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Short communication

The hidden isotope fractionation: How temperature of pyrolysis coupled to compound-specific isotope analysis shapes $\delta^{13}C$ results

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ABSTRACT

Pyrolysis compound-specific isotope analysis (Py-CSIA) is a relatively novel hyphenated technique for which no standard materials have yet been developed. For conventional CSIA (GC-C/IRMS), isotopically characterized standards are routinely used to construct calibration curves and to validate and correct analytical data. In this work, we test the suitability of the C4 CSIA standard (Indiana University, Stable Isotope Laboratory), a mixture of five odd-chain *n*-alkanes (C_{17}–C_{25} in decreasing concentration dissolved in hexane), as a reference material for $\delta^{13}C$ measurements by Py-CSIA and evaluate the effect of pyrolysis temperature on carbon isotope composition. Aliquots of the C4 standard were deposited onto glass fibre discs in deactivated steel capsules and pyrolysed at five temperatures (250, 300, 400, 500 and 600°C) in a micro-furnace pyrolizer coupled online to a GC-C/IRMS system; an additional direct injection (DI) GC-C/IRMS analysis of C4 was used as the reference. Each condition was analysed in ten replicate runs. Overall, $\delta^{13}C$ values obtained by Py-CSIA showed excellent agreement with DI measurements, with no significant isotope fractionation observed across the tested temperature range, and coefficients of determination (R^2) greater than 0.96 for all temperatures. No statistically significant temperature effect was observed for C_{19}, C_{21}, C_{23}, or C_{25}, whereas C_{17} was the only compound showing a significant response. A slight visual ^{13}C-enrichment trend was observed at 500°C, although this was not statistically significant, while at 600°C the $\delta^{13}C$ values converged towards the DI reference values and reproducibility improved. The more negative $\delta^{13}C$ values observed at 250°C are more consistently explained by incomplete volatilization and/or incomplete transfer of the heavier *n*-alkanes than by clear pyrolytic fractionation, although minor thermal transformation effects cannot be fully excluded. These results indicate that the C4 saturated linear *n*-alkane mixture is suitable as a working standard for Py-CSIA under the analytical conditions tested, and that elevated pyrolysis temperatures, particularly 600°C, provide the most robust balance between isotopic fidelity and reproducibility for this compound class. Further work is needed to determine whether this behaviour also applies to other compound classes and more complex organic matrices.

1. Introduction

Compound-specific isotope analysis (CSIA) has revolutionized our understanding of biogeochemical processes by enabling the precise determination of stable isotope ratios of light bioelements—such as $\delta^{13}C$, $\delta^{15}N$, and $\delta^{2}H$—at the level of individual molecular compounds [1,2]. Among the various CSIA techniques, pyrolysis-based compound-specific isotope analysis (Py-CSIA) has gained increasing attention for its ability to analyse complex and often refractory organic materials without prior chemical extraction or derivatization. This approach is particularly valuable in studies of soils [3,4], sediments [5], lava tube speleothems [6], and polymers/other heterogeneous organic matrices [7–9] where conventional extraction-based methods may alter or miss important fractions of organic matter. Moreover, in some cases the amount of sample is so small that it is not possible to carry out an effective pre-treatment.

Despite its analytical power, Py-CSIA presents a series of methodological challenges that are not yet fully understood or standardized. One of the most critical and underappreciated variables is the temperature at which pyrolysis is performed. Pyrolysis consists of a high-temperature

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process that thermochemically cleaves macromolecular organic matter into smaller volatile fragments [10]. In analytical terms, this process has been used for analysing these volatile fragments as amenable to gas chromatography [11]. When pyrolysis is coupled with isotope ratio mass spectrometry (IRMS), the determination of the carbon isotope ($\delta^{13}C$) composition of pyrolysis fragments can be significantly influenced by operational conditions, particularly temperature. Increasing pyrolysis temperature alters the extent and pathways of thermal degradation by modulating bond cleavage mechanisms, secondary reactions, and volatilization behaviour. For example, in an open-system shale pyrolysis study, rising temperatures led to systematic shifts in $\delta^{13}C$ values: methane became isotopically lighter (enriched in ^{12}C), while ethane became heavier (enriched in ^{13}C), a trend attributed to temperature-driven differences in reaction rates of ^{12}C- and ^{13}C-containing radicals during bond cleavage and recombination [12].

