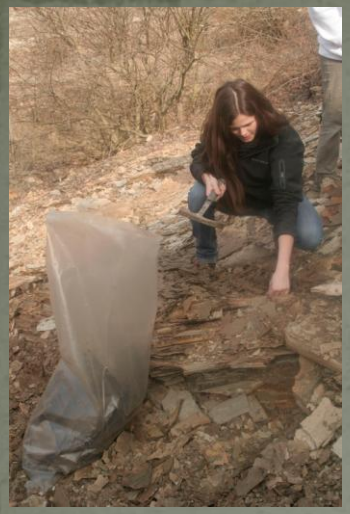



Application of near infrared spectroscopy

Distinguishing fossil and recent carbon in post mining soils

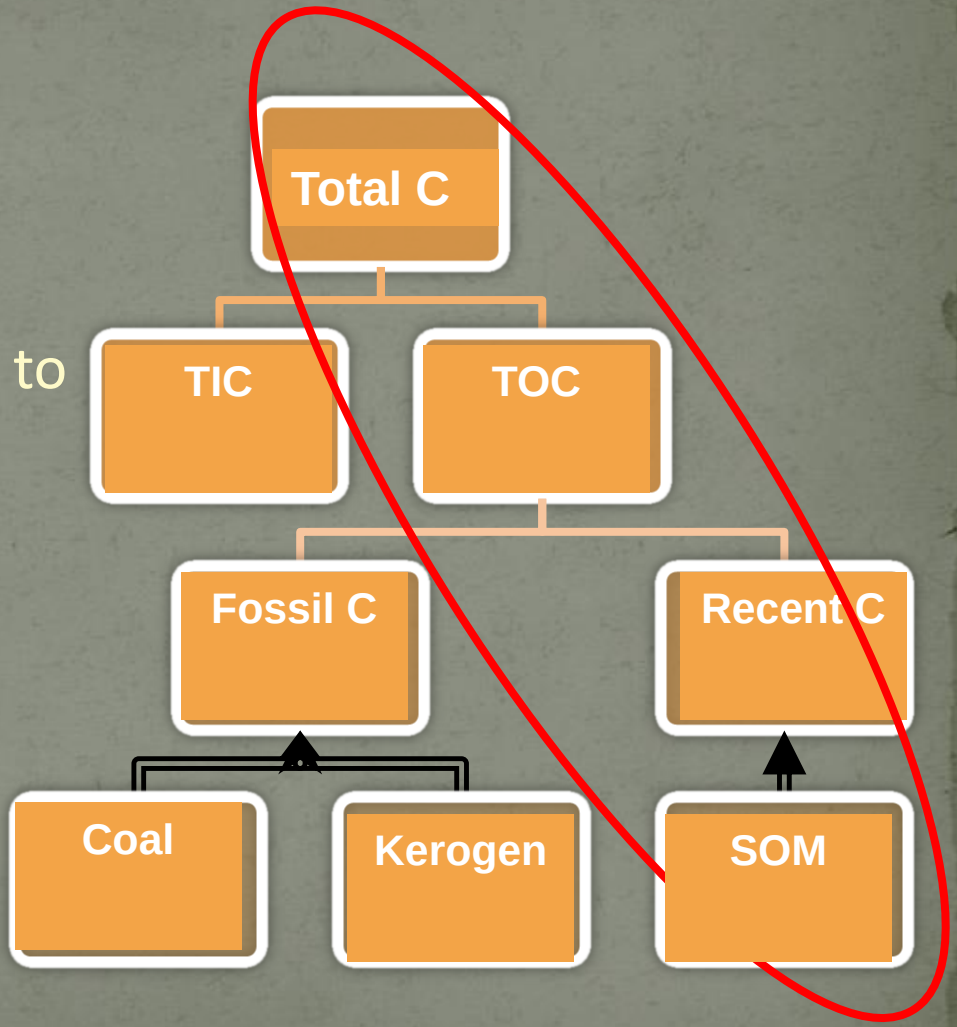
Bc. Olga Vindušková

Supervisor: prof. Ing. Mgr. Jan Frouz, CSc.

