

*Black Carbon Determination in
Sediments and Soils Using Multi-
Elemental Scanning Thermal Analysis
(MESTA)*

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What is BC?

One of the original conceptual definitions was proposed by Goldberg (1985) as:

An impure form of the element (C) produced by incomplete combustion of fossil fuels or biomass. It contains over 60% carbon with the major accessory elements of hydrogen, oxygen, nitrogen and sulfur.

- *To atmospheric scientists, the interest of BC is in its surface properties much more so than its bulk chemical properties.*
- *To most biogeochemists, the interest of BC is in its bulk biochemical properties rather than the surface properties.*

There are various forms of BC in the environment. BC may need to be defined differently accordingly the questions that we ask in our studies.

No matter what, determination of BC ought to base on chemical nature rather than pure operational. Because we need to know what are we studying and make comparison with other studies. We also need to know the relationship between the chemical identity of BC and its environmental behavior.

Current methods to determine BC:

1. *Visual/microscopic methods*

2. *Chemical oxidation methods*

3. *Thermal oxidation methods*

4. *Thermal/optical methods*

5. *Chemical/thermal oxidation methods*

6. *Molecular marker methods*

7. *¹³C CP/MAS NMR method*

Comparison of BC Ring Trial methods (Hammes et al., 2007)

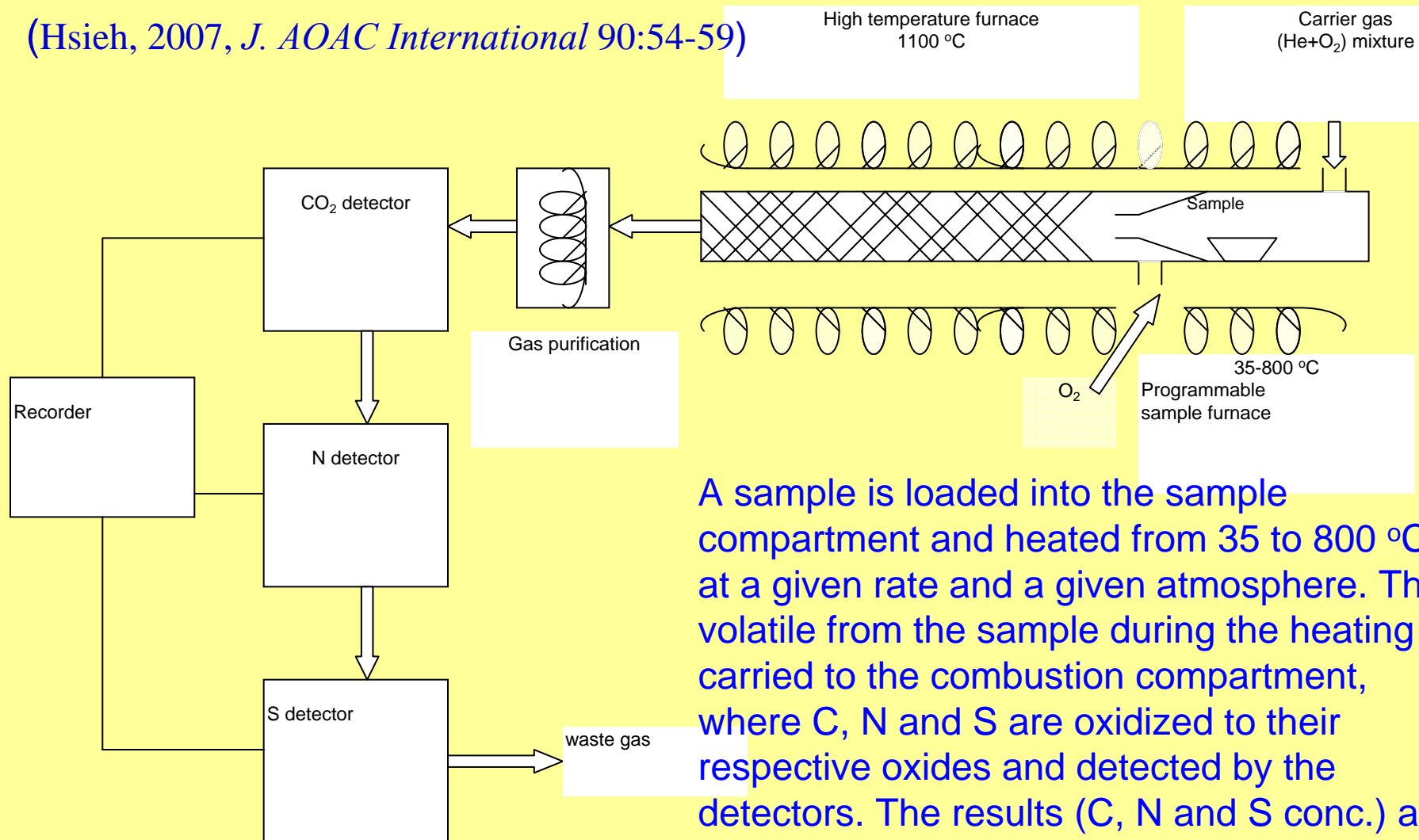
| Sample | % BC/TOC | | | | |
|-----------------------|----------|-----------|--------------------|-----------|---------|
| | CTO 375 | BPCA | Acid Dichromate | TOR/TOC | TGA-DSC |
| Chernozem | 4.1±3.1 | 19.7±5.3 | 7.3±4.7 | 20.2±13.5 | 57.5 |
| Vertisol | 2.6±1.6 | 15.7±6.2 | 15.0±9.3 | 26.5±7.6 | 49.5 |
| SRM1649a | 8.4±3.9 | 8.1±2.5 | 35.8±11.7 | 37.3±11.5 | 65.0 |
| Wood char | 0.0 | 24.6±13.0 | 70.4±15.0 | 87.7±13.7 | 95.3 |
| Grass char | 1.5±1.2 | 26.1±3.4 | 34.8±8.6 | 82.3±13.6 | 58.2 |
| <i>n</i> -hexane soot | 46.9±1.9 | 26.0±22.5 | 51.0±10.8 | 96.3±4.3 | 91.3 |

- *Due to the complexity of BC in the environment, may require more than one method to quantify BC properly. We need to look at the problem from more than just one angle.*

- *We report in this study an alternative rapid method to determine BC in soils and sediments using a multi-element scanning thermal analysis (MESTA) method.*
- *We compare the results of MESTA with those of the BC Ring Trial using the same reference materials.*

What is a MESTA?

