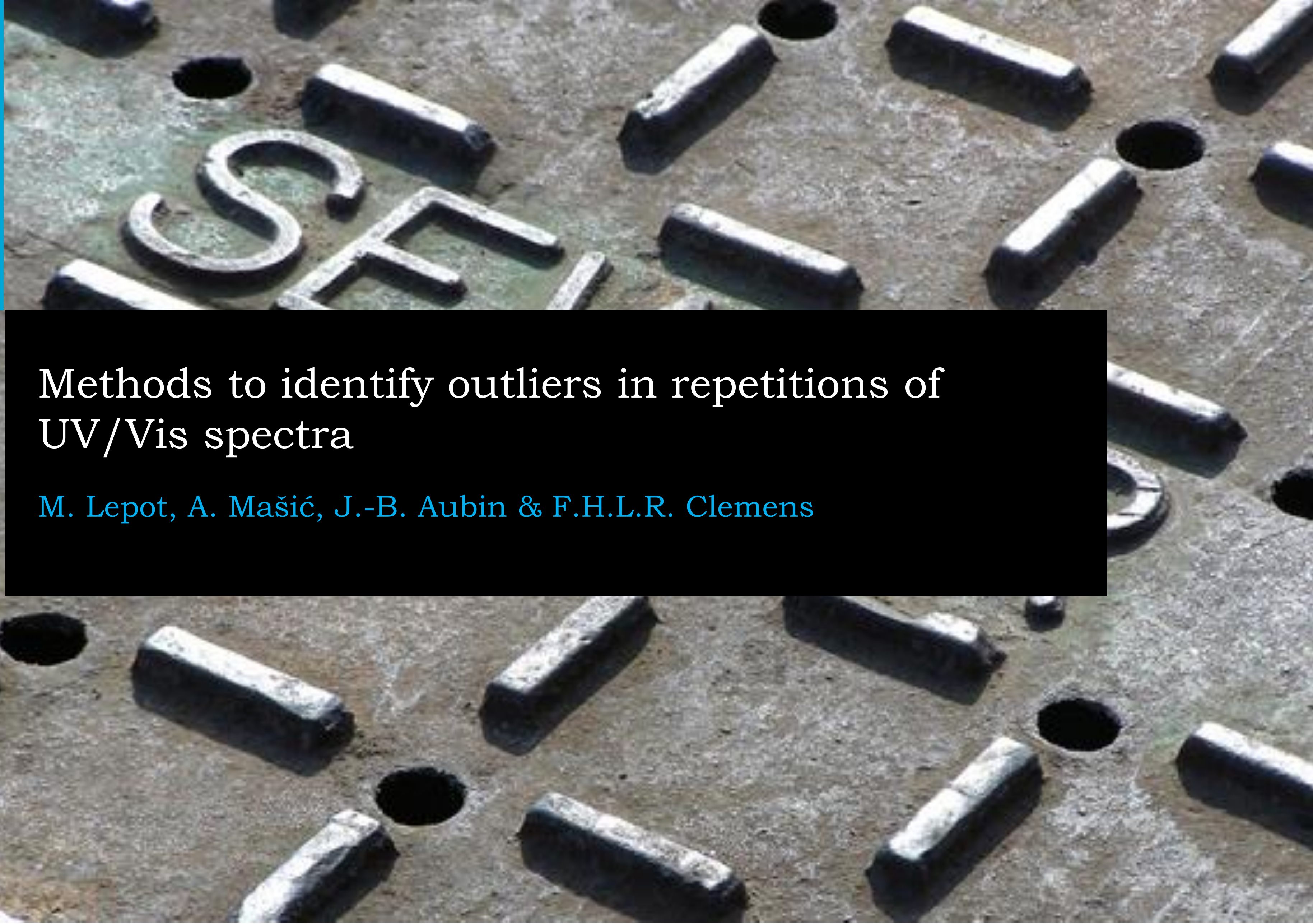
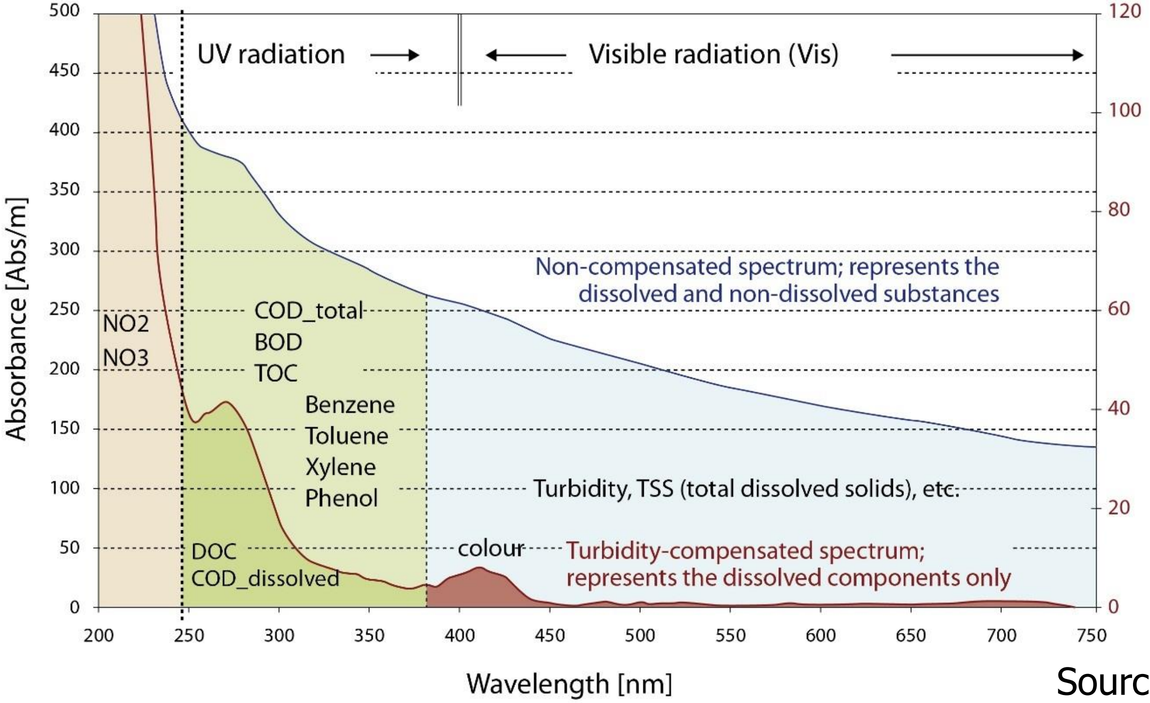