Why do we need to distinguish them?

- Soil organic matter
  - indicator of soil quality
  - global carbon pool
  - in most soils proportional to organic carbon content
    - Corg ~ 58% SOM

    => SOM = 1.724 * Corg

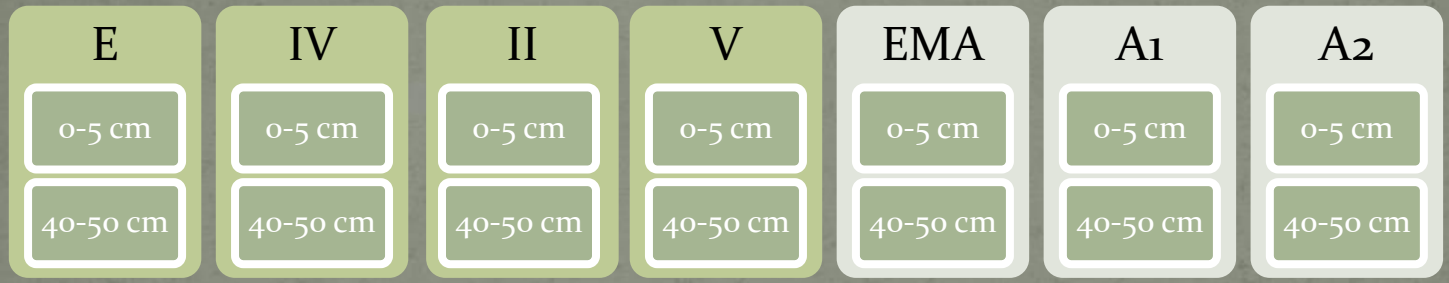


Aims

- assess, what is the error connected with regularly used methods to quantify SOM
