SPECTRO

AMETEK
MATERIALS ANALYSIS DIVISION

(ED) XRF – Calculation of Results

Versatility vs. Accuracy

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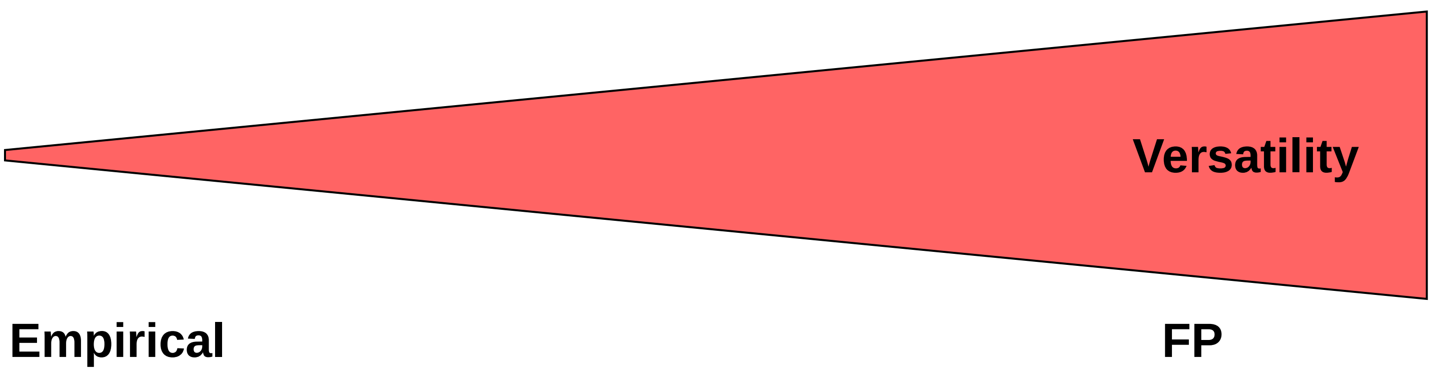
Kristiansand

SPECTRO

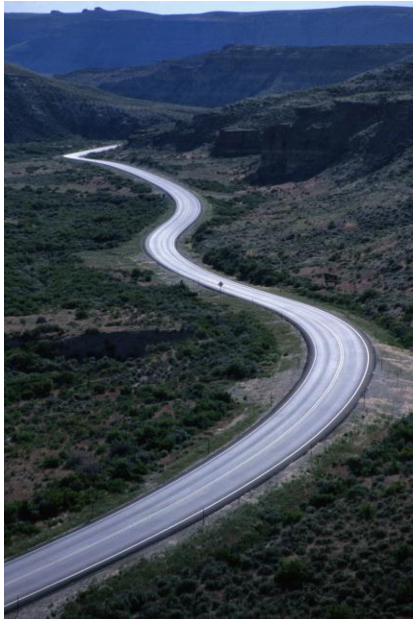
Motivation

- …much has been said already about the capabilities and the performance of analytical programs based on fundamental parameters. They are fast, versatile, accurate…
- …for a wide range of various samples like alloys, oil, water, oxides prepared as fused beads,…
- …many people, especially in process control using powder samples (slag, ferro alloys,…) applications prefer empirical calibrations
- When or why to use one or the other?



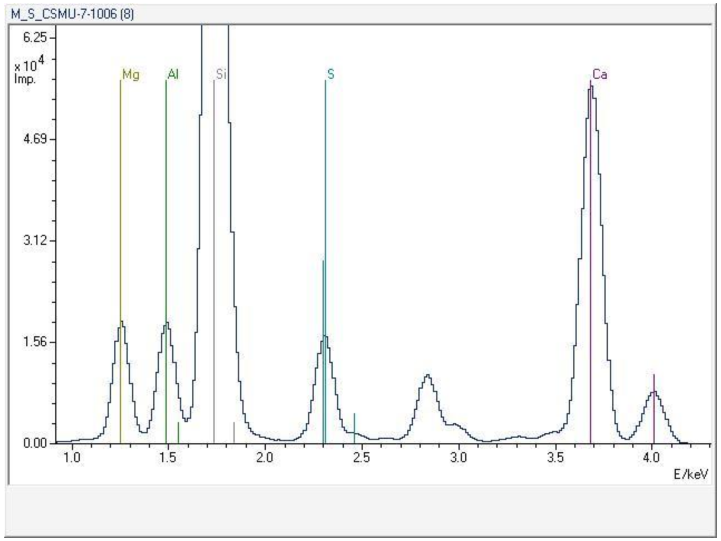
Agenda

- Pre-calibrated fundamental parameters calibration examples
- Compton normalization example
- Empirical calibration example
  - Precision
  - Application range
  - Results outside the calibrated range