(Hsieh, 2007, *J. AOAC International* 90:54-59)



A sample is loaded into the sample compartment and heated from 35 to 800 °C at a given rate and a given atmosphere. The volatile from the sample during the heating is carried to the combustion compartment, where C, N and S are oxidized to their respective oxides and detected by the detectors. The results (C, N and S conc.) are expressed against the volatile temperature as the thermogram of the sample.

Materials

- *n-hexane soot (From Dwight Smith, University of Denver, USA.)*
- *Mollisol (or Chernozem, Germany soil collected under the auspices of the “International Steering Committee for Black Carbon Reference Materials, i.e., ISCBCRM)*
- *Vertisol, (Australia soil collected under the auspices of the ISCBCRM)*
- *Wood char (laboratory-charred chestnut wood from Karen Hamme of University of Zurich, Zurich, Switzerland)*
- *Grass char (laboratory-charred grass straw from Karen Hammes of the University of Zurich, Zurich, Switzerland)*
- *SRM 1649a, (a urban dust sample from US NIST)*

Materials (cont'd)

- *Activated charcoal (from JT Baker Chemical Co.)*
- *CRM-coal, (a certified reference coal material from High Purity Standards)*
- *Graphite powder (Grade #38, 99.6 % C by wt., Fisher Chemical)*

Methods

1. MESTA:

Heating rate: 50 °C/min.

Carrier gas: 40% oxygen and 60% helium

Combustion gas: 100% oxygen

Heating temperature range: 35 – 750 °C

Sample size: 5 – 100 µg C

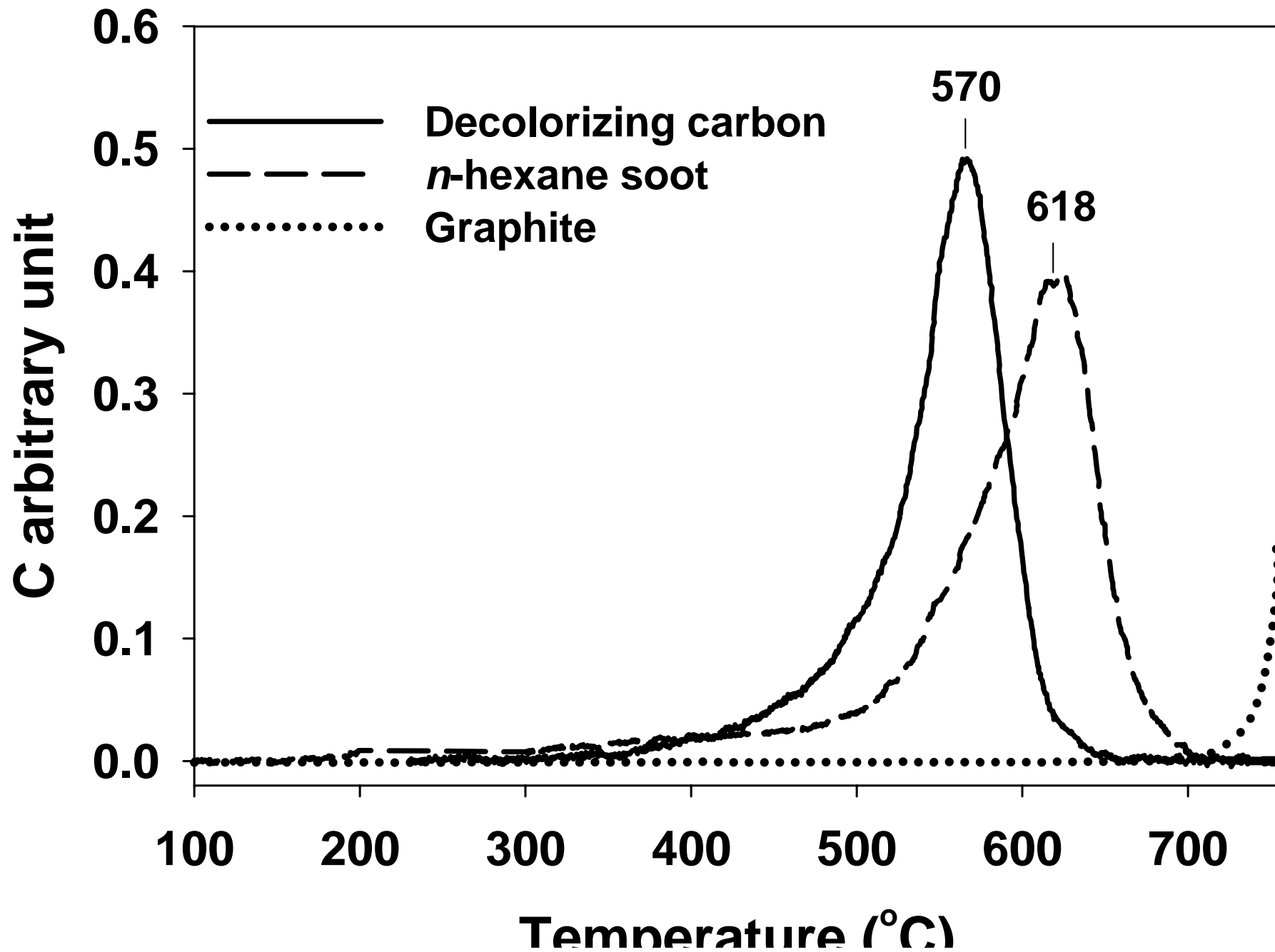
Calibration materials: cystine and glucose (C and N)

