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. ^{13}C CP/MAS NMR method

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

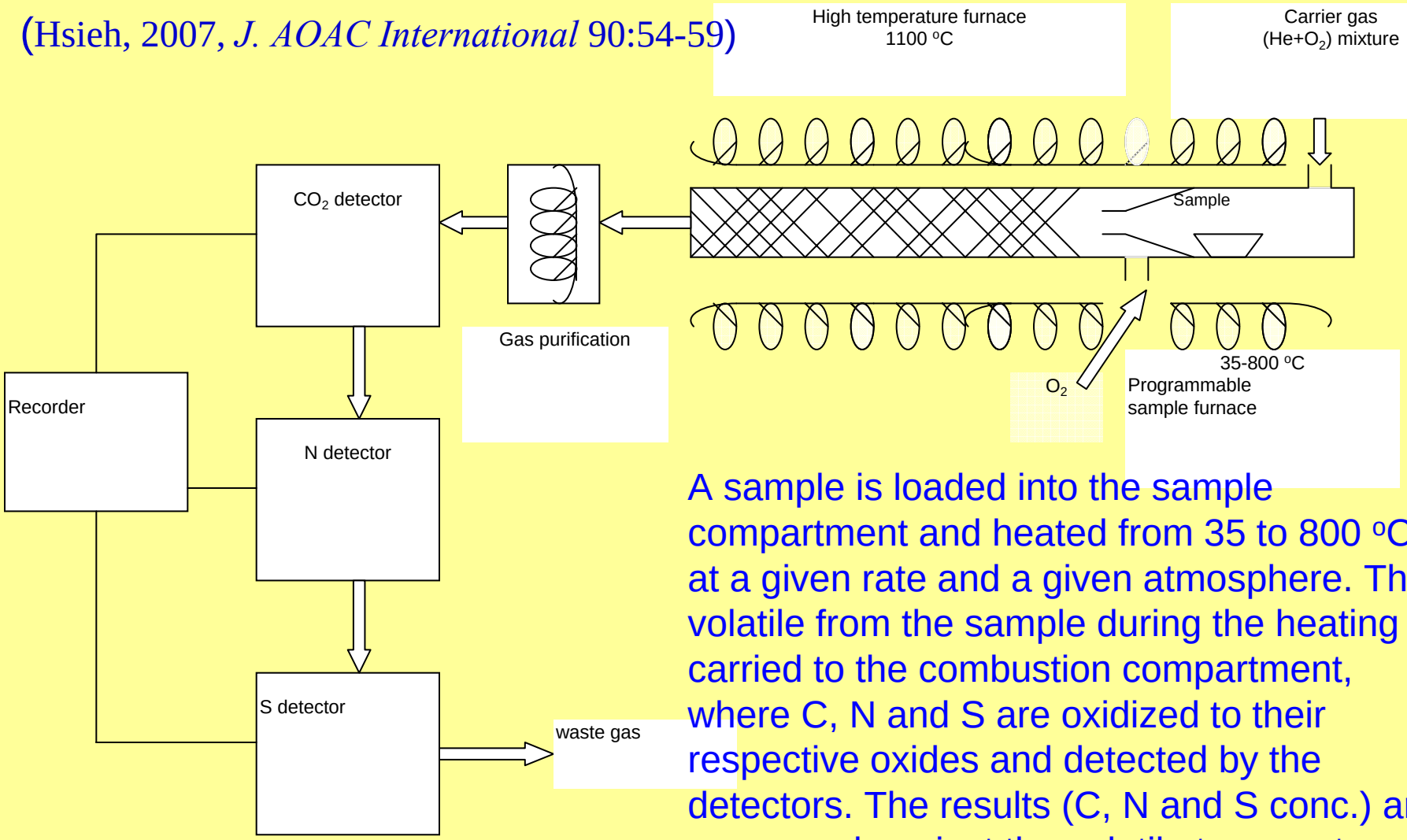
Sample	% BC/TOC				
	CTO 375	BPCA	Acid Dichromate	TOR/TOC	TGA-DSC
Chernozem	4.1±3.1	19.7±5.3	7.3±4.7	20.2±13.5	57.5
Vertisol	2.6±1.6	15.7±6.2	15.0±9.3	26.5±7.6	49.5
SRM1649a	8.4±3.9	8.1±2.5	35.8±11.7	37.3±11.5	65.0
Wood char	0.0	24.6±13.0	70.4±15.0	87.7±13.7	95.3
Grass char	1.5±1.2	26.1±3.4	34.8±8.6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

