR3 co-eluted compounds	Carbon ratio	Peak area	Peak ratio (%)	Adjusted Peak ratio by carbon	Carbon Purity (normalized peak ratio by carbon) (%)
3.125	Hydroperoxide, 1-methylhexyl	0.6364				
5.315	n/a					
7.110	Cyclohexasiloxane, dodecamethyl	0.3243				
8.695	3-Butoxy-1,1,1,7,7,7-hexamethyl-3,5,5-tris(trimethylsiloxy)tetrasiloxane	0.3864	18706.95	0.14	0.06	0.08
10.080	Cyclooctasiloxane,hexadecamethyl	0.3243	20175.45	0.15	0.05	0.07
11.265	n/a					
12.335	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322				
13.525	n/a					
13.985	Cholesterol	0.8394	69390.75	0.53	0.45	0.65
14.080	Z,E-2,13-Octadecadien-1-ol	0.8120	92086.8	0.70	0.57	0.83
14.910	Cyclononasiloxane, octadecamethyl	0.3243				
15.995	n/a					
16.100	Heptasiloxane,hexadecamethyl	0.3609	43135.5	0.33	0.12	0.17
16.955	n/a					
17.150	DEHP peak	0.7375	12057828.9	92.17		
18.035	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322	363610.65	2.78	0.92	1.35
18.900	Heptasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecamethyl	0.3333	204999.15	1.57	0.52	0.76
19.875	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322	155845.5	1.19	0.40	0.58
21.025	n/a (counted as siloxane)	0.3237	55789.2	0.43	0.14	0.20
22.435	n/a					
	Purity within DEHP peak by deconvolution			93.31		
	DEHP	0.7374		86.01	63.42	**92.40**
	Residual with DEHP peak by deconvolution calculated as siloxane C_2H_6SiO	0.3237		6.17	2.00	2.91

Table A 3.13 BTR4 Shimadzu® QP2010S GC-EIMS peak identification, deconvolution and carbon purity calculation (Trial 1)

t_R (min)	BTR4 co-eluted compounds	Carbon ratio	Peak area	Peak ratio (%)	Adjusted Peak ratio by carbon	Carbon Purity (normalized peak ratio by carbon) (%)
3.125	Hydroperoxide, 1-methylhexyl	0.6364				
5.315	n/a					
7.110	Cyclohexasiloxane, dodecamethyl	0.3243				
8.695	3-Butoxy-1,1,1,7,7,7-hexamethyl-3,5,5-tris(trimethylsiloxy)tetrasiloxane	0.3864				
10.080	Cyclooctasiloxane,hexadecamethyl	0.3243	15889.2	0.26	0.08	0.12
11.265	n/a (counted as siloxane)	0.3237	20071.2	0.33	0.11	0.15
12.335	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322	16689.75	0.27	0.09	0.13
13.525	n/a (counted as siloxane)	0.3237	14752.95	0.24	0.08	0.11
13.985	Cholesterol	0.8394	16916.7	0.28	0.23	0.34
14.080	Z,E-2,13-Octadecadien-1-ol	0.8120	20095.2	0.33	0.27	0.38
14.910	Cyclononasiloxane, octadecamethyl	0.3243	22483.65	0.37	0.12	0.17
16.100	Heptasiloxane,hexadecamethyl	0.3609	30091.95	0.49	0.18	0.26
17.150	DEHP	0.7375	5947997.1	96.89		
18.035	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322	26254.5	0.43	0.14	0.21
18.900	Heptasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecamethyl	0.3333	7848	0.13	0.04	0.06
19.875	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322				
21.025	n/a (counted as siloxane)	0.3237				
21.835	n/a (counted as siloxane)	0.3237				
22.435	n/a (counted as siloxane)	0.3237				
	Purity within DEHP peak by deconvolution			90.67		
	DEHP	0.7374		87.85	64.78	**93.83**
	Residual with DEHP peak by deconvolution calculated as siloxane C_2H_6SiO	0.3237		9.04	2.93	4.24

Table A 3.14 BTR4 Shimadzu® QP2010S GC-EIMS peak identification, deconvolution and carbon purity calculation (Trial 2)

t_R (min)	BTR4 co-eluted compounds	Carbon ratio	Peak area	Peak ratio (%)	Adjusted Peak ratio by carbon	Carbon Purity (normalized peak ratio by carbon) (%)
3.125	Hydroperoxide, 1-methylhexyl	0.6364				
5.315	n/a					
7.110	Cyclohexasiloxane, dodecamethyl	0.3243	5112.9	0.08	0.03	0.04
8.695	3-Butoxy-1,1,1,7,7,7-hexamethyl-3,5,5-tris(trimethylsiloxy)tetrasiloxane	0.3864	19871.7	0.32	0.12	0.18
10.080	Cyclooctasiloxane,hexadecamethyl	0.3243	23942.7	0.38	0.12	0.18
11.265	n/a (counted as siloxane)	0.3237	21079.2	0.34	0.11	0.16
12.335	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322	27572.1	0.44	0.15	0.22
13.525	n/a (counted as siloxane)	0.3237	25842.6	0.41	0.13	0.20
13.985	Cholesterol	0.8394	5421.45	0.09	0.07	0.11
14.080	Z,E-2,13-Octadecadien-1-ol	0.8120	7769.4	0.12	0.10	0.15
14.910	Cyclononasiloxane, octadecamethyl	0.3243	43979.7	0.70	0.23	0.34
16.100	Heptasiloxane,hexadecamethyl	0.3609	62204.7	0.99	0.36	0.53
17.150	DEHP	0.7375	5783204.7	91.91		
18.035	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322	101178.9	1.61	0.53	0.79
18.900	Heptasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecamethyl	0.3333	71226.3	1.13	0.38	0.56
19.875	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322	44127.9	0.70	0.23	0.35
21.025	n/a (counted as siloxane)	0.3237	27266.55	0.43	0.14	0.21
21.835	n/a (counted as siloxane)	0.3237	1724.55	0.03	0.01	0.01
22.435	n/a (counted as siloxane)	0.3237	20512.2	0.33	0.11	0.16
	Purity within DEHP peak by deconvolution			91.76		
	DEHP	0.7374		84.34	62.19	**92.19**
	Residual with DEHP peak by deconvolution calculated as siloxane C_2H_6SiO	0.3237		7.57	2.45	3.63