Methods to identify outliers in repetitions of UV/Vis spectra

M. Lepot, A. Mašić, J.-B. Aubin & F.H.L.R. Clemens

Introduction

- UV/Vis spectrophotometers
  - Used since ca. 2000
  - Record absorbance spectra
  - Concentrations (TSS, COD, NO_3, *etc.*)



Source: s::can

Introduction

- A local calibration is needed
    - Using the provided global calibration
    - Using the spectral data

- Spectrum measurement & laboratory analysis

- Repeated measurement of spectra
    - To avoid artefact and potential bias
    - To assess uncertainty

Problems

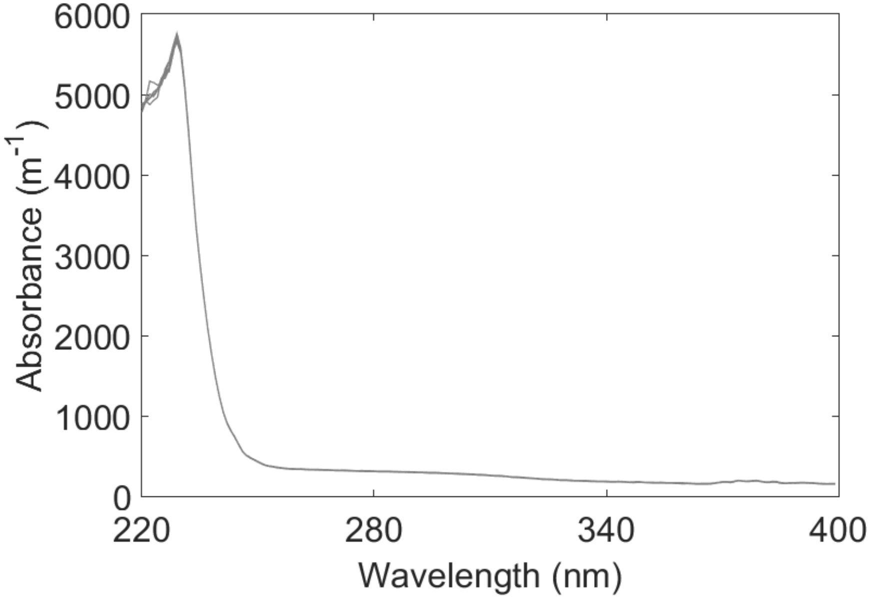
- Is there, at least, one outlier for this sample?