Additional studies have confirmed this trend, showing that $\delta^{13}C$ values of CH_4 initially become more negative and then less negative with increasing temperature [13,14]. This nonlinear behaviour is chemically explained by the kinetic isotope effect (KIE), where ^{12}C–C bonds crack and recombine more readily than ^{13}C–C bonds, leading to variable isotope fractionation during hydrocarbon generation from kerogen [15, 16].

A comparable effect is observed in biomass pyrolysis systems. Studies involving lignin and cellulose have shown that at elevated temperatures (>400 °C), primary depolymerization is followed by complex secondary reactions such as demethylation, decarboxylation, and repolymerization [17,18]. These transformations can further modulate both the molecular composition and isotope signatures of the pyrolysis products. Despite these observations, the effect of pyrolysis temperature on the carbon isotope composition of gases released from certified reference materials remains poorly constrained, particularly in the context of compound-specific isotope analysis (CSIA). This gap underscores the need for systematic investigations under controlled experimental conditions.

While the temperature-dependent mechanisms influencing carbon isotope composition during pyrolysis are becoming better understood, efforts to generalize these findings across compound classes and sample types remain ongoing. Emerging evidence suggests that increasing pyrolysis temperatures may introduce systematic biases in $\delta^{13}C$ measurements due to thermal isotope fractionation. This "hidden" fractionation can distort the original isotope signals of source compounds, potentially leading to misinterpretation of carbon sources, degradation pathways, and ecosystem dynamics. These effects are particularly problematic in comparative studies and long-term monitoring programs, where analytical consistency is critical for detecting genuine environmental trends [4].

To date, the potential for temperature-induced $\delta^{13}C$ fractionation in Py-CSIA has not been thoroughly quantified, and its implications remain largely overlooked in environmental isotope research. Most studies assume isotope fidelity between pyrolysis products and their precursors without testing the robustness of this assumption across temperature gradients [4,6–8,19,20]. As a result, there is a pressing need to systematically investigate how pyrolysis temperature affects the $\delta^{13}C$ values of representative organic compounds across different sample types.

In this study, we address this critical knowledge gap by evaluating the influence of pyrolysis temperature on $\delta^{13}C$ measurements in a controlled Py-CSIA setting. Using a saturated *n*-alkane mixture standard, we examine the carbon isotope variation correlated with increasing thermal energy and assess the extent to which observed variations reflect analytical artefacts versus true compositional differences. By disentangling these effects, we aim to provide a methodological framework to enhance the accuracy, reproducibility, and interpretative reliability of Py-CSIA data.

2. Materials and methods

2.1. Standard material

The experiment was carried out using a saturated *n*-alkane mixture (heptadecane - C_{17}, nonadecane - C_{19}, heneicosane - C_{21}, tricosane - C_{23}, and pentacosane - C_{25}) type C4 standard (Biogeochemical Laboratories, Indiana University, U.S.A). The $\delta^{13}C$ of individual compounds from C4 standard was produced by the Biogeochemical Laboratories (Indiana University, U.S.A).

2.2. Pyrolysis-Compound-Specific isotopic analysis ($\delta^{13}C$ Py-CSIA)

The saturated *n*-alkanes mixture standard carbon isotope composition ($\delta^{13}C$) of individual compounds was determined by direct Py-GC-C/IRMS (hereafter, Py-CSIA). This was performed by a double-shot pyrolyzer model 3030D (Frontier Laboratories Ltd., Fukushima, Japan). Aliquots of the *n*-alkane mixture standard (5 μL) were poured on ultra-clean glass wool discs and introduced into small pyrolysis capsules (Eco-Cup LF – Frontier Laboratory). The capsules were introduced into a pre-heated microfurnace at 5 different temperatures (250, 300, 400, 500, and 600 °C), with an interface at 250°C, heated for 1 min and the evolved gases directly injected into the GC/C-IRMS for analysis.