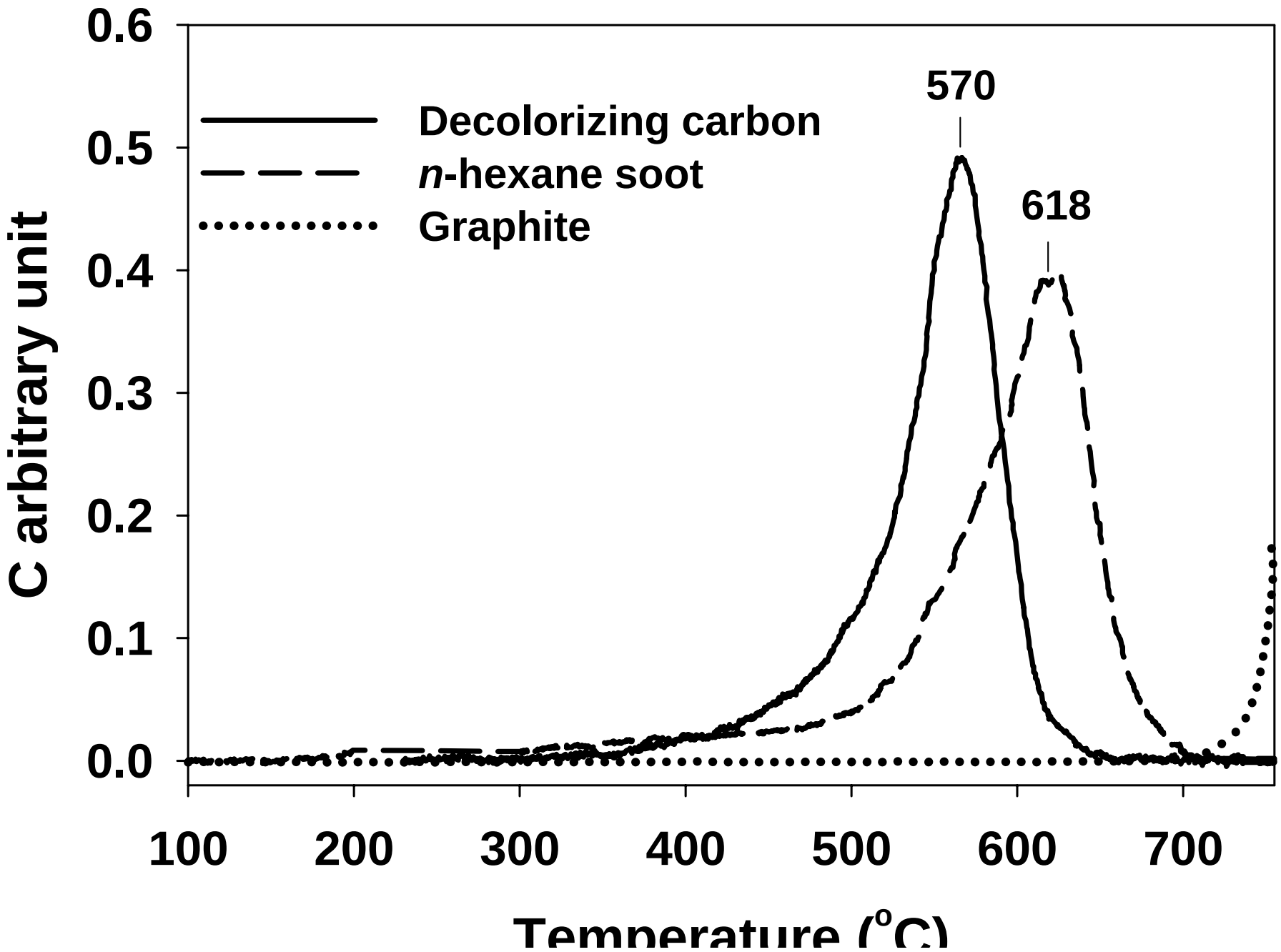
Calibration materials: cystine and glucose (C and N)

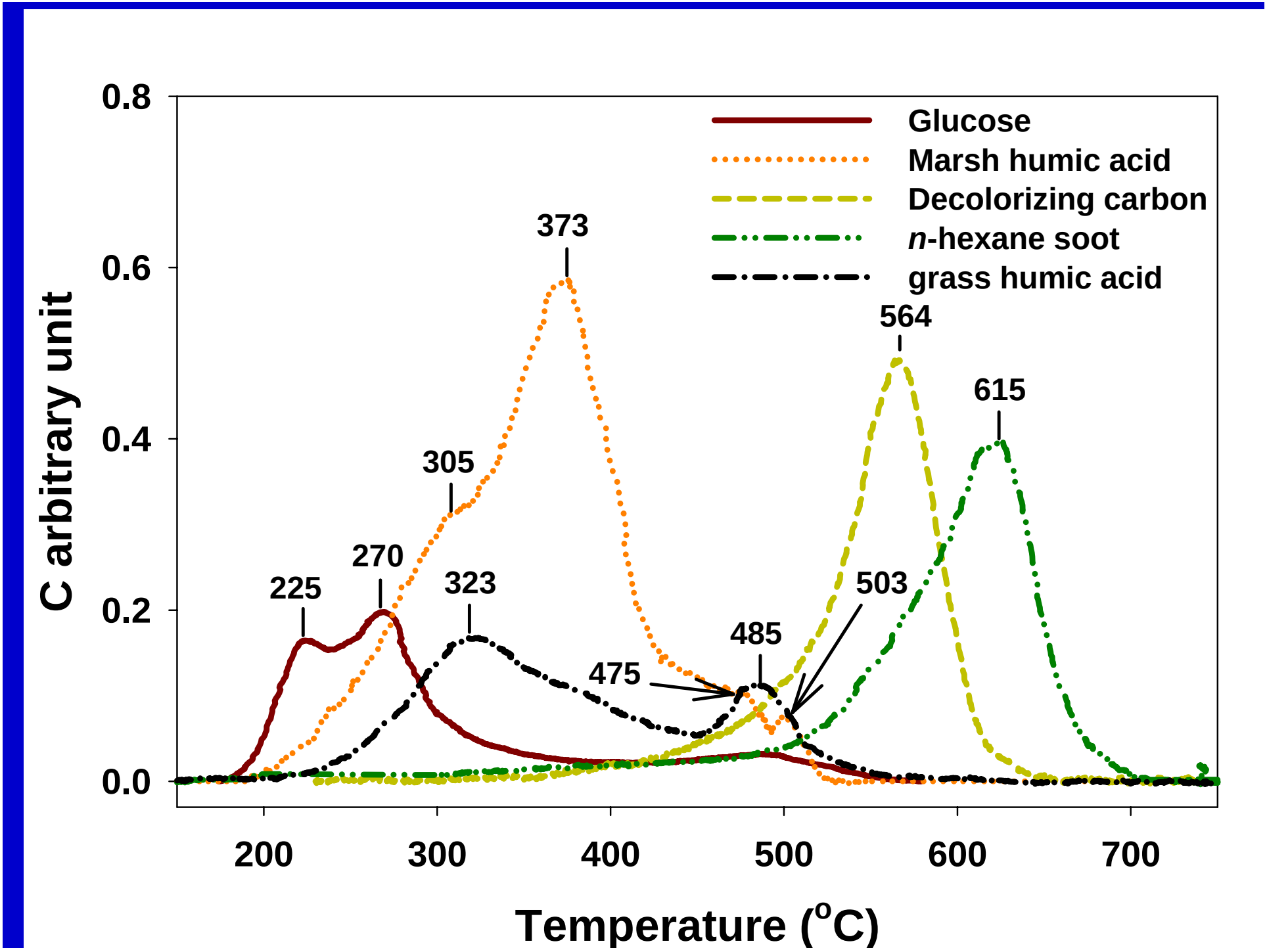
Internal temperature standards: S_8 and Ag_2S.