- How to identify spectrum(a) that can be outlier(s)?

- Among the remaining ones, which ones to choose for subsequent calculation (e.g. calibration)?

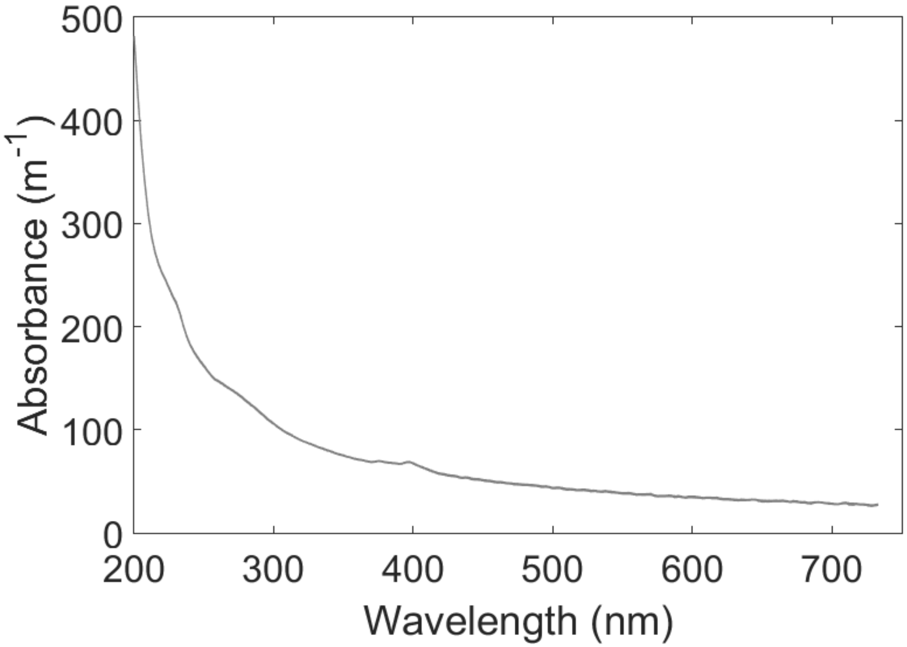
Materials and methods

- Sensors and data sets
  - EAWAG (Switzerland)
    - 4 x 30 samples of (un)filtered/(un)diluted urine
    - 5 spectra recorded per sample
    - (s::can, spectro::lyser, 0.5 mm, UV, 1nm)



Materials and methods

- INSA Lyon (France)
  - 94 samples (inlet of the WWTP, dry weather)
  - Up to 25 spectra recorded per sample
  - (s::can, spectro::lyser, 2 mm, UV/Vis, 2.5nm)



Materials and methods

Methods – two approaches: PCA & DDT/ED

Principal Component Analysis (PCA)

Scores of the first principal component in PCA

- Step 1: Data preprocessing – mean-centering
- Step 2: Singular value decomposition
- Step 3: Score matrix

- Outlier detection
  - PCA_Expert: visual inspection of the PC1 scores
  - PCA_2: automated selection based on mean±2std
- Identification of the MRS
  - PCA_2: smallest distance between PC1 score and median

PCA_Expert

PCA_2

Materials and methods

Data Depth Theory (DDT) & Euclidean Distance (ED)