The pyrolyzer is attached to a Trace GC Ultra system (Thermo Scientific), which is connected to a GC-IsoLink II system (Thermo Scientific). This GC interface is equipped with a micro-reactor for combustion (C), set at 1020°C. The GC system is coupled to a Delta V Advantage isotope ratio mass spectrometer (Thermo Scientific) via a ConFlo IV universal interface (Thermo Scientific).

The chromatographic separation of the *n*-alkane compounds was performed using an Agilent J&W HP-5 ms UI capillary column (30 m × 250 μm × 0.25 μm). The GC oven temperature was held at 50°C for 1 min and then increased to 100°C at 20°C min^{-1}, increased from 100 to 300°C at 10°C min^{-1}, and maintained at 300°C for 10 min. The carrier gas used was He at a controlled flow of 1 mL min^{-1}. Each chromatographic compound was gasified in the IsoLink System, and pure CO_2 and H_2 were mixed into the He carrier flow as pulses of reference gases.

The stable isotope determinations are reported in the delta (δ) notation (e.g., $\delta^{13}C$) relative to an international measurement standard. The isotope value is defined in [21], according to Eq.1.

$$\delta^{13}C_{sample} = \frac{R\left(\frac{^{13}C}{^{12}C}\right)sample}{\left(\frac{^{13}C}{^{12}C}\right)standard} - 1 \quad (1)$$

Where "*R*" is the molar ratio of the heavy (^{13}C) to light (^{12}C) most abundant isotope of carbon. The "δ" values are reported in per mil (‰). The stable isotope standard for reporting carbon measurements is the Vienna Pee Dee Belemnite limestone (V-PDB scale). The final isotope value was corrected using background subtractions using an individual peak definition strategy, using the ISODAT 3.0 software (Thermo Scientific, Bremen, Germany).

2.3. Statistical analyses

The precision of measurements, expressed as the standard deviation ('σ') obtained from at least 10 replicate analyses of the *n*-alkane mixture standard at each pyrolysis temperature, was up to 0.5 ‰ for $\delta^{13}C$. Control charts were made as part of the statistical approach to evaluate the stability of the analytical measurements. In these charts, the variable of interest ($\delta^{13}C$ values of individual *n*-alkanes) was plotted against the number of measurements for each *n*-alkane compound. The central line corresponded to the mean value of the dataset for each parameter, including warning limits (mean ± 2 σ) and control limits (mean ± 3 σ). These limits define the acceptable range of analytical variability within

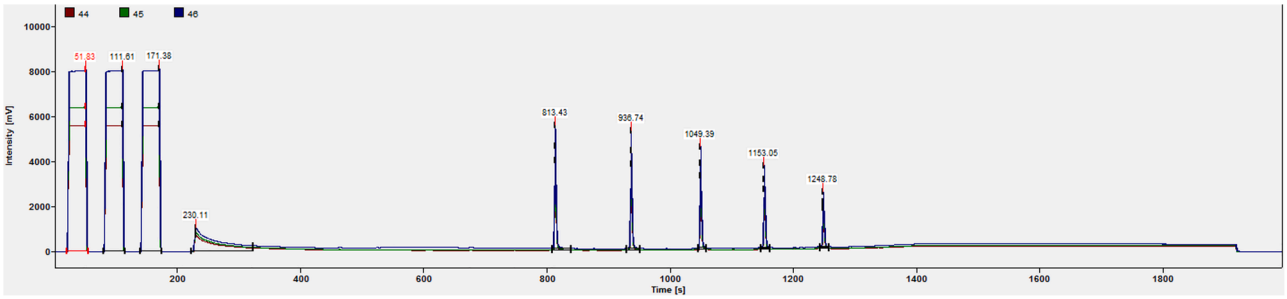

Fig. 1. Py-GC-C/IRMS $\delta^{13}C$ chromatogram of n-alkane mixture. Peaks shown in order: heptadecane - C_{17}, nonadecane - C_{19}, heneicosane - C_{21}, tricosane - C_{23}, and pentacosane - C_{25}. The first three peaks of the chromatogram panel are reference gas signals; the fourth correspond to the solvent (hexane).