Test example for this investigation

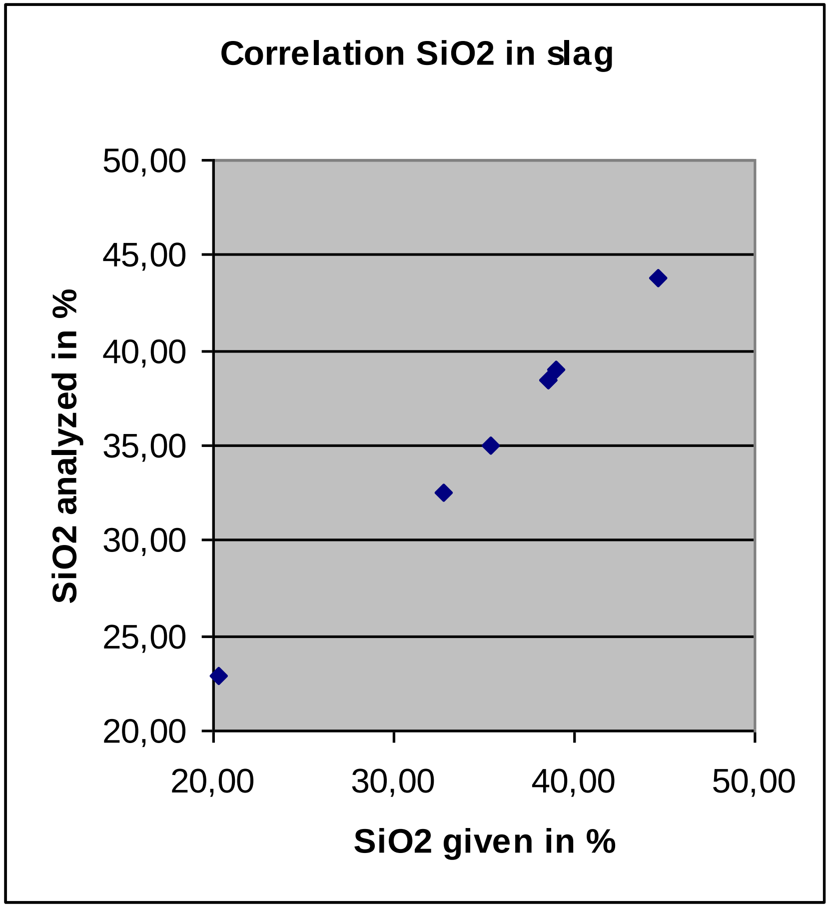
- The main application is the analysis of powders, e.g. slag samples, having similar composition
  - Measurement time 60…90 s per sample
- Every now and then different matrices (e.g. cement samples and environmental samples) have to be analyzed as well
- What quality of results can we expect from the different types of calibration for powders?



Pre-calibrated fundamental parameters (FP) models

- Fundamental parameters (FP) calibrations are typically very accurate if the intensities of all matrix elements can be determined or if the the matrix (oxidic, sulfidic, water, oil,…) of a sample is known

- I ~ C (+ corrections)
  - Matrix related corrections are calculated based on physics
  - Only two free parameters per element (slope and intercept) are optimized with the calibration
  - Corrections also can be necessary in case of line overlaps, those are based on intensities



Pre calibrated FP calibration – validation

- The calibration is based on a set of eight certified slag samples from “Slovensky Metrologicky Ustav”
- The sample matrix is defined as oxidic
- One sample of the same sample set was not used for calibration and analyzed as validation sample to check the calibration

	Certified in %	Analyzed in %
MgO	16.8 ± 0.4	17.20 ± 0.05
Al2O3	7.05 ± 0.08	6.37 ± 0.03
SiO2	38.5 ± 0.2	38.42 ± 0.06
CaO	(32.7)	33.18 ± 0.06
Fe	0.59 ± 0.05	0.495 ± 0.004

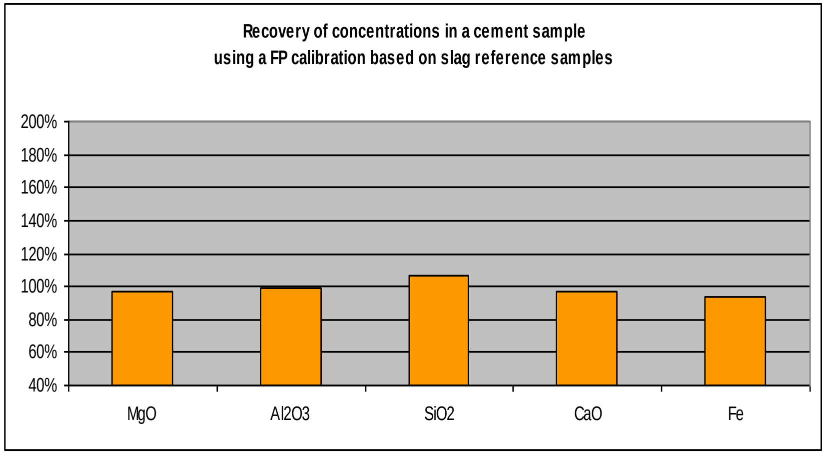
Pre calibrated FP calibration – precision