- optimalize current methods and test new alternative approaches
- identify the most suitable method

Methods

- 14 soil samples



- „basic“ components:
  - claystone (2 types)
  - coal
  - fermentation layer

- 125 artificial mixtures

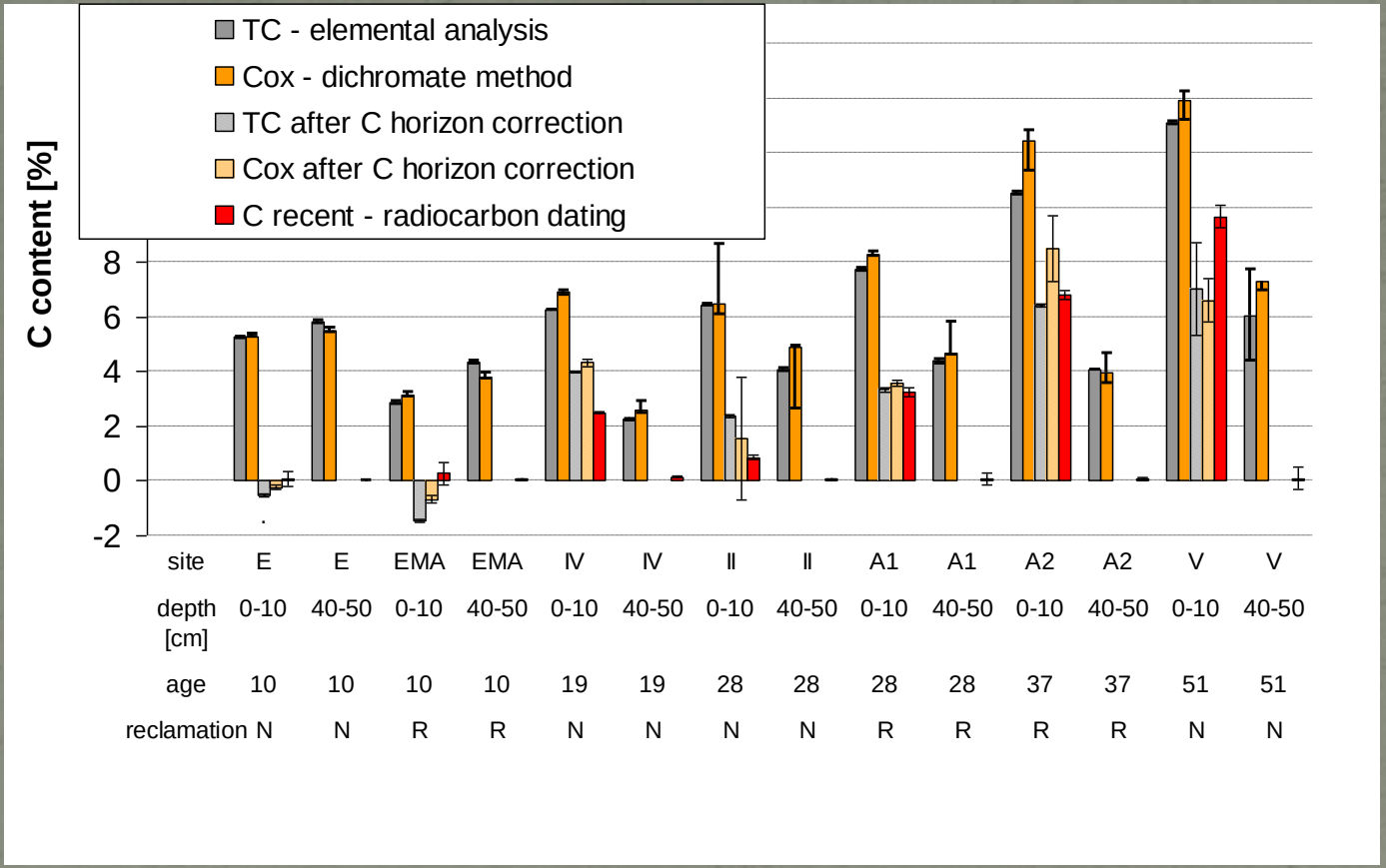
» 14C AMS, 13C/12C
» CN
» Cox (dichromate)
» LOI (150-850°C)

