

Figure S1. ¹H NMR spectra of lime, rape, acacia and multifloral Polish honey samples in spectral region from 0 to 11 ppm.

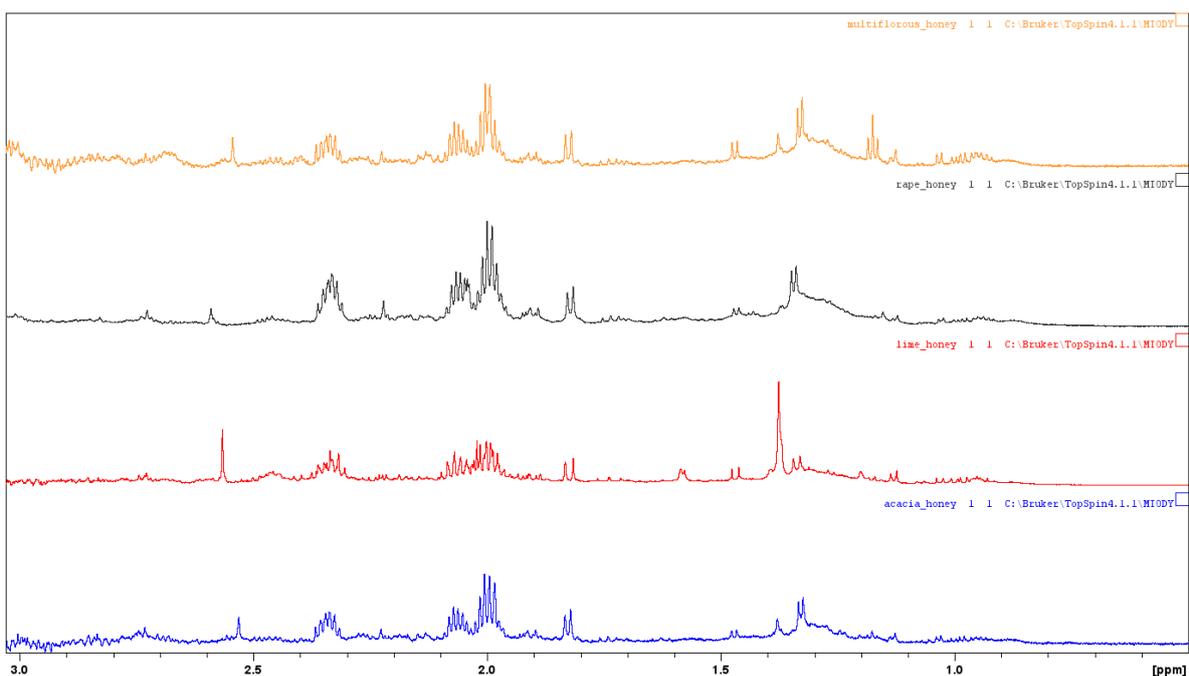


Figure S2. ¹H NMR spectra of lime, rape, acacia and multifloral Polish honey samples in spectral region from 0 to 3 ppm.