Table A 3.15 BTR4 Shimadzu® QP2010S GC-EIMS peak identification, deconvolution and carbon purity calculation (Trial 3)

t_R (min)	BTR4 co-eluted compounds	Carbon ratio	Peak area	Peak ratio (%)	Adjusted Peak ratio by carbon	Carbon Purity (normalized peak ratio by carbon) (%)
3.125	Hydroperoxide, 1-methylhexyl	0.6364				
5.315	n/a					
7.110	Cyclohexasiloxane, dodecamethyl	0.3243	8755.8	0.14	0.05	0.07
8.695	3-Butoxy-1,1,1,7,7,7-hexamethyl-3,5,5-tris(trimethylsiloxy)tetrasiloxane	0.3864	21872.7	0.35	0.13	0.20
10.080	Cyclooctasiloxane,hexadecamethyl	0.3243	22417.95	0.36	0.12	0.17
11.265	n/a (counted as siloxane)	0.3237	24498	0.39	0.13	0.19
12.335	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322	28892.1	0.46	0.15	0.23
13.525	n/a (counted as siloxane)	0.3237	39404.55	0.63	0.20	0.30
13.985	Cholesterol	0.8394				
14.080	Z,E-2,13-Octadecadien-1-ol	0.8120				
14.910	Cyclononasiloxane, octadecamethyl	0.3243	43995.3	0.70	0.23	0.34
16.100	Heptasiloxane,hexadecamethyl	0.3609	61040.1	0.97	0.35	0.52
17.150	DEHP	0.7375	5723554.35	91.09		
18.035	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322	114705	1.83	0.61	0.91
18.900	Heptasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecamethyl	0.3333	85534.95	1.36	0.45	0.68
19.875	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322	70538.4	1.12	0.37	0.56
21.025	n/a (counted as siloxane)	0.3237	37882.8	0.60	0.20	0.29
21.835	n/a (counted as siloxane)	0.3237				
22.435	n/a (counted as siloxane)	0.3237				
	Purity within DEHP peak by deconvolution			91.11		
	DEHP	0.7374		83.00	61.20	**91.61**
	Residual with DEHP peak by deconvolution calculated as siloxane C_2H_6SiO	0.3237		8.10	2.62	3.92

Table A 3.16 BTR5 Shimadzu® QP2010S GC-EIMS peak identification, deconvolution and carbon purity calculation (Trial 1)

t_R (min)	BTR5 co-eluted compounds	Carbon ratio	Peak area	Peak ratio (%)	Adjusted Peak ratio by carbon	Carbon Purity (normalized peak ratio by carbon) (%)
3.115	Hydroperoxide, 1-methylhexyl	0.6364				
5.315	n/a					
7.110	Cyclohexasiloxane, dodecamethyl					
8.695	3-Butoxy-1,1,1,7,7,7-hexamethyl-3,5,5-tris(trimethylsiloxy)tetrasiloxane	0.3864				
10.080	Cyclooctasiloxane,hexadecamethyl	0.3243	12635.1	0.10	0.03	0.05
11.265	n/a (counted as siloxane)	0.3237	16601.7	0.14	0.04	0.06
12.335	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322	9592.95	0.08	0.03	0.04
13.525	n/a					
13.985	Cholesterol	0.8394	22281.6	0.18	0.15	0.21
14.080	Z,E-2,13-Octadecadien-1-ol	0.8120	32411.85	0.26	0.21	0.30
14.910	Cyclononasiloxane, octadecamethyl	0.3243				
16.100	Heptasiloxane,hexadecamethyl	0.3609	21169.35	0.17	0.06	0.09
16.955	n/a (counted as siloxane)	0.3237	27272.25	0.22	0.07	0.10
17.150	DEHP	0.7375	12108346.2	98.54		
18.035	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322	37952.4	0.31	0.10	0.14
18.900	Heptasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecamethyl	0.3333				
19.875	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322				
	Purity within DEHP peak by deconvolution			93.86		
	DEHP	0.7374		92.49	68.20	**96.24**
	Residual with DEHP peak by deconvolution calculated as siloxane C_2H_6SiO	0.3237		6.05	1.96	2.76

Table A 3.17 BTR5 Shimadzu® QP2010S GC-EIMS peak identification, deconvolution and carbon purity calculation (Trial 2)

t_R (min)	BTR5 co-eluted compounds	Carbon ratio	Peak area	Peak ratio (%)	Adjusted Peak ratio by carbon	Carbon Purity (normalized peak ratio by carbon) (%)
3.115	Hydroperoxide, 1-methylhexyl	0.6364				
5.315	n/a					
7.110	Cyclohexasiloxane, dodecamethyl					
8.695	3-Butoxy-1,1,1,7,7,7-hexamethyl-3,5,5-tris(trimethylsiloxy)tetrasiloxane	0.3864				
10.080	Cyclooctasiloxane,hexadecamethyl	0.3243				
11.265	n/a (counted as siloxane)	0.3237				
12.335	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322	6248.85	0.05	0.02	0.02
13.525	n/a					
13.985	Cholesterol	0.8394	18597.15	0.16	0.13	0.19
14.080	Z,E-2,13-Octadecadien-1-ol	0.8120	27006.6	0.23	0.19	0.26
14.910	Cyclononasiloxane, octadecamethyl	0.3243				
16.100	Heptasiloxane,hexadecamethyl	0.3609				
16.955	n/a (counted as siloxane)	0.3237				
17.150	DEHP	0.7375	11622163.05	99.56		
18.035	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322				
18.900	Heptasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecamethyl	0.3333				
19.875	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322				
	Purity within DEHP peak by deconvolution			95.57		
	DEHP	0.7374		95.15	70.16	**97.54**
	Residual with DEHP peak by deconvolution calculated as siloxane C_2H_6SiO	0.3237		4.41	1.43	1.98

