

High-Throughput FIA-MS/MS and LC-MS/MS Polyphenolics for the Authentication of Teas Adulterated with Chicory

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INTRODUCTION & AIM

Tea is a worldwide consumed beverage made by pouring hot (or boiling) water over fresh or cured leaves of the plant *Camelia sinensis*, native to China and East Asia; nowadays, its production has expanded to Europe, among other regions. Drinking tea is appreciated by society because of its characteristic flavor and aroma, as well as its health-beneficial attributes such as antioxidant, anti-inflammatory, anti-hypertensive, antimicrobial, neuroprotective, and anticarcinogenic properties, among others.

Tea can be found among the beverages more susceptible to fraudulent practices due to its high worldwide consumption and the increases in prices for some specific varieties due to climate changes and instability in the world of geopolitics. Tea adulteration with other plants, including chicory, is a common practice to gain an illicit profit. Polyphenols are the most abundant bioactive substances in tea, determining its quality and health function. In addition, they can be employed as secondary markers to address authentication issues.

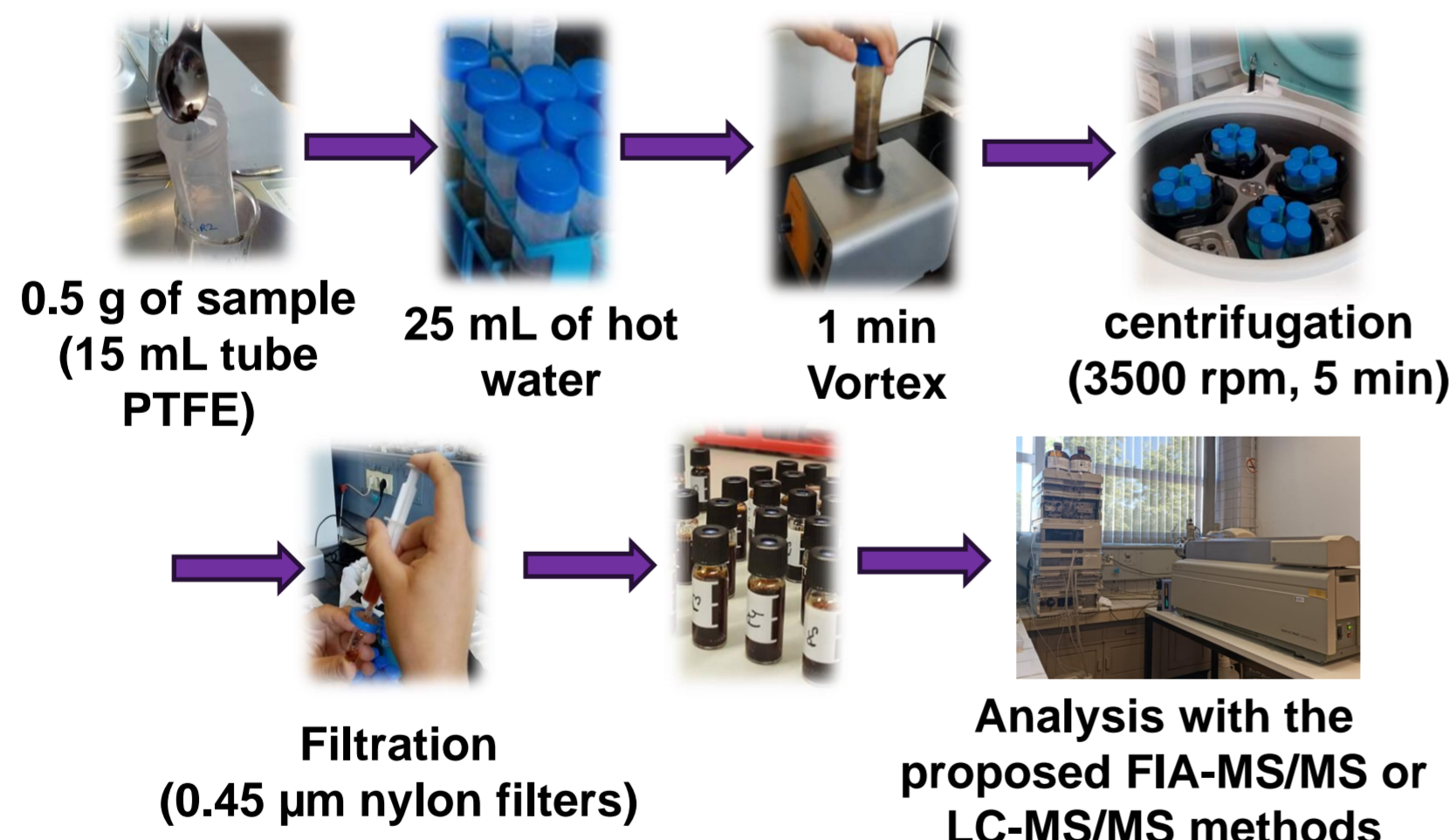
The aim of the present contribution is to evaluate the potential of FIA-MS/MS and LC-MS/MS polyphenolic profiling to address the authentication of teas adulterated with chicory.