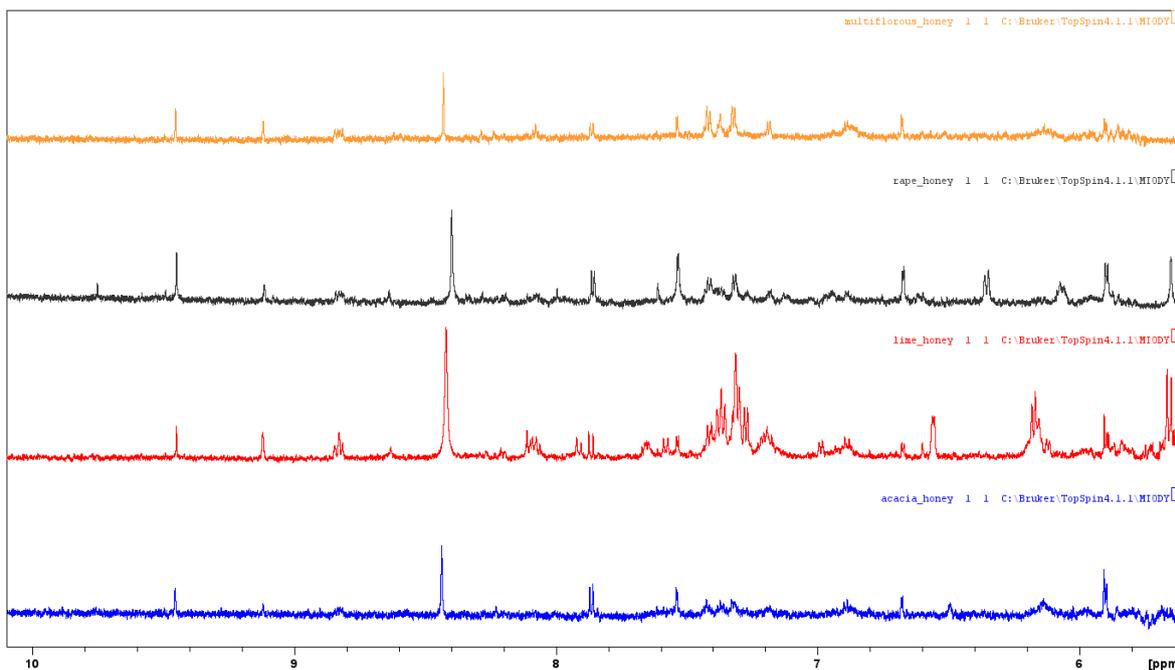


Figure S3. ^1H NMR spectra of lime, rape, acacia and multiflorous Polish honey samples in spectral region from 5.6 to 10 ppm.

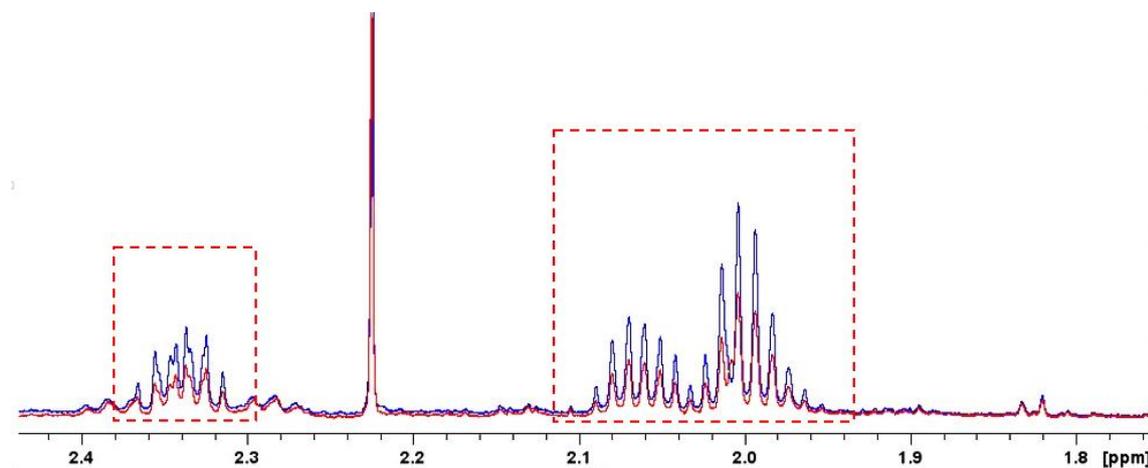


Figure S4. Expanded region of ^1H NMR spectrum of acacia honey sample (red spectrum) spiked with proline solution (blue spectrum).

^{13}C NMR spectra of analyzed honeys consisted mainly of fructose (fructofuranose and fructopyranose), glucose and sucrose signals.

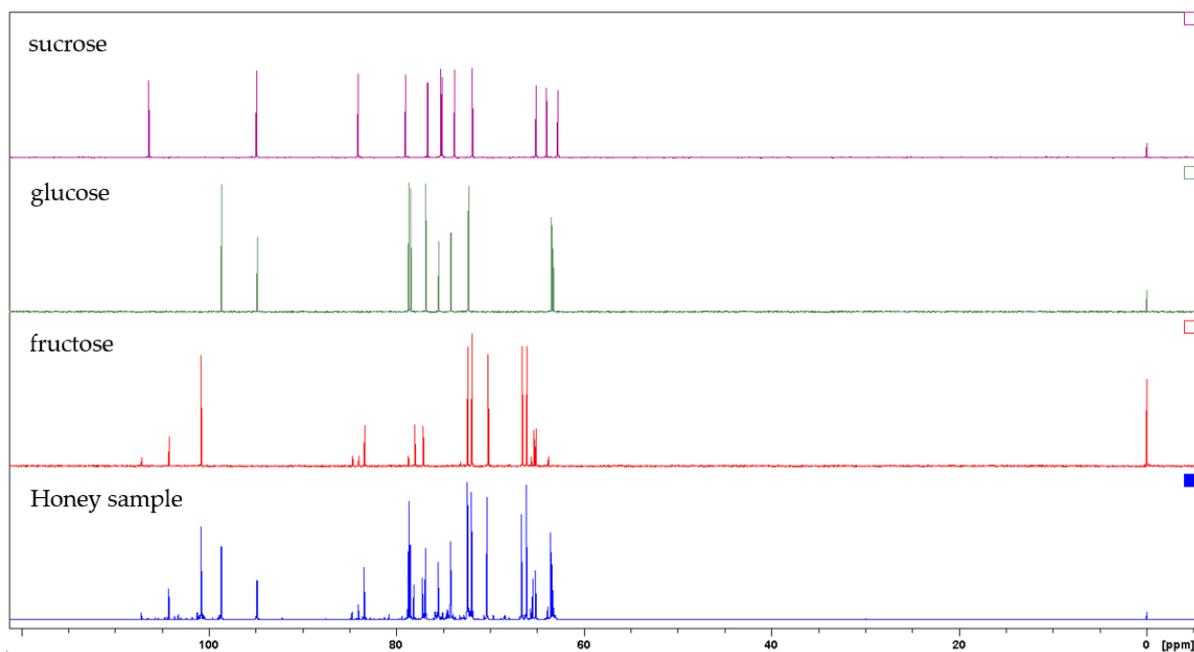


Figure S5. ^{13}C NMR spectrum of lime honey sample with ^{13}C spectra of standard sample of fructose, glucose and sucrose.