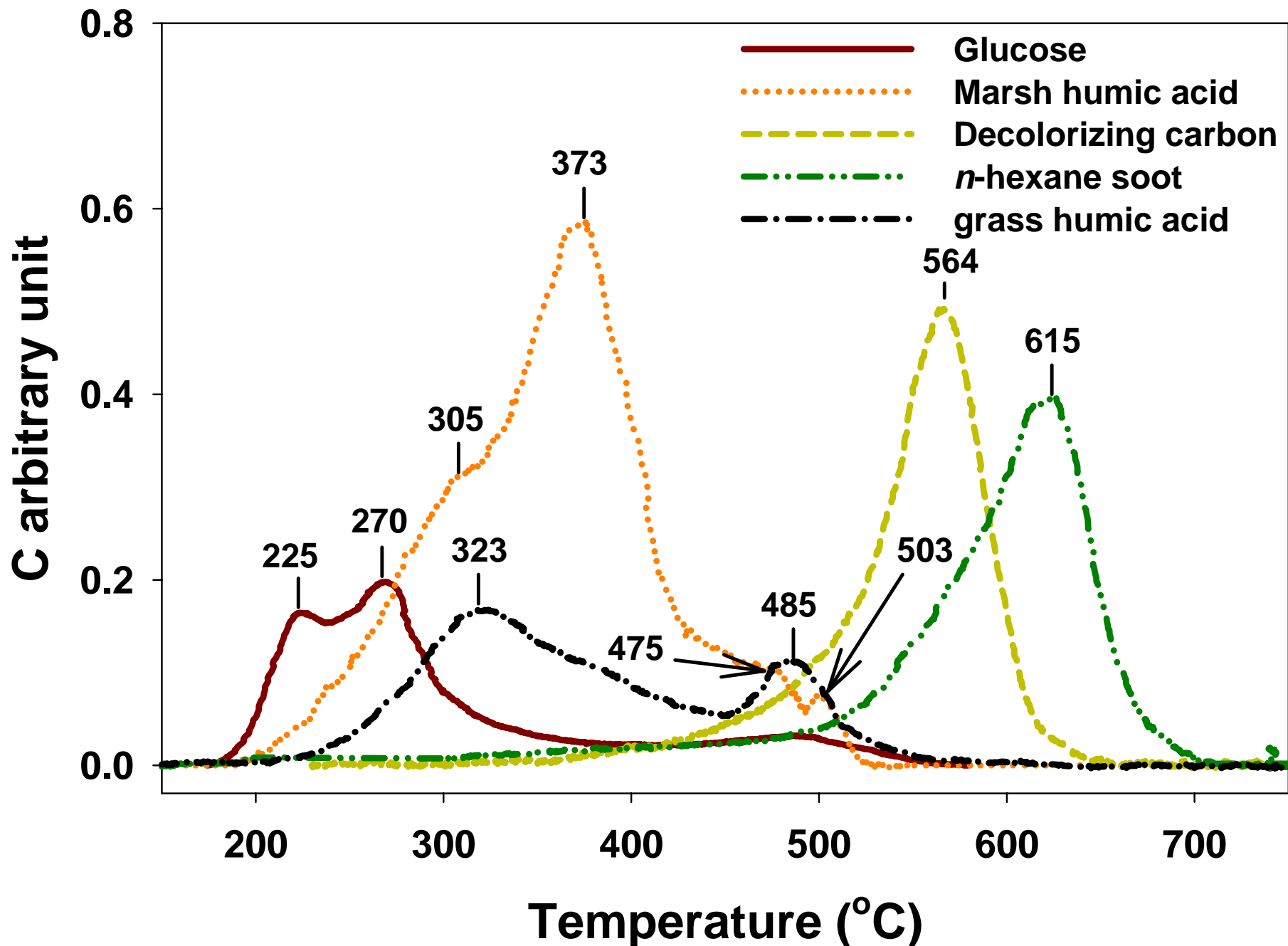
Internal temperature standards: S₈ and Ag₂S.

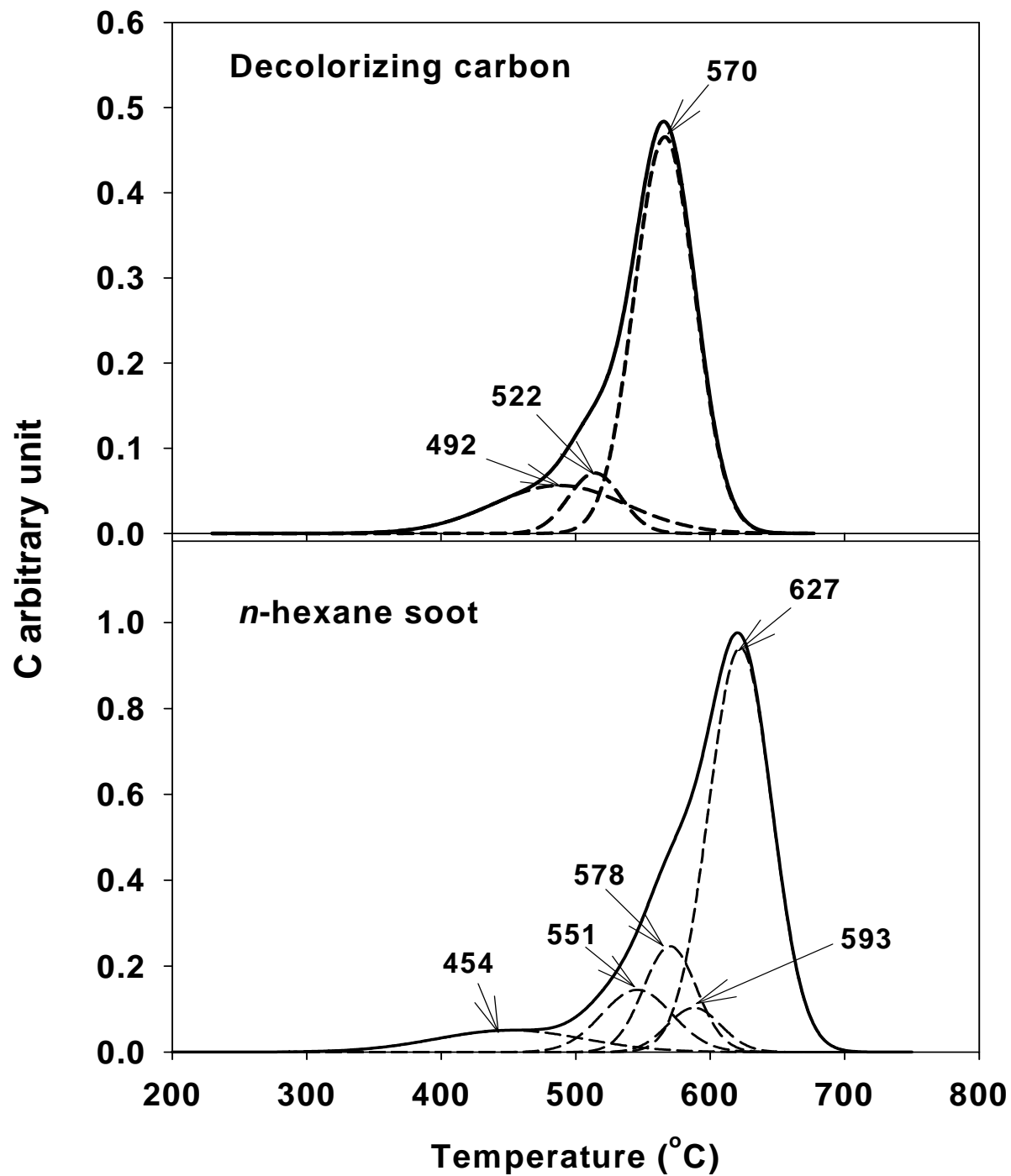
Methods (cont'd)

