The New Developments of Adulteration Detection for Honey

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Content

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- 2. Overview of honey adulteration detection techenologies
- 3. The new method for honey adulteration detection after 2010.

1. The current development of honey adulteration

- Honey is the natural sweet substance, produced by bees from nectar and honey dew of plants or from secretions of living parts of plants or excretions of plant-sucking insects on the living parts of plants.

- The mainly ingredients of honey are carbohydrates such as fructose, glucose, sucrose, and the other sugar. Apart from these, honey also contains vitamins, minerals, amino acids and bio-enzymes.

Raw materials added into pure honey

- Initial stage: water, sucrose, maltose, starch, and so on
- Development stage: high fructose corn syrup(HFCS), corn syrup, sugarcane syrup, and so on
- Advanced stage: Beet sugar syrup, rice syrup. And these syrup can pass the different test.

2. Overview of honey adulteration detection techenologies before 2011

- 2.1 Identified by sensory evaluation
- 2.2 Identified by physical and chemical indexes such as HMF, L-proline
- 2.3 Identified by TLC method
- 2.4 Identified by EA-IRMS method
- 2.5 Identified by LC-IRMS method
- 2.6 Identified by foreign enzyme method (BFF)

2.1 Identified by sensory evaluation

- Conventional method
- Identified by experienced experts according to the color, odor, taste, viscosity of honey
- Disadvantage: different people have different opinion

2.2 Identified by physical and chemical indexes

- Including water content, the composition of sugar, amylase activities, HMF content, L-proline content, and so on

- The quality of honey could be controled by detecting these insexes

2.3 Identified by TLC method

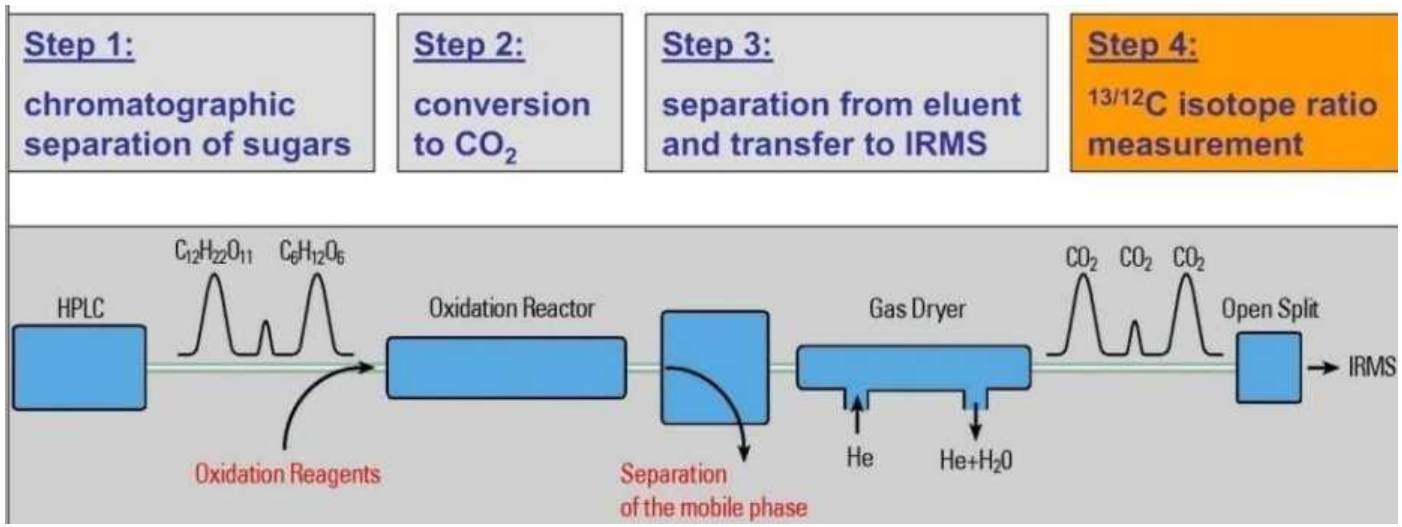
- Test acoording to GB/T 18932.2
- oligosaccharide in sample was enrichment by charcoal column and seperated by thin layer chromatography on silicon gel plate.
- This method could be used to detect honey adulterated with HFCS.
- However, qualified HFCS has been presented in market!