» NIR spectroscopy

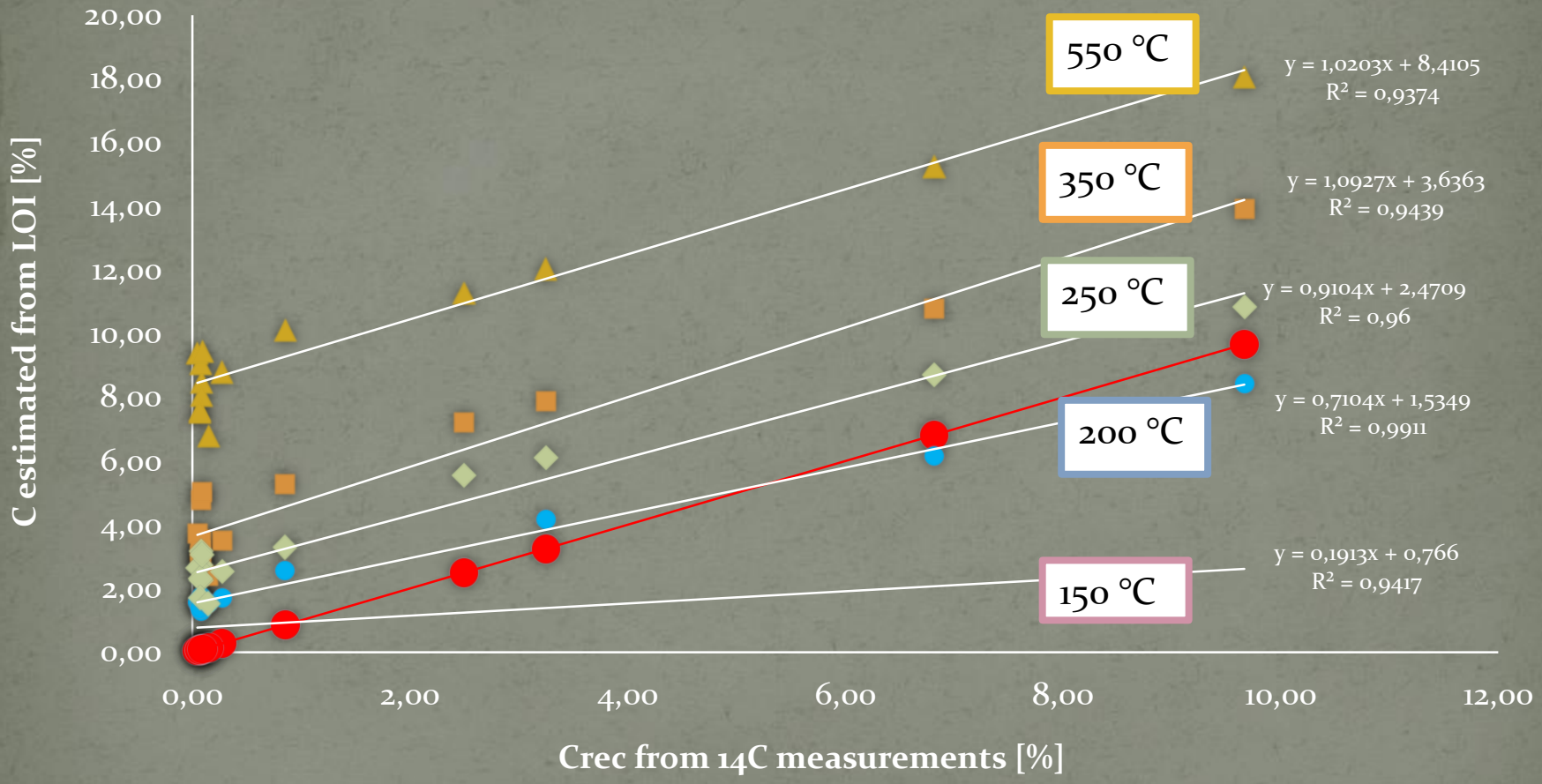
Results

	TC [%]		Cox [%]		LOI/1,724 [%]						
					250°C	350°C	450°C	550°C	650°C	750°C	850°C
„gray“ clay	4,31	± 0,02	3,61	± 0,06	**1,06**	2,26	5,00	**7,49**	8,75	8,96	9,28
„brown“ clay	13,70	± 0,12	12,76	± 6,47	**3,35**	8,70	11,56	**12,79**	13,27	13,61	14,83
ferm. layer	38,04	± 0,30	43,57	± 4,95	**32,16**	41,82	45,78	**46,47**	47,03	47,13	47,14
coal	51,56	± 1,80	78,27	± 12,62	**22,20**	50,88	53,88	**54,27**	53,88	54,01	54,30

Results


TC - elemental analysis
Cox - dichromate method
TC after C horizon correction
Cox after C horizon correction
C recent - radiocarbon dating
C content [%]
8
6
4
2
0
-2
site E E EMA EMA IV IV II II A1 A1 A2 A2 V V
depth [cm] 0-10 40-50 0-10 40-50 0-10 40-50 0-10 40-50 0-10 40-50 0-10 40-50 0-10 40-50
age 10 10 10 10 19 19 28 28 28 28 37 37 51 51
reclamation N N R R N N N N R R R R N N