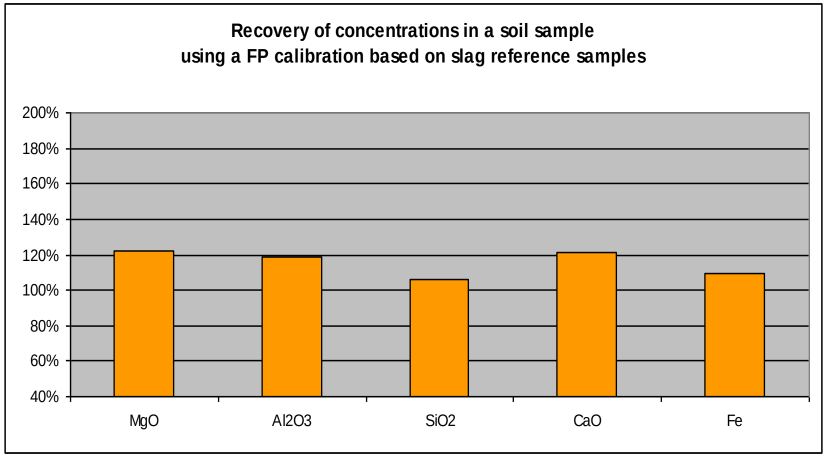
- The same validation sample was analyzed 10-times to check the repeatability and to compare the statistical error of the individual analysis with the standard deviation of the repeats
- The calculation of the concentration is based on the concentrations of all elements
- The error in the determination of all elements will contribute to the std. dev.

	Average	Stat. Error	Std. Dev.
MgO	17. 20	0.05	0.06
Al_2O_3	6.37	0.02	0.04
SiO_2	38.42	0.06	0.09
CaO	33.20	0.06	0.09
Fe	0.497	0.004	0.006

Pre calibrated FP calibration – versatility

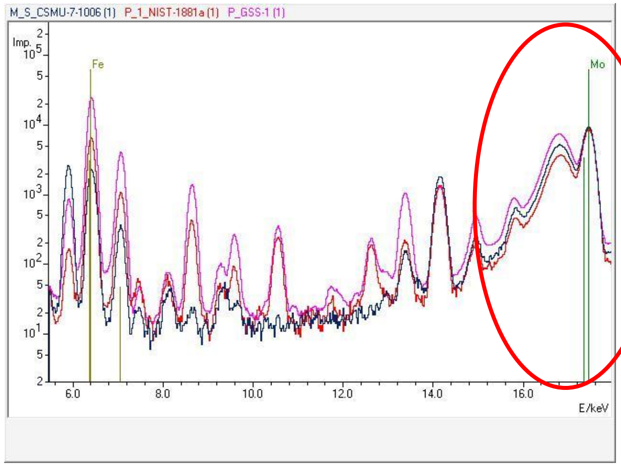
- FP based calibrations can be very versatile for a wide range of matrices
- The accuracy of the analysis is influenced by the fact, whether the matrix is selected properly
- The calibration is limited in corrections for organics, H_2O,…

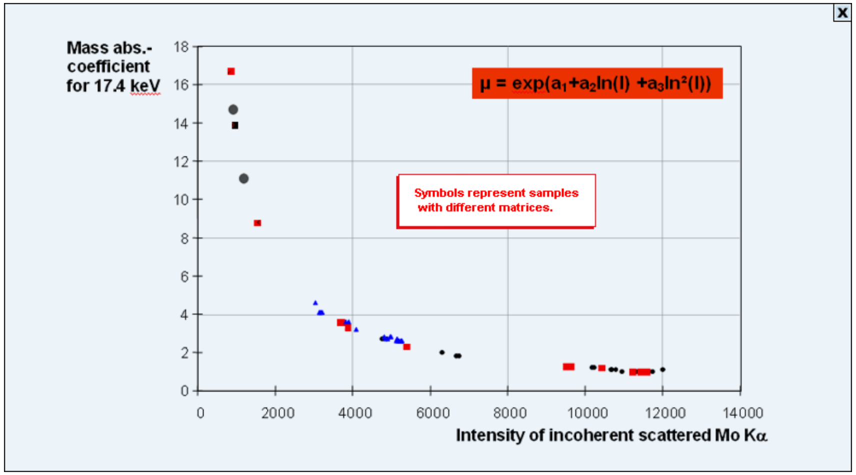




Turboquant calibration (pre calibrated FP for fluorescence)

- Turboquant methods combine the benefits from the FP calibration with the matrix information from the Compton scatter
- No additional matrix information (oxidic, metallic, water, oil,…) is required
- I ~ C (+ corrections)
  (+ corrections based on Compton scatter information)
  - Matrix related corrections are calculated based on physics
  - Corrections also can be necessary in case of line overlaps, those are based on intensities





Pre calibrated Turboquant – validation

- Besides other samples the calibration is based on a set of eight certified slag samples from “Slovensky Metrologicky Ustav”

- One sample of the same sample set was not used for calibration and analyzed as validation sample to check the calibration