2.4 Identified by EA-IRMS method

- As the carbon isotope of C3 and C4 plants in photosynthetic cycles are different, the $^{13}C/^{12}C$ ratios of C3 and C4 plants fall in the range of -28~-23‰ and -15~-9‰, respectively.
- As bees mainly produce honey from C3 plants, honey samples having $\delta^{13}C$ less negative than -23.5‰ could be suspicious.
- EA-IRMS method could be used to detect honey adulterated with syrup product from C4 plants
- Disadvantage: This method can't be used to detect honey adulterated with syrup product from C3 plants!!!

2.5 Identified by LC-IRMS method

- Coupling an isotope ratio mass spectrometer to a liquid chromatography
- The fructose, glucose, di- and tri-saccharides were separated by LC and tested by IRMS.



The limits for $\Delta\delta^{13}C$ values of pure honey

- $\Delta\delta^{13}C$ (‰) $_{P - H}$
  (differences between protein and honey $\delta^{13}C$ values): ≥ -1.0‰
- $\Delta\delta^{13}C$ (‰) $_{fru\text{-}glu}$
  (differences between fructose and glucose $\delta^{13}C$ values): $\leq \pm 1.0$‰
- $\Delta\delta^{13}C$ (‰) $_{max.}$
  (maximum difference between all measured $\delta^{13}C$ values): $\leq \pm$ 2.1‰

2.6 Identified by foreign enzyme method (BFF)

- BFF was used to transfer the beet sucrose to fructose and glucose (1:1)
- The composition of the product is very close to the component of pure honey, therefore, it is very difficult to detect the adulteration with the product
- This method was developed for the determination of beta-fructofuranosidase activity in honey. to verify the adulteration of honey.

3. The New Methods for Honey Adulteration Detection

- 3.1 SM-R method for rice syrup (2011)
- 3.2 SM-B method for beet syrup (2012)
- 3.3 TMR methdo for rice syrup (2012)
- 3.3 oligosaccharide method (2012)

3.1 SM-R method

- This is a new and typical marker which was found to be presented in rice syrup and unable to be detected in pure honey

- This method could be used to detect the adulteration of honey with rice surup by the LC-MS/MS