Table A 3.18 BTR5 Shimadzu® QP2010S GC-EIMS peak identification, deconvolution and carbon purity calculation (Trial 3)

t_R (min)	BTR5 co-eluted compounds	Carbon ratio	Peak area	Peak ratio (%)	Adjusted Peak ratio by carbon	Carbon Purity (normalized peak ratio by carbon) (%)
3.115	Hydroperoxide, 1-methylhexyl	0.6364				
5.315	n/a					
7.110	Cyclohexasiloxane, dodecamethyl					
8.695	3-Butoxy-1,1,1,7,7,7-hexamethyl-3,5,5-tris(trimethylsiloxy)tetrasiloxane	0.3864				
10.080	Cyclooctasiloxane,hexadecamethyl	0.3243				
11.265	n/a (counted as siloxane)	0.3237				
12.335	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322	9342.45	0.08	0.03	0.04
13.525	n/a					
13.985	Cholesterol	0.8394	20731.2	0.18	0.15	0.21
14.080	Z,E-2,13-Octadecadien-1-ol	0.8120	20447.1	0.17	0.14	0.20
14.910	Cyclononasiloxane, octadecamethyl	0.3243				
16.100	Heptasiloxane,hexadecamethyl	0.3609	7439.7	0.06	0.02	0.03
16.955	n/a (counted as siloxane)	0.3237				
17.150	DEHP	0.7375	11627427.75	99.44		
18.035	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322	7238.4	0.06	0.02	0.03
18.900	Heptasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecamethyl	0.3333				
19.875	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322				
	Purity within DEHP peak by deconvolution			95.76		
	DEHP	0.7374		95.23	70.22	**97.60**
	Residual with DEHP peak by deconvolution calculated as siloxane C_2H_6SiO	0.3237		4.22	1.362	1.90

Table A 3.19 BTR6 Shimadzu® QP2010S GC-EIMS peak identification, deconvolution and carbon purity calculation (Trial 1)

t_R (min)	BTR6 co-eluted compounds	Carbon ratio	Peak area	Peak ratio (%)	Adjusted Peak ratio by carbon	Carbon Purity (normalized peak ratio by carbon) (%)
3.125	Hydroperoxide, 1-methylhexyl	0.6364				
5.315	n/a					
7.110	Cyclohexasiloxane, dodecamethyl	0.3243				
8.695	3-Butoxy-1,1,1,7,7,7-hexamethyl-3,5,5-tris(trimethylsiloxy)tetrasiloxane	0.3864				
10.080	Cyclooctasiloxane,hexadecamethyl	0.3243				
11.265	n/a (counted as siloxane)	0.3237				
13.250	n/a (counted as siloxane)	0.3237				
13.985	Cholesterol	0.8394				
14.080	Z,E-2,13-Octadecadien-1-ol	0.8120	36186.15	0.39	0.32	0.45
15.995	n/a (counted as siloxane)	0.3237	17839.2	0.19	0.06	0.09
16.100	Heptasiloxane,hexadecamethyl	0.3609				
16.605	n/a (counted as siloxane)	0.3237				
17.150	DEHP	0.7375	9123937.5	99.41		
18.100	n/a (counted as siloxane)	0.3237				
18.220	n/a (counted as siloxane)	0.3237				
19.975	n/a (counted as siloxane)	0.3237				
	Purity within DEHP peak by deconvolution			92.76		
	DEHP	0.7374		92.21	68.00	**96.16**
	Residual with DEHP peak by deconvolution calculated as siloxane C_2H_6SiO	0.3237		7.20	2.33	3.29

Table A 3.20 BTR6 Shimadzu® QP2010S GC-EIMS peak identification, deconvolution and carbon purity calculation (Trial 2)

t_R (min)	BTR6 co-eluted compounds	Carbon ratio	Peak area	Peak ratio (%)	Adjusted Peak ratio by carbon	Carbon Purity (normalized peak ratio by carbon) (%)
3.125	Hydroperoxide, 1-methylhexyl	0.6364				
5.315	n/a					
7.110	Cyclohexasiloxane, dodecamethyl	0.3243	1560.45	0.02	0.01	0.01
8.695	3-Butoxy-1,1,1,7,7,7-hexamethyl-3,5,5-tris(trimethylsiloxy)tetrasiloxane	0.3864				
10.080	Cyclooctasiloxane,hexadecamethyl	0.3243				
11.265	n/a (counted as siloxane)	0.3237	2261.55	0.03	0.01	0.01
13.250	n/a (counted as siloxane)	0.3237	1527.45	0.02	0.01	0.01
13.985	Cholesterol	0.8394				
14.080	Z,E-2,13-Octadecadien-1-ol	0.8120	18670.2	0.21	0.17	0.24
15.995	n/a (counted as siloxane)	0.3237	1059.9	0.01	0.00	0.01
16.100	Heptasiloxane,hexadecamethyl	0.3609				
16.605	n/a (counted as siloxane)	0.3237				
17.150	DEHP	0.7375	8875409.85	99.69		
18.100	n/a (counted as siloxane)	0.3237	2075.55	0.02	0.01	0.01
18.220	n/a (counted as siloxane)	0.3237				
19.975	n/a (counted as siloxane)	0.3237				
	Purity within DEHP peak by deconvolution			94.63		
	DEHP	0.7374		94.34	69.57	**97.29**
	Residual with DEHP peak by deconvolution calculated as siloxane C_2H_6SiO	0.3237		5.35	1.73	2.42