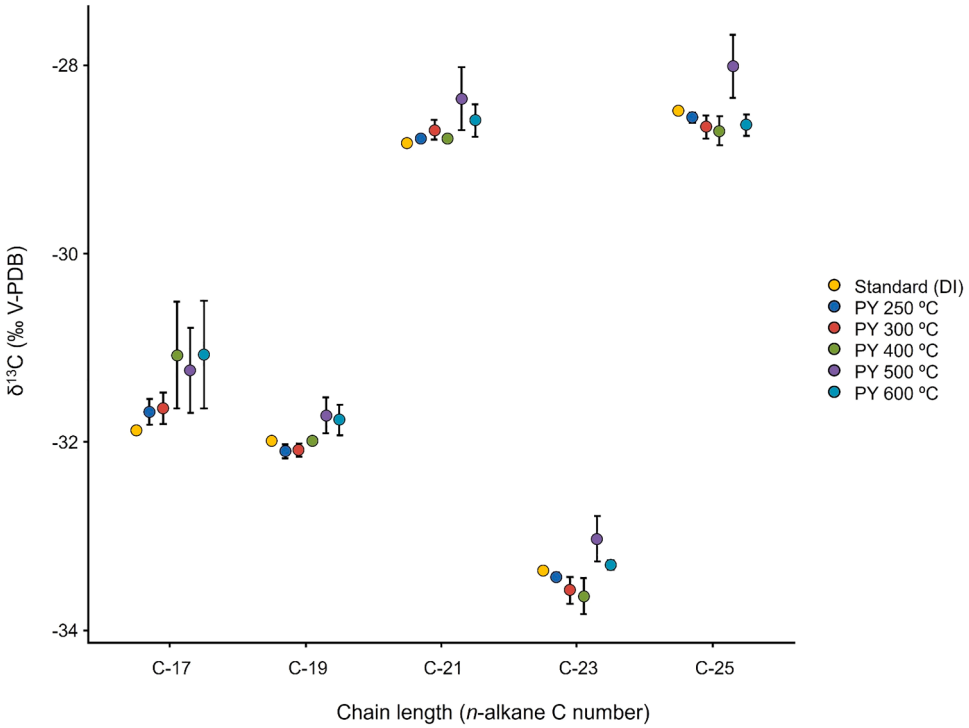

Fig. 2. Carbon isotope measurements of the n-alkane mixture type C4 standard by GC-C/IRMS and by Py-CSIA at different pyrolysis temperatures. The 'standard' refers to the direct injection values of the reference material.

which the measured values are not expected to significantly affect data quality [22]. An analysis of variance (two-way factorial ANOVA) was performed when the assumptions of normal distribution and homogeneity of variance were met using the Kolmogorov–Smirnov test and the Levene test, respectively.

3. Results and discussion

3.1. Carbon isotope value of individual n-alkane compounds

A typical Py-CSIA chromatograph of the *n*-alkane mixture is shown in Fig. 1, where a great baseline resolution was achieved for the four *n*-alkane compounds. Fig. 2 depicts the $\delta^{13}C$ value of the individual *n*-alkane compounds present in the C4 standard. The red dots represent the standardized carbon isotope values, analyzed through the direct

Table 1
$\delta^{13}C$ values (‰, VPDB) of selected n-alkanes (C_{17}–C_{25}) obtained at different pyrolysis temperatures. Values are expressed as mean ± standard deviation (n = 10). One-way ANOVA was performed to evaluate the effect of pyrolysis temperature on $\delta^{13}C$ values; F and p values are reported.

n-alkane C number	Standard values	Pyrolysis temperature					F	*p*-value
		250 °C	300 °C	400 °C	500 °C	600 °C		
C_{17}	-31.87 ± 0.02	-31.69 ± 0.14	-31.64 ± 0.17	-31.08 ± 0.57	-31.24 ± 0.45	-31.07 ± 0.57	9.16	<0.001
C_{19}	-31.99 ± 0.01	-32.10 ± 0.08	-32.09 ± 0.07	-31.99 ± 0.00	-31.72 ± 0.19	-31.77 ±0.16	2.17	0.088
C_{21}	-28.83 ± 0.02	-28.78 ± 0.03	-28.69 ± 0.10	-28.78 ± 0.04	-28.36 ± 0.34	-28.58 ± 0.17	1.73	0.160
C_{23}	-33.37 ± 0.03	-33.43 ± 0.04	-33.58 ± 0.15	-33.64 ± 0.19	-33.03 ± 0.24	-33.30 ± 0.05	2.56	0.052
C_{25}	-28.48 ± 0.02	-28.56 ± 0.05	-28.66 ± 0.12	-28.70 ± 0.15	-28.01 ± 0.33	-28.64 ± 0.11	2.97	0.060