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Rice syrup

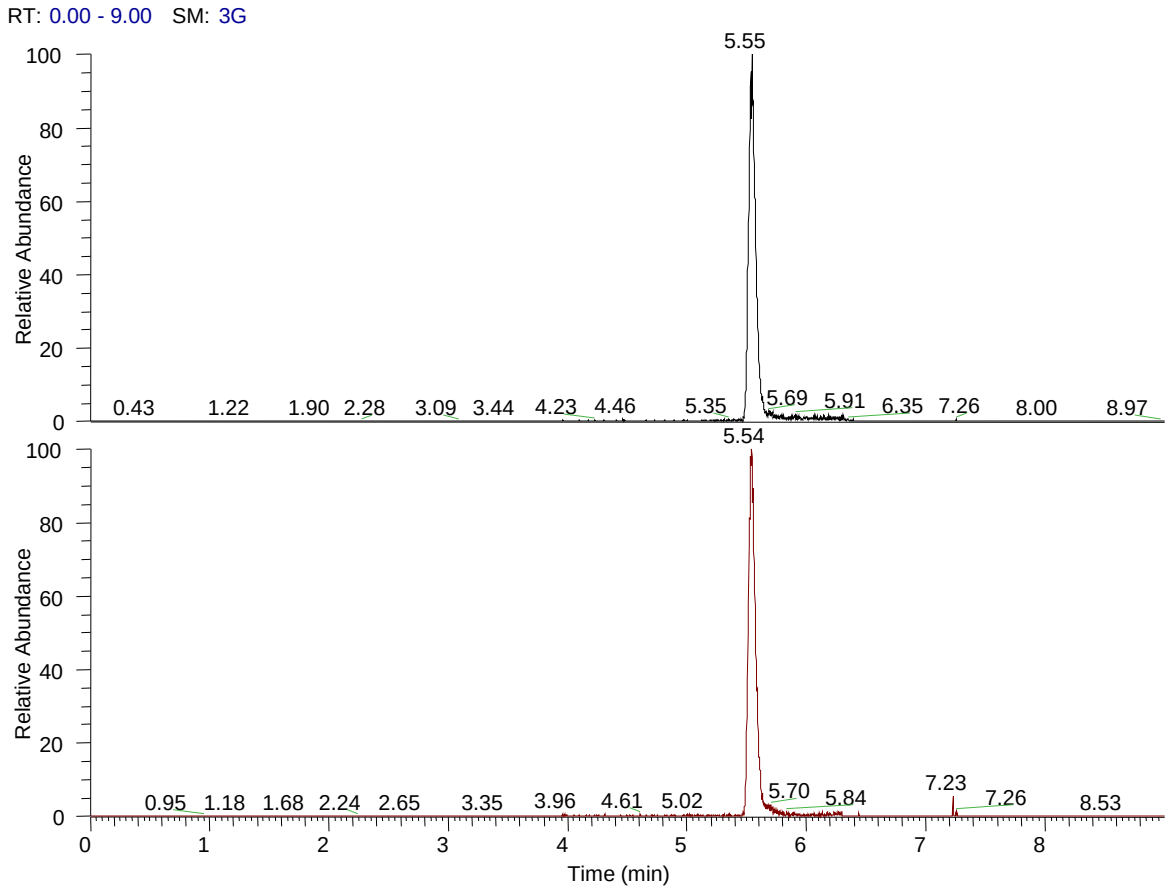


Fig.1 Chromatogram of rice syrup with rice syrup marker (SM-R)

Pure honey

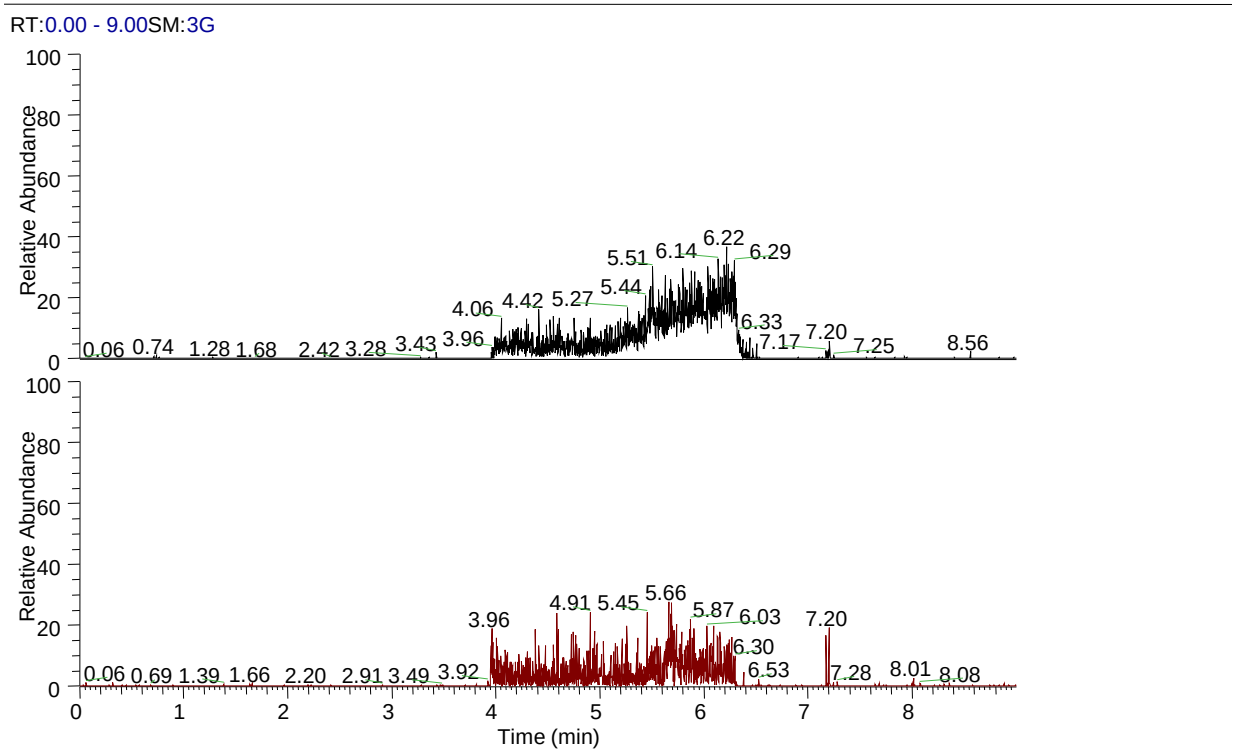


Fig.2 Chromatogram of pure honey

3.2 SM-B method

- This is a typical marker in beet syrup.

