Qualitative analysis of dental material ingredients, composite resins and sealants using liquid chromatography coupled to quadrupole time of flight mass spectrometry

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Introduction

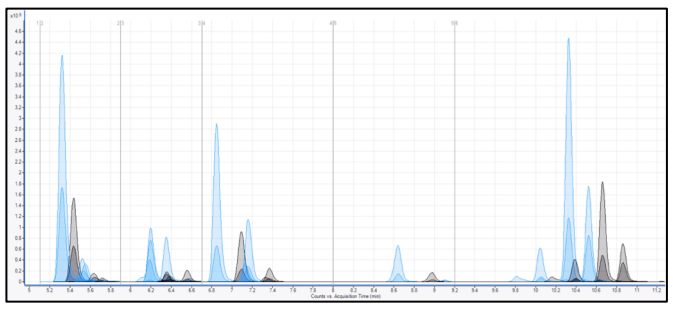
Composite resins have an increased use after the phase-down of the use of amalgam for dental restorations. These resins consist of inorganic fillers, monomers, photoinitiators, etc. However, the exact composition of these composite resins is not known as it is regarded a trade secret. In order to perform studies on the (long-term) release, degradation and metabolism of the monomers in these resins, it is necessary to identify the ingredients and possible impurities of the different materials.

Objectives

1. Develop an LC-QTOF-MS/MS method for identification of dental material ingredients
2. Identify impurities in dental material ingredients
3. Identify ingredients of composite resins & sealants

LC-QTOF-MS/MS Method Development

Initial choice of additive 2 mM NH_4Ac + Acetic acid based on Putzeys et al[1].



Optimal results for pH 3.5 in exploratory experiments (black).

Increased sensitivity when replaced by 1 mM NH_4F (blue).

Column:
Agilent Poroshell EC-C18 (3.0 x 100 mm, 2.7 µm)

Mobile Phase A:
H_2O (MilliQ) + 1 mM NH_4F

Mobile Phase B:
MeOH + 1 mM NH_4F

Temperature: 40°C

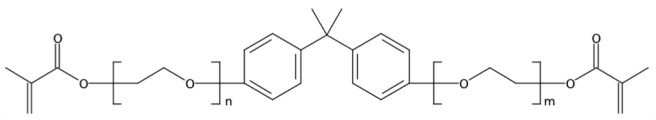
Flow: 0.4 mL / min

T (min)	%B
0	15
0.6	15
1.5	70
3	70
10	95
13	95
13.1	15
19	15

Suspect screening dental material ingredients

Analysis of 1 ng/µL reference standards using custom in-house library

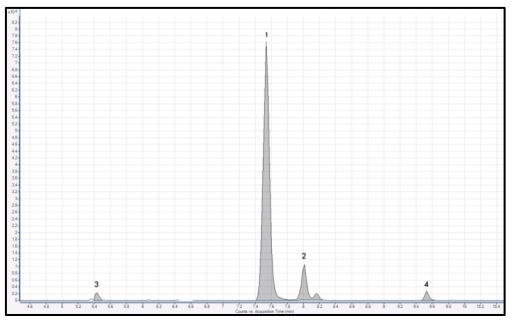
BisEMA

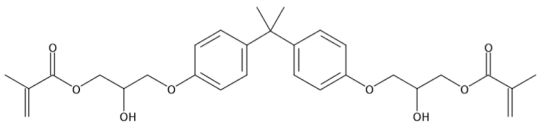


BisEMA is a group of oligomers with different amounts of ethoxy groups. In standards of different BisEMA a variety of oligomers has been identified with ethoxy groups ranging from 2 – 13 (n + m).