- Outlier detection (DDT or ED)
  - ED

$$ED_j = \frac{1}{N_T}\sqrt{\sum_{i=1}^{n_x}\left(Abs_{j,i} - Abs_{k\neq j,i}\right)^2}$$

$$ED_j > k_M \times median\left(\left[ED_1 \colon ED_{N_T}\right]\right)$$

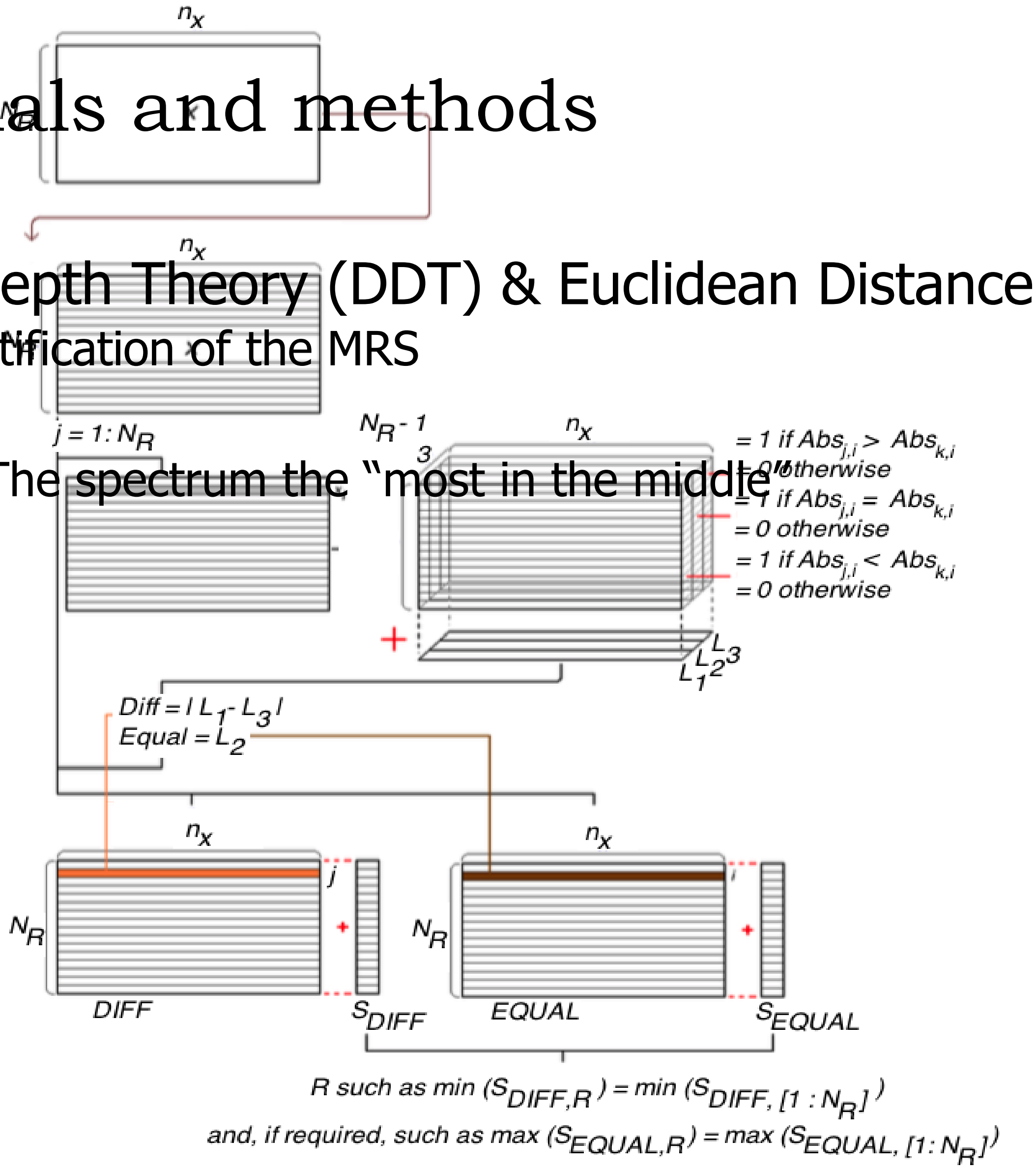
DDT_ED_1
DDT_ED_2
DDT_ED_3

  - DDT
    - Removal of every spectra always below or above the other ones

DDT_DDT

Materials and methods

- Data Depth Theory (DDT) & Euclidean Distance (ED)
  - Identification of the MRS
    - The spectrum the "most in the middle"