Table A 3.21 BTR6 Shimadzu® QP2010S GC-EIMS peak identification, deconvolution and carbon purity calculation (Trial 3)

t_R (min)	BTR6 co-eluted compounds	Carbon ratio	Peak area	Peak ratio (%)	Adjusted Peak ratio by carbon	Carbon Purity (normalized peak ratio by carbon) (%)
3.125	Hydroperoxide, 1-methylhexyl	0.6364				
5.315	n/a					
7.110	Cyclohexasiloxane, dodecamethyl	0.3243	2158.05	0.02	0.01	0.01
8.695	3-Butoxy-1,1,1,7,7,7-hexamethyl-3,5,5-tris(trimethylsiloxy)tetrasiloxane	0.3864				
10.080	Cyclooctasiloxane,hexadecamethyl	0.3243				
11.265	n/a (counted as siloxane)	0.3237				
13.250	n/a (counted as siloxane)	0.3237				
13.985	Cholesterol	0.8394	1803.45	0.02	0.02	0.02
14.080	Z,E-2,13-Octadecadien-1-ol	0.8120	20270.7	0.22	0.18	0.24
15.995	n/a (counted as siloxane)	0.3237	5596.8	0.06	0.02	0.03
16.100	Heptasiloxane,hexadecamethyl	0.3609				
16.605	n/a (counted as siloxane)	0.3237	134562.3	1.43	0.46	0.64
17.150	DEHP	0.7375	9143716.2	97.29		
18.100	n/a (counted as siloxane)	0.3237				
18.220	n/a (counted as siloxane)	0.3237	5778.9	0.06	0.02	0.03
19.975	n/a (counted as siloxane)	0.3237	84125.7	0.90	0.29	0.40
	Purity within DEHP peak by deconvolution			94.51		
	DEHP	0.7374		91.95	67.81	**93.68**
	Residual with DEHP peak by deconvolution calculated as siloxane C_2H_6SiO	0.3237		5.34	1.73	2.39

Table A 3.22 BTR7 Shimadzu® QP2010S GC-EIMS peak identification, deconvolution and carbon purity calculation (Trial 1)

t_R (min)	BTR7 co-eluted compounds	Carbon ratio	Peak area	Peak ratio (%)	Adjusted Peak ratio by carbon	Carbon Purity (normalized peak ratio by carbon) (%)
5.090	n/a (count as siloxane)	0.3237				
8.695	3-Butoxy-1,1,1,7,7,7-hexamethyl-3,5,5-tris(trimethylsiloxy)tetrasiloxane	0.3864				
9.040	n/a	0.3237				
10.080	Cyclooctasiloxane,hexadecamethyl	0.3243				
11.265	n/a					
12.335	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322				
13.525	n/a					
13.985	Cholesterol	0.8394	18462.9	0.45	0.38	0.54
14.080	Z,E-2,13-Octadecadien-1-ol	0.8120	18310.5	0.45	0.36	0.52
14.910	Cyclononasiloxane, octadecamethyl	0.3243				
16.100	Heptasiloxane,hexadecamethyl	0.3609				
17.150	DEHP	0.7375	4065726.9	99.10		
18.035	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322				
18.900	Heptasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecamethyl	0.3333				
	Purity within DEHP peak by deconvolution			89.78		
	DEHP	0.7374		88.98	65.61	**94.23**
	Residual with DEHP peak by deconvolution calculated as siloxane C_2H_6SiO	0.3237		10.13	3.28	4.71

Table A 3.23 BTR7 Shimadzu® QP2010S GC-EIMS peak identification, deconvolution and carbon purity calculation (Trial 2)

t_R (min)	BTR7 co-eluted compounds	Carbon ratio	Peak area	Peak ratio (%)	Adjusted Peak ratio by carbon	Carbon Purity (normalized peak ratio by carbon) (%)
5.090	n/a (count as siloxane)	0.3237	1888.65	0.05	0.01	0.02
8.695	3-Butoxy-1,1,1,7,7,7-hexamethyl-3,5,5-tris(trimethylsiloxy)tetrasiloxane	0.3864				
9.040	n/a	0.3237				
10.080	Cyclooctasiloxane,hexadecamethyl	0.3243				
11.265	n/a					
12.335	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322				
13.525	n/a					
13.985	Cholesterol	0.8394	5780.7	0.14	0.12	0.17
14.080	Z,E-2,13-Octadecadien-1-ol	0.8120				
14.910	Cyclononasiloxane, octadecamethyl	0.3243				
16.100	Heptasiloxane,hexadecamethyl	0.3609				
17.150	DEHP	0.7375	4076268.3	99.81		
18.035	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322				
18.900	Heptasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecamethyl	0.3333				
	Purity within DEHP peak by deconvolution			92.14		
	DEHP	0.7374		91.97	67.82	**96.21**
	Residual with DEHP peak by deconvolution calculated as siloxane C_2H_6SiO	0.3237		7.85	2.54	3.60

Table A 3.24 BTR7 Shimadzu® QP2010S GC-EIMS peak identification, deconvolution and carbon purity calculation (Trial 2)

t_R (min)	BTR7 co-eluted compounds	Carbon ratio	Peak area	Peak ratio (%)	Adjusted Peak ratio by carbon	Carbon Purity (normalized peak ratio by carbon) (%)
5.090	n/a (count as siloxane)	0.3237	2358.75	0.06	0.02	0.03
8.695	3-Butoxy-1,1,1,7,7,7-hexamethyl-3,5,5-tris(trimethylsiloxy)tetrasiloxane	0.3864				
9.040	n/a	0.3237	1176.6	0.03	0.01	0.01
10.080	Cyclooctasiloxane,hexadecamethyl	0.3243				
11.265	n/a					
12.335	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322				
13.525	n/a					
13.985	Cholesterol	0.8394				
14.080	Z,E-2,13-Octadecadien-1-ol	0.8120	1010.1	0.02	0.02	0.03
14.910	Cyclononasiloxane, octadecamethyl	0.3243				
16.100	Heptasiloxane,hexadecamethyl	0.3609				
17.150	DEHP	0.7375	4218950.7	99.89		
18.035	Octasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl	0.3322				
18.900	Heptasiloxane,1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecamethyl	0.3333				
	Purity within DEHP peak by deconvolution			92.07		
	DEHP	0.7374		91.97	67.82	**96.29**
	Residual with DEHP peak by deconvolution calculated as siloxane C_2H_6SiO	0.3237		7.92	2.56	3.64