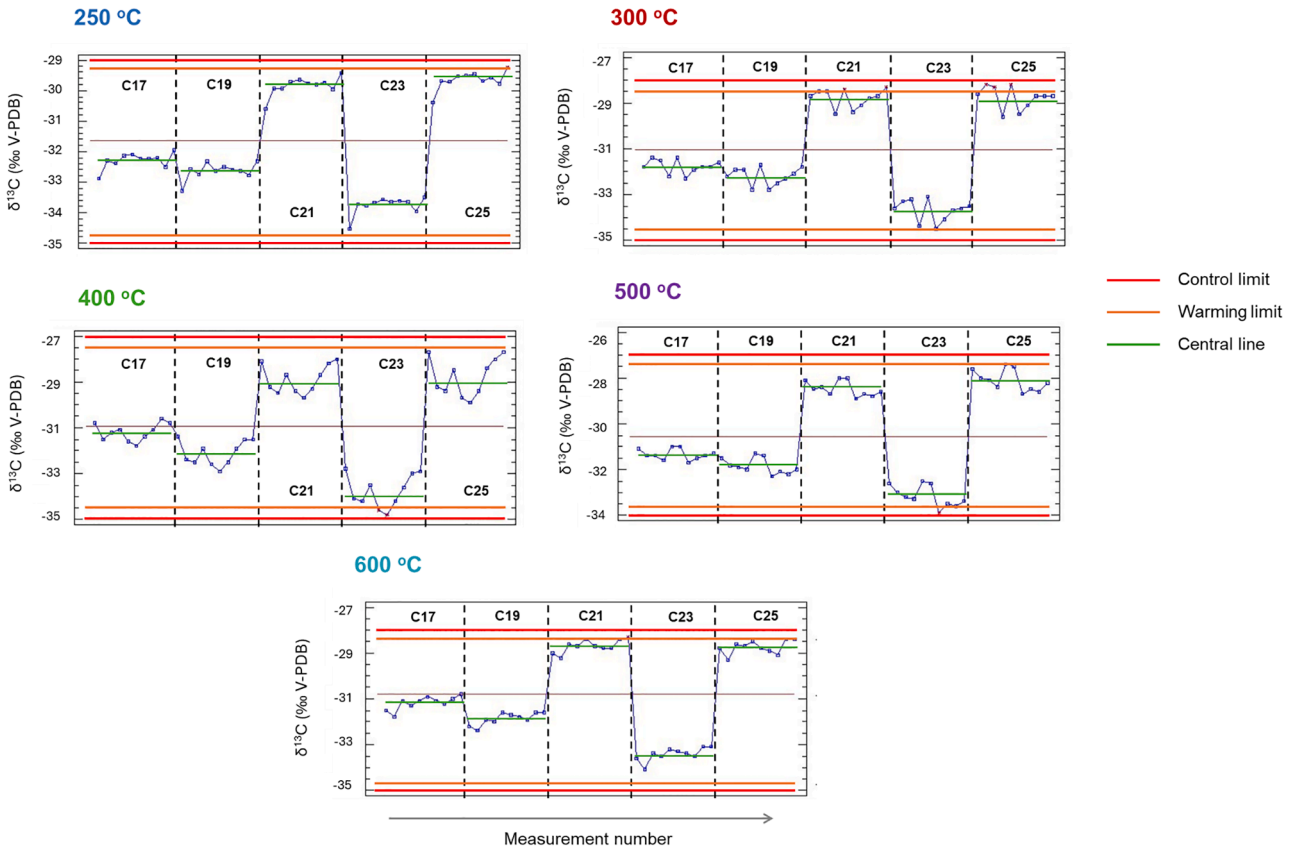

Fig. 3. Control charts for the $\delta^{13}C$ values of the n-alkane C4 reference measured by Py-CSIA at the different pyrolysis temperatures.