	BisEMA-3	BisEMA-6	BisEMA-10
BisEMA-2	X	X	
BisEMA-3	X	X	
BisEMA-4	X	X	X
BisEMA-5	X	X	X
BisEMA-5	X	X	X
BisEMA-6	X	X	X
BisEMA-7	X	X	X
BisEMA-8		X	X
BisEMA-9		X	X
BisEMA-10		X	X
BisEMA-11		X	X
BisEMA-12		X	X
BisEMA-13			X

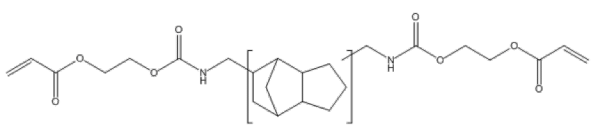
BisGMA



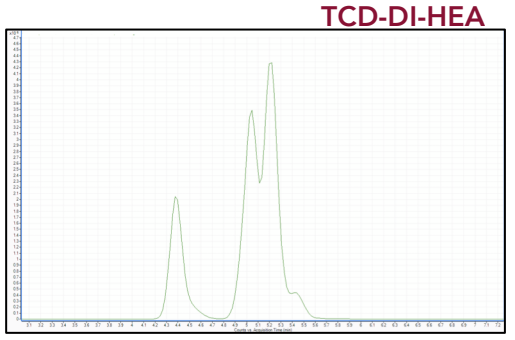


1: BisGMA
2: iso-BisGMA (isomer)
3: BisGMA-H (monomethacrylate)
4: BisGMA-M (trimethacrylate)

TCD-DI-HEA



Different isomers present in standard of TCD-DI-HEA, MS/MS fragments did not help to elucidate structure of these isomers



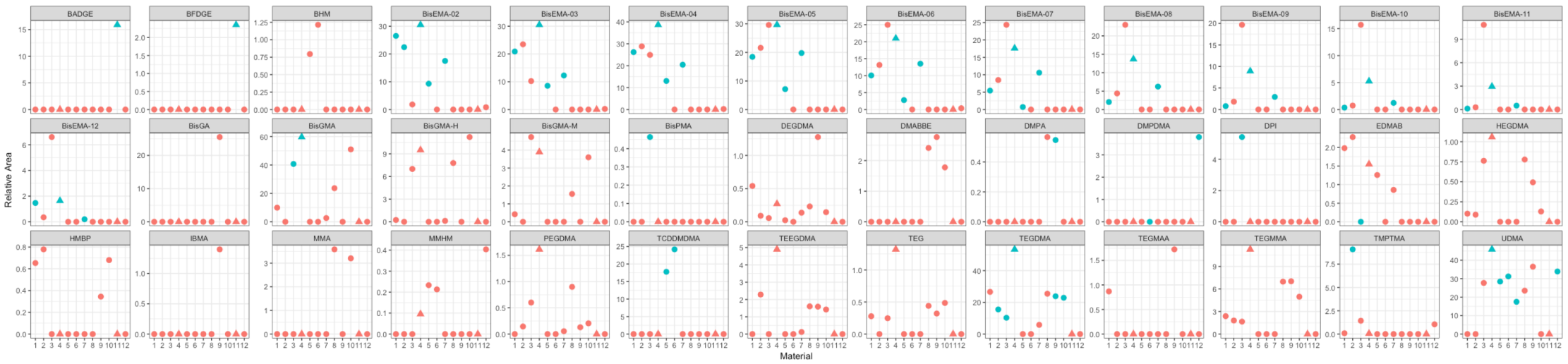
Suspect screening dental materials

Sample Preparation & Analysis

50 mg material + 50 mL MeOH → Vortex (30") + Sonicate (30') (2 cycles) → Centrifuge 5' @ 2000 rpm → 160 µL aliquot + 40 µL IS → Filter + LC-QTOF-MS analysis → Suspect Screening using in-house library

Results

For all identified features, the area in each sample was divided by the area of the deuterated internal standard (IS, d-UDMA) to obtain relative areas, allowing to compare the amount of the compound between samples. Next, safety data sheets of materials (MSDS) were checked to control whether the feature was listed or not (colored resp. blue or red).



Stated on MSDS
●: True
●: False

Material Type
●: Composite
▲: Sealant

Material
1: Ceram.X Universal ; **2:** Dyract Extra ; **3:** Filtek Supreme Flow ; **4:** Fissurit FX ; **5:** G-ænial posterior ; **6:** Gradia Direct Posterior ; **7:** N'Durance ; **8:** Quadrant Anterior ; **9:** Solitaire 2 ; **10:** Venus ; **11:** AH Plus ; **12:** G-ænial anterior

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References

1. Putzeys, E. et al., Journal of Separation Science 40(5), 2017: 1063-1075