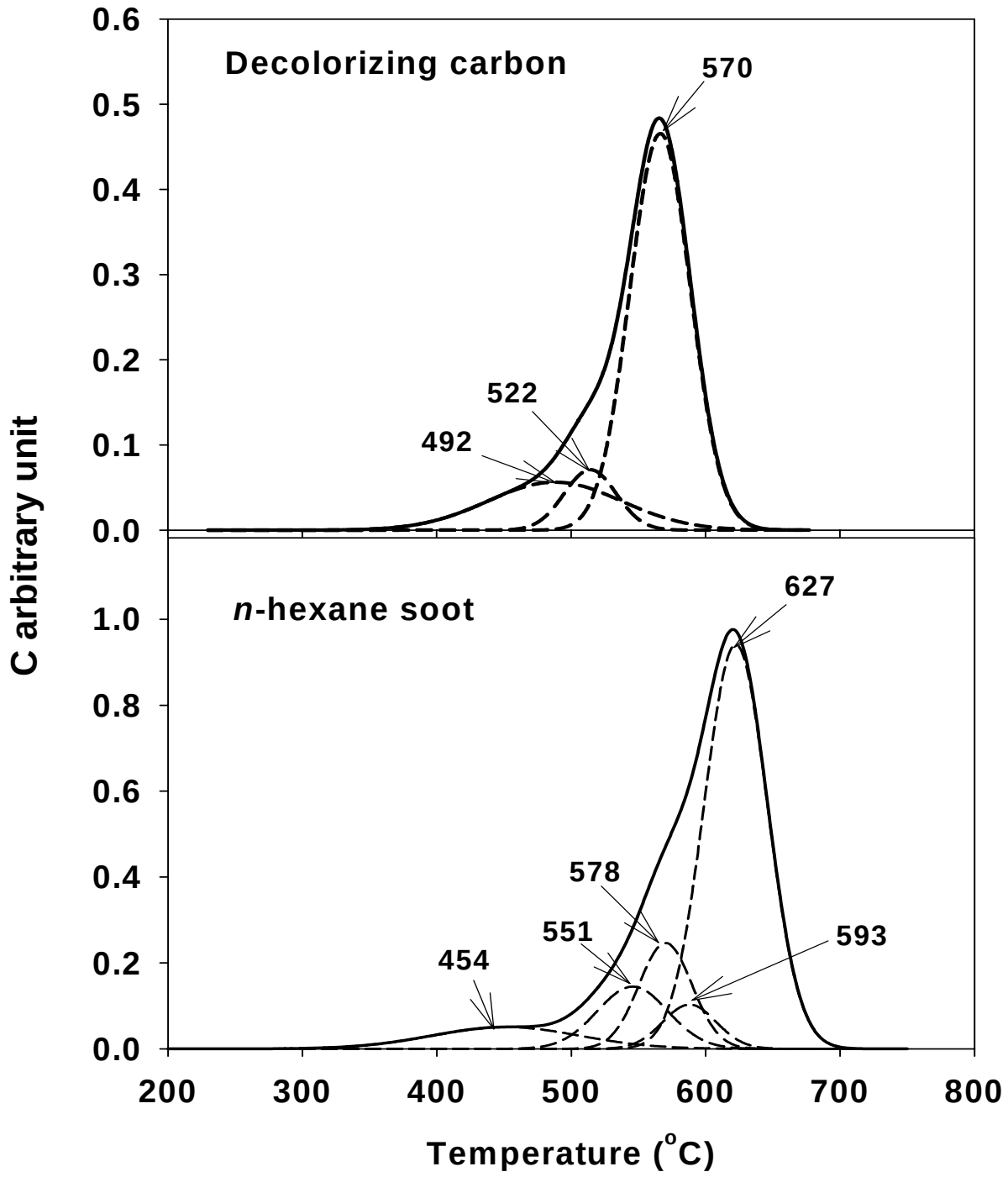
Methods (cont'd)

2. *Dichromate oxidation: Digested in 0.25 M dichromate and 2 M H_2SO_4 solution for 406 hr. at room temperature (23 ^oC)*
3. *Thermal oxidation: 350 ^oC for 2 hr. in the air.*