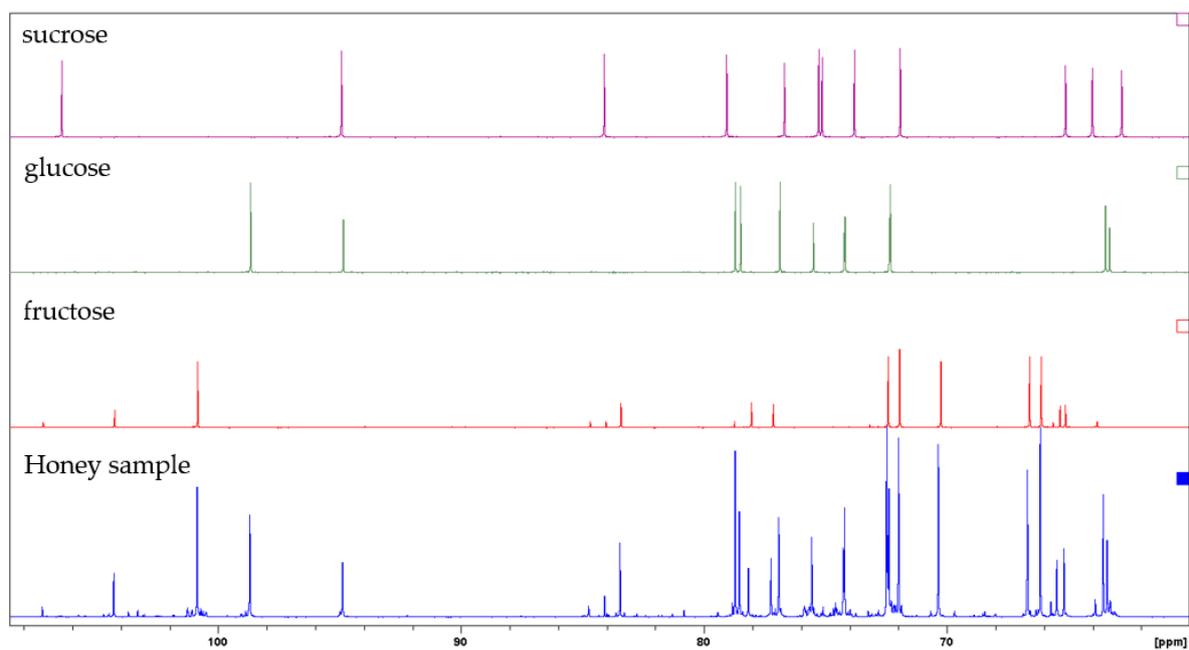


Figure S6. Expanded region of ^{13}C NMR spectrum of lime honey sample with ^{13}C spectra of standard sample of fructose, glucose and sucrose.

Table S1. The main compounds assigned in ^1H NMR spectra of honey samples, their diagnostic ^1H signals, chemical shifts δ_{H} , coupling constants, and multiplicities.

| | Compound | Chemical shift [ppm] (multiplet) |
|-----------|---------------------------------------|--|
| 1 | Valine | 0.97 (d), 1.03 (d), J=7.0 Hz |
| 2 | Ethanol | 1.18 (t), J=7.1 Hz |
| 3 | Lactic acid | 1.33 (d), J=6.9 Hz |
| 4 | Dimethyl succinic acid | 1.37 (s), 2.56 (s) |
| 5 | Alanine | 1.47 (d), J=7.2 Hz |
| 6 | Proline | 1.95-2.10 (m) 2.29-2.38 (m) |
| 7 | Fructose | 4.11(d), J=3.7 Hz |
| 8 | Arabinose | 4.49 (d), J=7.8 Hz |
| 9 | β -glucose α -glucose | 4.64 (d), J=7.9 Hz 5.22 (d), J=3.8 Hz |
| 10 | Sucrose | 5.44 (d), J=3.8 Hz |
| 11 | Tyrosine | 6.91 (d), J=8.3 Hz 7.18 (d), J=8.3 Hz |
| 12 | Phenylalanine | 7.28 (d) J=7.6 Hz 7.37 (t) 7.40(t) |
| 13 | 5-(hydroxymethyl)furfural | 6.67 (d), J=3.7 Hz 7.53 (d), J=3.7 Hz 9.45 (s) |
| 14 | 4-chlorobenzoic acid | 7.58 (d), J=8.5 Hz 7.86 (d), j=8.5 Hz |
| 15 | Formic acid* | 8.45 (s) |

*Formic acid was not detected in most of the samples. In four samples it was found in small amounts of 0.54 -0.96 mg/kg.