	Certified in %	Analyzed in %
MgO	16.8 ± 0.4	17.16 ± 0.05
Al2O3	7.05 ± 0.08	6.33 ± 0.03
SiO2	38.5 ± 0.2	36.42 ± 0.06
CaO	(32.7)	31.14 ± 0.06
Fe	0.59 ± 0.05	0.515 ± 0.004

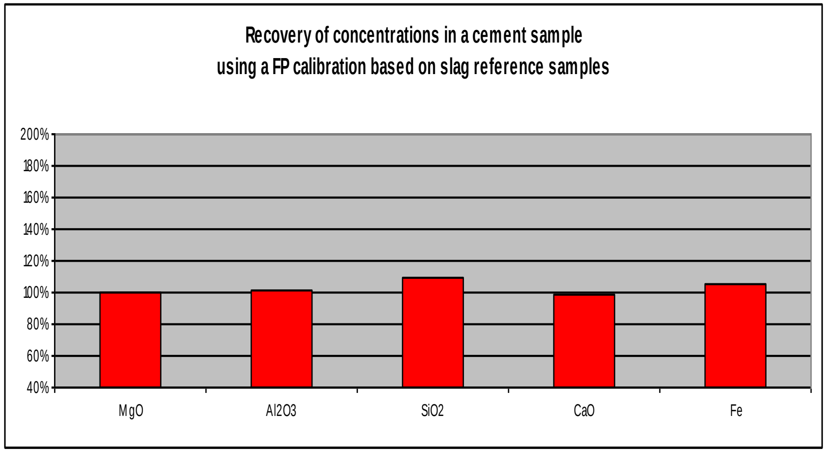
Turboquant calibration – precision

- The same validation sample was analyzed 10-times to check the repeatability and to compare the statistical error of the individual analysis with the standard deviation of the repeats
- The calculation of the concentration is based on the concentrations of all elements
- The error in the determination of all elements (plus the error in Compton intensity) will contribute to the std. dev.

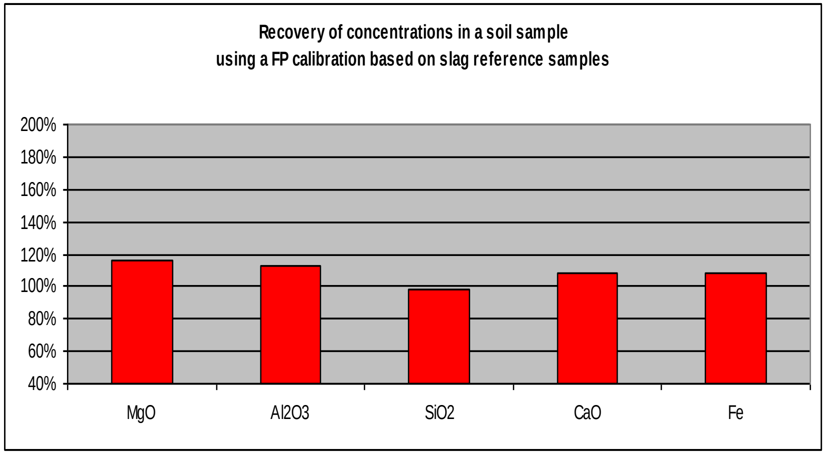
	Average	Stat. Error	Std. Dev.
MgO	17.16	0.05	0.06
Al_2O_3	6.33	0.02	0.04
SiO_2	36.42	0.06	0.09
CaO	31.14	0.06	0.09
Fe	0.515	0.004	0.006

Turboquant calibration – Versatility

- Turboquant calibrations are even more versatile compared to FP based calibrations.