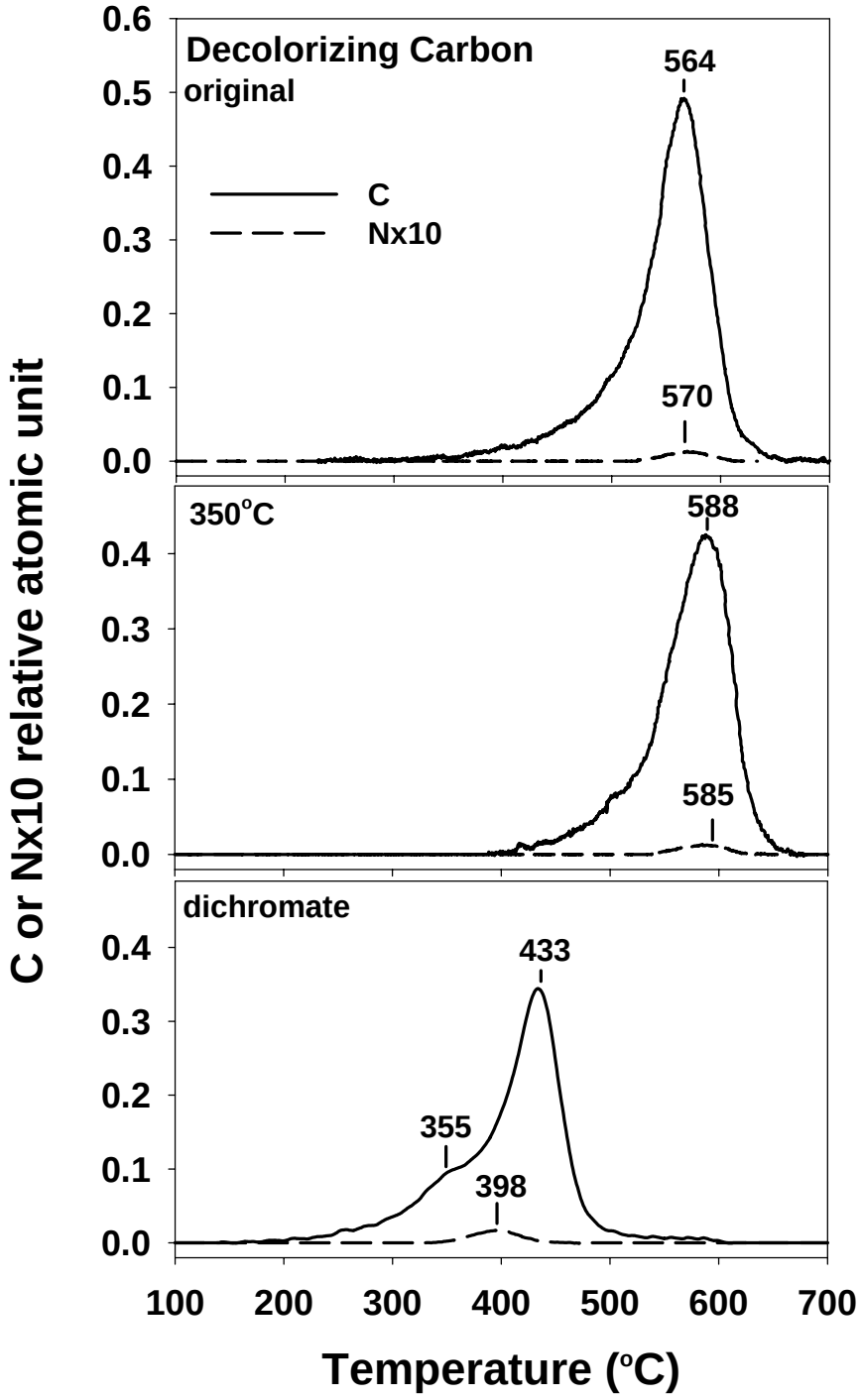
Results

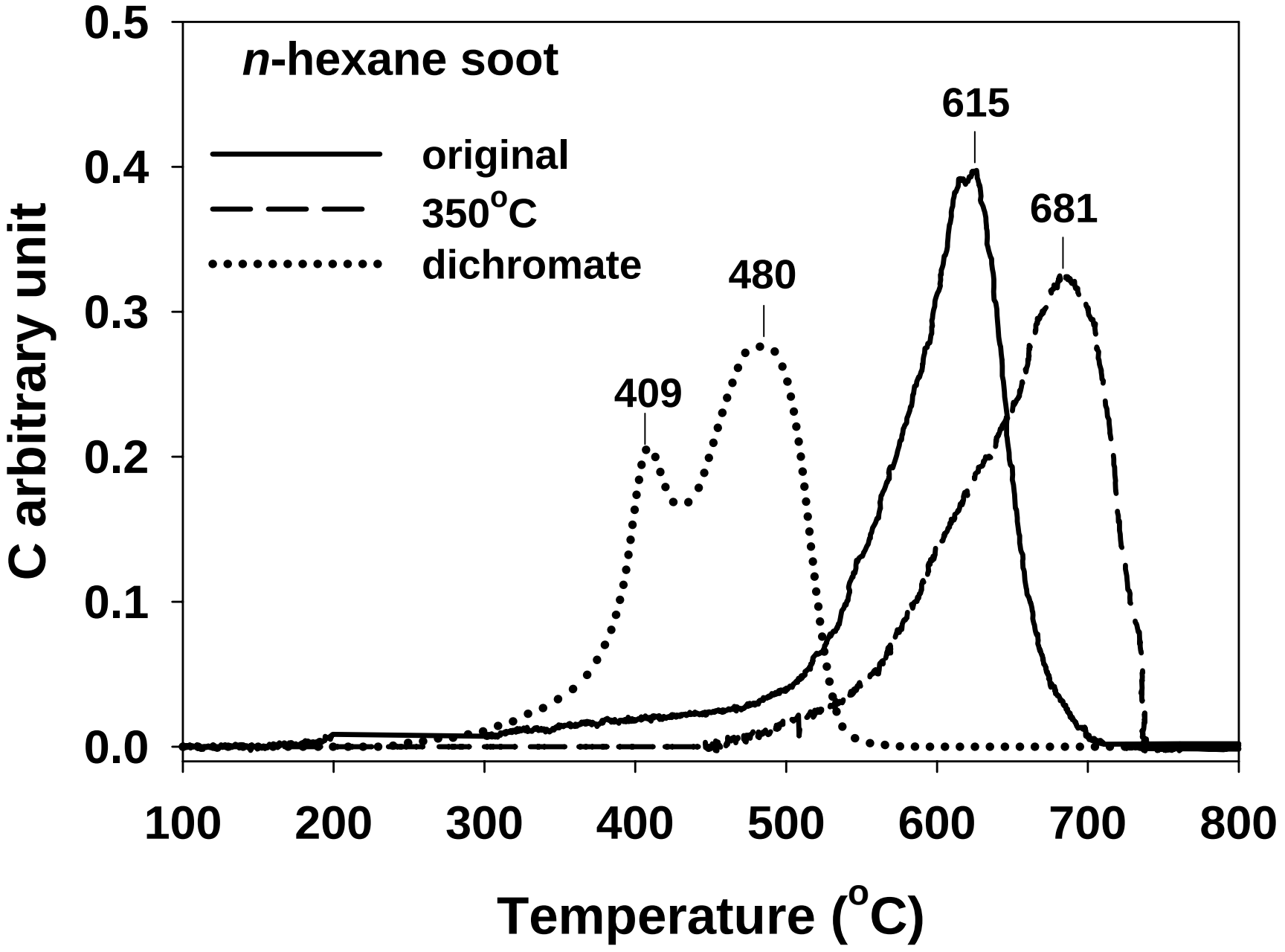

0.6
0.5
0.4
0.3
0.2
0.1
0.0
C arbitrary unit
Decolorizing carbon
n-hexane soot
Graphite
570
618
100
200
300
400
500
600
700
Temperature (°C)