injection (DI) in the GC-C/IRMS, while the remaining points indicate the $\delta^{13}C$ values for each *n*-alkane analyzed at the different pyrolysis temperatures (250, 300, 400, 500, and 600 °C). The replicate variability of these measurements for each *n*-alkane compared its theoretical mean value is shown in Figure S1 (Supplementary Information). The comparative analysis between the mean isotopic value of the alkane mixture measured by direct injection (DI) and at each of the selected temperatures showed no statistically significant differences between a conventional CSIA (DI) analysis and the $\delta^{13}C$ values at any of the temperatures considered in this study (Table 1). A slight visual trend towards ^{13}C-enrichment was nevertheless observed at 500 °C in some compounds (Fig. 2), although this pattern should be interpreted as an observable tendency rather than as a statistically significant effect. In contrast, C_{17} was the only *n*-alkane showing a significant temperature

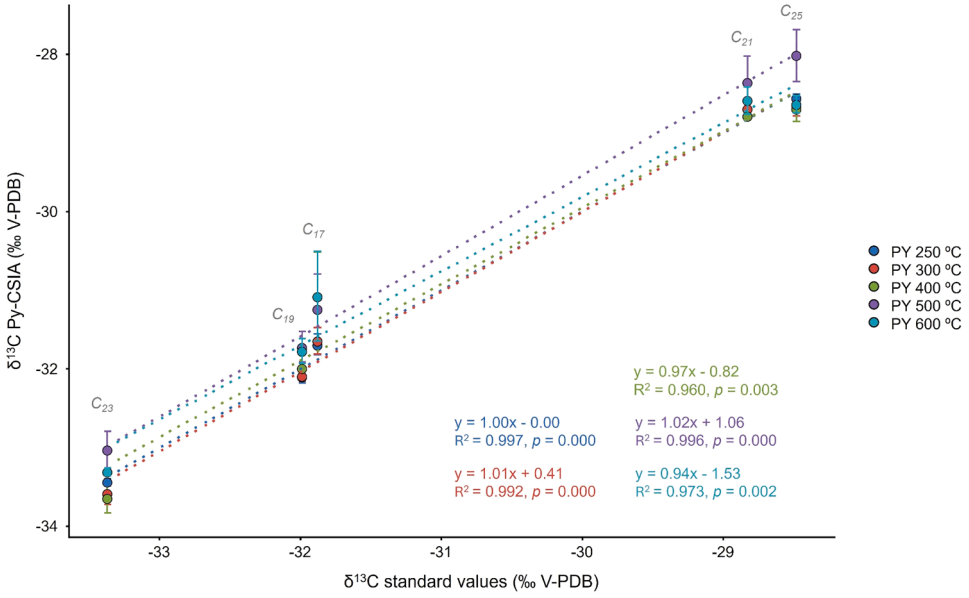

Fig. 4. Carbon isotope ($\delta^{13}C$) values measured by Py-CSIA for the n-alkane mixture (n = 10 replicates) plotted against the corresponding theoretical $\delta^{13}C$ reference values provided for the standard mixture.

effect (Table 1). The significant ($p < 0.05$) ^{13}C depletion observed at 250 °C may be attributed to a limited volatilization of high molecular weight *n*-alkanes (e.g., C_{25}) and/or incomplete transfer of the higher-molecular-weight *n*-alkanes into the analytical system, although minor thermal transformation effects during heating cannot be fully excluded. No evident thermal decomposition of the target *n*-alkanes was observed in the pyrochromatograms at 500 or 600°C, likely because the residence time in the microfurnace was relatively short (1 min), which may have limited extensive thermal cracking under the analytical conditions applied. Such processes could decrease the relative contribution of ^{13}C-enriched compounds in the volatilized fraction, yielding more negative $\delta^{13}C$ values. At 600°C, alkanes with chain lengths greater than 19 carbon atoms showed no differences relative to the DI values. The absence of carbon isotope enrichment at 600°C may be related to a forced release of both the heavy and light isotopes, resulting in isotope values that remain close to those obtained by DI.