- This method could be used to detect the adulteration of honey with rice surup by the LC-MS/MS

Beet syrup

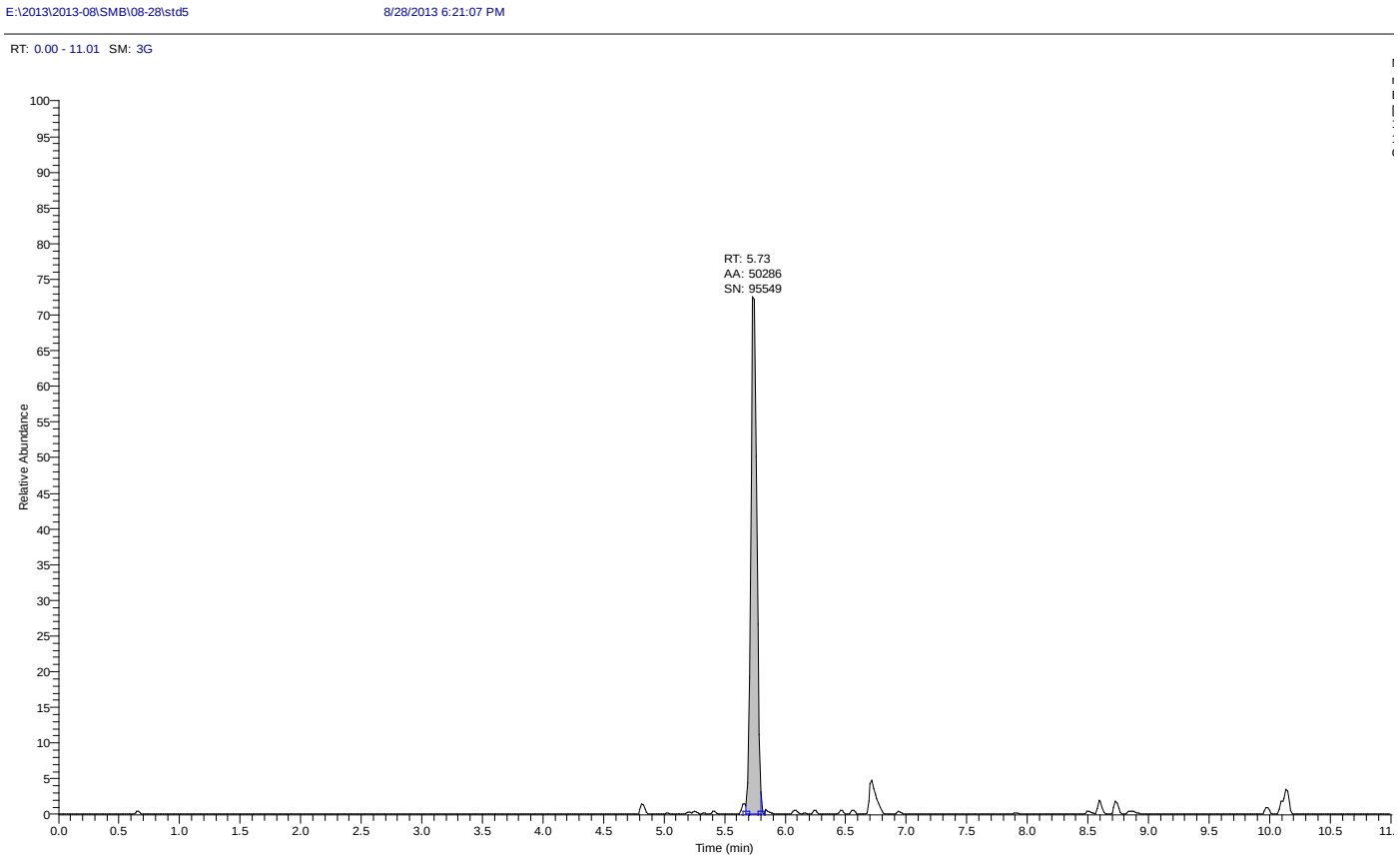


Fig.3 Chromatogram of beet syrup with beet syrup maker (SM-B)