n_x
N_R
n_x
N_R
$j = 1 : N_R$
$N_R - 1$
3
n_x
$= 1$ if $Abs_{j,i} > Abs_{k,i}$
$= 0$ otherwise
$= 1$ if $Abs_{j,i} = Abs_{k,i}$
$= 0$ otherwise
$= 1$ if $Abs_{j,i} < Abs_{k,i}$
$= 0$ otherwise
+
L_3
L_2
L_1
$Diff = | L_1 - L_3 |$
$Equal = L_2$
n_x
n_x
j
N_R
+
N_R
+
DIFF
S_{DIFF}
EQUAL
S_{EQUAL}
R such as min $(S_{DIFF,R}) = \min (S_{DIFF, [1 : N_R]})$
and, if required, such as max $(S_{EQUAL,R}) = \max (S_{EQUAL, [1 : N_R]})$

Results

- Identification of sample containing outlier(s): ca 75% of consistency (TP – TN / FP – FN)

WWTP (94 samples)						
Method	DDT_ED_1 94	DDT_ED_2 89	DDT_ED_3 69	DDT_DDT 39	PCA_Expert 82	PCA_2 60
DDT_ED_1	-	89 - 0 / 5 - 0	69 - 0 / 25 - 0	39 - 0 / 55 - 0	82 - 0 / 12 - 0	60 - 0 / 34 - 0
DDT_ED_2		-	69 - 5 / 20 - 0	41 - 5 / 48 - 0	81 - 3 / 9 - 1	60 - 6 / 28 - 0
DDT_ED_3			-	39 - 25 / 29 - 1	66 - 8 / 4 - 16	60 - 22 / 10 - 2
DDT_DDT				-	38 - 11 / 1 - 44	34 - 29 / 5 - 26
PCA_Expert					-	58 - 11 / 23 - 2
PCA_2						-