Appendix 4 : Isoprime® IR-MS $\delta^{13}C$ Measurements

Table A 4.1 Isoprime® IR-MS $\delta^{13}C$ measurements (the 1st batch)

Sample ID	*Date*	*RT (Sec)*	*Trap Current (μA)*	*Height (nA)*	*Weight (mg)*	*^{13}C*	*^{18}O*	*delta^{18}O w.r.t. SMOW*	*Elemental Composition*	*$\delta^{13}C$_corr*	*$\delta^{13}C$_corr _avg*	*$\delta^{13}C$_corr _stdev*
urea-R1	9/10/12 14:28	292.7	150	2.9806	0.049	-31.9499	-1.2512	29.5701	20.7276	-29.4833	-29.3166	0.1463
urea-R2	9/10/12 14:37	296.7	150	3.3386	0.055	-31.7057	-1.8001	29.0044	21.3666	-29.2391		
urea-R3	9/10/12 14:46	296.8	150	6.2098	0.104	-31.6237	-2.2719	28.5180	20.9155	-29.1571		
urea-R4	9/10/12 14:55	298.3	150	4.9332	0.094	-31.8535	-2.6859	28.0912	18.4129	-29.3869		
BTR1	9/6/12 13:34	265.7	100	1.2934	0.018	-33.8844	-3.2150	27.5458	26.4941	-31.2298	-31.0393	0.2694
BTR2	9/6/12 13:43	265.9	100	1.1800	0.025	-33.5034	-3.0105	27.7566	17.3809	-30.8488		
CTP1	9/10/12 15:04	299.4	150	4.6141	0.038	-23.5454	-2.7940	27.9798	42.7927	-21.0788	-21.1936	0.1623
CTP2	9/10/12 15:12	303.1	150	2.9864	0.028	-23.7749	-2.7474	28.0278	38.2622	-21.3083		
urea-R5	9/10/12 15:21	303.9	150	5.6470	0.105	-31.9697	-3.0164	27.7505	19.3407	-29.5031	-29.5368	0.0476
urea-R6	9/10/12 15:30	304.6	150	8.0605	0.151	-32.0371	-3.0402	27.7259	19.2367	-29.5705		

Table A 4.2 Isoprime® IR-MS $\delta^{13}C$ measurements (the 2nd batch)

Sample ID	*Date*	*RT (Sec)*	*Trap Current (μA)*	*Height (nA)*	*Weight (mg)*	*^{13}C*	*^{18}O*	*delta^{18}O w.r.t. SMOW*	*Elemental Composition*	*$\delta^{13}C$_corr*	*$\delta^{13}C$_corr _avg*	*$\delta^{13}C$_corr _stdev*
urea-R1	12/20/12 12:59 PM	236.8	100	8.19	0.10	-31.81	-5.71	24.98	18.91	-29.3432	-29.3900	0.0648
urea-R2	12/20/12 1:05 PM	236.8	100	8.23	0.09	-31.84	-6.48	24.18	20.53	-29.3628		
urea-R3	12/20/12 1:12 PM	236.5	100	9.00	0.10	-31.94	-7.07	23.57	20.38	-29.4640		
CTP3	12/20/12 1:19 PM	236.8	100	6.77	0.03	-23.52	-6.89	23.76	62.59	-21.0414		
CTP4	12/20/12 1:26 PM	236.3	100	15.58	0.03	-23.58	-7.20	23.44	118.88	-21.0929		
CTP5	12/20/12 1:33 PM	236.4	100	14.00	0.03	-23.69	-6.98	23.66	106.75	-21.1984		
CTP6	12/20/12 1:39 PM	236.5	100	8.51	0.03	-23.62	-6.57	24.09	67.23	-21.1285		
CTP7[a]			150							-20.8978		
BTR3	12/20/12 1:53 PM	236.8	100	2.56	0.01	-27.09	-5.53	25.16	99.72	-24.5889		
BTR4	12/20/12 2:00 PM	236.5	100	2.73	0.01	-30.25	-5.22	25.48	63.34	-27.7415		
BTR5	12/20/12 2:06 PM	236.5	100	4.81	0.01	-30.24	-4.84	25.87	122.89	-27.7264		
BTR6	12/20/12 2:13 PM	236.4	100	5.21	0.01	-27.75	-4.80	25.91	132.79	-25.2311		
BTR7[b]			150							-23.4246		
urea-R4	12/20/12 2:33 PM	236.2	100	7.67	0.09	-31.90	-4.29	26.44	19.90	-27.5679	-29.3900	0.0321
urea-R5	12/20/12 2:40 PM	236.4	100	8.38	0.09	-31.95	-4.04	26.69	20.29	-29.3673		

[a,b] Only $\delta^{13}C$ data provided.

