Detection of Maple Syrup Adulteration by Sugars

By N. Martin Ph.D., A. Clément Ph.D., B. Panneton Ph. D.

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ACER
Centre de recherche, de développement et de transfert technologique acéricole Inc.

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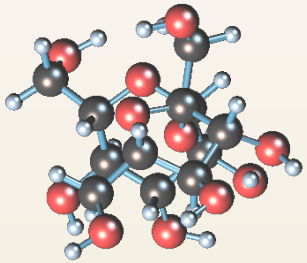
Chemical Composition of Maple Syrup



Sucrose

Reducing sugars
(glucose and fructose)

Amino acids

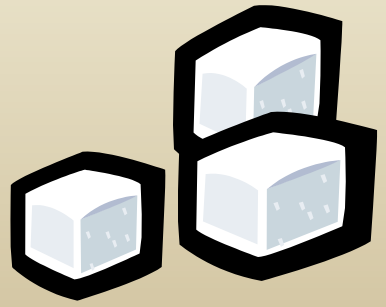
Organic acids

Minerals

Phenolic compounds

Adulteration of Maple Syrup

- Sucrose can also be obtained from other vegetal sources;
- Maple syrup is a luxury product;
- Maple syrup can be adulterated by adding comparatively cheaper sugars for economic gains;
- Adulteration of maple syrup by the addition of other types of sugars violates state, provincial, and federal laws; defrauds consumers; and is damaging to the maple industry;



Maple Syrup Authenticity and Quality Control

- Maple syrup is 100% natural, pure and free of any coloring or additives;
- Canadian laws and regulations for maple syrup production ensure the quality of maple syrup production. Each province has its own maple syrup regulations;
- Producers must adhere to strict quality control standards throughout the production process (food safety and authenticity);
- At the request of the Federation of Quebec Maple Syrup Producers, ALL barrels of maple syrup produced in Quebec are inspected and classed according to various quality parameters.

Simple, cost-effective, quick, accurate and non-destructive methods are required for routine analysis

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Detection of Adulteration – Laboratory Methods

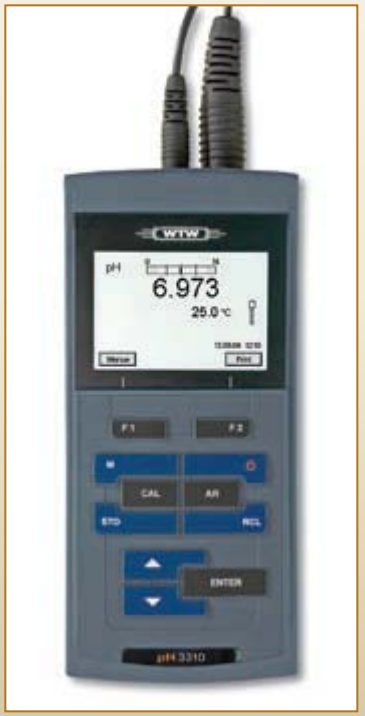
- ^{13}C Isotope Ratio Mass Spectrometry (IRMS)
- Oligosaccharide Fingerprinting : High-performance anion exchage liquid chromatography-pulse amperometric detection (HPAQ-PAD)
- Site-specific nuclear isotope fragmentation –nuclear magnetic resonance (^{2}H SNIF-NMR)
- Stable isotope ratio analysis based on ethanol fermentation from sugars (^{13}C SIRA-MS)

Time-consuming and expensive methods, destructive testing

Detection of Adulteration – Field Tests

- Electrical conductivity: indirect method for the determination of mineral substances in food;

- The electrical conductivity of maple syrup is a measure of it's ability to conduct an electric current and depends on its soluble ion content;



- Can be measured by a portable conductivity-meter;