Results

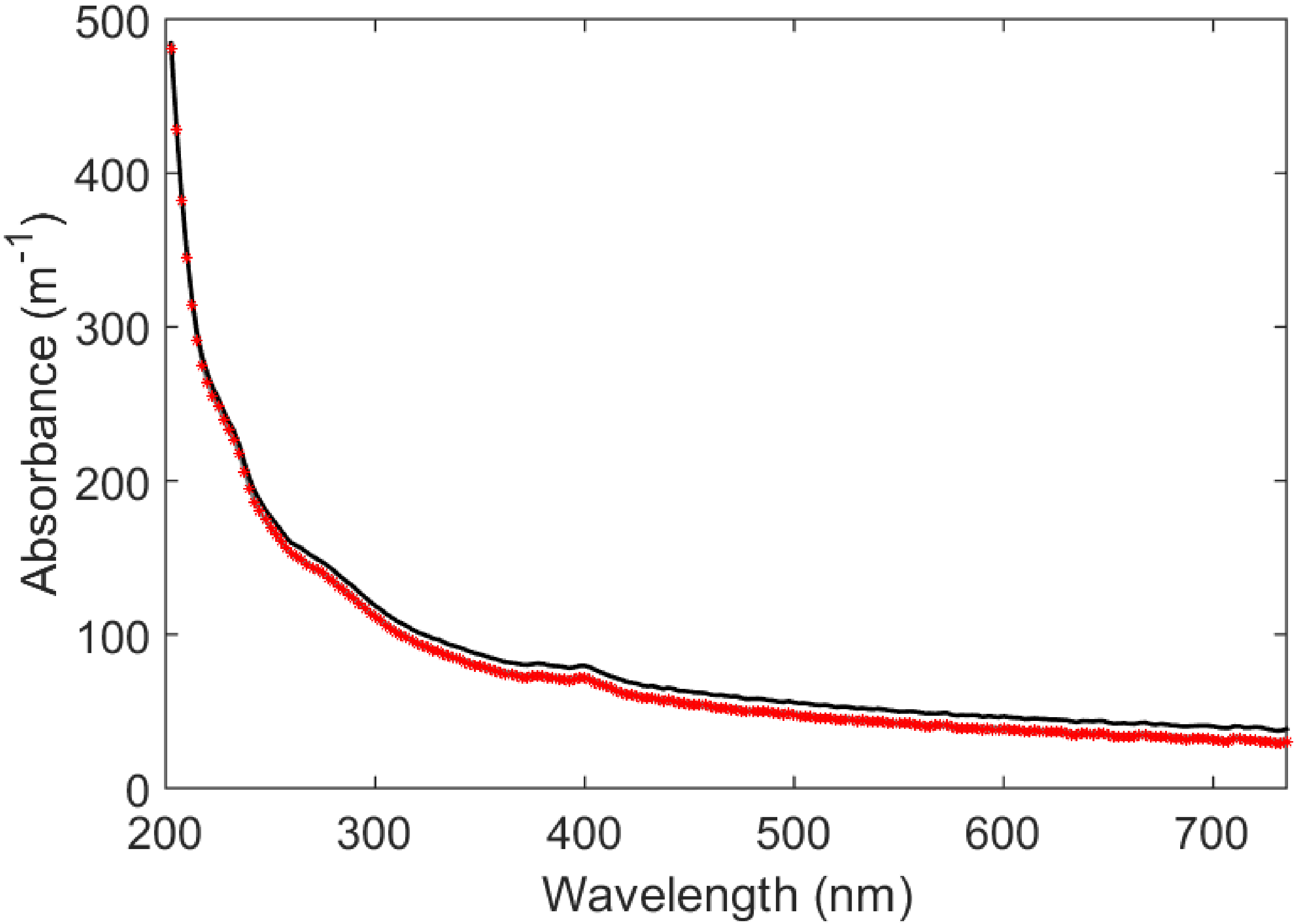
FU (30 samples)						
Method	DDT_ED_1 30	DDT_ED_2 7	DDT_ED_3 4	DDT_DDT 0	PCA_Expert 6	PCA_2 0
DDT_ED_1	-	7 - 0 / 23 - 0	4 - 0 / 26 - 0	0 - 0 / 30 - 0	6 - 0 / 24 - 0	0 - 0 / 30 - 0
DDT_ED_2		-	4 - 23 / 3 - 0	0 - 23 / 7 - 0	5 - 22 / 2 - 1	0 - 23 / 7 - 0
DDT_ED_3			-	0 - 26 / 4 - 0	4 - 24 / 0 - 2	0 - 26 / 4 - 0
DDT_DDT				-	0 - 24 / 0 - 6	0 - 30 / 0 - 0
PCA_Expert					-	0 - 24 / 6 - 0
PCA_2						-

