

# High Throughput Analysis of Anti-Fungal Parabens in Personal-Care Products at 9 seconds per sample using Laser Diode Thermal Desorption Mass Spectrometry

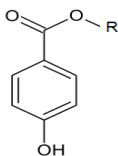
Annie-Claude Bolduc, Jean Lacoursière, Serge Auger & Pierre Picard  
Phytronix Technologies, Québec, Canada,

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## Introduction

Different varieties of cosmetics and personal-care products use parabens as an anti-fungal agent. There is controversy in the use of parabens, since adverse effects are not fully understood for concentrations typically used in body-care or cosmetics. Over the last several years, parabens have been targeted as a possible health hazard and consumers are seeking out paraben-free alternatives.

To evaluate the levels of paraben in cosmetic products, we developed a method using LDTD-MS/MS to quantify methyl, ethyl, propyl and butyl paraben in 9 seconds sample-to-sample. Sample pre-treatment consists of a liquid-liquid extraction.



**Figure 1 Paraben chemical structure**

- Methyl paraben: R=CH<sub>3</sub>
- Ethyl paraben: R= CH<sub>2</sub>-CH<sub>3</sub>
- Propyl paraben: R= CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>
- Butyl paraben: R= CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>

## LDTD-MS/MS System



**Figure 2 LDTD system on SCIEX 5500 Qtrap™ Mass Spectrometer**

## Sample Method

### Personal-care products preparation

Samples are dissolved in HCl (1N) at 1 mg/mL. Solutions are then filtered on 0.2 µm nylon to remove suppression. Two different sample dilutions of filtered solutions were performed in HCl (1N) to obtain 200 µg/mL and 20 µg/mL of cream.

### Liquid-liquid extraction

200 µL sample or calibration curve  
400 µL Ethyl Acetate  
Vortex  
Phase separation  
Transfer 5 µL of the upper organic layer onto a LazWell™ plate  
Analyze after complete solvent evaporation

### LDTD-MS/MS Parameters

Mass Spectrometer :	Sciex 5500 QTrap®	
APCI :	Negative	
Time :	20 msec	
DP :	100	
LDTD Gas Flow:	3 L/min	
Laser pattern:	Time (s)	
	0	Power (%)
	1	0
	4	0
	4.1	55
	4.2	55
		0

**Table 1 MRM method parameters for paraben**

Analyte	Q1	Q3	CE (V)
Methyl paraben	151	92	-25
Ethyl paraben	165	92	-25
Propyl paraben	179	92	-25
Butyl paraben	193	92	-25

## Results and Discussion

### Linearity

A calibration curve (0.0125-0.5000 g/kg) has been prepared in HCl (1N) and analyzed in triplicate. Correlations were all over 0.9973. **Figure 3** presents a typical calibration curve for methyl paraben.

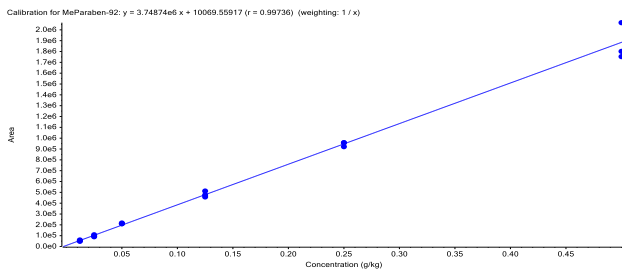


Figure 3 Typical methyl paraben standard curve

### Intra-run precision and accuracy

Reproducibility and accuracy were calculated. Results for methyl paraben have a precision lower than 15.4% and accuracy between 95.1 and 100.8%. **Table 2** shows the QCs results for methyl paraben. Similar results are obtained with ethyl, propyl and butyl paraben.

Table 2 Intra-run precision and accuracy for methyl paraben

	LLOQ	QCL	QCM	QCH	ULOQ
Conc (g/kg)	0.0125	0.0250	0.1250	0.2500	0.5000
N	3	3	3	3	3
Mean (g/kg)	0.0121	0.0238	0.1260	0.2493	0.4973
%RSD	15.4	10.5	6.0	2.4	9.0
%NOM	96.9	95.1	100.8	99.7	99.5

### Inter-run precision and accuracy

Reproducibility and accuracy were calculated. Methyl paraben results have a precision lower than 13.7% and accuracy between 97.2 and 101.6%. **Table 3** shows the QCs results for methyl paraben. Similar results are obtained with ethyl, propyl and butyl paraben.

Table 3 Inter-run precision and accuracy for methyl paraben

	QCL	QCM	QCH
Conc (g/kg)	0.0250	0.1250	0.2500
N	9	9	9
Mean (g/kg)	0.0254	0.1215	0.2450
%RSD	13.7	11.8	9.8
%NOM	101.6	97.2	98.0

### Matrix effect analysis

Samples containing parabens are evaluated with two different matrix dilutions (dilution 1: 20 µg/mL and dilution 2: 200 µg/mL). Sample

concentrations are evaluated in the standard curve. The paraben samples' content are then evaluated using the paraben amount in the samples. **Table 4** shows the content of two parabens obtained from different sample dilutions. % of difference lower than 10 is obtained.

Table 4 Matrix effect evaluation for methyl and ethyl paraben

	Dilution 1	Dilution 2	%Diff
	g/kg	g/kg	%
Methyl paraben	0.3950	0.3577	9.9
Ethyl paraben	0.1325	0.1228	7.6

### Personal-care product analysis

Three samples are analyzed. No parabens are named on the tube for sample 1 and 3. Methyl, ethyl and propyl paraben are showed in the ingredients section for sample 2. Results were reported in **Table 5**. Low concentrations of methyl and ethyl paraben are detected in sample 1 (claim: no paraben). Paraben concentration limits within the industry: the maximum of individual paraben concentration allowed in cosmetic formulas is 4 g/kg with a maximum of 8 g of total paraben per kg of product.

Table 5 Personal-care sample product results

	Sample 1	Sample 2	Sample 3
	g/kg	g/kg	g/kg
Methyl paraben	0.01875	0.3763	<0.0125
Ethyl paraben	0.01855	0.1277	<0.0125
Propyl paraben	<0.0125	0.0316	<0.0125
Butyl paraben	<0.0125	<0.0125	<0.0125



Figure 4 Sample 1



Figure 5 Sample 2



Figure 6 Sample 3

### Conclusions

LDTD technology provides a selective, accurate, sensitive and ultra-rapid analysis method, **9 seconds per sample**, for the detection and quantification of 4 parabens in personal-care products. Good linearity, precision and accuracy are obtained at concentrations ranging from 0.0125 to 0.5000 g/kg. No carryover and matrix effects were observed.

For more information about your specific application, visit [www.phytronix.com](http://www.phytronix.com)

Phytronix Technologies  
Parc technologique du Québec métropolitain  
4535, boulevard Wilfrid-Hamel, suite 120, Québec (Qc) Canada G1P 2J7  
[www.phytronix.com](http://www.phytronix.com)