Carbon content estimated from loss-on-ignition at different temperatures

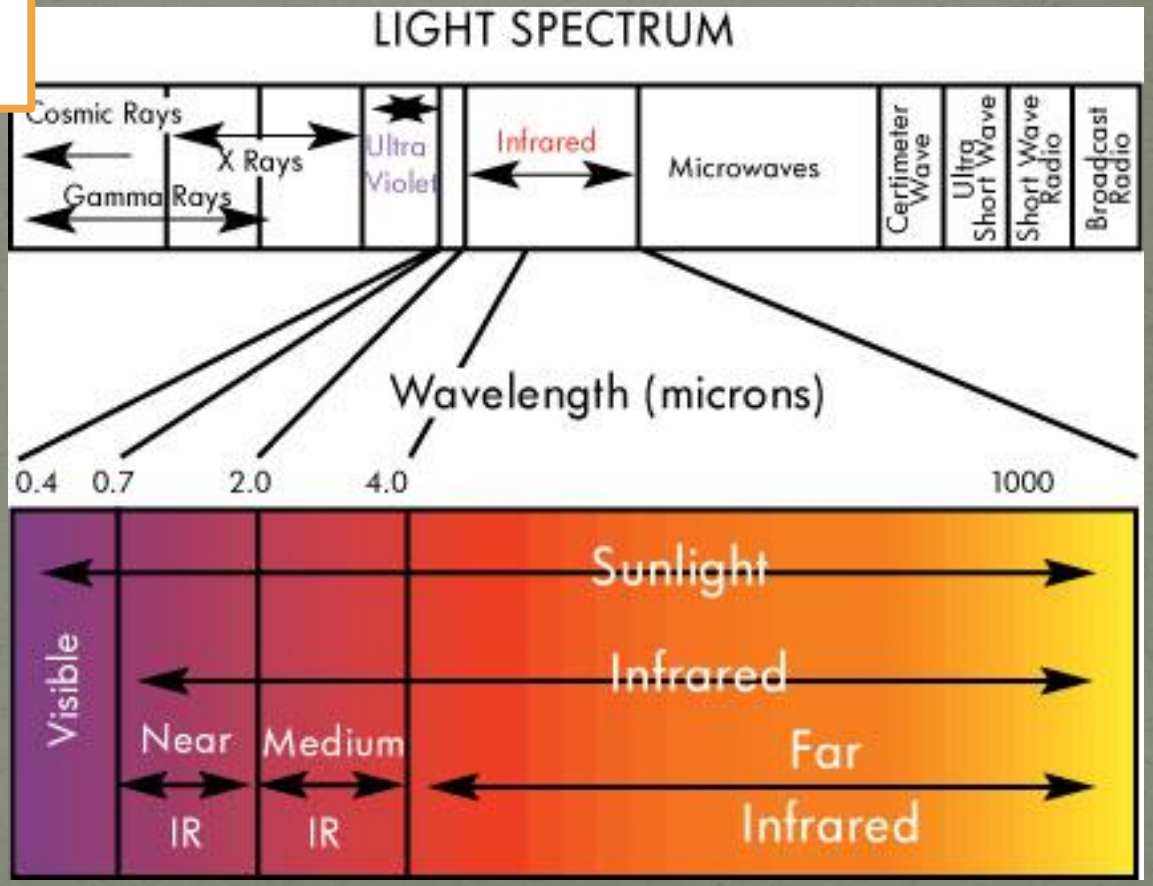


Near infrared (diffuse reflectance) spectroscopy

750 nm – 2500 nm
12 500 – 4000 cm-*1*

