Potential strategy of universal calibrations independant of the type of NIR instrument

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Is the time for standardization and transfer of NIR spectral databases over ?

To provide a **quick solution of calibration** to any types of NIR spectrometers, the **classical procedure** consists in a **transfer of spectral databases**. Usually **reference commodities (standards optic)** are scanned **in sealed cups** on both device for which the calibrations are required (**Master**) and the device used to build the database (**Slave**). Then, an **algorithm of transfer** can be used to **simulate** the NIR data of the slave on the master.
This method presents some **limitations** :

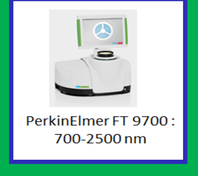
- The **measurement dates** on both instruments must be **relatively close** which can be problematic when the instruments are not on the same country or not easily accessible;
- It is **time consuming** to send the standard optics at different locations and difficult to manage when dealing with a large number of spectrometers;
- The sample compartment of the instruments or the instrument itself must be **compatible with the sealed cups;**
- Usually a transfer is not enough and it is necessary to **add spectra of the master** in the simulated spectral database of the slave;
- A **validation step** is **mandatory** at the end of the procedure.

In order to cope with those limitations, a large experiment has been set up :


ASD : 350-2500 nm


DS2500 : 400-2500 nm


Buchi : 1100-2500 nm


PerkinElmer FT 9700 : 700-2500 nm


VIAVI : 950-1650 nm


Spectrale engine 3477 : 1550-1950 nm

80 samples of white flour divided into **4 batches** have been scanned on **12 different NIR devices** (all anonymized) and analyzed by **wet chemistry** for the determination of the **protein content**.

➢ **8 devices** have **the full classical NIR** spectral range (1100-2500 nm) : ASD Fieldspec, Bruker MPA, Buchi NIRMaster, Foss DS2500, Foss XDS, PerkinElmer FT 9700, Thermofisher Antaris, Unity Spectra Star XT

➢ **4 devices** have a **reduced NIR** spectral range : Perten DA7200 (950-1650 nm), Spectral engine 3477 (1550-1950 nm), Spectral engine 3487 (1750-2150 nm) , VIAVI (950-1650 nm)


Unity : 680-2600 nm


Bruker : 1100-2500 nm


Antaris : 1100-2500 nm


XDS : 400-2500 nm


Perten DA7200 : 950-1650 nm


Spectrale engine 3487 : 1750-2150 nm

A first calibration (initial calibration) was calculated from the **Initial Calibration Set (ICS)** using the **batches 1 and 3** of **only 4 instruments**: 2 FT systems and 2 monochromator systems having the **full classical NIR range** (1100-2500 nm).

Then, for **every instrument**, a **new specific calibration** has been established with the **initial calibration set + the batch 2** of each respective device.

All the calibrations have been calculated **automatically** by Winisi with **maximum 10 factors** PLS and by applying **SNV** and a **first derivative** as preprocessing.

The **batch 4** for **each device** constitutes the **final validation.**

Table 1 shows the data structure :

	NIR Instrument	Spectra of			
		Batch 1 (Monday)	Batch 2 (Tuesday)	Batch 3 (Wednesday)	Batch 4 (Thursday)
Table 1	Device 1 - FT 1	Initial calibration set	Added in the initial calibration set	Initial calibration set	Validation set 1
	Device 2 - FT 2	Initial calibration set	Added in the initial calibration set	Initial calibration set	Validation set 2
	Device 3 - Monochromator 1	Initial calibration set	Added in the initial calibration set	Initial calibration set	Validation set 3
	Device 4 - Monochromator 2	Initial calibration set	Added in the initial calibration set	Initial calibration set	Validation set 4
	Device 5 - Full range	Data not used	Added in the initial calibration set	Data not used	Validation set 5
	Device 6 - Full range	Data not used	Added in the initial calibration set	Data not used	Validation set 6
	Device 7 - Full range	Data not used	Added in the initial calibration set	Data not used	Validation set 7
	Device 8 - Full range	Data not used	Added in the initial calibration set	Data not used	Validation set 8
	Device 9 - Reduced range	Data not used	Added in the initial calibration set	Data not used	Validation set 9
	Device 10 - Reduced range	Data not used	Added in the initial calibration set	Data not used	Validation set 10
	Device 11 - Reduced range	Data not used	Added in the initial calibration set	Data not used	Validation set 11
	Device 12 - Reduced range	Data not used	Added in the initial calibration set	Data not used	Validation set 12

Table 2 indicatives the performances expressed as SEC and SECV on both calibrations : the initial calibration and all specific calibrations