METHOD

ANALYZED SAMPLES

Sample Class	Sample Type	Number of Samples
Tea	Black tea	20
	Green tea	20
	Oolong tea	20
	Red tea	20
	White tea	20
Chicory	Chicory	20

SAMPLE TREATMENT



INSTRUMENTATION



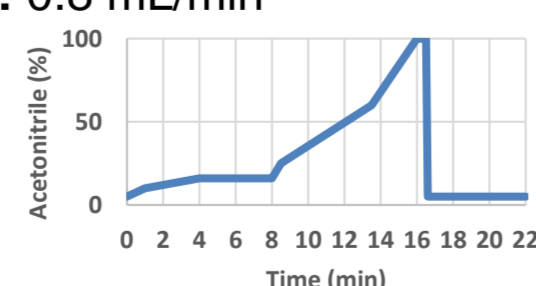
LC-MS/MS method

Column: Kinetex C18 (10 cm x 4.6 mm I.D., 2.6 µm)

Mobile phase: (A) 0.1% formic acid in water (B) Acetonitrile

Flow-rate: 0.8 mL/min

Gradient:



FIA-MS/MS method

No column

Mobile phase: 0.1% formic acid in water:acetonitrile (1:1 v/v)

Flow-rate: 0.15 mL/min

Other common conditions:

Sample injection volume: 5 µL

Ionization source: Electrospray negative ionization mode

Acquisition: Multiple reaction monitoring (MRM) mode

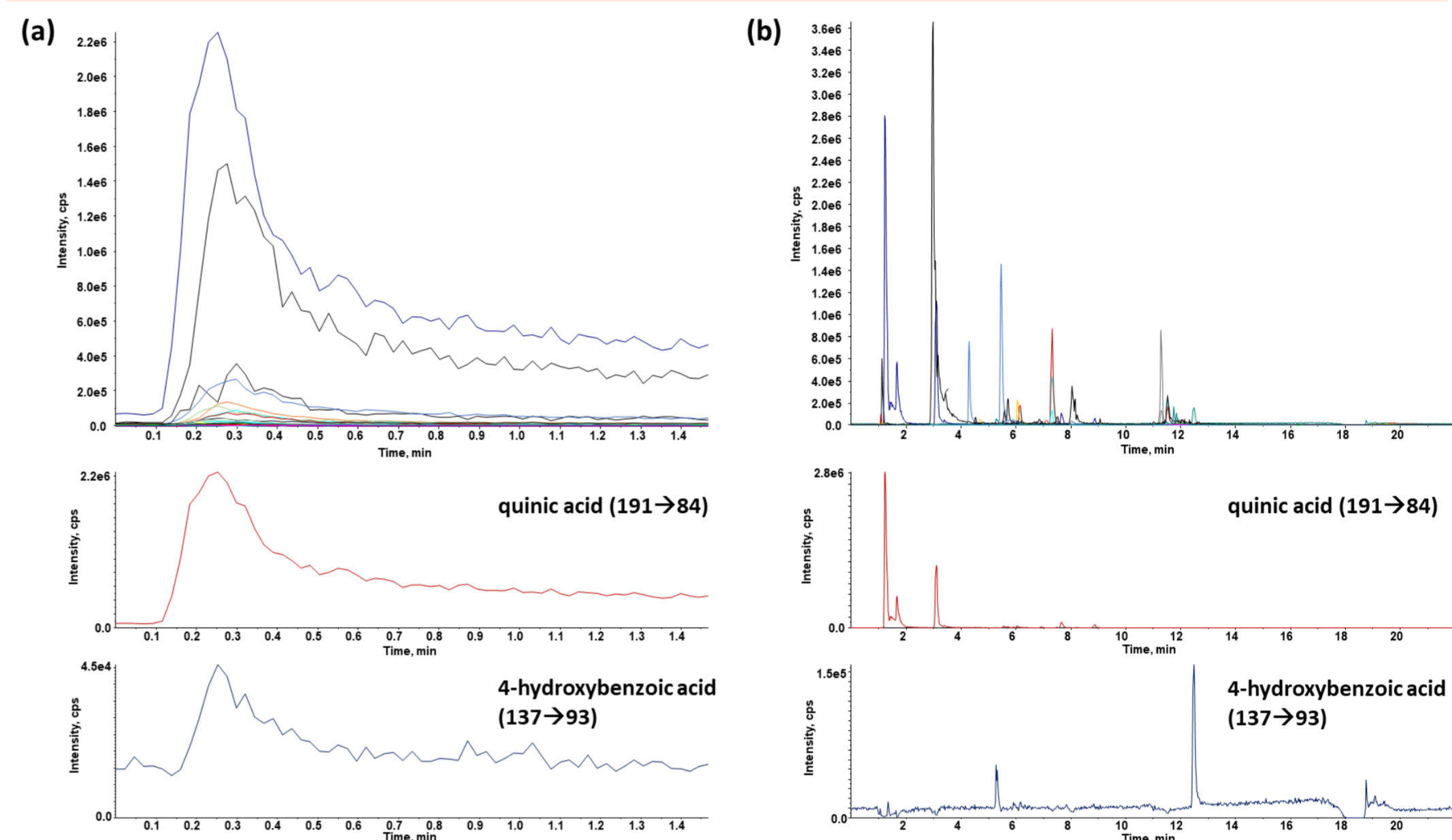
Transitions were optimized for up to 55 phenolic compounds