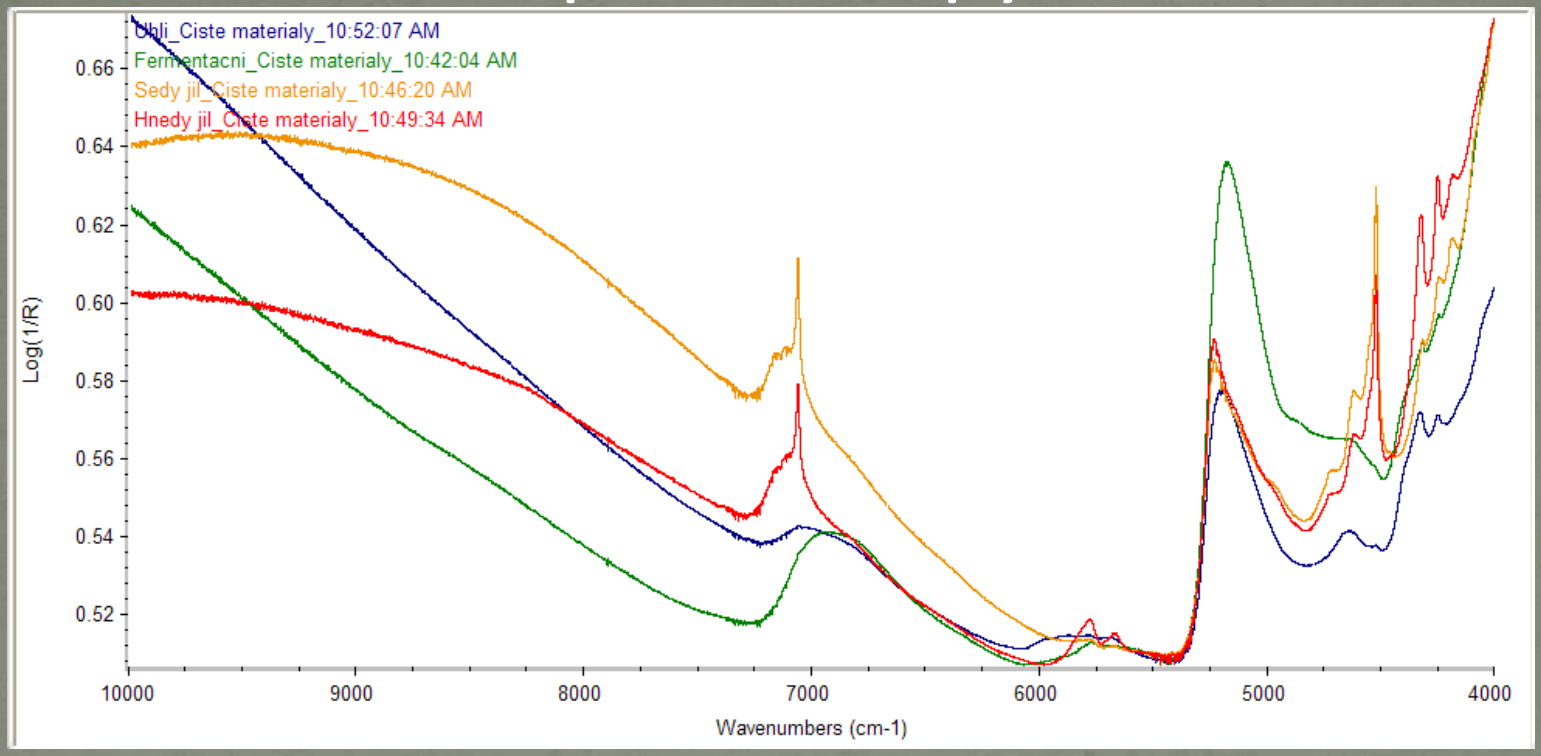
- (A = log [1/reflectance]

(DRIFTS) (FT-IR)



- Stretching and bending of functional groups
- -NH, -CH, -OH, -COOH,
- Combinations and overtones from mid-IR