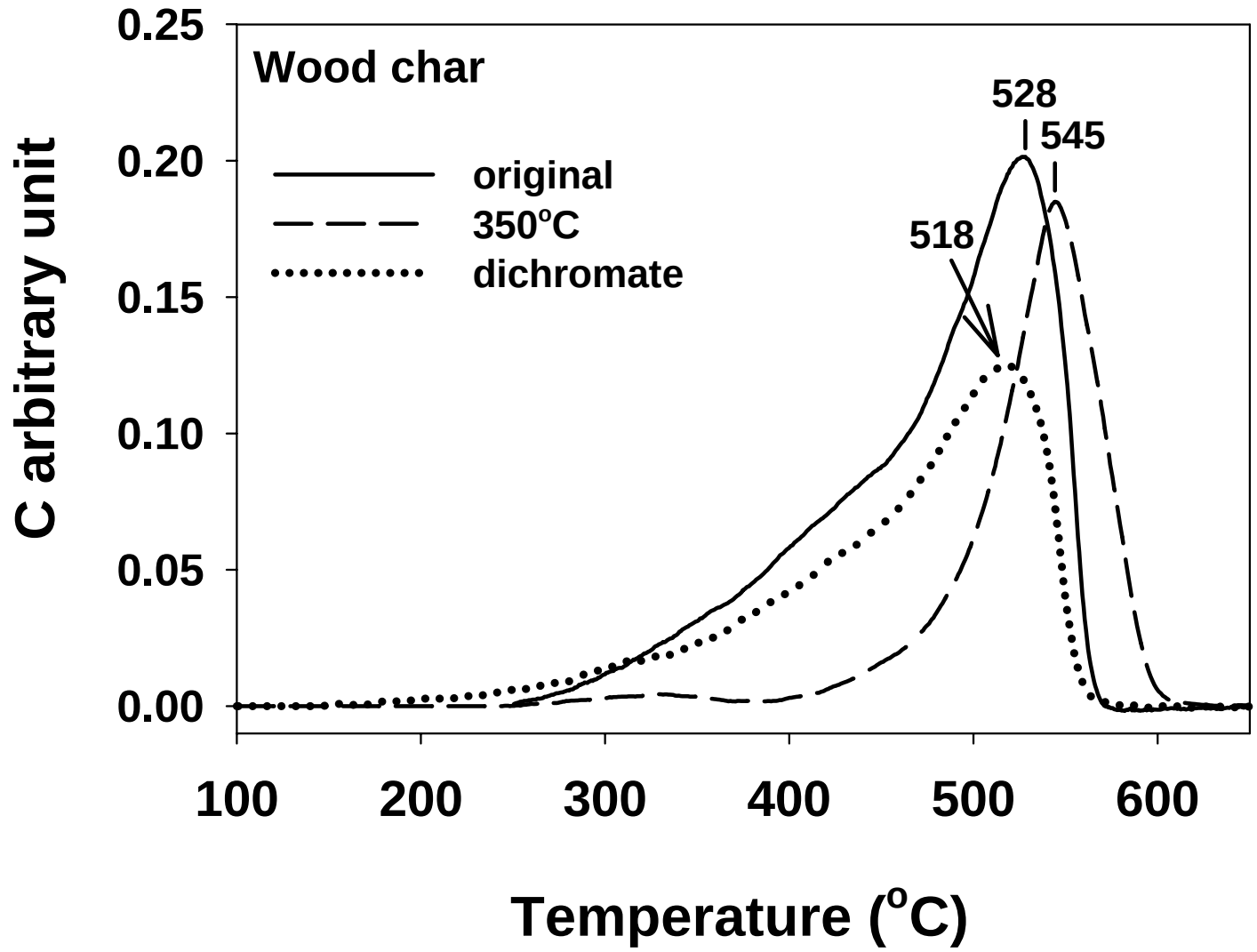

0.8
0.6
0.4
0.2
0.0
C arbitrary unit
200
300
400
500
600
700
Temperature (°C)
Glucose
Marsh humic acid
Decolorizing carbon
n-hexane soot
grass humic acid
373
564
615
305
270
225
323
503
485
475

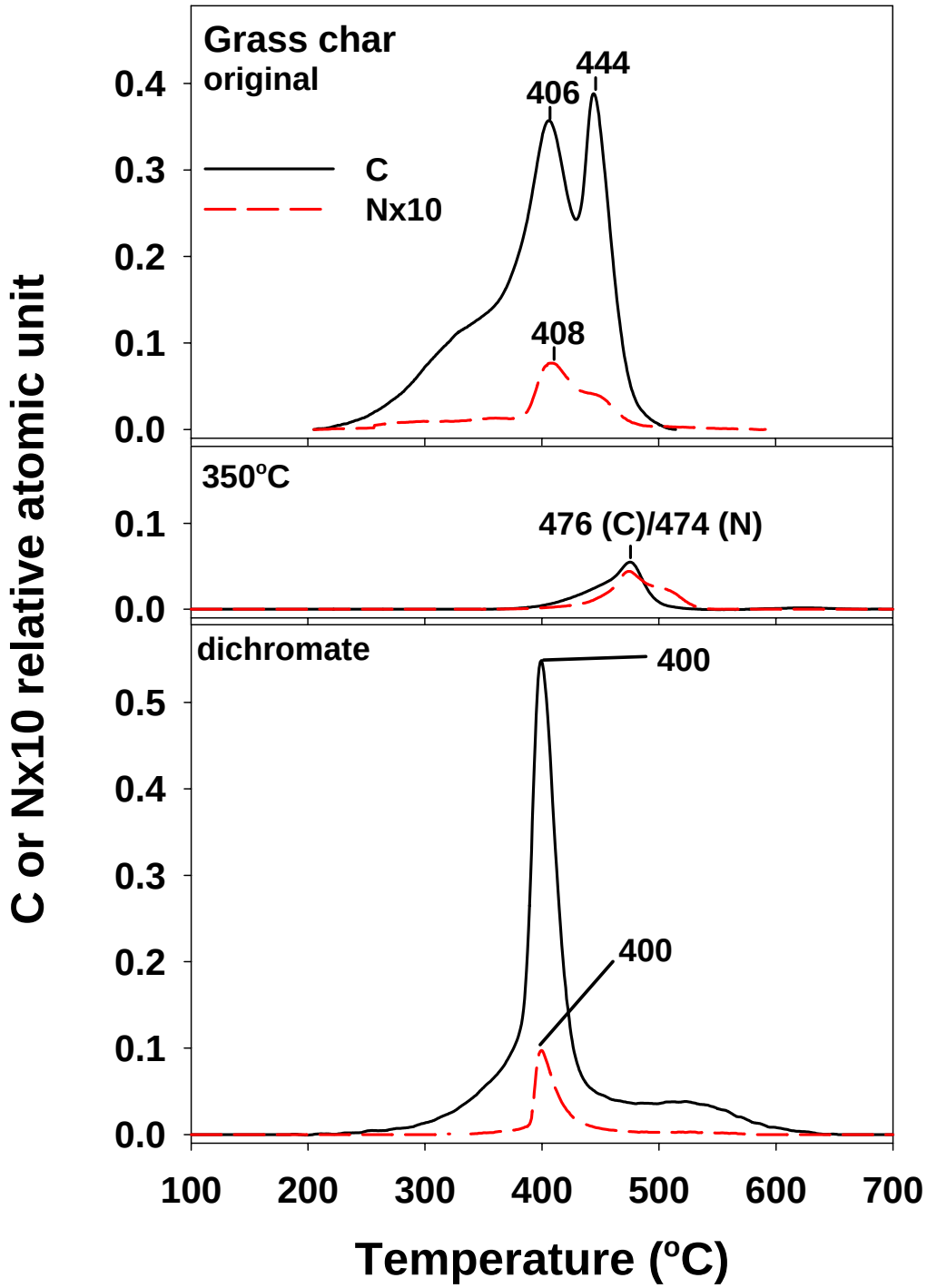

Decolorizing carbon
570
522
492
n-hexane soot
627
578
551
593
454
C arbitrary unit
Temperature (°C)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.0
0.2
0.4
0.6
0.8
1.0
200
300
400
500
600
700
800