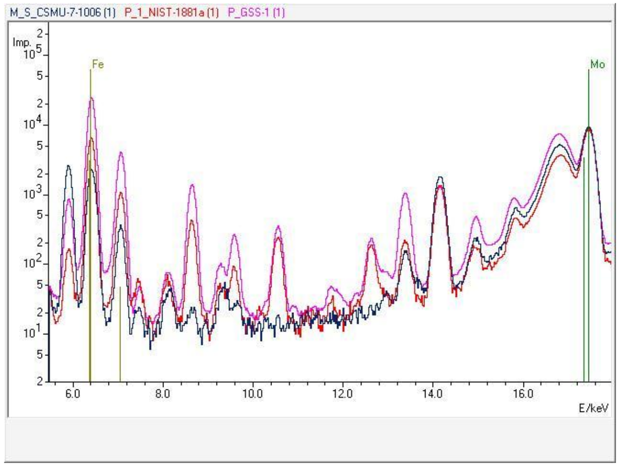


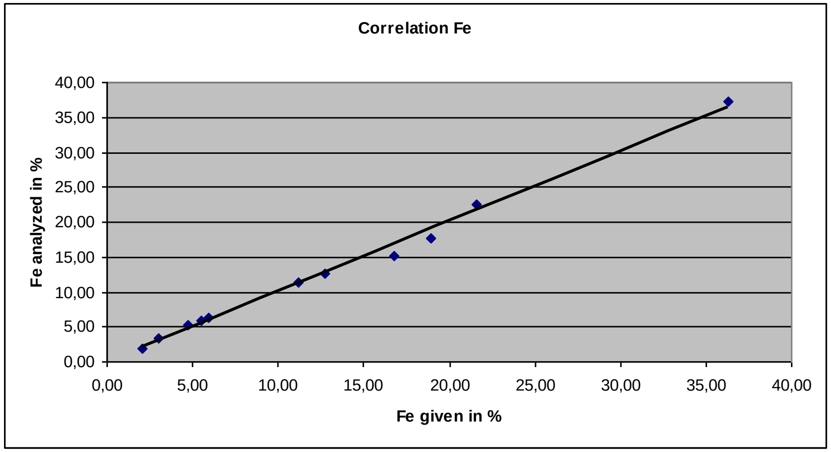
- The matrix correction is done automatically



Semi- Empirical calibration (Compton)

- A so-called Compton calibration uses the Compton scattered primary information as additional matrix correction
- A Compton calibration typically is used for Z ≥ 22
- $I / I_{Compton}$ ~ C (+ corrections)
  - Matrix related corrections are calculated based on concentrations and are determined based on standards
  - Number of free parameters is limited
  - Corrections also can be necessary in case of line overlaps, those are based on intensities





Compton calibration – validation

- The calibration is based on a set of eight certified slag samples from “Slovensky Metrologicky Ustav”
- One sample of the same sample set was not used for calibration and analyzed as validation sample to check the calibration

	Certified in %	Analyzed in %
MgO	16.8 ± 0.4	
Al2O3	7.05 ± 0.08	
SiO2	38.5 ± 0.2	
CaO	(32.7)	34.19 ± 0.06
Fe	0.59 ± 0.05	0.623 ± 0.005

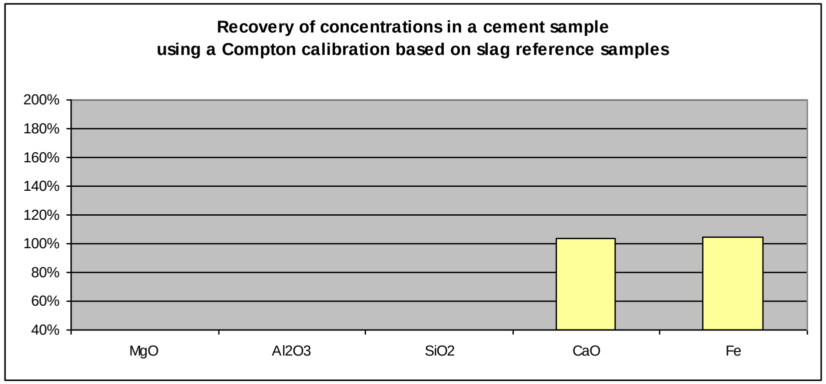
Compton calibration – validation

- The same validation sample was analyzed 10-times to check the repeatability and to compare the statistical error of the individual analysis with the standard deviation of the repeats
- The calculation of the concentration is based on the intensities
- The error in the determination of the intensity of the element of interest plus the error of the Compton intensity will contribute to the std. dev.

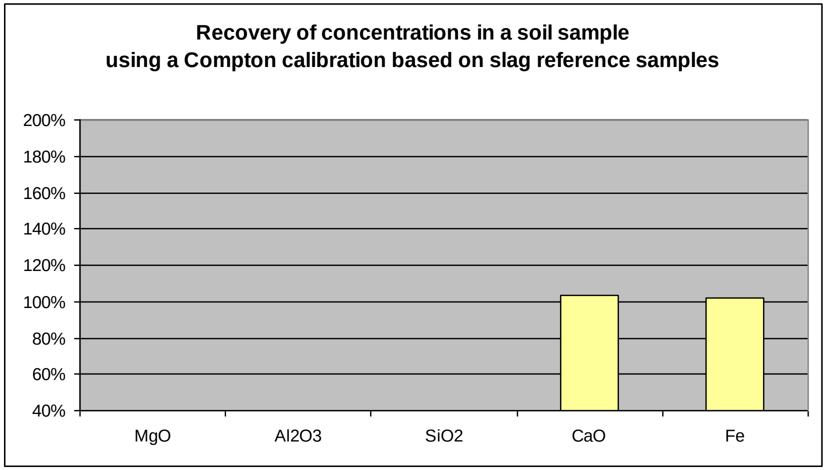
	Average	Stat. Error	Std. Dev.
MgO			
Al_2O_3			
SiO_2			
CaO	34.17	0.05	0.05
Fe	0.625	0.005	0.005

Compton calibration – versatility

- For higher atomic numbers Compton based calibrations can be very versatile as long as the concentration of the elements is within the calibrated range



- The normalization on the Compton scatter information will correct for influences from varying matrices