- 2. Dichromate oxidation: Digested in 0.25 M dichromate and 2 M H₂SO₄ solution for 406 hr. at room temperature (23 °C)*
- 3. Thermal oxidation: 350 °C for 2 hr. in the air.*

Results

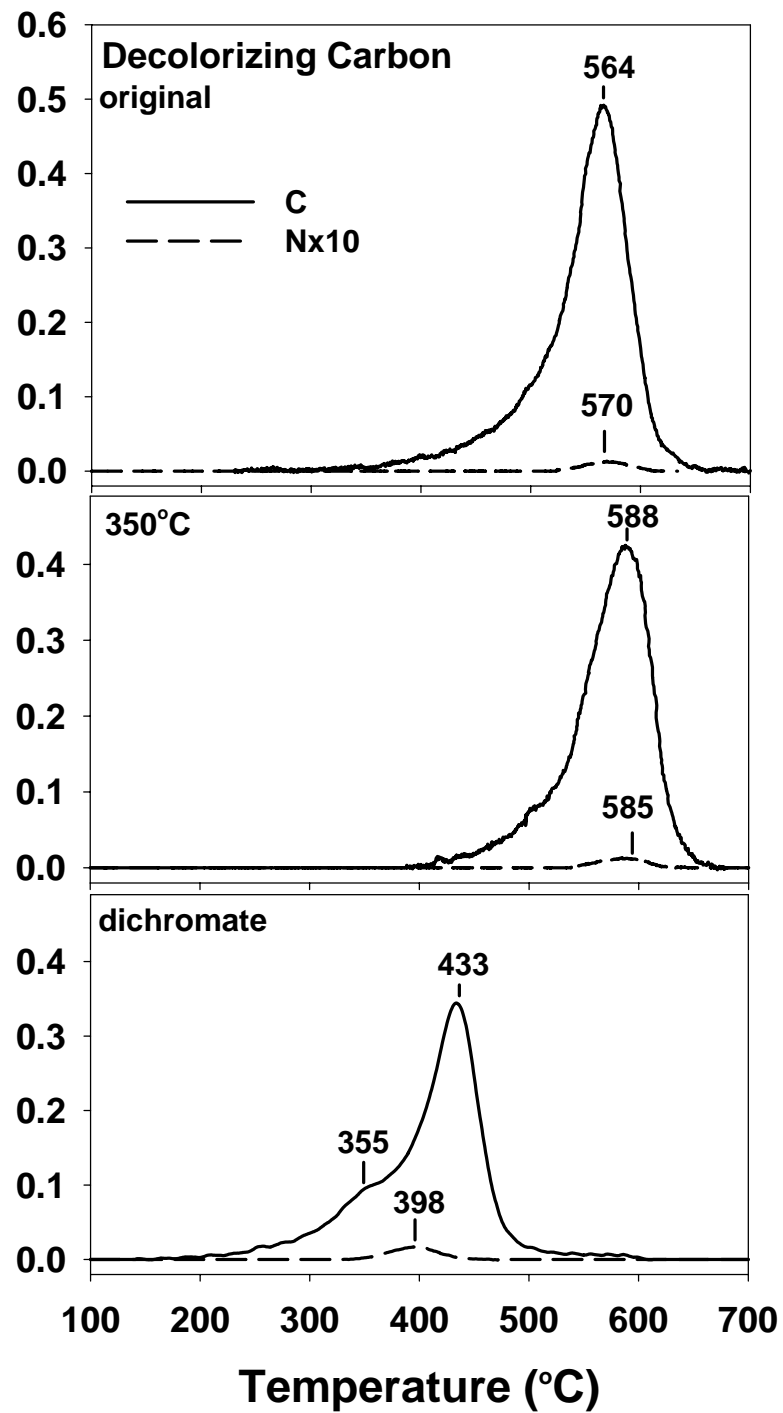