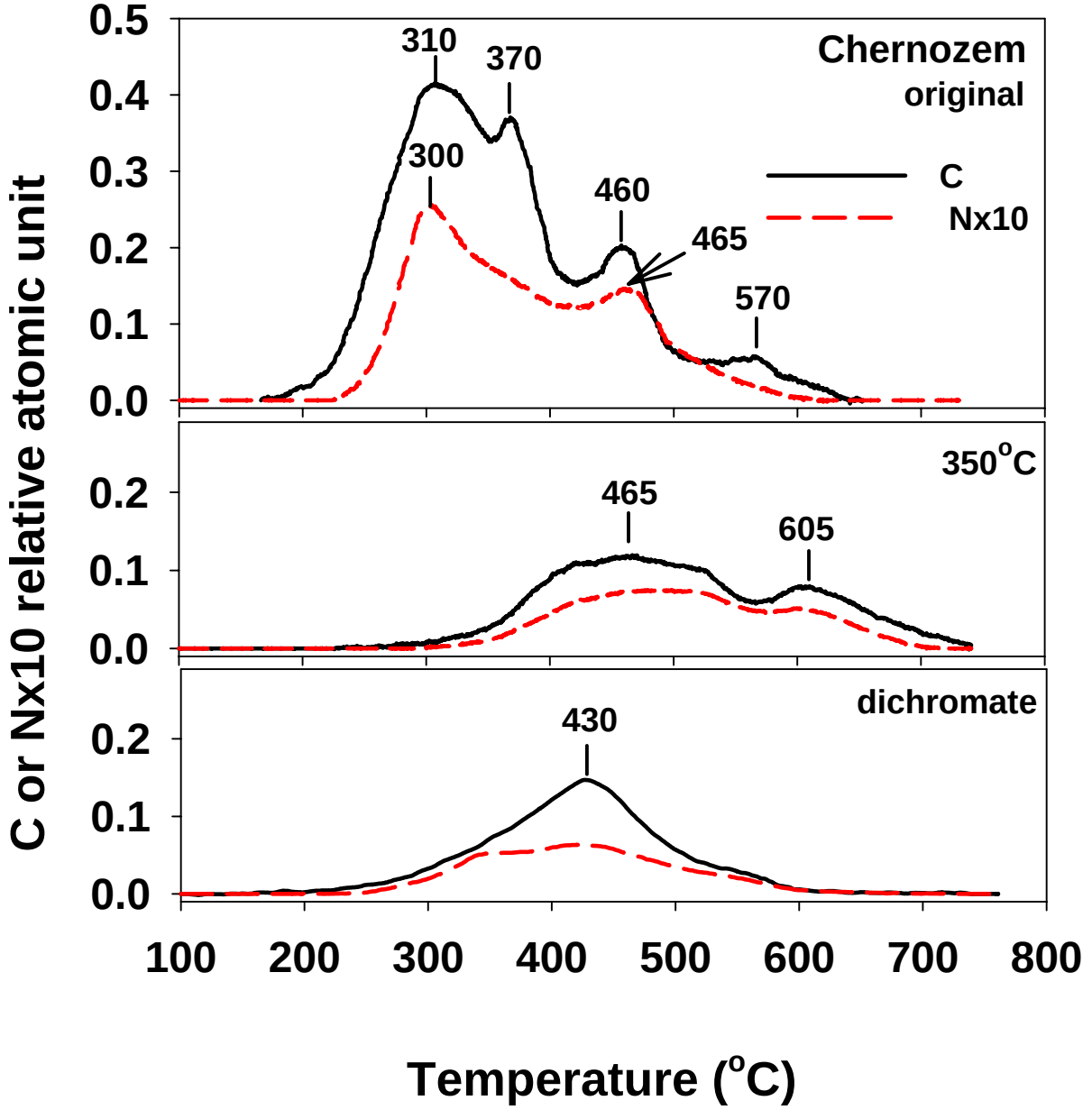
- *We set a BC criteria in MESTA as the C thermal decomposition peak ≥ 550 °C under the set of MESTA conditions.*