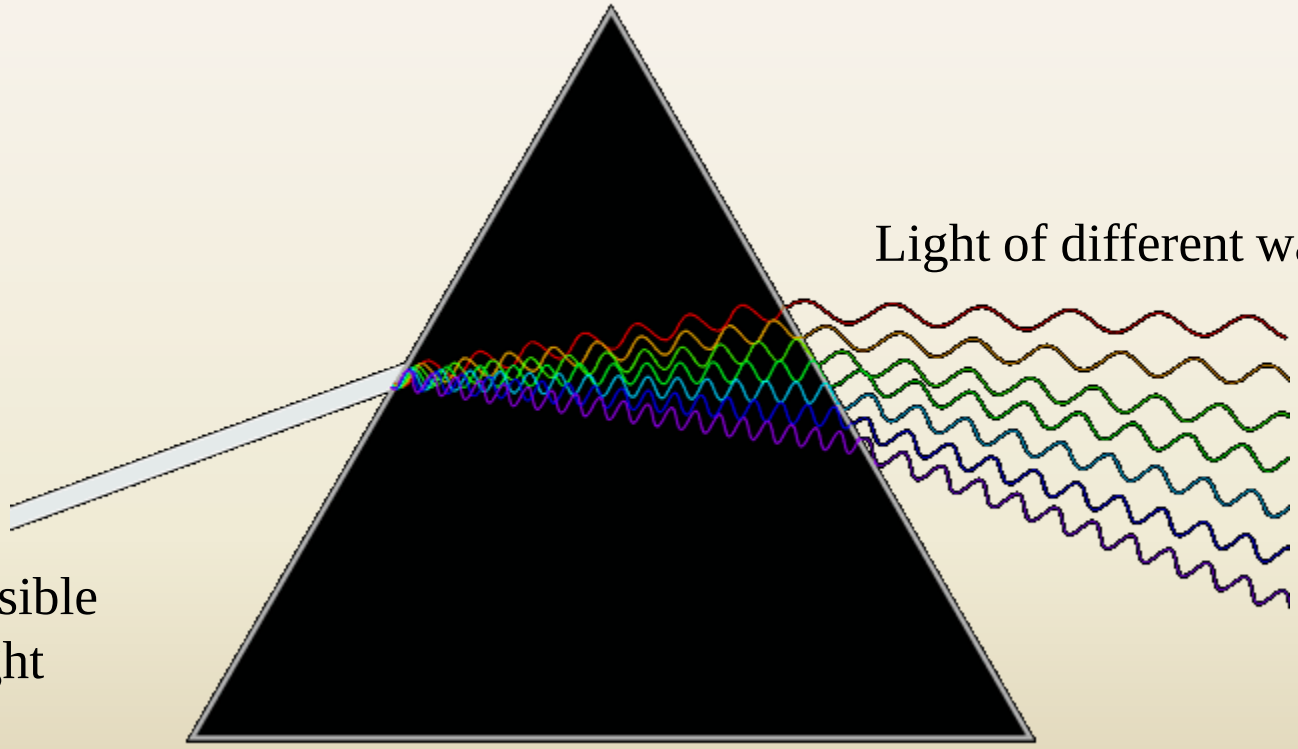
Not an accurate method for determining authenticity (Too many false-positive samples $$$)