3.2. Precision of Py-CSIA at different temperatures

In order to evaluate the variability of Py-CSIA measurements, the reference *n*-alkane mixture was analyzed at 5 different temperatures over a certain period of time, shown in control charts (Fig. 3). A noticeable increase in the variability (i.e., reduced precision) of the $\delta^{13}C$ measurements is observed beginning at 300 °C. This effect persists at 400 °C but begins to diminish at 500 °C. The highest measurement precision across the ten replicates for each *n*-alkane compound is achieved at 250 °C and 600 °C, where the difference between the minimum and maximum $\delta^{13}C$ values does not exceed 1.1 ‰. In contrast, at 300 °C and 400 °C, this difference increases to 1.5 ‰, which indicated a substantial decline in isotope measurement precision at these intermediate temperatures. At 500 °C, the precision improves markedly, with the range between minimum and maximum values reduced to 0.9 ‰. These results suggest that both low (250 °C) and high (>500 °C) pyrolysis temperatures yield more consistent $\delta^{13}C$ values, while mid-range temperatures introduce greater isotope variability. However, although 250 °C yielded comparatively low replicate variability, the associated isotopic depletion indicates that precision at this temperature does not necessarily imply optimal isotopic fidelity.

3.3. Correlation between CSIA and Py-CSIA

Fig. 4 illustrates the correlation between carbon isotope values obtained by conventional CSIA and those measured by Py-CSIA across a range of pyrolysis temperatures. At all tested temperatures, a strong linear relationship was observed between the $\delta^{13}C$ values of the five *n*-alkane compounds, with coefficients of determination (R^2) exceeding 0.96. These correlations were also statistically significant in every case, as all *p*-values were below 0.05.

As observed in Fig. 2, the correlation between the values obtained by DI and those at 500°C shows a slight visual ^{13}C-enrichment along the alkane series. However, this enrichment is not statistically significant. This indicates that, although a minor enrichment may occur at higher temperatures, working at elevated pyrolysis temperatures can substantially improve reproducibility and make the analysis more robust without introducing meaningful isotopic bias. This approach is therefore well suited for the study of highly recalcitrant organic matter that requires high pyrolysis temperatures, such as the characterization of organic matter in highly complex natural matrices (e.g., soil, sediment, PyOM).

4. Conclusions

This study demonstrates that, under the Py-CSIA conditions evaluated here, the C4 saturated linear *n*-alkane mixture (C_{17}– C_{25}) can be used as a suitable working standard for compound-specific $\delta^{13}C$ measurements. Py-CSIA values remained in close agreement with direct-injection GC-C/IRMS data across the tested temperature range, with no statistically significant temperature effect for C_{19}, C_{21}, C_{23}, or C_{25}, and a significant response detected only for C_{17}. Although a slight visual ^{13}C-enrichment tendency was apparent at 500°C, this effect was not statistically significant, whereas analyses performed at 600°C yielded $\delta^{13}C$ values closer to the direct-injection reference together with improved reproducibility. The isotopic depletion observed at 250°C is more consistently explained by incomplete volatilization and transfer of the heavier *n*-alkanes than by clear pyrolytic fractionation, although a minor contribution of thermal transformation cannot be ruled out. Overall, these results support the use of elevated pyrolysis temperatures as a robust analytical compromise for accurate and reproducible $\delta^{13}C$ measurements in the saturated linear *n*-alkanes investigated here.

Further work is needed to evaluate the extent to which these findings can be extended to other compound classes and more complex organic matrices, in which pyrolysis-induced isotope effects may depend more strongly on molecular structure and thermal reaction pathways.

CRediT authorship contribution statement

Layla M. San-Emeterio: Writing – review & editing, Writing – original draft, Visualization, Validation, Investigation, Formal analysis, Data curation. **Gonzalo Correa-López:** Writing – original draft, Formal analysis, Data curation. **Desiré Carrere:** Writing – original draft, Methodology, Formal analysis. **José A. González-Pérez:** Writing – review & editing, Resources, Investigation. **Nicasio T. Jiménez-Morillo:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Methodology, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2026.466919.

Data availability

Data will be made available on request.

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