Pure honey

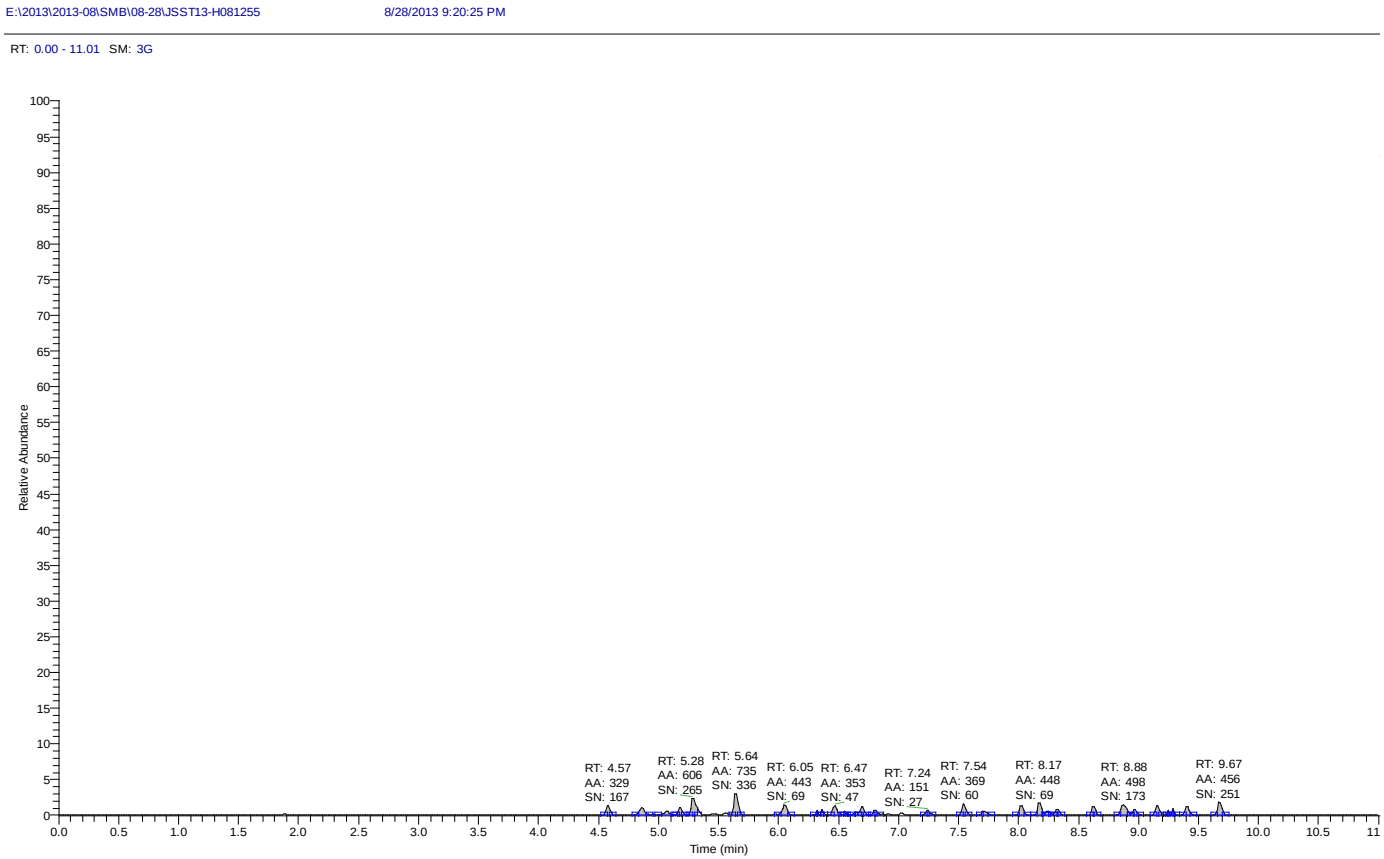


Fig.4 Chromatogram of pure honey

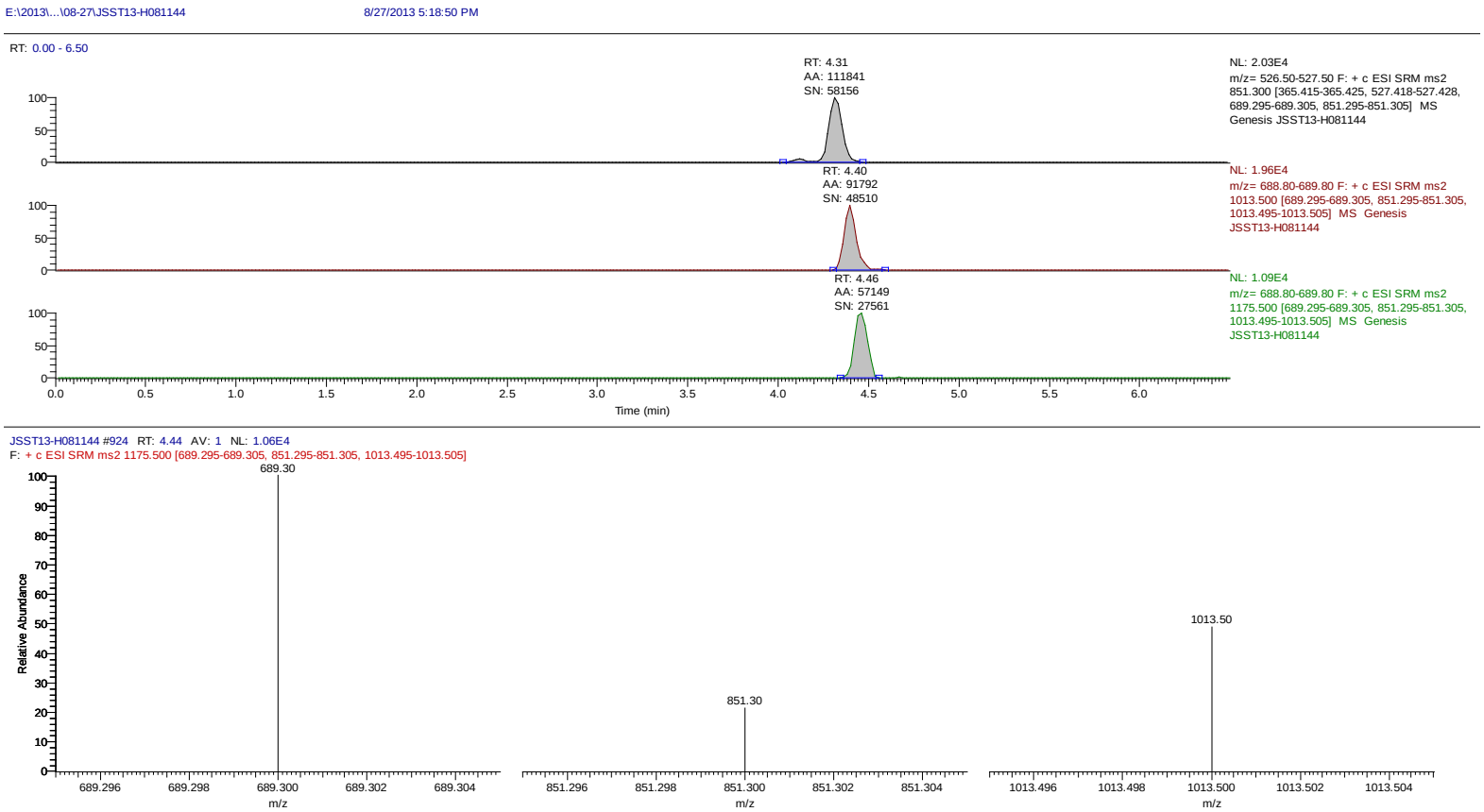
3.3 TMR method

- The method was proposed by the Intertek in 2012.
- The method detect the Arsenic in the honey to confirm the adulteration.
- The positive limit is 15ppb.