3. Calibration curves for quantified compounds.

To check linearity of proposed method ^1H NMR spectra for 8 series of selected compounds were recorded. In the case of glucose solutions (0.48, 0.96, 1.92, 4.21, 8.43, 17.50, 33.71 and 66.82 g/100g) ^1H NMR spectra were measured with two different repetition time: $T_r = 6\text{s}$ and 8.5s . Calibration curves for Glc were presented in the main manuscript. Each sample was analyzed in triplicate with random order. The criteria of acceptance: the recovery between 98 to 102%.

Table S2. Accuracy of applied method for Glc solutions measured with repetition time $T_r = 8.5\text{s}$.

| Number of sample | Theoretical mass [g] | Experimental mass [g] | Recovery [%] |
|------------------|----------------------|-----------------------|--------------|
| 1 | 66.82 | 67.05 ± 0.04 | 100.34 |
| 2 | 33.71 | 33.68 ± 0.03 | 99.91 |
| 3 | 17.50 | 17.48 ± 0.04 | 99.86 |
| 4 | 8.43 | 8.46 ± 0.03 | 100.35 |
| 5 | 4.21 | 4.24 ± 0.03 | 100.71 |
| 6 | 1.92 | 1.95 ± 0.04 | 101.56 |
| 7 | 0.96 | 1.07 ± 0.01 | 111.45 |
| 8 | 0.48 | 0.49 ± 0.04 | 102.08 |

Table S3. Accuracy of applied method for Glc solutions measured with repetition time $T_r = 6\text{s}$.

| Number of sample | Theoretical mass [g] | Experimental mass [g] | Recovery [%] |
|------------------|----------------------|-----------------------|--------------|
| 1 | 66.82 | 65.71 ± 0.01 | 98.34 |
| 2 | 33.71 | 33.90 ± 0.02 | 100.56 |
| 3 | 17.50 | 17.51 ± 0.03 | 100.06 |
| 4 | 8.43 | 8.40 ± 0.02 | 99.64 |
| 5 | 4.21 | 4.19 ± 0.05 | 99.52 |
| 6 | 1.92 | 1.91 ± 0.03 | 99.47 |
| 7 | 0.96 | 0.96 ± 0.02 | 100.00 |
| 8 | 0.48 | 0.47 ± 0.03 | 97.91 |

Calibration curve for fructose

In the case of fructose solutions (0.5, 5.22, 15.10, 30.26, 45.62, 60.12, 85.44 and 100 g/100g) ^1H NMR spectra were measured with selected repetition time: $T_r = 6\text{s}$. Each sample was analyzed in triplicate with random order. The criteria of acceptance: the recovery between 98 to 102%.

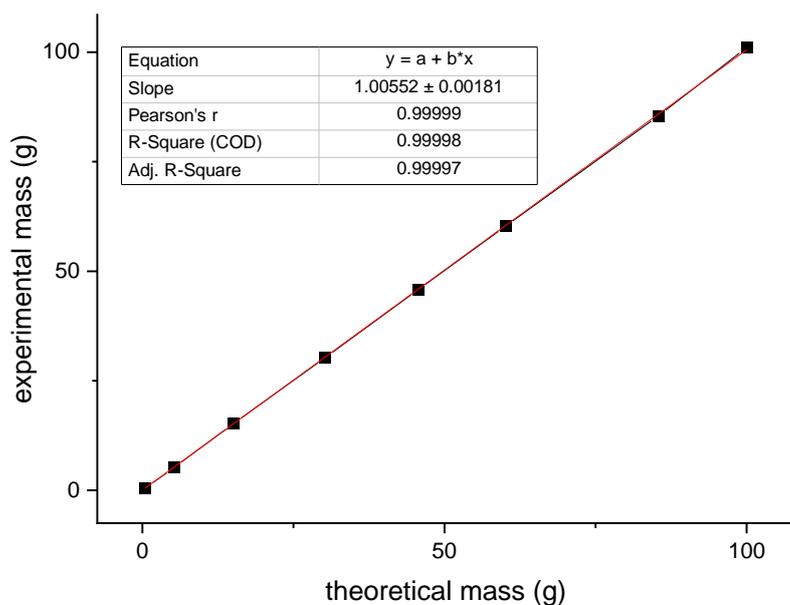


Figure S7. Linearity of the method for fructose with repetition time equals 6s.