Results

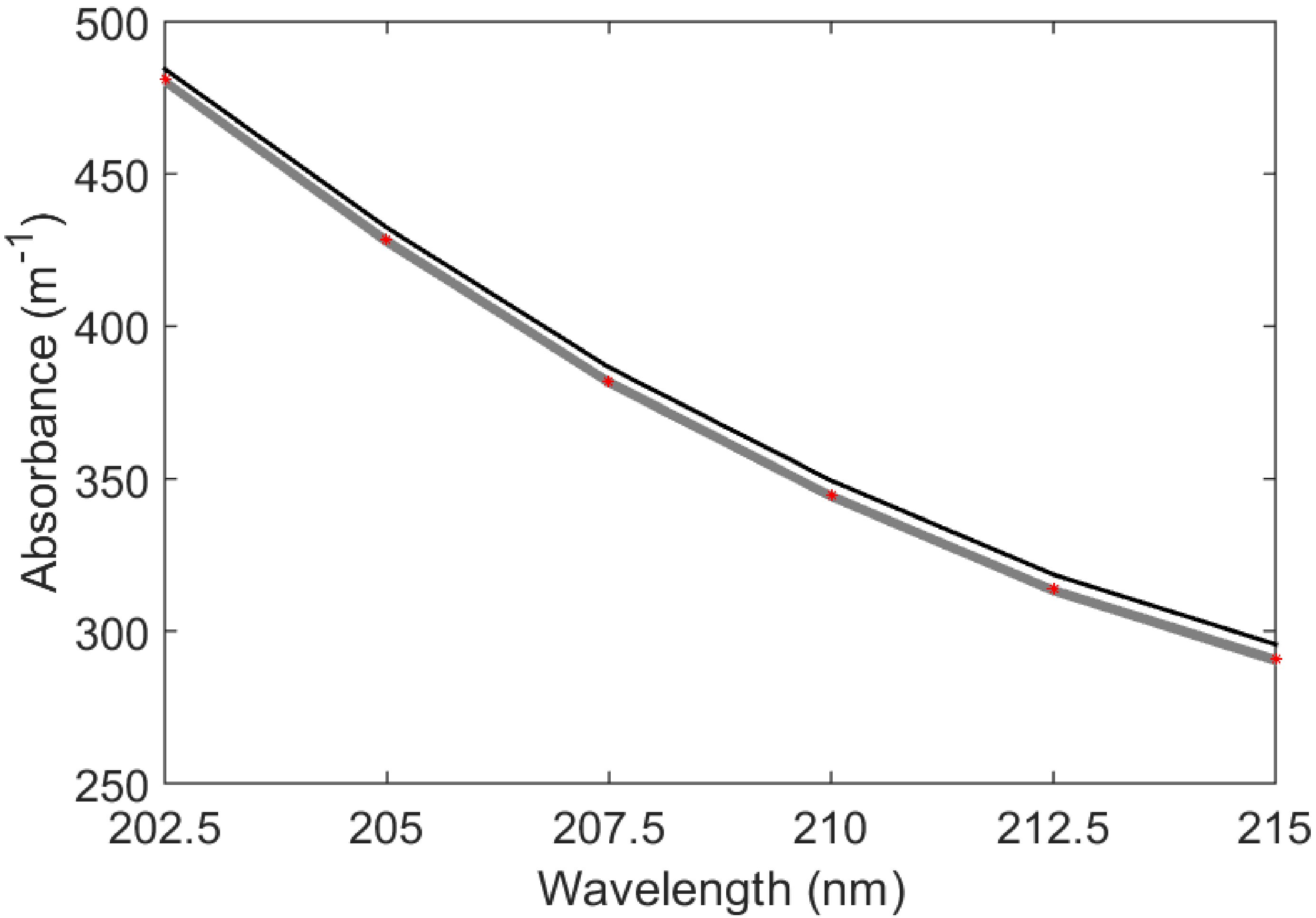
- Identification of the outlier(s): ca 95% of consistency (consistency ratios for at least one outlier in common)

WWTP (94 samples)						
Method	DDT_ED_1 94	DDT_ED_2 89	DDT_ED_3 69	DDT_DDT 39	PCA_Expert 82	PCA_2 60
DDT_ED_1	1	1	1	1	0.99	1
DDT_ED_2		1	1	1	1	1
DDT_ED_3			1	0.97	0.99	0.99
DDT_DDT				1	0.98	0.99
PCA_Expert					1	1
PCA_2						1

Results


500
400
300
200
100
0
Absorbance (m^{-1})
200
300
400
500
600
700
Wavelength (nm)