Optical Spectroscopy

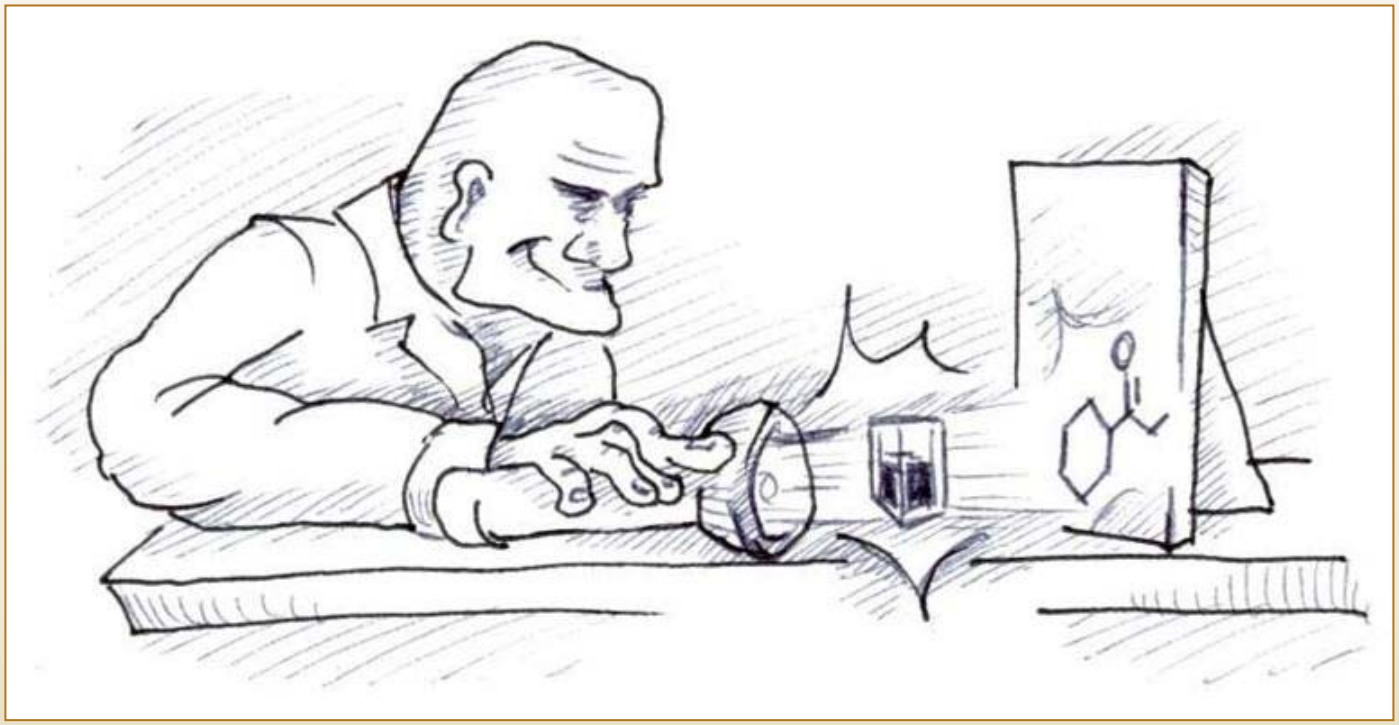
Optical spectroscopy methods are:

- Based on the interaction between light and food;
- Simple, cost-effective, quick, and non-destructive;
- Often used for the detection of adulteration in other industries where the procedure has been properly calibrated and validated;
- Coupled with chemometrics to extract the relevant information.

Division of light in spectral colors



Optical Spectroscopy



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Identification of substances through the spectrum emitted from or absorbed by them.

What is Chemometrics?

- Science of extracting information from chemical systems by means of mathematical and statistical methods;
- Correlates quality parameters or physical properties to analytical instrument data (spectroscopy spectra);
- Patterns in the data are modeled (pure maple syrup); these models can then be routinely applied to future data to detect abnormal samples (monitoring adulteration);
- Selection of samples and variables to include in the modeling is of major importance (needs very large and complex datasets).

Investigation of an alternative method for the detection of maple syrup adulteration

Research Project Description

- **Requested by the Federation of Quebec Maple Syrup Producers;**

- **Funded by Provincial and Federal Programs :**
  - ✓ Programme d'appui financier aux regroupements et aux associations de producteurs désignés – MAPAQ
  - ✓ Developing Innovative Agri-Products Programm-AAC

- **Work done in collaboration with optical spectroscopy and chemometrics specialists:**
  - ✓ Alain Clément, Ph.D., FRDC-AAC
  - ✓ Bernard Panneton, Ph.D., HRDC-AAC

Specific Goals of the Study

1. To investigate the efficiency of different spectroscopic methods for the detection of maple syrup adulteration;

2. To characterize maple syrup and adulterants with the chosen methods (sampling, data acquisition, calibration and validation);