Table S4. Accuracy of applied method for fructose solutions measured with repetition time $T_r = 6\text{ s}$.

| Number of sample | Theoretical mass [mg] | Experimental mass [mg] | Recovery [%] |
|------------------|-----------------------|------------------------|--------------|
| 1 | 0.50 | 0.49 ± 0.03 | 98.00 |
| 2 | 5.12 | 5.17 ± 0.02 | 100.97 |
| 3 | 15.10 | 15.24 ± 0.01 | 100.93 |
| 4 | 30.26 | 30.31 ± 0.03 | 101.16 |
| 5 | 45.62 | 45.78 ± 0.03 | 100.35 |
| 6 | 60.12 | 60.29 ± 0.04 | 100.28 |
| 7 | 85.44 | 85.47 ± 0.03 | 100.04 |
| 8 | 100.00 | 101.1 ± 0.02 | 101.10 |

Calibration curve for sucrose

In the case of sucrose solutions (0.05, 0.25, 0.63, 1.44, 2.88, 5.22, 7.89 and 10 g/100g) ^1H NMR spectra were measured with selected repetition time: $T_r=6\text{s}$. Each sample was analyzed in triplicate with random order. The criteria of acceptance: the recovery between 98 to 102%.

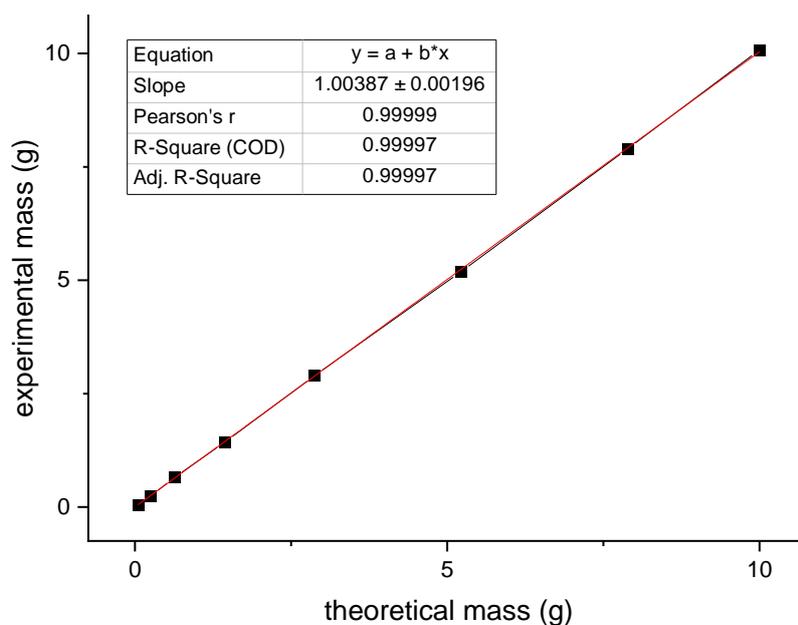


Figure S8. Linearity of the method for sucrose with repetition time equals 6s.

Table S5. Accuracy of applied method for sucrose solutions measured with repetition time $T_r=6\text{ s}$.

| Number of sample | Theoretical mass [mg] | Experimental mass [mg] | Recovery [%] |
|------------------|-----------------------|------------------------|--------------|
| 1 | 0.05 | 0.051 ± 0.01 | 102.00 |
| 2 | 0.25 | 0.24 ± 0.03 | 96.00 |
| 3 | 0.63 | 0.65 ± 0.01 | 103.17 |
| 4 | 1.44 | 1.43 ± 0.02 | 99.31 |
| 5 | 2.88 | 2.90 ± 0.03 | 100.69 |
| 6 | 5.22 | 5.19 ± 0.02 | 99.43 |
| 7 | 7.89 | 7.90 ± 0.02 | 100.13 |
| 8 | 10.00 | 10.08 ± 0.01 | 100.80 |

Calibration curve for Alanine

In the case of Ala solutions (0.49, 1.11, 1.64, 4.34, 6.03, 7.25, 8.48 and 10 mg/100g) ^1H NMR spectra were measured with selected repetition time: $T_r = 6\text{s}$. Each sample was analyzed in triplicate with random order. The criteria of acceptance: the recovery between 98 to 102%.