Appendix 5 : Ion Chromatography Data

Table A 5.1 Stock solution of sodium carbonate for IC

Sample ID	*Mass of Na2CO3 (g)*	*Flask Vol. (mL)*	*Concentration (mol/L)*
	0.51229		
CBNSTK1	0.51230		
	0.51229		
Mean	0.51229	50.00	0.09666
Standard deviation (1σ)	0.00001		0.00001
	0.08190		
CBNSTK2	0.08191		
	0.08192		
Mean	0.08191	50.00	0.01545
Standard deviation (1σ)	0.00001		0.00001

Table A 5.2 IC calibrants for carbonates contents measurements in butter

Sample ID	*Vol. of stock CBNSTK1 (mL)*	*Final vol. (mL)*	*Concentration (mol/L)*	*Peak Area*	*Retention Time bin #*	*Initial Time bin #*	*End Time bin #*
				2.6108	599	536	1099
CBN1-1	1.00	25.00		2.4591	599	528	1099
				2.6565	599	514	1099
Mean			0.00387				
Standard deviation (1σ)			0.00001				
				0.4719	592	542	843
CBN1-2	0.20	25.00		0.4722	592	544	813
				0.4815	592	540	800
Mean			0.00077				
Standard deviation (1σ)			0.00001				
				0.724	594	544	824
CBN1-3	0.30	25.00		0.7236	593	542	856
				0.7623	594	539	873
Mean			0.00116				
Standard deviation (1σ)			0.00001				
				1.141	594	532	1003
CBN1-4	0.50	25.00		1.3141	594	535	1008
				1.2754	595	540	928
Mean			0.00193				
Standard deviation (1σ)			0.00001				
				2.0819	599	540	1099
CBN1-5	0.80	25.00		2.0277	600	540	980
				2.0894	599	503	1024
Mean			0.00309				
Standard deviation (1σ)			0.00001				

Table A 5.3 IC calibrants for method derived carbonates contents measurements

Sample ID	*Vol. of stock CBNSTK2 (mL)*	*Final vol. (mL)*	*Concentration (mol/L)*	*Peak Area*	*Retention Time bin #*	*Initial Time bin #*	*End Time bin #*
				-0.9711	585	519	849
CBN2-1	1	25		-0.9862	586	513	848
				-0.9892	582	519	849
Mean			0.00062				
Standard deviation (1σ)			0.00001				
				-0.5795	583	520	830
CBN2-2	2	25		-0.5556	584	515	835
				-0.5441	586	516	840
Mean			0.00124				
Standard deviation (1σ)			0.00001				
				-0.163	582	518	771
CBN2-3	3	25		-0.1717	581	521	771
				-0.1602	583	515	780
Mean			0.00185				
Standard deviation (1σ)			0.00001				
				-0.6252	579	522	828
CBN2-4	1.6	25		-0.7019	582	526	791
				-0.7092	580	516	804
Mean			0.00099				
Standard deviation (1σ)			0.00001				
				-0.3146	577	519	787
CBN2-5	2.6	25		-0.309	582	522	785
				-0.3061	585	519	799
Mean			0.00161				
Standard deviation (1σ)			0.00001				
				-1.236	590	537	800
CBN2-6	0	25		-1.1586	586	520	904
				-1.1751	585	523	885
Mean			0				
Standard deviation (1σ)			-				

Appendix 6 : Simulation parameters and fraction of contemporary plots

The following matrix was perturbated 50000 times with the described Monte Carlo Method. The fraction modern and fraction of contemporary were computed as the mean value and standard deviation for each set of perturbation respectively.

Table A 6.1 Parameters, initial input values and output values for Monte Carlo simulation

Index	***Parameters***	***BTR3***	***BTR4***	***BTR5***	***BTR6***	***BTR7***
	Inputs					
1	$m_{DEHP,total}$	77.85	104.89	70.83	65.73	66.76
2	uncertainty (1σ)	11.27	12.64	11.07	10.03	10.35
3	m_{mtd}	1.08	0.73	0.79	0.87	0.87
4	uncertainty (1σ)	0.08	0.06	0.07	0.19	0.19
5	$f_{m,mtd}$	0.0009	0.0009	0.0009	0.0009	0.0009
6	uncertainty (1σ)	0.0013	0.0013	0.0013	0.0013	0.0013
7	$f_{m,coe}$	1.0561	1.0561	1.0561	1.0561	1.0561
8	uncertainty (1σ)	0.00219	0.00219	0.00219	0.00219	0.00219
9	$purity_C$	0.9351	0.9254	0.9713	0.9571	0.9558
10	uncertainty (1σ)	0.0181	0.0115	0.0077	0.0185	0.0117
11	$f_{m,measured}$	0.6484	0.296	0.3045	0.667	0.9414
12	uncertainty (1σ)	0.0032	0.0021	0.0025	0.0027	0.0034
13	$f_{m,btr}$	1.0561	1.0561	1.0561	1.0561	1.0561
14	uncertainty (1σ)	0.00219	0.00219	0.00219	0.00219	0.00219
15	$\delta^{13}C_{sam}$	-24.59	-24.74	-27.73	-25.23	-23.42
16	uncertainty (1σ)	1.93	1.93	1.93	1.93	1.93
17	$\delta^{13}C_{btr}$	-21.11	-21.11	-21.11	-21.11	-21.11
18	uncertainty (1σ)	0.13	0.13	0.13	0.13	0.13
19	m_{LLNL}	247	200	143	221	990