LS System: Agilent 1100 Series HPLC

MS System: AB Sciex 4000 Qtrap hybrid Triple quadrupole/linear ion trap MS

RESULTS & DISCUSSION

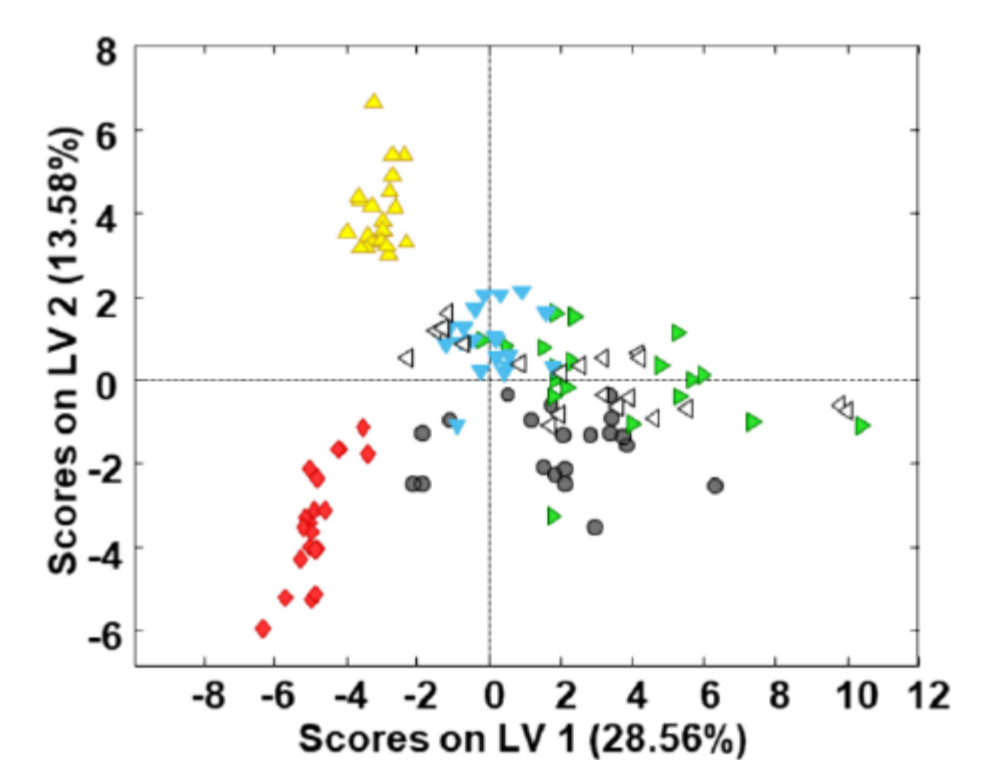
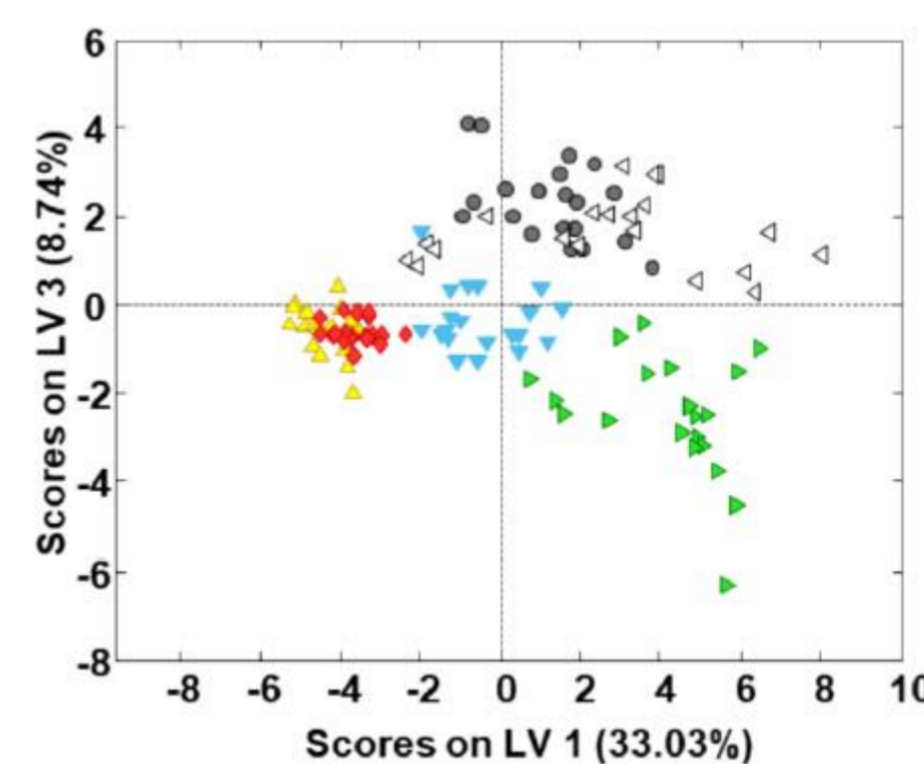
FIA-MS/MS and LC-MS/MS Polyphenolic Profiles



Polyphenolic and phenolic acid profiles (showing all the detected MRM transitions), and the extracted MRM transitions for quinic acid (191→84) and 4-hydroxybenzoic acid (137→93), obtained by (a) FIA-MS/MS and (b) LC-MS/MS.