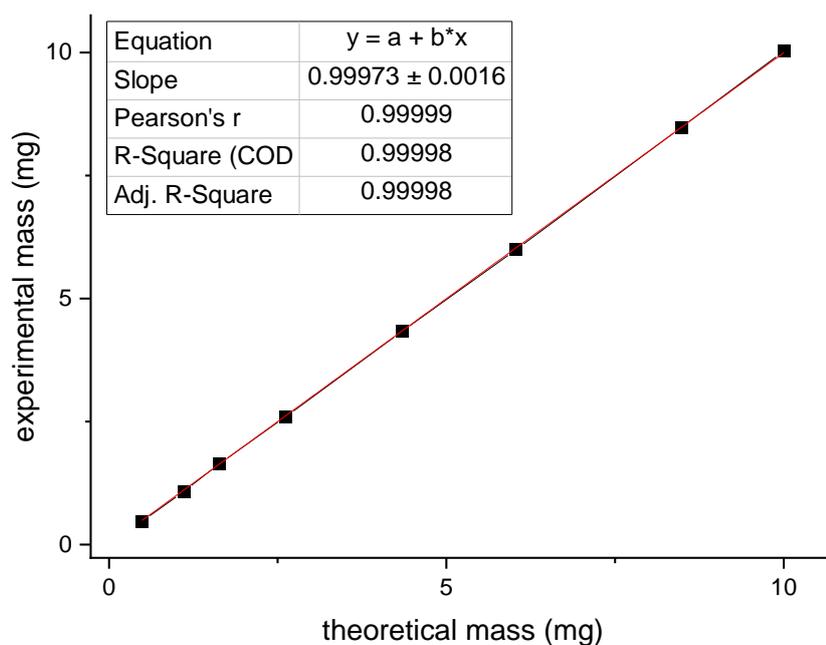


Figure S9. Linearity of the method for Ala with repetition time equals 6s.

Table S6 Accuracy of applied method for Ala solutions measured with repetition time $T_r = 6\text{s}$.

| Numer of sample | Theoretical mass [mg] | Experimental mass [mg] | Recovery [%] |
|-----------------|-----------------------|------------------------|--------------|
| 1 | 0.49 | 0.47±0.01 | 95.92 |
| 2 | 1.11 | 1.08±0.02 | 97.30 |
| 3 | 1.64 | 1.65±0.01 | 100.61 |
| 4 | 2.62 | 2.60±0.01 | 99.24 |
| 5 | 4.34 | 4.33±0.02 | 99.77 |
| 6 | 6.03 | 5.99±0.02 | 99.34 |
| 7 | 8.48 | 8.48±0.02 | 100.00 |
| 8 | 10.00 | 10.03±0.02 | 100.30 |

Calibration curve for Phenylalanine

In the case of Phe solutions (0.50, 1.52, 3.39, 6.55, 9.40, 11.53, 17.38 and 20 mg/100g) ^1H NMR spectra were measured with selected repetition time: $T_r = 6\text{s}$. Each sample was analyzed in triplicate with random order. The criteria of acceptance: the recovery between 98 to 102%.

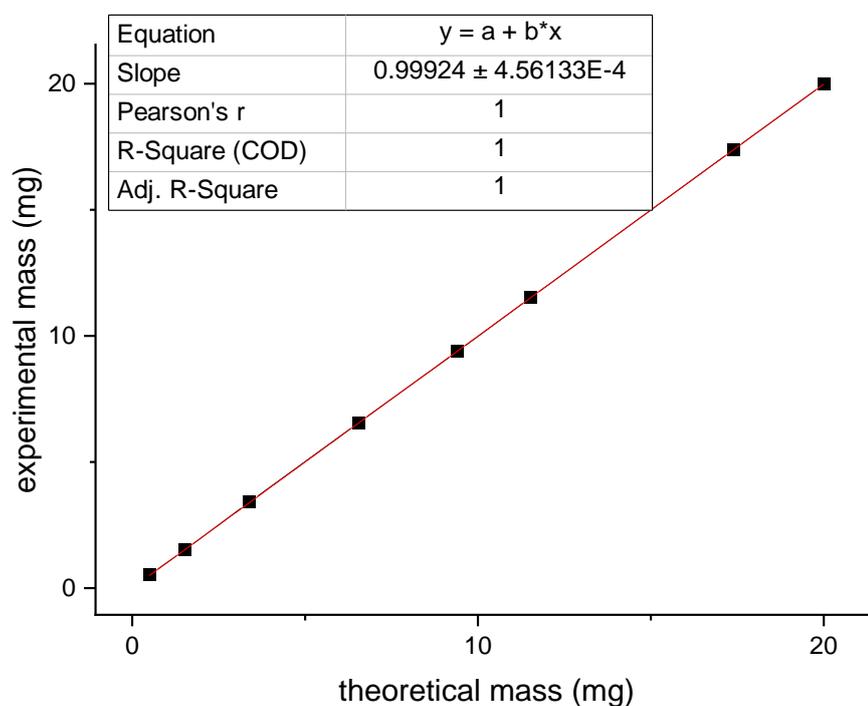


Figure S10. Linearity of the method for Phe with repetition time equals 6s.

Table S7. Accuracy of applied method for Phe solutions measured with repetition time $T_r = 6\text{s}$.

| Number of sample | Theoretical mass [mg] | Experimental mass [mg] | Recovery [%] |
|------------------|-----------------------|------------------------|--------------|
| 1 | 0.50 | 0.52 ± 0.04 | 104.00 |
| 2 | 1.52 | 1.51 ± 0.04 | 99.34 |
| 3 | 3.39 | 3.41 ± 0.04 | 100.59 |
| 4 | 6.55 | 6.56 ± 0.03 | 100.15 |
| 5 | 9.40 | 9.38 ± 0.04 | 99.79 |
| 6 | 11.53 | 11.52 ± 0.03 | 99.91 |
| 7 | 17.38 | 17.37 ± 0.01 | 99.94 |
| 8 | 20.00 | 19.98 ± 0.02 | 99.90 |

Calibration curve for tyrosine

In the case of Tyr solutions (0.48, 1.55, 3.26, 7.31, 10.45, 13.50, 16.40 and 20.07 mg/100g) ^1H NMR spectra were measured with selected repetition time: $T_r = 6\text{s}$. Each sample was analyzed in triplicate with random order. The criteria of acceptance: the recovery between 98 to 102%.