20	uncertainty (1σ)	12	10	7	11	50
21	$m_{exo,carbMtd}$	31.2	31.2	31.2	31.2	31.2
22	uncertainty (1σ)	7.2	7.2	7.2	7.2	7.2
23	$f_{m,exo,carbMtd}$	0.4213	0.4213	0.4213	0.4213	0.4213
24	uncertainty (1σ)	0.1797	0.1797	0.1797	0.1797	0.1797
25	$m_{exo,postHPLC}$	1.79	22.22	20.43	1.79	21.33
26	uncertainty (1σ)	9.1	9.7	9.7	9.1	9.7
27	$f_{m,exo,postHPLC}$	0.0209	0.0209	0.0209	0.0209	0.0209
28	uncertainty (1σ)	0.0050	0.0050	0.0050	0.0050	0.0050
29	$f_{m,exo,carbBtr}$	1.0561	1.0561	1.0561	1.0561	1.0561
30	uncertainty (1σ)	0.0022	0.0022	0.0022	0.0022	0.0022
	Outputs					
31	$m_{exo,carbBtr}$	130.7496	33.0111	18.6712	119.3179	867.8953
32	uncertainty (1σ)	20.7091	20.9107	18.0799	19.0462	52.6404
33	$f_{m,exo}$	0.9223	0.5381	0.4495	0.9124	1.0104
34	uncertainty (1σ)	0.0755	0.1944	0.2307	0.0804	0.0139
35	F_{iso}	1.0067	1.0070	1.0127	1.0079	1.0044
36	uncertainty (1σ)	0.0037	0.0037	0.0037	0.0037	0.0037
37	m_{coe}	5.4270	8.4748	2.0919	2.9774	3.0916
38	uncertainty (1σ)	1.8133	1.7581	0.6663	1.4254	0.9896
39	m_{exo}	163.7437	86.5267	70.1614	152.3177	920.4226
40	uncertainty (1σ)	17.1553	17.0322	13.4215	15.2371	51.2743
41	$m_{totalBlank}$	170.2507	95.7312	73.0433	156.1636	924.3837
42	uncertainty (1σ)	16.5303	16.1494	13.1339	14.8774	51.1728
43	$f_{m,totalBlank}$	0.9209	0.5855	0.4647	0.9102	1.0096
44	uncertainty (1σ)	0.0724	0.1619	0.2152	0.0783	0.0139
45	$f_{m,actual}$	0.0175	0.0008	0.0901	0.0531	-0.0470
46	uncertainty (1σ)	0.2403	0.1965	0.2618	0.2629	0.2937
47	fc	0.0167	0.0008	0.0864	0.0507	-0.0447
48	uncertainty (1σ)	0.2290	0.1874	0.2511	0.2509	0.2794

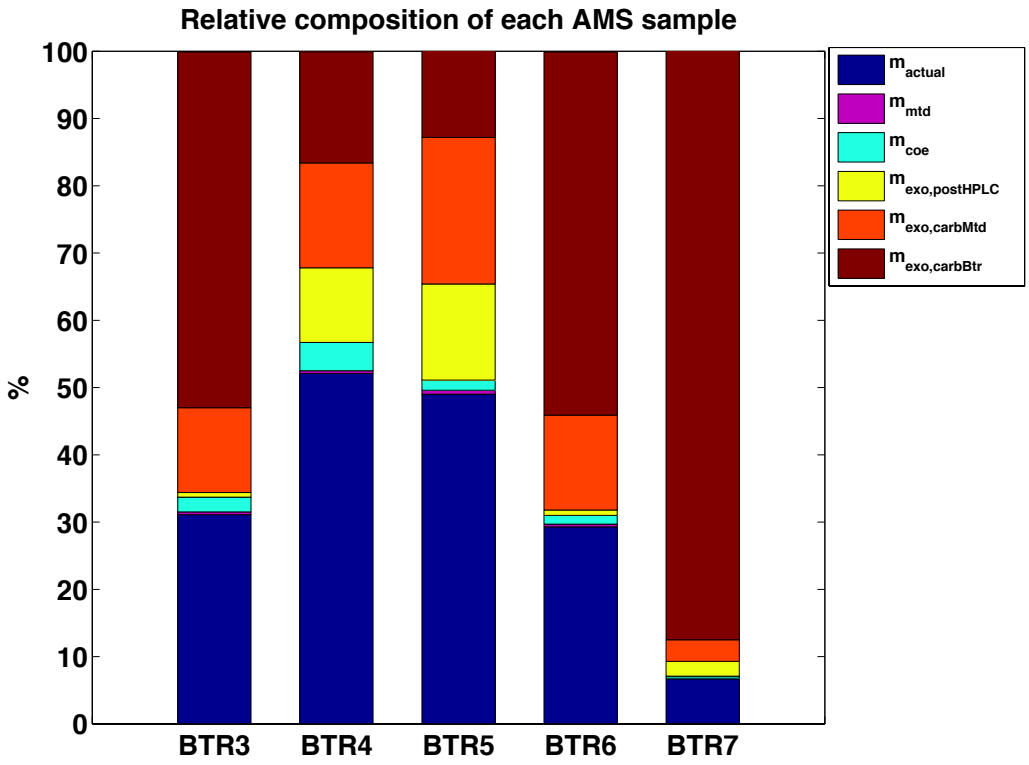
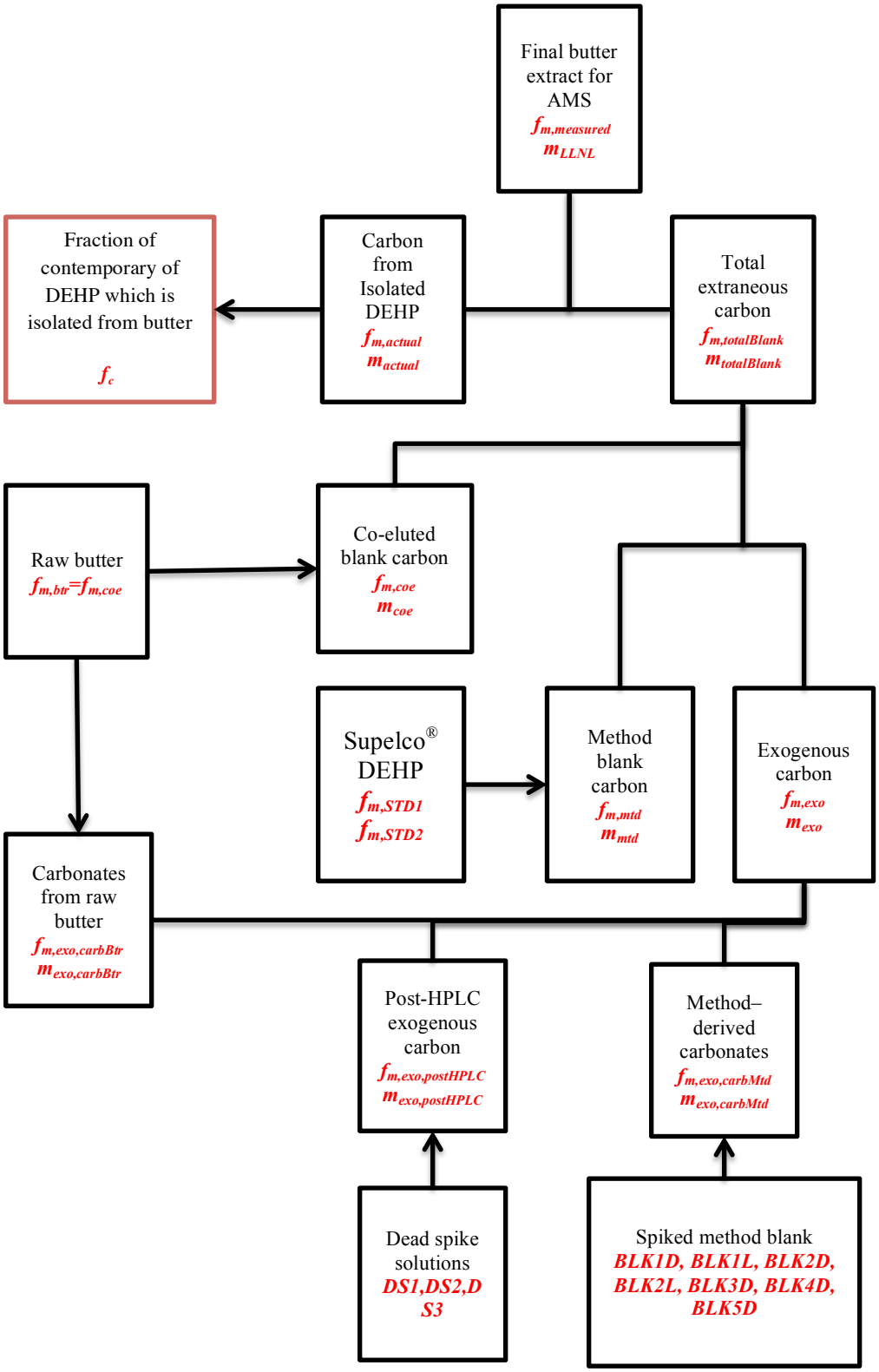