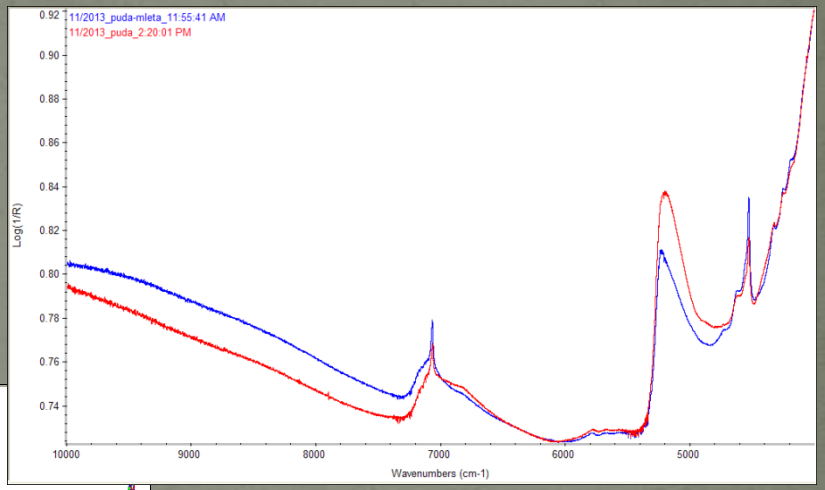
Near infrared spectroscopy

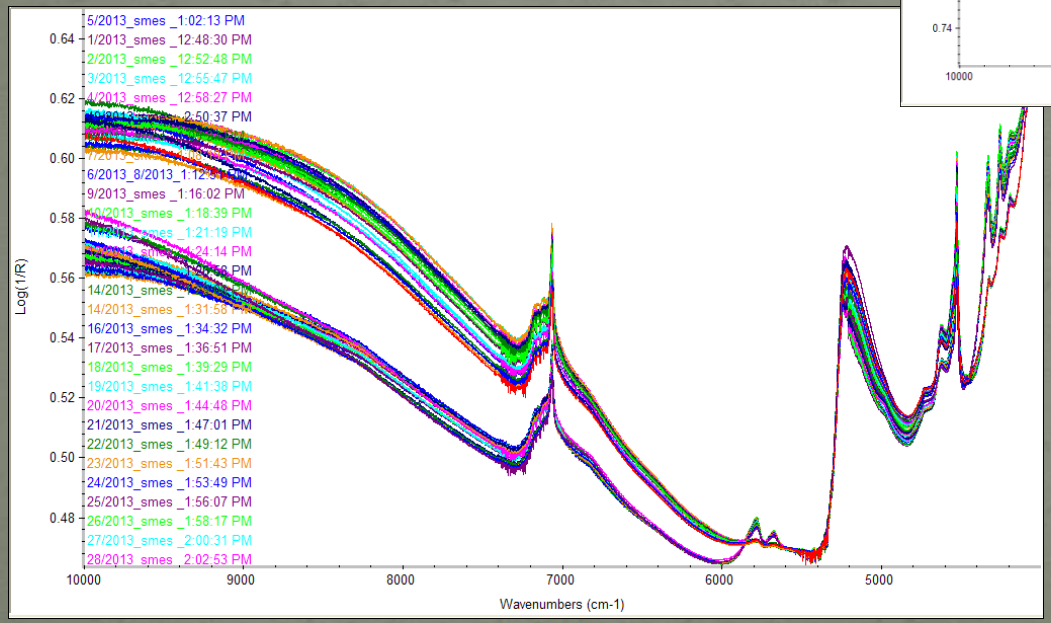


- 14 soil samples
- 125 artificial mixtures

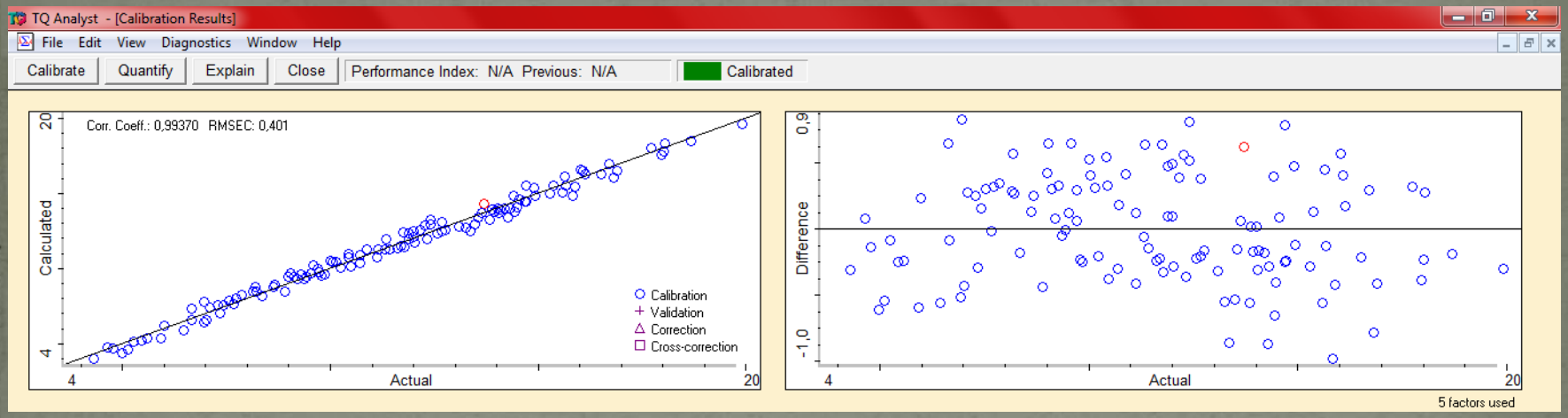
Near infrared spectroscopy

- Sample scanning
- Fine vs normal grinding





Near infrared spectroscopy



Calibration Results Table

Index	Spectrum Title	Actual	Calculated	Diff. x Path
2	2/2013_smes/mleta_12:21:33 PM	0,00	-0,05	-0,05
3	3/2013_smes/mleta_12:23:31 PM	0,00	0,11	0,11
4	4/2013_smes/mleta_12:26:37 PM	0,00	0,09	0,09
5	5/2013_smes/mleta_12:29:20 PM	0,00	0,19	0,19
6	6/2013_smes/mleta_12:32:09 PM	0,38	0,43	0,05
7	7/2013_smes/mleta_12:34:24 PM	0,38	0,50	0,12
8	8/2013_smes/mleta_12:38:43 PM	0,38	0,40	0,02
9	8/2013_smes/mleta_12:48:24 PM	0,38	0,36	-0,02
10	10/2013_smes/mleta_12:53:26 PM	0,38	0,55	0,17
11	11/2013_smes/mleta_12:55:29 PM	0,77	0,68	-0,09
12	12/2013_smes/mleta_12:57:10 PM	0,77	0,65	-0,12
13	13/2013_smes/mleta_12:59:40 PM	0,76	0,83	0,07
14	14/2013_smes/mleta_1:02:16 PM	0,76	0,96	0,20
15	15/2013_smes/mleta_1:04:31 PM	0,76	1,04	0,28
16	16/2013_smes/mleta_1:07:21 PM	1,90	1,77	-0,13
17	17/2013_smes/mleta_1:10:16 PM	1,91	1,79	-0,12
18	18/2013_smes/mleta_1:12:14 PM	1,90	1,68	-0,22

- Calibration – Partial least squares (PLS) regression
- Ctot, Crec, Cclay, Ccoal