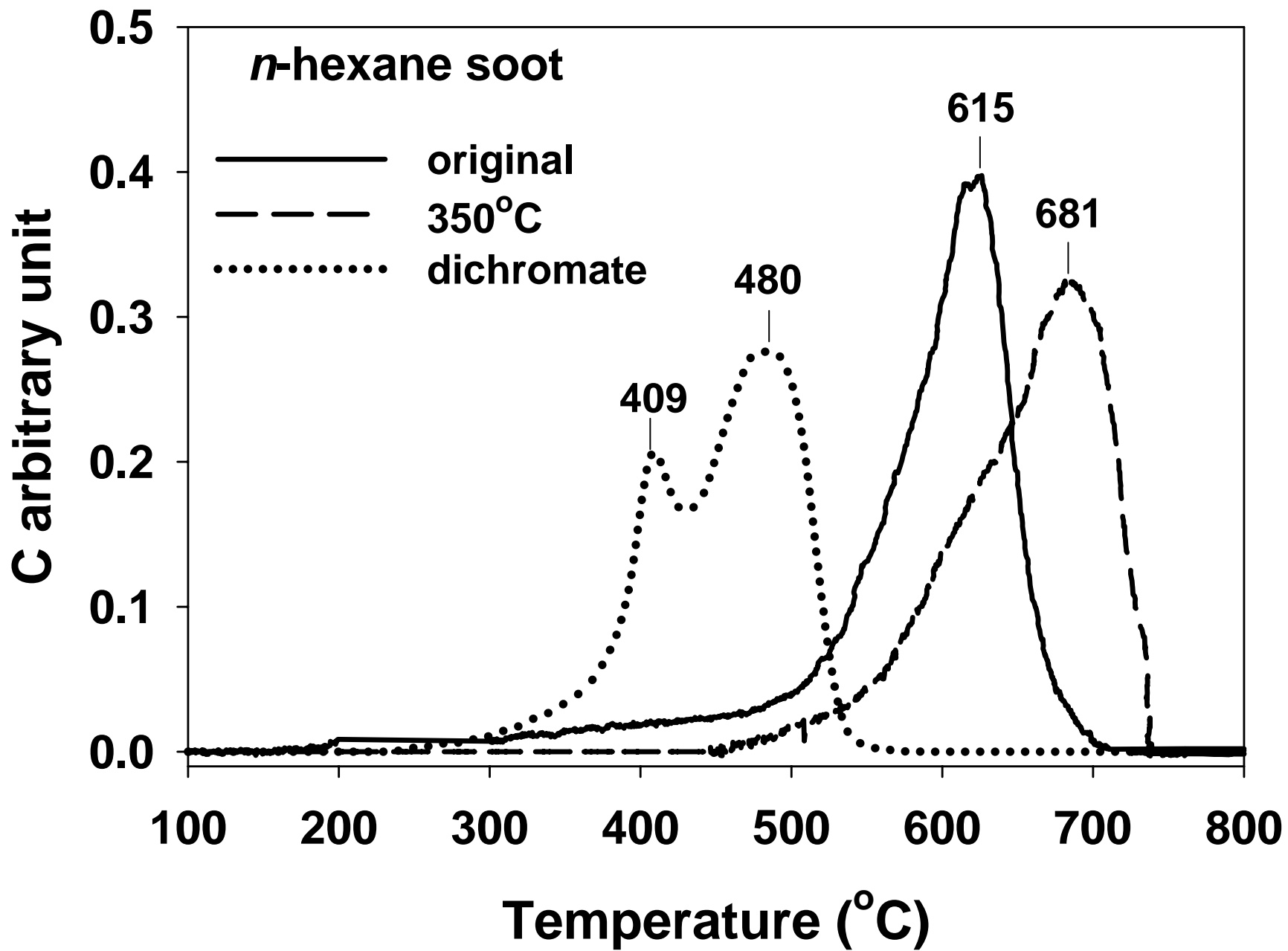


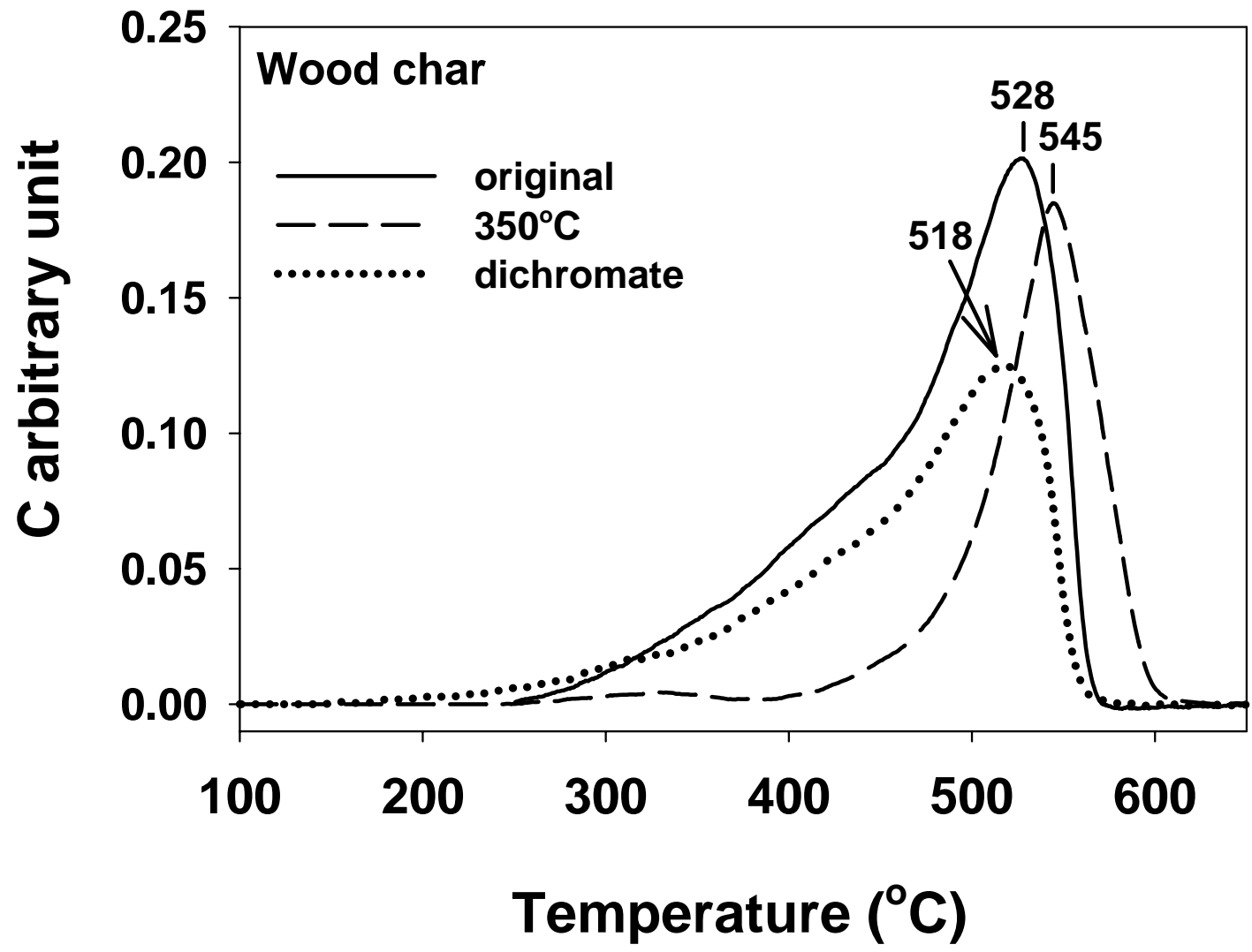


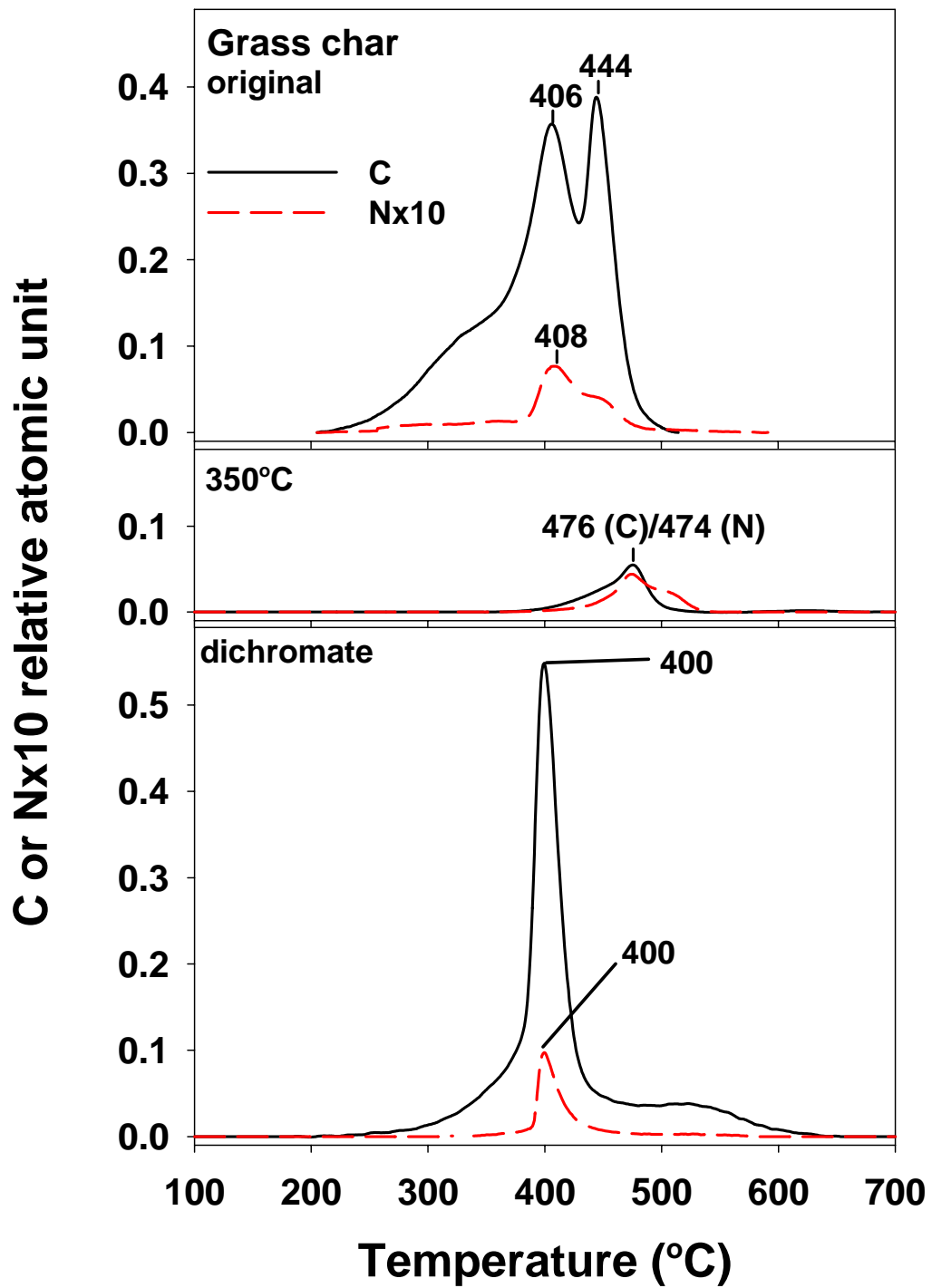
- *We set a BC criteria in MESTA as the C thermal decomposition peak ≥ 550 °C under the set of MESTA conditions.*