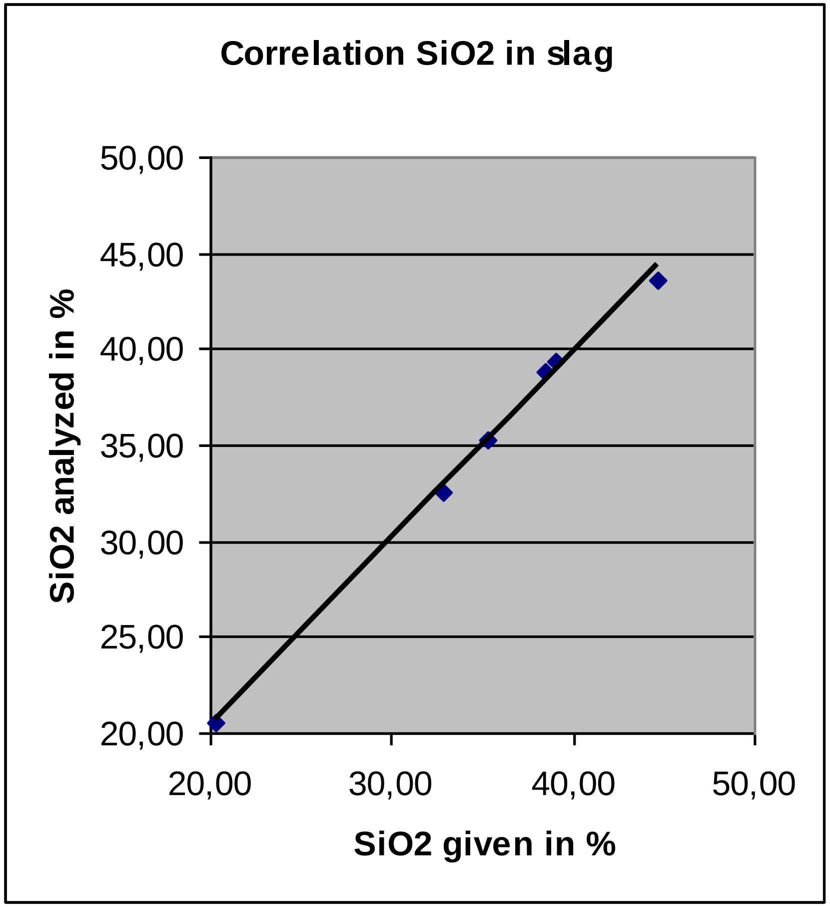


Empirical intensity calibration models

- Calibration is **only** based on intensities

- C ~ I (+ corrections)

  - Matrix related corrections
  - Number of free parameters is depending on the number of available independent standards
  - Method allows line overlaps
  - All are based on intensities



Empirical intensity calibration – validation

- The calibration is based on a set of eight certified slag samples from “Slovensky Metrologicky Ustav”
- One sample of the same sample set was not used for calibration and analyzed as validation sample to check the calibration

	Certified in %	Analyzed in %
MgO	16.8 ± 0.4	17.01 ± 0.05
Al2O3	7.05 ± 0.08	6.83 ± 0.03
SiO2	38.5 ± 0.2	38.83 ± 0.06
CaO	(32.7)	32.85 ± 0.06
Fe	0.59 ± 0.05	0.526 ± 0.004

Empirical intensity calibration – precision

- The same validation sample was analyzed 10-times to check the repeatability and to compare the statistical error of the individual analysis with the standard deviation of the repeats
- The calculation of the concentration is based on the intensities
- The error in the determination of the intensity of the element of interest plus the error of the intensities from corrections will contribute to the std. dev.

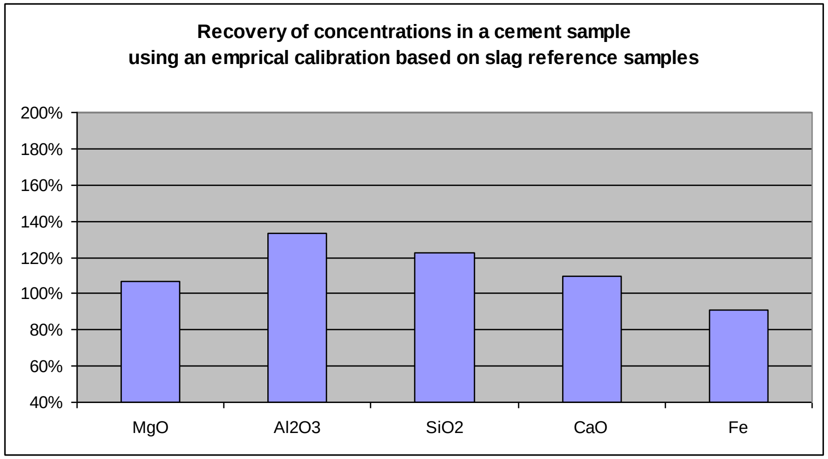
	Average	Stat. Error	Std. Dev.
MgO	17.03	0.05	0.05
Al_2O_3	6.85	0.02	0.03
SiO_2	38.80	0.06	0.06
CaO	32.70	0.06	0.08
Fe	0.527	0.004	0.004