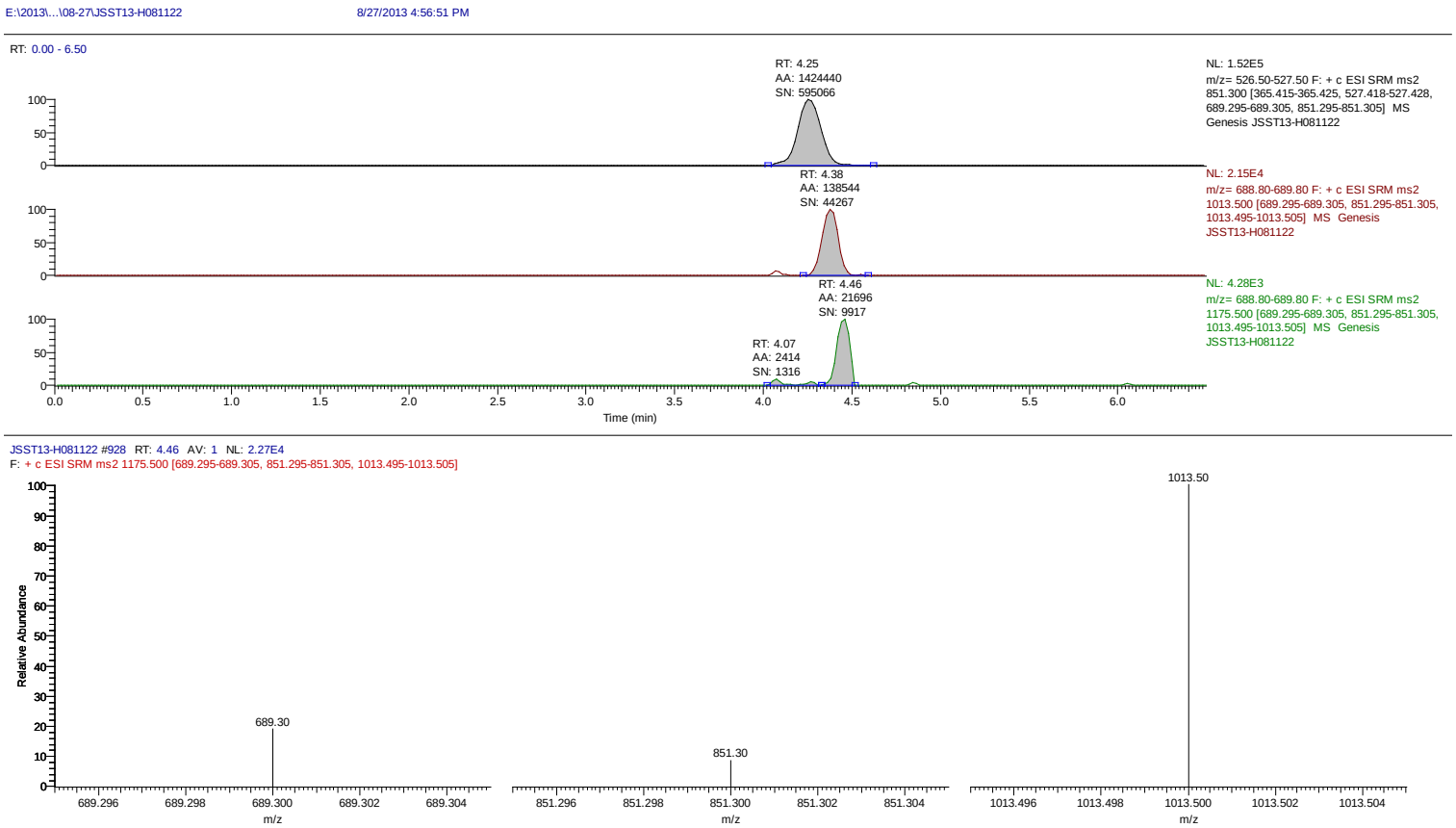
3.4 oligosaccharide method

- Improvement for the TLC method for oligosaccharide analysis.
- The method can indentify the oligosaccharide from the syrup and honeydew honey.

Syrup sample



Pure honey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Relative Abundance
689.30
851.30
1013.50
m/z

Thank you!

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