Figure A 6.1 Relative composition of each AMS sample

Appendix 7 : Flow Diagram



Glossary

A_{abs}	Absolute international standard activity of oxalic acid standard
AMS	Accelerator Mass Spectrometry
A_{ON}	Normalized activity of oxalic acid standard
A_S	Measured activity of the analyte
A_{SN}	Normalized activity of the analyte
BLK	Blank, prepared with the identical method
BTR	Isolated DEHP from butter
CPM	Counts per minute
CSIA	Compound specific isotope analysis
CTP	Unprocessed contemporary butter
D	Distribution factor
DEHP	Bis (2-ethylhexyl) phthalate
DPM	Decays per minute
f_c	Fraction of contemporary of carbon as DEHP in butter
F_{iso}	Isotopic fractionation correction coefficient
$f_{m,actual}$	Fraction modern of carbon as DEHP in butter
$f_{m,btr}$	Fraction modern of the raw butter reported by LLNL
$f_{m,coe}$	Fraction modern of the co-eluted compound
$f_{m,exo}$	Fraction modern of the exogenous carbon
$f_{m,exo,carbBtr}$	Fraction modern of carbon as carbonates from raw butter
$f_{m,exo,carbMtd}$	Fraction modern of carbon as carbonates from sample preparation procedures
$f_{m,exo,postHPLC}$	Fraction modern of exogenous carbon introduced after HPLC handling

$f_{m,measured}$	Fraction modern of the sample reported by LLNL
$f_{m,mtd}$	Fraction modern of carbon as DEHP from coetaneous method blank
$f_{m,totalBlank}$	Fraction modern of carbon as total blank
f_p	Fraction petrogenic
HOxI	SRM 4990B, oxalic acid created by NIST in 1955 AD (one batch, 1000 lb.).
HOxII	Oxalic acid, prepared by NIST from French beat harvests in 1970s.
K_{ah}	Partition coefficient between acetonitrile and hexane
LLNL-CAMS	Lawrence Livermore National Laboratory Center for Accelerator Mass Spectrometry
LSC	Liquid Scintillation Counting (LSC)
m_{actual}	Carbon mass of the isolated DEHP in butter
m_{coe}	Carbon mass of co-eluted compounds
$m_{DEHP,total}$	Carbon mass of DEHP measured with GC-EIMS
m_{exo}	Carbon mass of total exogenous carbon
$m_{exo,carbBtr}$	Carbon mass as carbonates from raw butter
$m_{exo,carbMtd}$	Carbon mass as carbonates from sample preparation procedures
$m_{exo,postHPLC}$	Carbon mass of exogenous carbon introduced after HPLC handling
m_{LLNL}	Carbon mass of the sample determined manometrically at LLNL
m_{MC}	Mass of Modern carbon
$m_{MC,coe}$	Modern carbon mass of each co-eluted blanks
$m_{MC,mtd}$	Modern carbon mass of the method blank
m_{mtd}	Carbon mass of DEHP that was from coetaneous method blank
m_{mtd}	Carbon mass of the method blank
$m_{totalBlank}$	Carbon mass of total blank carbon, which includes method blank, co-eluted compounds and total exogenous carbon

n	Number of perturbations
PDB	Pee Dee Belemnite
pM	Percent Modern
$purity_C$	Carbon purity of the isolated DEHP determined by GC-MS
R	isotopic ratio, either $^{14}C/^{12}C$ or $^{14}C/^{13}C$
R_{modern}	Normalized isotopic ratio of oxalic acid standard, corrected from isotopic fractionation
$R_{normSample}$	Normalized isotopic ratio of sample, corrected from isotopic fractionation
SF	Separation factor
SIM	Selected ion monitoring
$t_{1/2}$	Half-life, the Cambridge value of ^{14}C is 5730 ± 40 years
$\delta^{13}C_{btr}$	$\delta^{13}C$ fractionation for the raw butter
$\delta^{13}C_{sam}$	$\delta^{13}C$ fractionation for the isolate DEHP sample

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