	Origin of calibrations	N	Mean	SD	Est. Min	Est. Max	SEC	SECV	R^2	RPD_{CV}
Table 2	eqa 1 : Initial calibration based on the initial calibration set (ICS)	156	11.15	1.19	7.59	14.72	0.13	0.16	0.98	7.4
	ICS + batch 2 of device 1 - FT 1	175	11.10	1.19	7.54	14.66	0.13	0.16	0.98	7.6
	ICS + batch 2 of device 2 - FT 2	174	11.12	1.18	7.57	14.66	0.13	0.16	0.98	7.3
	ICS + batch 2 of device 3 - Monochromator 1	175	11.09	1.18	7.54	14.65	0.12	0.15	0.98	7.7
	ICS + batch 2 of device 4 - Monochromator 2	175	11.11	1.18	7.56	14.66	0.12	0.16	0.98	7.4
	ICS + batch 2 of device 5 - Full range	174	11.09	1.19	7.53	14.66	0.12	0.15	0.98	8.1
	ICS + batch 2 of device 6 - Full range	174	11.09	1.18	7.55	14.62	0.13	0.15	0.98	7.8
	ICS + batch 2 of device 7 - Full range	175	11.12	1.20	7.51	14.72	0.13	0.16	0.98	7.3
	ICS + batch 2 of device 8 - Full range	175	11.09	1.18	7.54	14.65	0.12	0.15	0.98	8.1
	ICS + batch 2 of device 9 - Reduced range	177	11.08	1.18	7.55	14.62	0.21	0.25	0.96	4.8
	ICS + batch 2 of device 10 - Reduced range	177	11.10	1.19	7.54	14.66	0.24	0.26	0.95	4.6
	ICS + batch 2 of device 11 - Reduced range	178	11.09	1.19	7.52	14.67	0.22	0.24	0.96	4.9
	ICS + batch 2 of device 12 - Reduced range	178	11.08	1.18	7.55	14.61	0.25	0.28	0.94	4.2

Table 3 represents the SEPC (error of prediction corrected for the bias) for the initial calibration and the specific calibrations

		SEPC	
		Initial calibration	ICS + batch 2 of each respective device
Table 3	Device 1 - FT 1	0.215	0.178
	Device 2 - FT 2	0.118	0.107
	Device 3 - Monochromator 1	0.170	0.145
	Device 4 - Monochromator 2	0.164	0.150
	Device 5 - Full range	0.142	0.100
	Device 6 - Full range	0.105	0.086
	Device 7 - Full range	0.105	0.088
	Device 8 - Full range	0.247	0.134
	Device 9 - Reduced range	0.206	0.187
	Device 10 - Reduced range	0.330	0.281
	Device 11 - Reduced range	0.635	0.449
	Device 12 - Reduced range	1.201	0.358

As expected, the results are better when real spectra are added into the initial calibration set with usually RPDC (SD=SEPC) values larger than 3. Even without adding spectra, the devices 6 and 7 have better performances of predictions than the 4 instruments used to built the initial calibration set.
For devices having a reduced range, the performances are really lower.
Figure 1 illustrates the RPDC obtained with the initial calibration and the 12 specifics calibrations

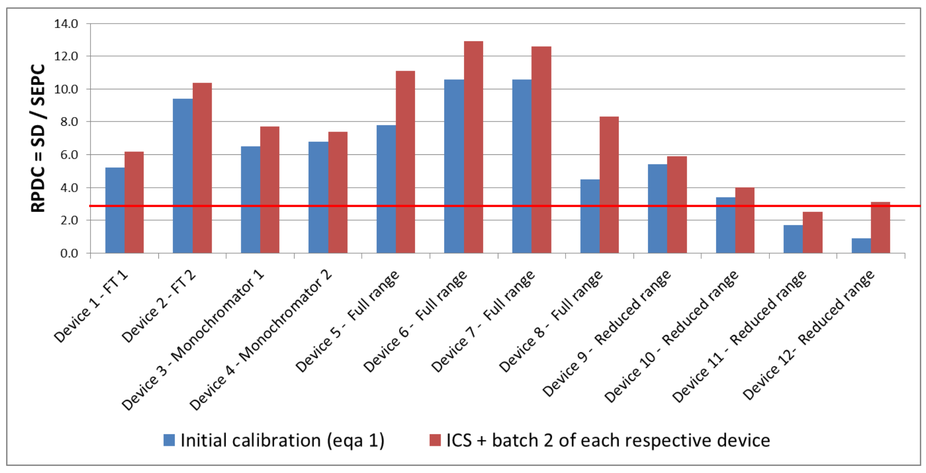


Table 4 describes the GH (Mahalanobis distance) and NH (Neighborhood distance) values. Adding only 20 real spectra allows to reduce considerably the values proving that it is possible to adapt easily the calibrations

		Average GH		Average NH	
		No real spectra added	20 real spectra added	No real spectra added	20 real spectra added
Table 4	Device 1 - FT 1	2.1	1.6	0.5	0.5
	Device 2 - FT 2	1.0	1.0	0.2	0.2
	Device 3 - Monochromator 1	0.9	0.7	0.1	0.1
	Device 4 - Monochromator 2	0.9	0.7	0.1	0.1
	Device 5 - Full range	13.2	12.6	8.5	8.2
	Device 6 - Full range	3.9	1.1	1.3	0.2
	Device 7 - Full range	4.2	1.3	2.2	0.3
	Device 8 - Full range	5.7	1.2	2.4	0.2
	Device 9 - Reduced range	35.6	1.7	21.9	0.4
	Device 10 - Reduced range	497.8	1.6	463.7	0.1
	Device 11 - Reduced range	706.4	1.5	672.1	0.1
	Device 12 - Reduced range	36.0	2.3	29.0	0.5

Conclusion

Based on this study, it seems possible to skip the step of transfer of database between instruments provided the full spectral range is available. As a validation set is required anyway, just a **bias correction seems to be enough** provided that the calibration is based on spectra coming from different reliable devices.
Further study should be launched on more complicated products and constituents like forage for instance.

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