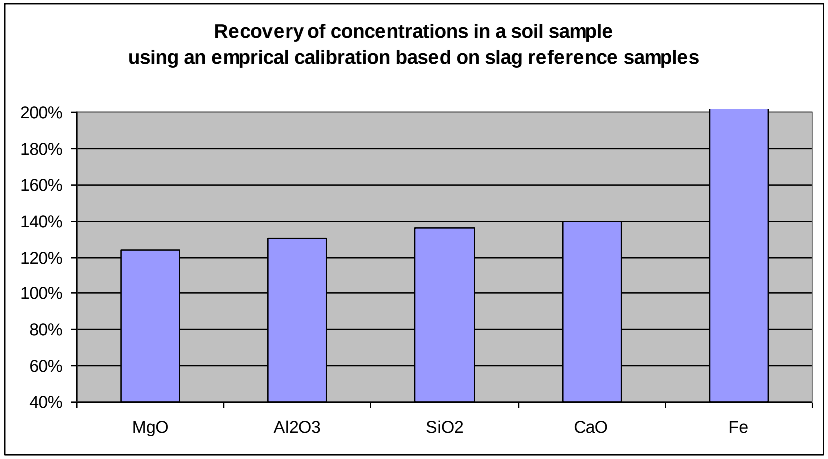
Empirical calibration – versatility

- No-one should use such a specialized empirical calibration outside the calibrated matrix range

- But what happens if we do that?

- Especially for “lighter” matrices (compared to the calibration samples) the concentrations will be overestimated