- mixtures / mixtures + soils
- Fine vs normal grinding

Calibration parameters

			calibration			cross-validation		
calibration model	**component**	**n**	**R2**	**RMSEC %**	ignored	**R2 CV %**	**RMSECV %**	**factors**
1A	C_{tot}	125	0,990	0,19	2	0,998	0,22	7
1A fine	C_{tot}	125	0,994	0,40	3	0,991	0,481	5
1B	C_{tot}	125 + 14	0,990	0,28	4	0,990	0,31	8
1B fine	C_{tot}	125 + 14	0,995	0,37	6	0,990	0,56	7
2A	C_{rec}	125	0,990	0,10	0	0,996	0,13	8
2A fine	C_{rec}	125	0,998	0,08	1	0,992	0,18	9
2B	C_{rec}	125 + 14	0,945	0,55	2	0,991	0,18	7
2B fine	C_{rec}	125 + 14	0,995	0,16	6	0,976	0,36	8
3A	C_{jil}	125	0,990	0,11	1	0,999	0,137	8
3A fine	C_{jil}	125	0,999	0,10	5	0,993	0,345	5
4A	C_{uhli}	125	0,994	0,20	1	0,990	0,26	8
4A fine	C_{uhli}	125	0,994	0,21	3	0,989	0,28	8

Conclusions on NIRS

- Good potential for quantifying total, recent and both types of fossil C in post-mining sites, but calibration based more on soils rather than artificial mixtures recommended

- Advantages:
- Easy sample preparation (drying, 2mm)
- low cost (60 CZK/sample)
- user-friendly, quick (5-10 mins per scan)

- Disadvantages:
- site-specific calibration needed
- high number of samples (calibration/validation)
- calibration is spectrometer-specific

Thank you for your attention!