Results

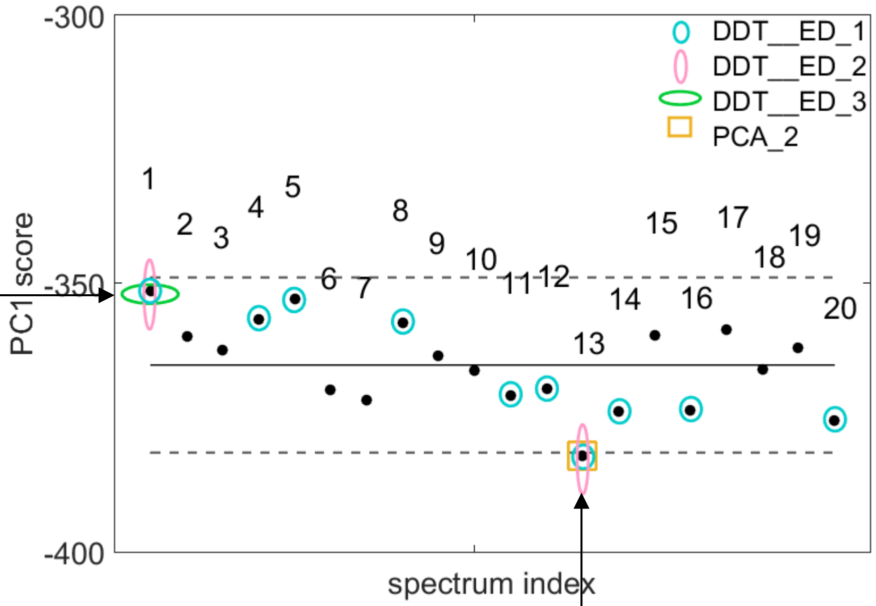

500
450
400
350
300
250
202.5
205
207.5
210
212.5
215
Absorbance (m^{-1})
Wavelength (nm)

Results

UD (30 samples)						
Method	DDT_ED_1 30	DDT_ED_2 4	DDT_ED_3 3	DDT_DDT 0	PCA_Expert 2	PCA_2 0
DDT_ED_1	1	1	1	--	0.5	--
DDT_ED_2		1	1	--	NSWOIC	--
DDT_ED_3			1	--	NSWOIC	--
DDT_DDT				1	--	--
PCA_Expert					1	--
PCA_2						1

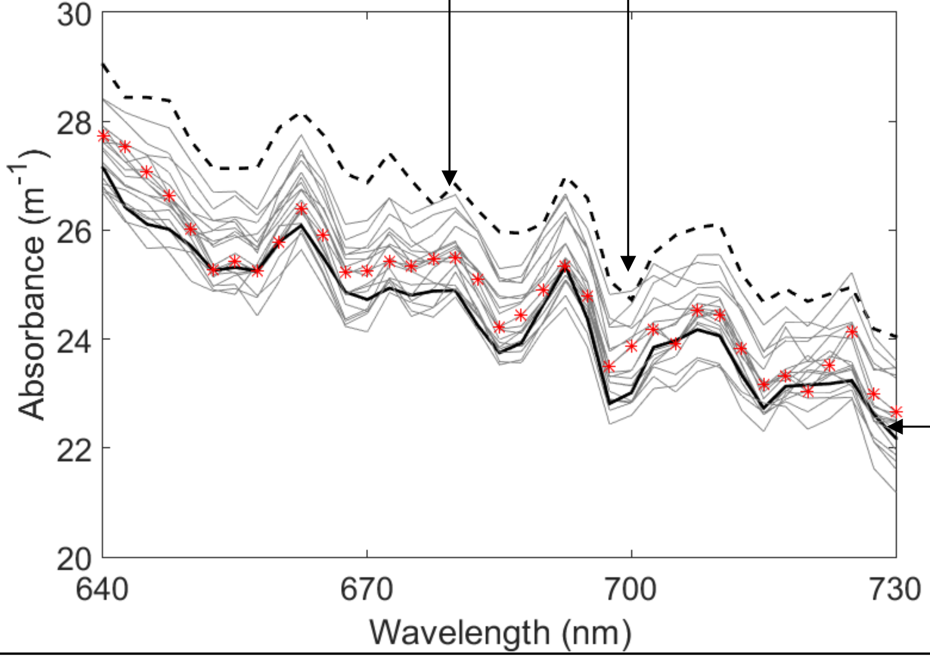
Results

Or by PCA



Identified by DDT_ED

But not by DDT_DDT



And by PCA_2

Identified by DDT_ED_1 and DDT_ED_2

Results

- Identification of the MRS: ca 28% of consistency (consistency ratios for the MRS identification)

WWTP (94 samples)					
Method	DDT_ED_1	DDT_ED_2	DDT_ED_3	DDT_DDT	PCA_2
DDT_ED_1	1	0.35	0.35	0.41	0.11
DDT_ED_2		1	0.81	0.71	0.13
DDT_ED_3			1	0.87	0.24
DDT_DDT				1	0.3
PCA_2					1

Conclusions

- Repeated spectra are required
- If only few spectra per sample: DDT_ED_2
- PCA and DDT are equivalent when more spectra are recorded (> 5)
- PCA and DDT are inconsistent for the identification of MRS
- A voting system?

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