CLASSIFICATION OF TEA AND CHICORY SAMPLES BY PARTIAL LEAST SQUARES-DISCRIMINANT ANALYSIS (PLS-DA)

Using FIA-MS/MS polyphenolics



Cross-validation results:

Sensitivity (%): 90-100

Specificity (%): 88.9-100

Classification error (%): 0-10.5

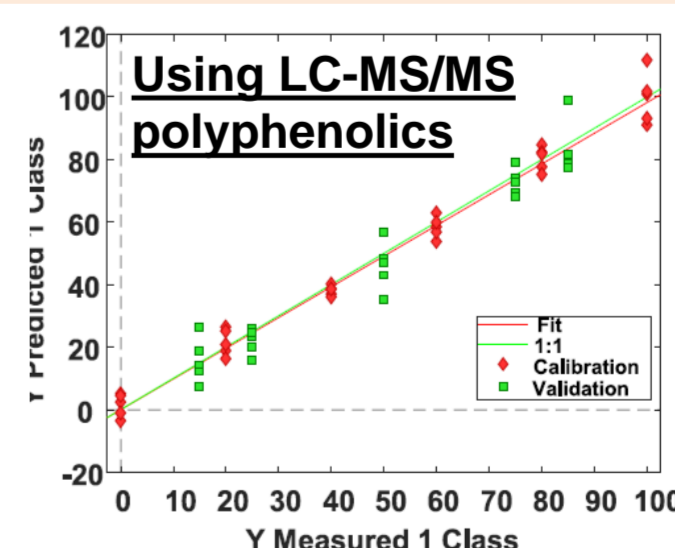
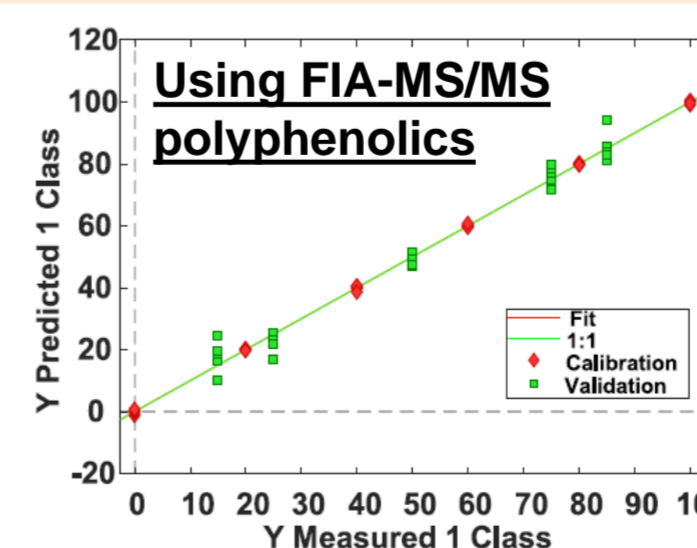
Cross-validation results:

Sensitivity (%): 95-100

Specificity (%): 86-99

Classification error (%): 0.5-14.5

DETECTION AND QUANTIFICATION OF TEA FRAUDS WITH CHICORY BY PARTIAL LEAST SQUARES (PLS) REGRESSION



Adulteration prediction errors:

FIA-MS/MS: 3.4-10.9%

LC-MS/MS: 6.5-14.8%

CONCLUSION

Both FIA-MS/MS and LC-MS/MS polyphenolic profiling strategies have shown good classification and chicory adulteration detection capabilities to assess tea authentication, being FIA-MS/MS advantageous as no chromatographic separation is required.

ACKNOWLEDGEMENTS

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