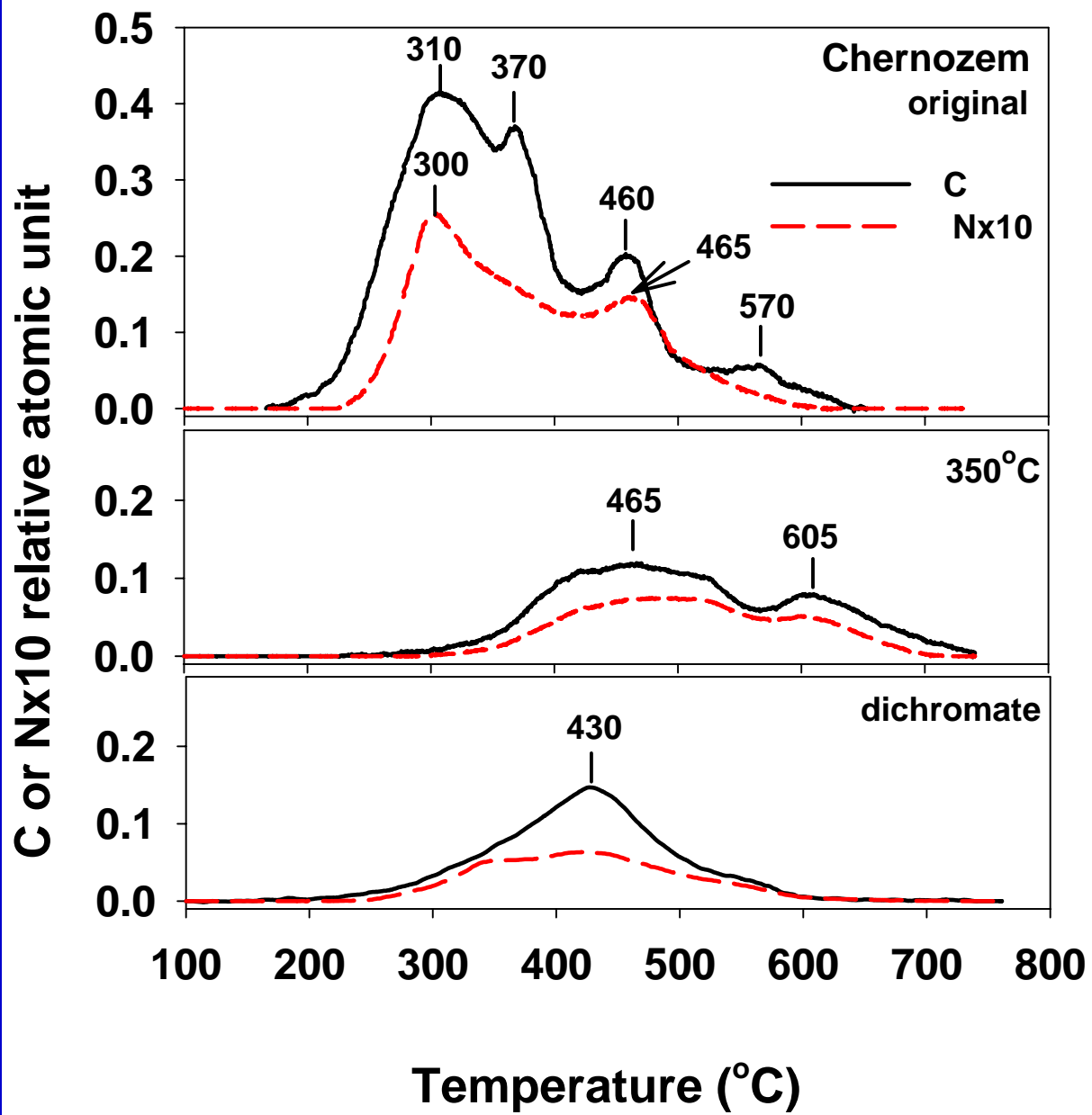
C or Nx10 relative atomic unit

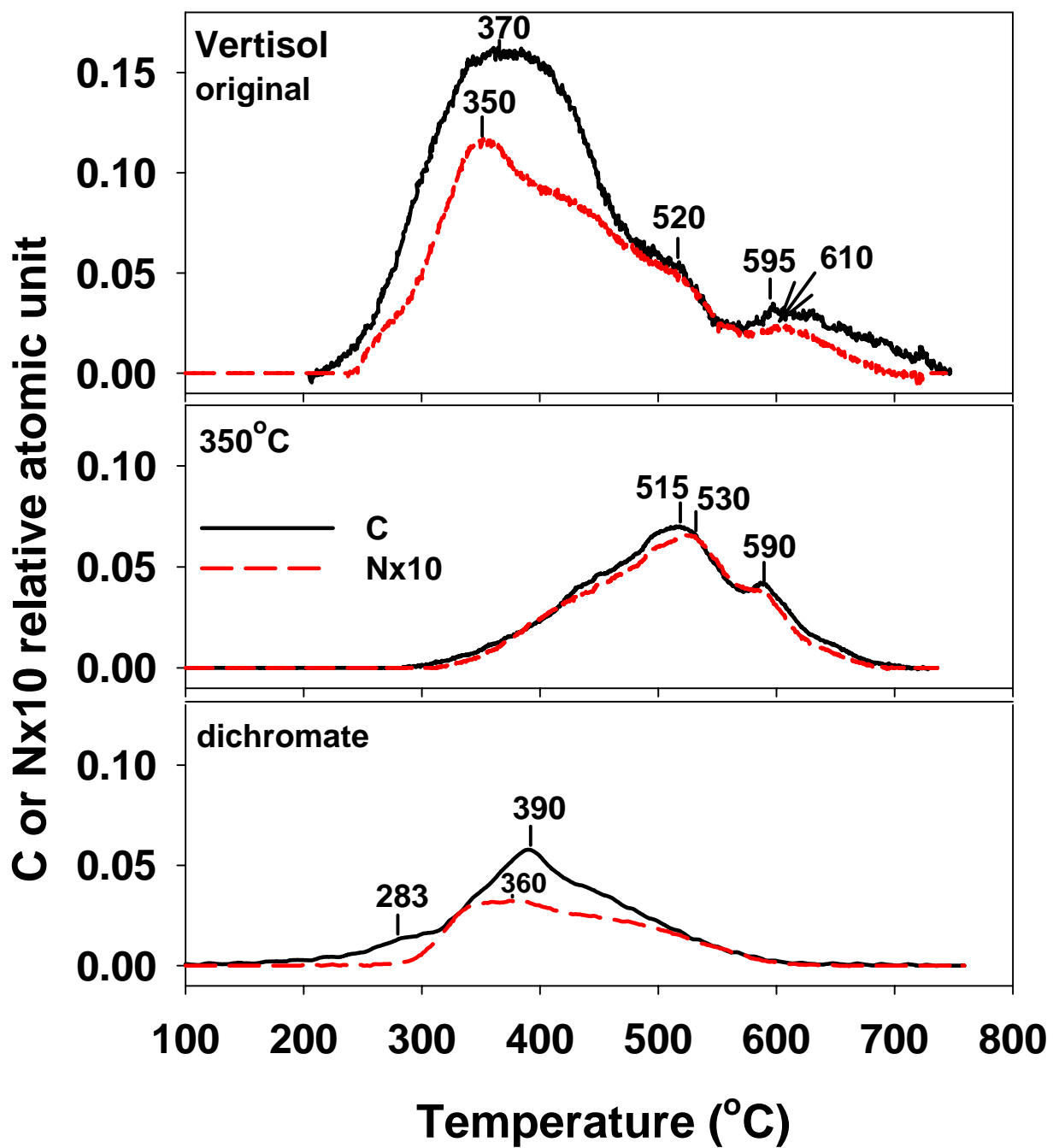


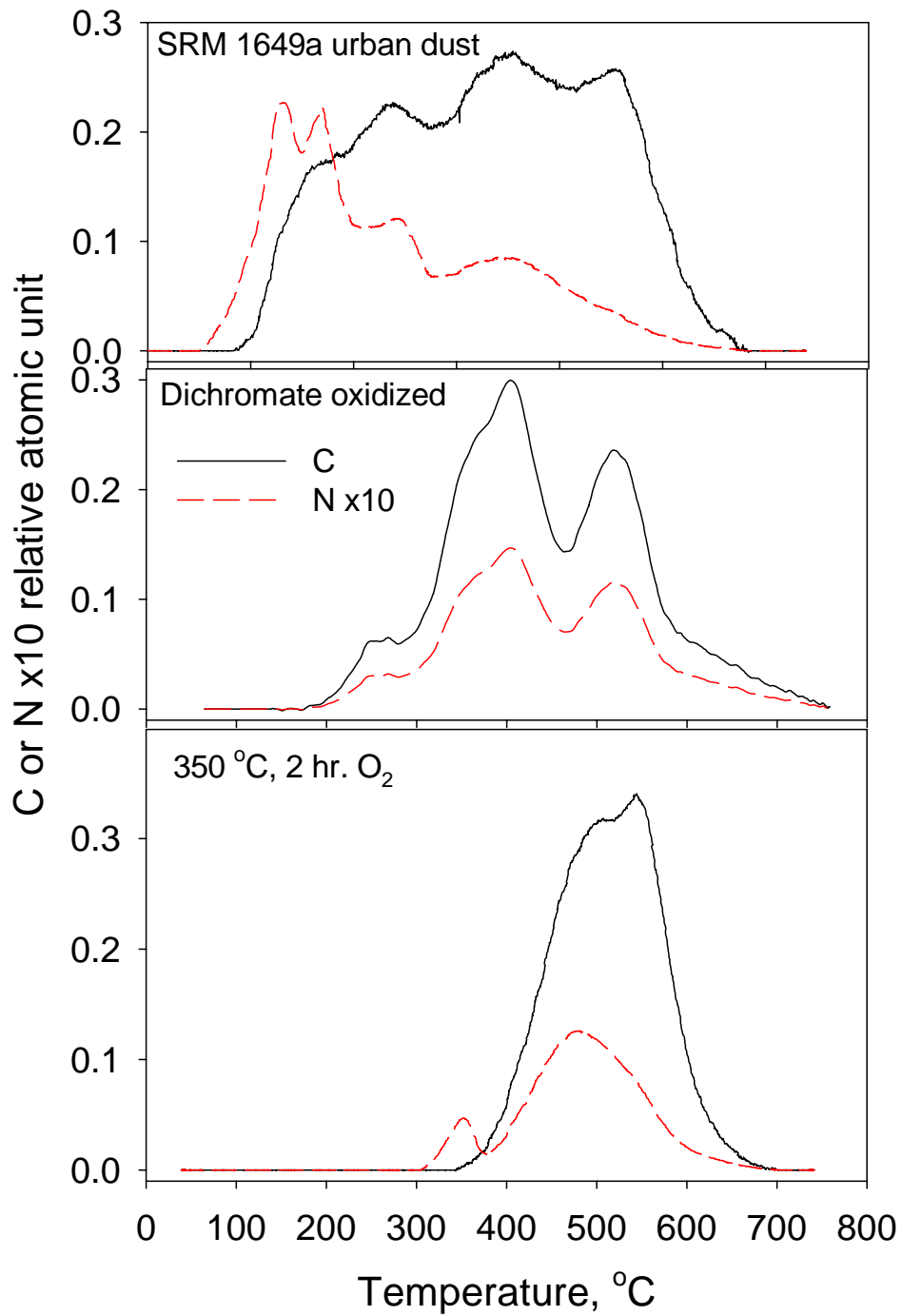


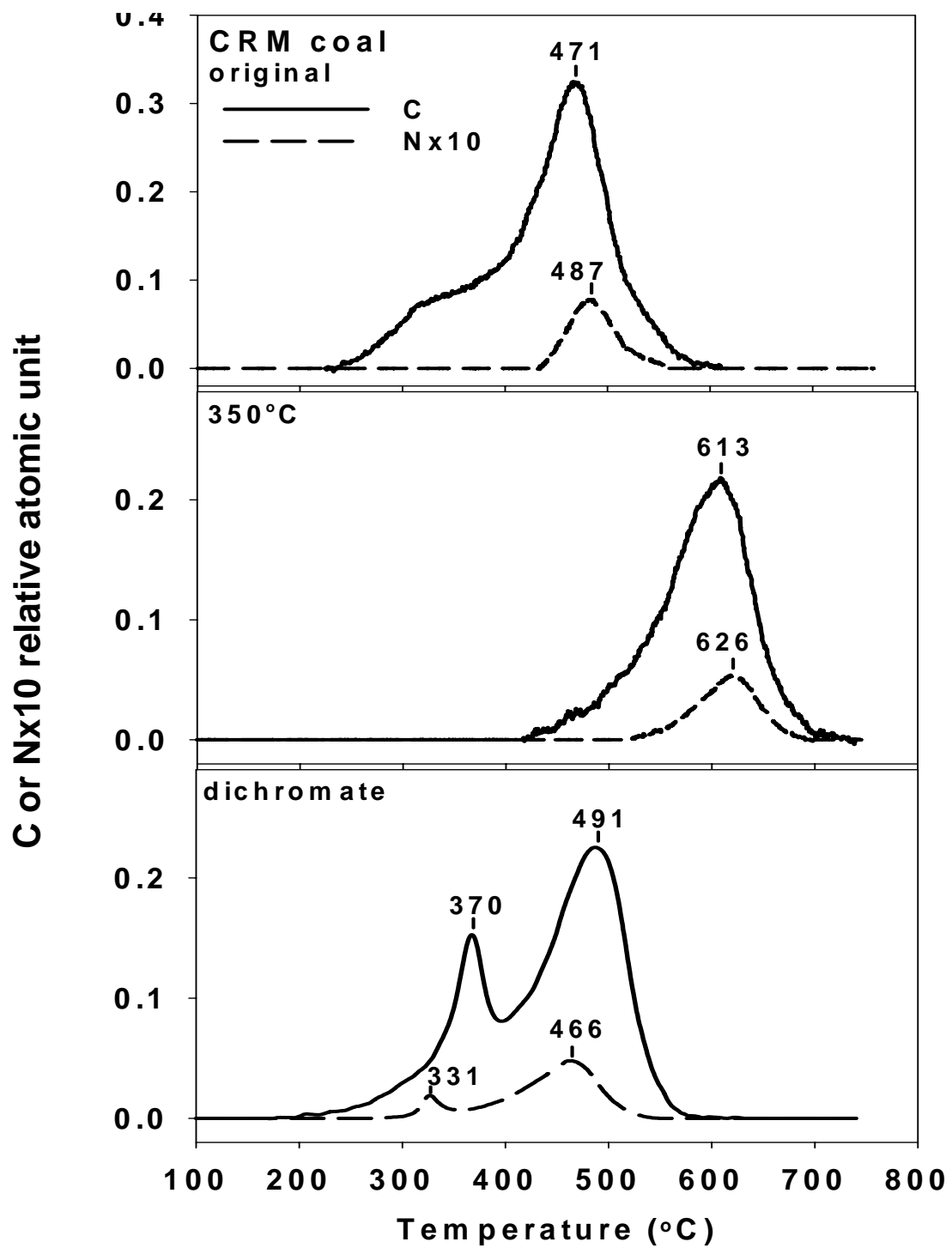












Conclusions

- *This study shows that MESTA can reveal an entire spectrum of OC/BC continuum with the co-decomposed N and S information in a sample.*
- *One of the advantages of the MESTA method is that it can accommodate modification of BC criteria later on without re-analyze a sample.*
- *Charring seems not significant in MESTA if the BC criteria is set for carbon peaks $\geq 550^{\circ}\text{C}$.*
- *MESTA indicates that dichromate method and C350 are not doing good job in separating BC from OC.*

Conclusions (cont'd)

- *MESTA reveals that mollisol and vertisol have high N containing BC-like matters. Are they BC? Do they behave like BC? If so, how about the behavior of the associated N? Is this black N?*
- *Application of MESTA in BC research needs to be further explored. The complexity of BC in the environment requires us to look at it from various angles that are relevant to the questions.*