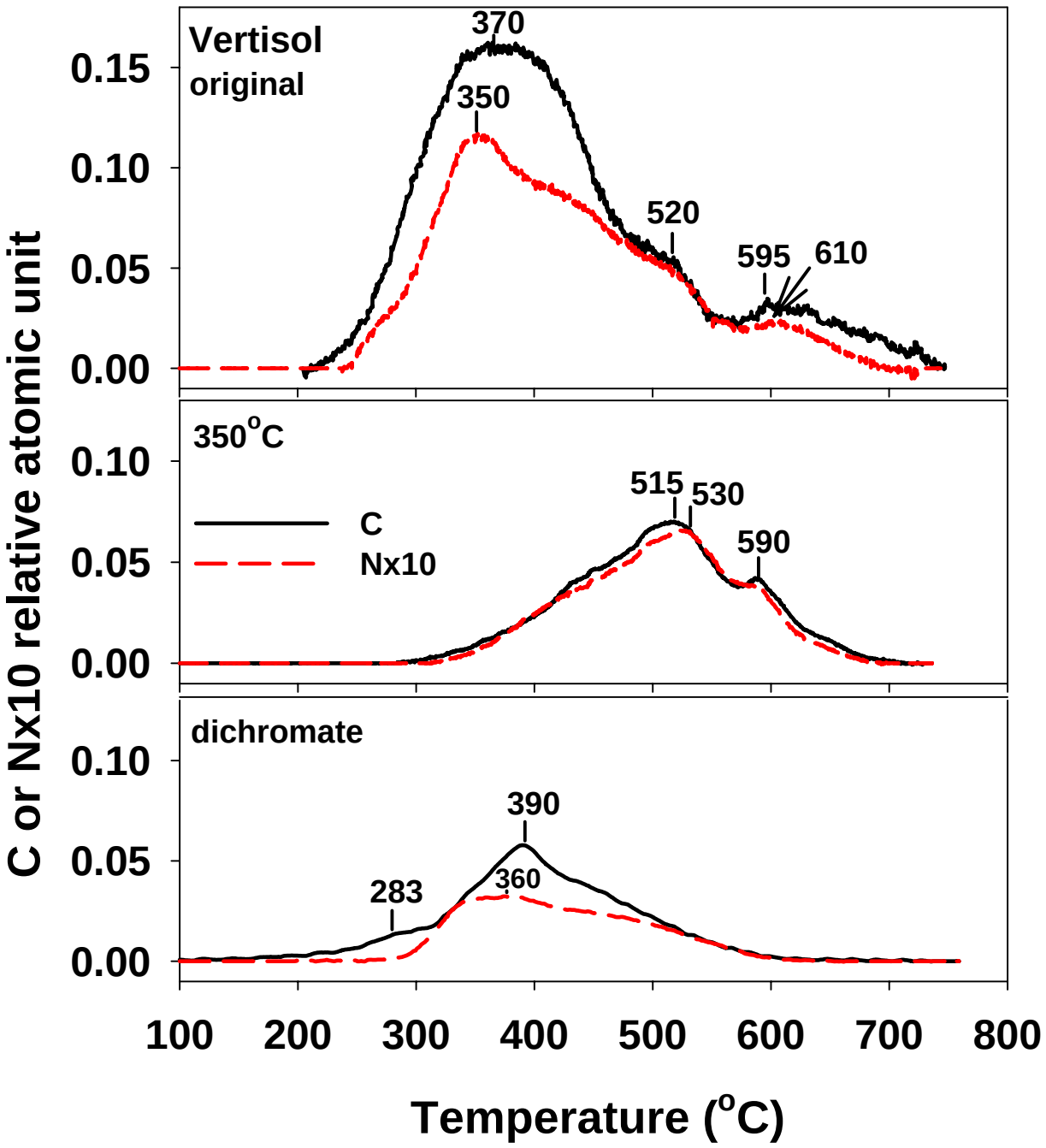

Decolorizing Carbon
original
C
Nx10
564
570
350°C
588
585
dichromate
433
355
398
C or Nx10 relative atomic unit
Temperature (°C)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
100
200
300
400
500
600
700

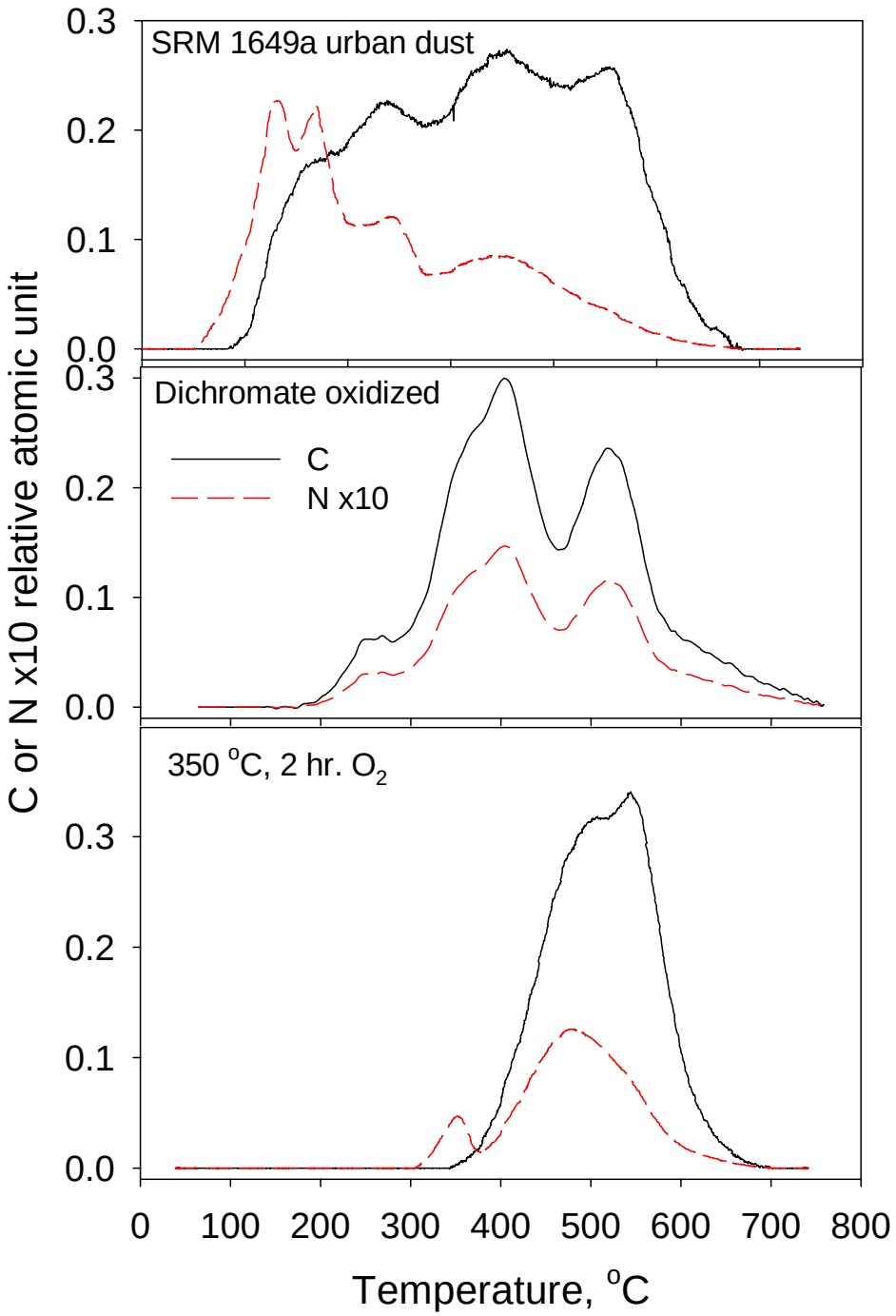

n-hexane soot
original
350°C
dichromate
615
681
480
409
0.5
0.4
0.3
0.2
0.1
0.0
C arbitrary unit
100
200
300
400
500
600
700
800
Temperature (°C)