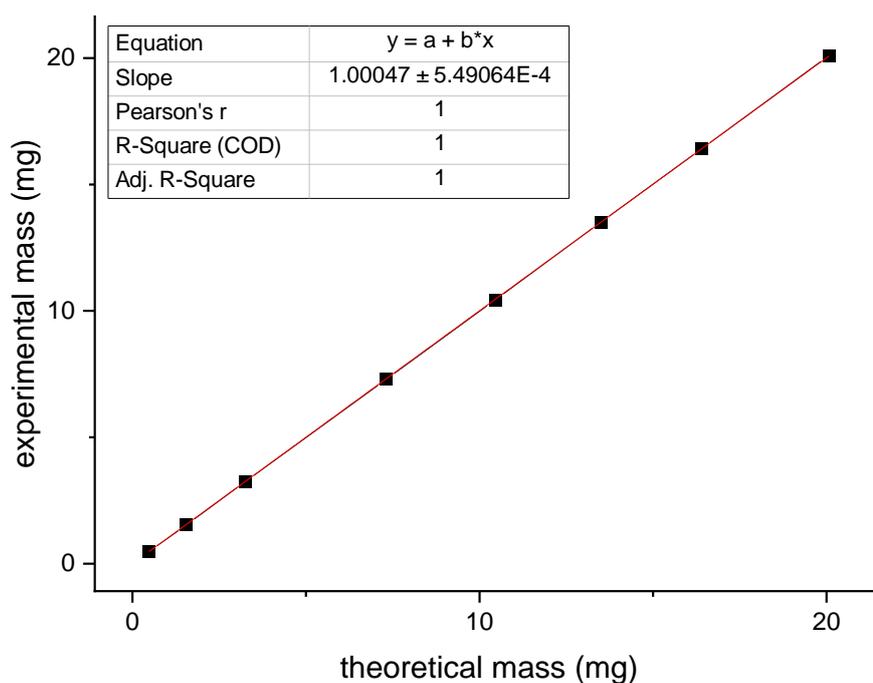


Figure S11. Linearity of the method for Tyr with repetition time equals 6s.

Table S8. Accuracy of applied method for Tyr solutions measured with repetition time $T_r = 6\text{s}$.

| Numer of sample | Theoretical mass [mg] | Experimental mass [mg] | Recovery [%] |
|-----------------|-----------------------|------------------------|--------------|
| 1 | 0.48 | 0.48 ± 0.02 | 100.00 |
| 2 | 1.55 | 1.53 ± 0.03 | 98.71 |
| 3 | 3.26 | 3.25 ± 0.02 | 99.69 |
| 4 | 7.31 | 7.29 ± 0.03 | 99.73 |
| 5 | 10.45 | 10.43 ± 0.03 | 99.81 |
| 6 | 13.50 | 13.51 ± 0.01 | 100.07 |
| 7 | 16.41 | 16.42 ± 0.02 | 100.06 |
| 8 | 20.07 | 20.10 ± 0.01 | 100.15 |

Calibration curve for proline

In the case of Pro solutions (0.52, 1.57, 4.98, 10.86, 22.18, 49.87, 67.32 and 80.12 mg/100g) ^1H NMR spectra were measured with selected repetition time: $T_r = 6\text{s}$. Each sample was analyzed in triplicate with random order. The criteria of acceptance: the recovery between 98 to 102%.

