Formulae for calculation of lignin content and relative abundance by $^{13}$C-IS py-GC-MS

$$ RRF_{\text{run},i} = RRF_{\text{start},i} \cdot \frac{A_{\text{WS ref},i}^{\text{WS ref}}}{A_{\text{WS ref},i}^{\text{WS ref}}} \cdot \frac{A_{\text{start},i}^{\text{start}}}{A_{\text{run},i}^{\text{run}}} \cdot \frac{\sum_{i=1}^{43} A_{\text{WS ref},i}^{\text{WS ref}}}{\sum_{i=1}^{43} A_{\text{run},i}^{\text{run}}} \cdot \frac{m_{\text{IS}}}{m_{\text{sample}}} \cdot 100 \quad (1) $$

where $i$ refers to compound number (Table S-1) (only initially monitored products included (1)), $A$ is peak area of reference wheat straw at system performance relative response factors (RRF) were determined (‘start’) and in each run performed (‘run’). $M_w$ is the molecular weight. Run refers to one sequence of measurements.

$$ \text{Lignin content (w/w)\%} = \frac{\sum_{i=1}^{49} A_{i}^{12C} M_{w12C} m_{\text{IS}}}{\sum_{i=1}^{49} A_{i}^{13C} M_{w13C} m_{\text{sample}}} \cdot 100 \quad (2) $$

where $i$ refers to compound number (Table S-1), $A$ is area, $RRF_{\text{run}}$ is corrected relative response factor, $m_{\text{IS}}$ is the amount of IS (corrected for purity) ($\mu$g; $^{13}$C-LIGpure), $m_{\text{sample}}$ is the amount of sample ($\mu$g).

$$ \text{Relative abundance (RA)} \quad (\%) = \frac{A_{i}}{\sum_{i=1}^{49} A_{i}} \cdot 100 \quad (3) $$

where $i$ refers to compound number (Table S-1), $A$ is area, $RRF_{\text{run}}$ is corrected relative response factor.

$$ \text{Relative abundance factor (RAF)}_{i}^{13C} = \frac{RA_{i}^{13C, IS}}{RA_{i}^{13C, \text{WS ref}}} \quad (4) $$

where $i$ refers to compound number (Table S-1), RA is relative abundance.

$$ \text{Relative abundance } i, \text{corrected} = \frac{RA_{i}}{RAF_{i}^{13C}} \cdot \left( \frac{100}{\sum_{i=1}^{49} RA_{i}} \right) \quad (5) $$

where $i$ refers to compound number (Table S-1), RA is relative abundance, RAF is relative abundance factor (eq 4)

**References**