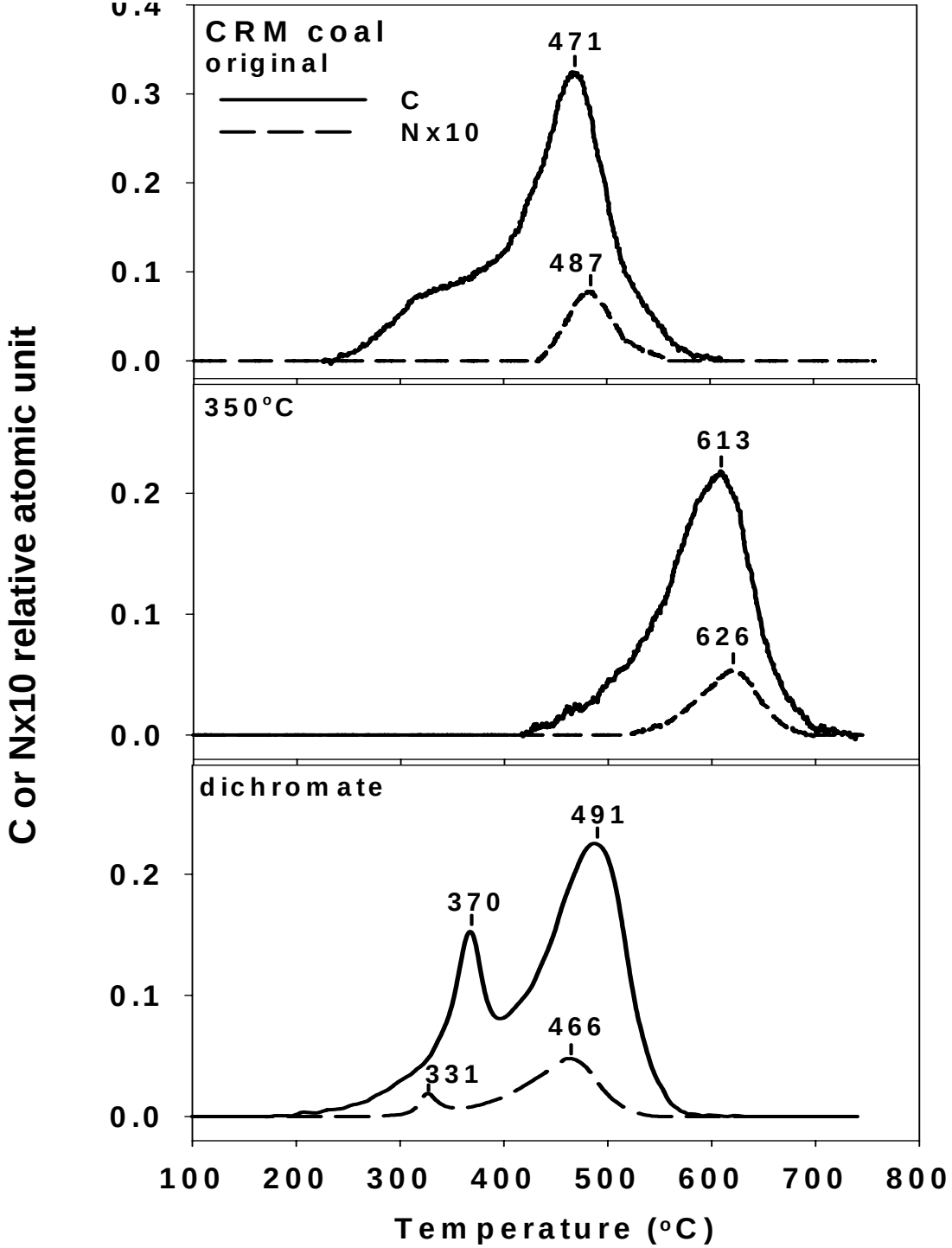

Wood char
original
350°C
dichromate
528
545
518
C arbitrary unit
0.25
0.20
0.15
0.10
0.05
0.00
100
200
300
400
500
600
Temperature (°C)


Grass char
original
444
406
C
Nx10
408
350°C
476 (C)/474 (N)
dichromate
400
400
0.0
0.1
0.2
0.3
0.4
0.5
100
200
300
400
500
600
700
C or Nx10 relative atomic unit
Temperature (°C)


C or Nx10 relative atomic unit
0.5
0.4
0.3
0.2
0.1
0.0
310
370
300
460
465
570
Chernozem
original
C
Nx10
350°C
465
605
dichromate
430
100
200
300
400
500
600
700
800
Temperature (°C)


Vertisol
original
370
350
520
595
610
350°C
515
530
590
C
Nx10
dichromate
390
360
283
0.15
0.10
0.05
0.00
100
200
300
400
500
600
700
800
C or Nx10 relative atomic unit
Temperature (°C)


SRM 1649a urban dust
Dichromate oxidized
C
N x10
350 °C, 2 hr. O2
C or N x10 relative atomic unit
Temperature, °C
0.0
0.1
0.2
0.3
0
100
200
300
400
500
600
700
800


CRM coal
original
C
Nx10
471
487
350°C
613
626
dichromate
491
370
466
331
C or Nx10 relative atomic unit
Temperature (°C)
0.0
0.1
0.2
0.3
0.4
100
200
300
400
500
600
700
800

Comparison of results of MESTA method with those of BC Ring Trial results (Hammes et al., 2007)

Sample	% BC/TOC					
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SRM1649a	8.4±3.9	8.1±2.5	35.8±11.7	37.3±11.5	65.0	24.6±5.7
Wood char	0.0	24.6±13.0	70.4±15.0	87.7±13.7	95.3	14.0±4.6
Grass char	1.5±1.2	26.1±3.4	34.8±8.6	82.3±13.6	58.2	0
n-hexane soot	46.9±1.9	26.0±22.5	51.0±10.8	96.3±4.3	91.3	89.2±3.6
Decolorizing Carbon	---	---	---	---	---	72.9±5.6
CRM coal	---	---	---	---	---	6.7±0.9

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 ≥550^{o}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.*