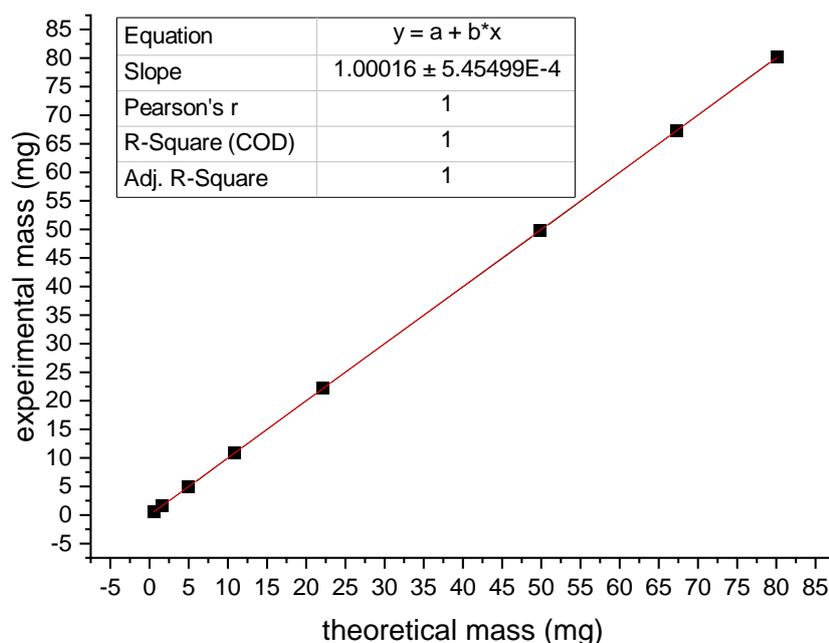


Figure S12. Linearity of the method for Pro with repetition time equals 6s.

Table S9. Accuracy of applied method for Pro solutions measured with repetition time $T_r = 6\text{s}$.

| Numer of sample | Theoretical mass [mg] | Experimental mass [mg] | Recovery [%] |
|-----------------|-----------------------|------------------------|--------------|
| 1 | 0.52 | 0.54± 0.03 | 103.85 |
| 2 | 1.57 | 1.59±0.01 | 98.59 |
| 3 | 4.98 | 4.91±0.02 | 99.82 |
| 4 | 10.86 | 10.84±0.03 | 100.09 |
| 5 | 22.18 | 22.20±0.03 | 99.76 |
| 6 | 49.87 | 49.75±0.03 | 100.04 |
| 7 | 67.32 | 67.35±0.04 | 100.10 |
| 8 | 80.12 | 80.20±0.02 | 101.27 |

Calibration curve for hydroxymethylfurfural

In the case of HMF solutions (0.50, 0.97, 1.48, 2.51, 5.52, 10.11, 18.66 and 30.25 mg/1000g) ^1H NMR spectra were measured with selected repetition time: $T_r = 6\text{ s}$. Each sample was analyzed in triplicate with random order. The criteria of acceptance: the recovery between 95 to 105%.

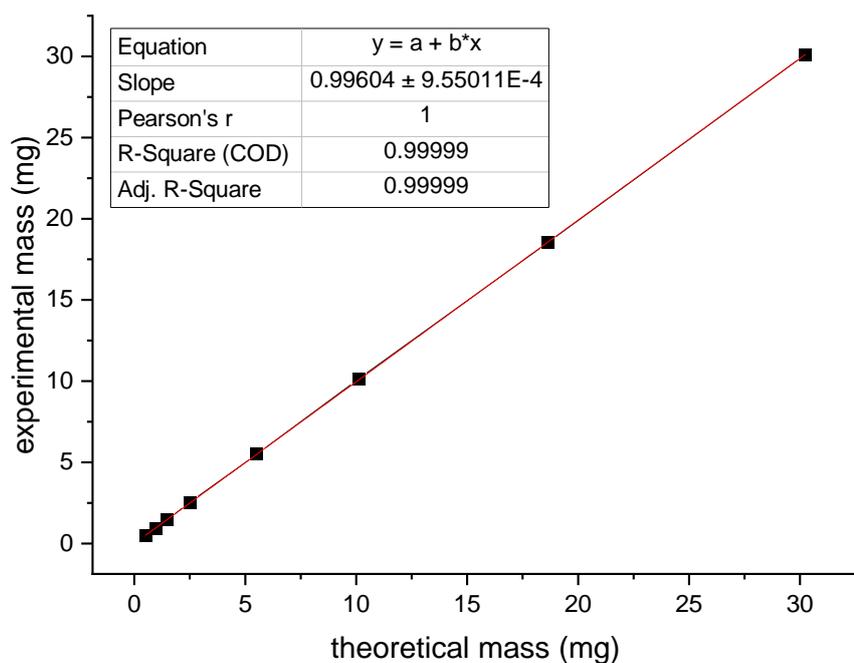


Figure S13. Linearity of the method for HMF with repetition time equals 6s.

Table S10. Accuracy of applied method for HMF solutions measured with repetition time $T_r = 6\text{ s}$.

| Numer of sample | Theoretical mass [mg] | Experimental mass [mg] | Recovery [%] |
|-----------------|-----------------------|------------------------|--------------|
| 1 | 0.50 | 0.48 ± 0.04 | 96.00 |
| 2 | 0.97 | 0.95 ± 0.03 | 97.94 |
| 3 | 1.48 | 1.46 ± 0.03 | 98.65 |
| 4 | 2.51 | 2.55 ± 0.02 | 101.59 |
| 5 | 5.52 | 5.50 ± 0.03 | 99.64 |
| 6 | 10.11 | 10.14 ± 0.02 | 100.30 |
| 7 | 18.66 | 18.56 ± 0.01 | 99.46 |
| 8 | 30.25 | 30.12 ± 0.01 | 99.57 |