3. To develop a prototype for quick detection of maple syrup adulteration intented for routine analysis (inspection).

Material and Methods

- **Reference pure maple syrup samples**
  - ✓ 230 samples taken from barrels from different producers
  - ✓ AA, A, B, C and D
  - ✓ Different regions across Quebec

- **Adulteration treatments**
  - ✓ Five types of adulterants (2 sources/type: A2, A3, A4, A5; 1 source: A1)
  - ✓ Four levels of adulteration
  - ✓ 40 maple syrup samples (AA, A, B, C and D)

Total of 1710 samples analysed

Material and Methods

Why so many samples?

- Wide variability in the maple syrup composition and not all chemical compounds have been identified yet;

- Composition of maple syrup varies from producer to producer, region to region, from season to season, and within a season;

- Several ways to adulterate maple syrup;

⇨ **Need to control all sources of variability**

Material and Methods

Controlling the nature of maple syrup :

- All samples were certified by the producers to be authentic (solemn declaration);

- Randomly chosen samples were submitted to CFIA for analysis (^{13}C IRMS).

A look into our first results

Detection capacity of the methods used

Falses-positives

Results using Spectroscopic Method No. 1				
From / To	No	Yes	Total	% Correct
No	241	29	270	89.3%
Yes	187	1253	1440	87.0%
Total	428	1282	1710	**87.4%**

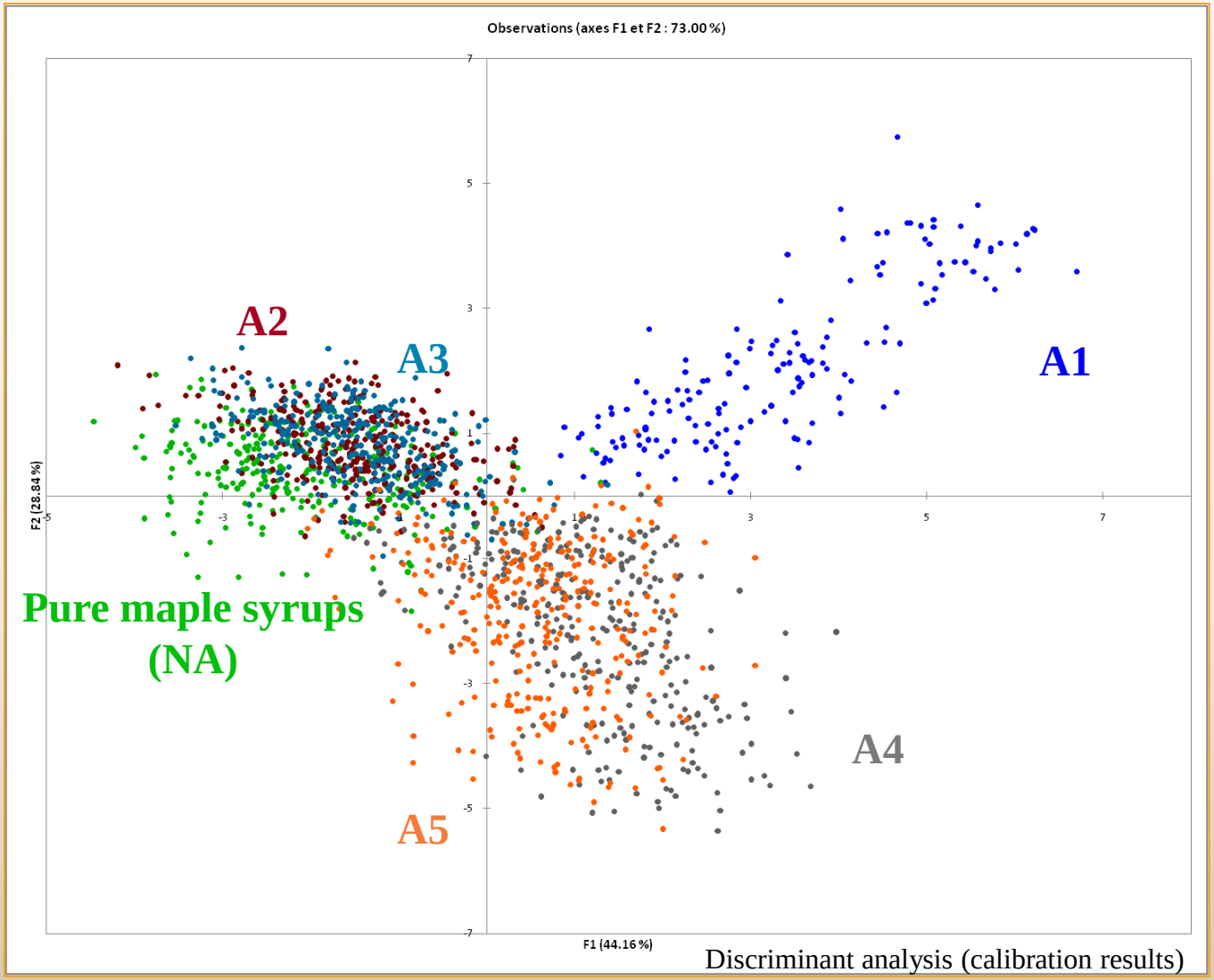
Results using Spectroscopic Method No.2				
From / To	No	Yes	Total	% Correct
No	234	36	270	86.7%
Yes	168	1272	1440	88.3%
Total	402	1308	1710	**88.1%**

Falses-negatives

Results combining both Spectroscopic Methods				
From / To	No	Yes	Total	% Correct
No	262	8	270	97.0%
Yes	95	1345	1440	93.4%
Total	357	1353	1710	**94.0%**

Statistical Approach: Discriminant Analysis (calibration results)

Differentiation of adulterants types



Discriminant analysis (calibration results)

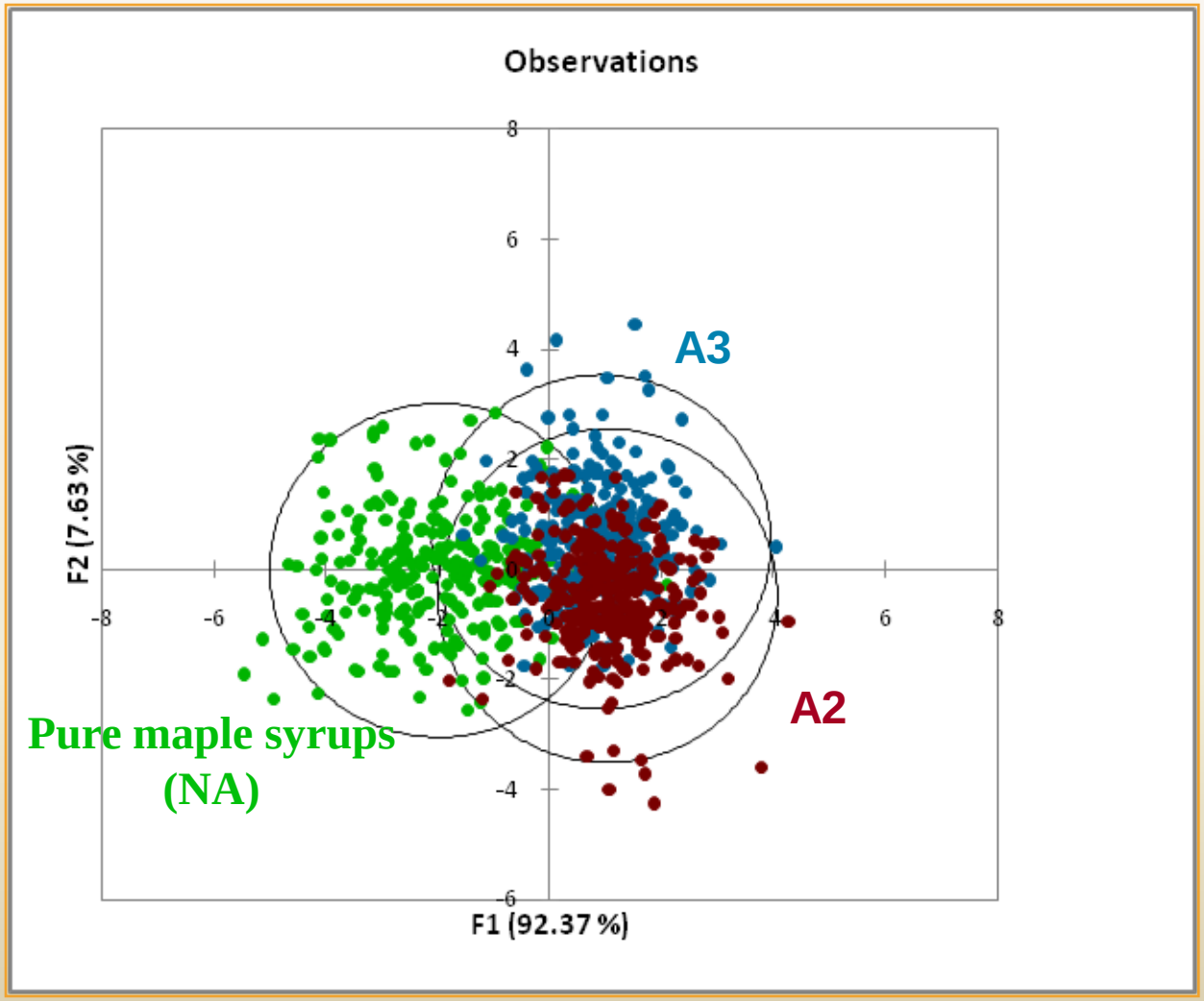
Differentiation capacity of the method

Classification matrix

	NA	A1	A2	A3	A4	A5	Total	% Correct
NA	239	1	10	11	3	6	270	88.5%
A1	0	152	2	2	3	1	160	95.0%
A2	4	0	219	91	0	6	320	68.4%
A3	6	0	85	224	2	3	320	70.0%
A4	1	0	5	6	270	38	320	84.4%
A5	3	2	6	10	37	262	320	81.9%
Total	253	155	327	344	315	316	1710	79.8%

Statistical Approach: Discriminant Analysis (calibration results)

A closer look at adulterants A2 and A3



Statistical Approach: Discriminant analysis on subsample (calibration results)

A closer look at adulterants A2 and A3

From \ To	NA	A2	A3	Total
NA	238	19	13	270
A2	8	212	100	320
A3	11	93	216	320
Total	257	324	329	910

% Correct classification (A2 and A3 confounded) : 94.4 %

% False Positive: 3.51%

% False Negative: 2.09%

Statistical Approach: Discriminant analysis on subsample (calibration results)

Conclusion

- Preliminary data analysis of the latest results shows that the chosen spectroscopic methods are powerful for detecting maple syrup adulteration (94% correct classification);

- The method is also able to identify the type of sugar used to adulterate the maple syrup;
  - ✓ Some sugars are very easily identified (A1=95%, A4 and A5 >80%)
  - ✓ More work is needed for the discrimination of A2 and A3

- More chemometrics work on the datasets will allow for refinement of the prediction models and determination of detection limits.

Future Work

- A set of 400 «unknown» samples will be submitted to analysis (blind testing) : testing the mathematical model's robustness;

- Method's performances will be validated in 2011
  - ✓ Assessment of maple syrup variability (effect of sampling season);
  - ✓ More maple syrup samples in each colour class
  - ✓ Updated hardware

- The hardware and the mathematical models belong to Centre ACER and FPAQ which allows us to adjust and refine the technology as necessary.

Acknowledgements

- ACER-Inspection division
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- Quebec Maple Syrup Producers (Affidavits)
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Thank you!

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