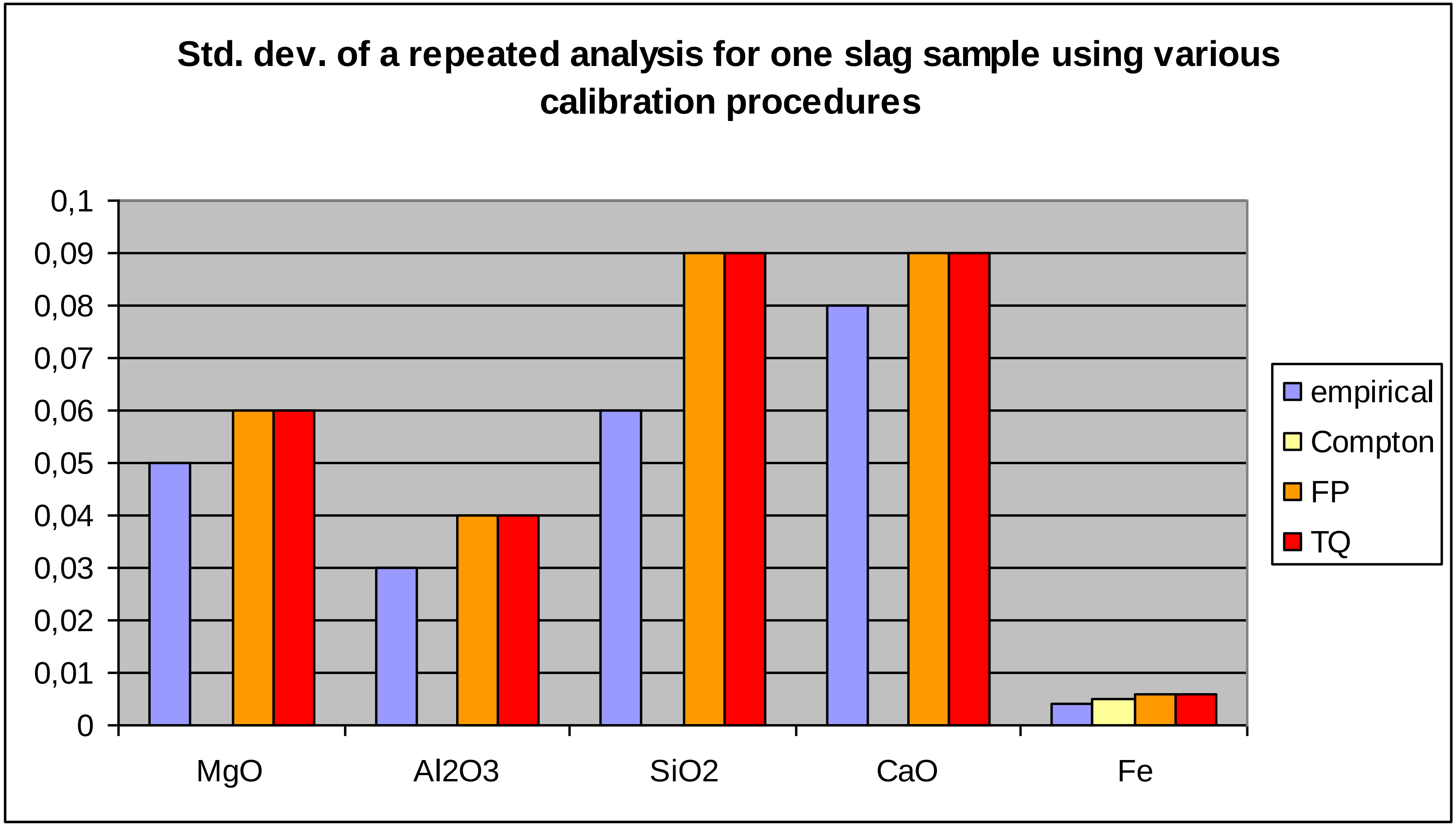




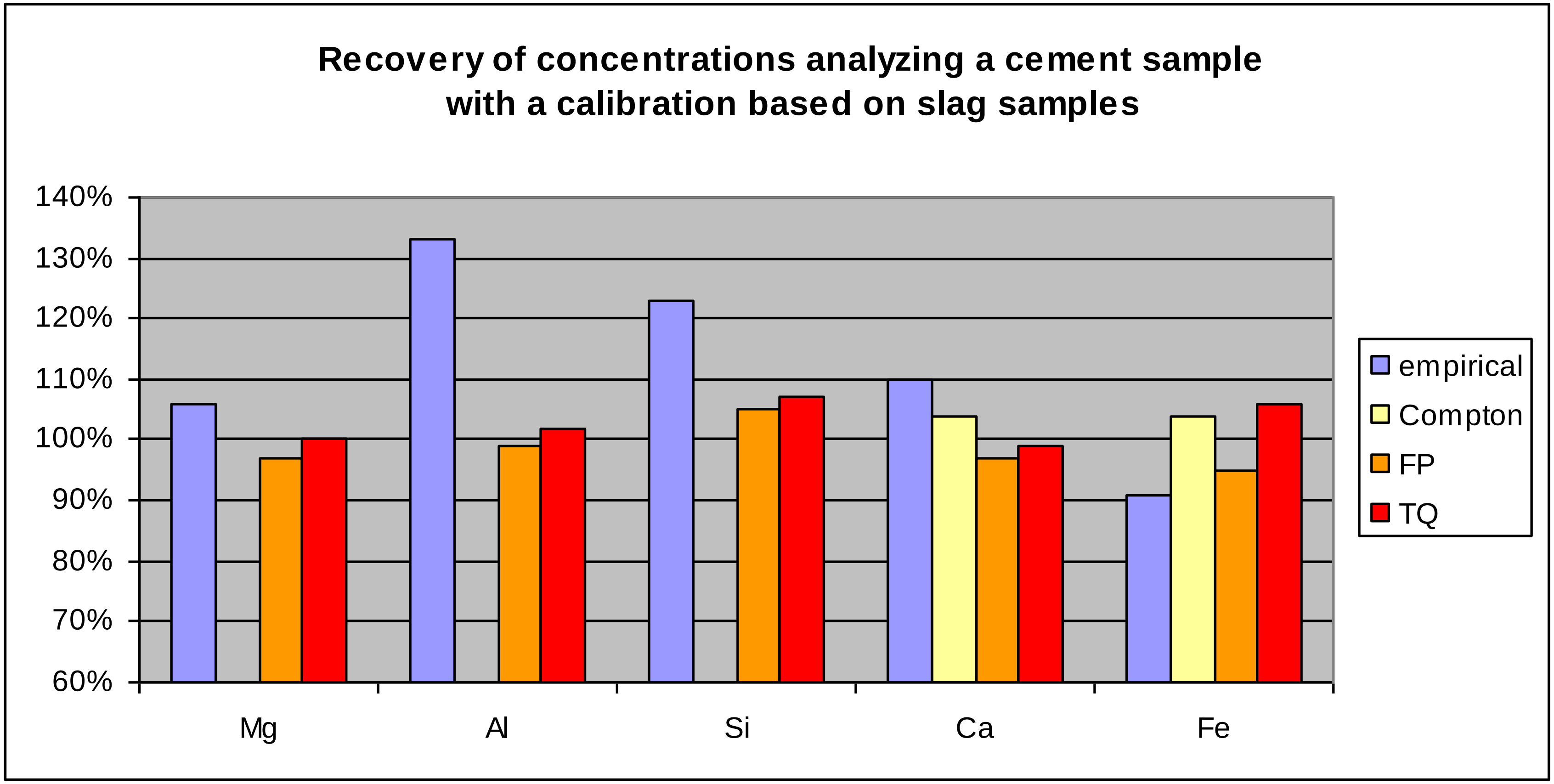
Comparison of validation results

	Certified in %	Analyzed in % FP	Analyzed in % TQ	Analyzed in % Compton	Analyzed in % emprical
MgO	16.8 ± 0.4	17.20 ± 0.05	17.16 ± 0.05		17.01 ± 0.05
Al2O3	7.05 ± 0.08	6.37 ± 0.03	6.33 ± 0.03		6.83 ± 0.03
SiO2	38.5 ± 0.2	38.42 ± 0.06	36. 42 ± 0.06		38.83 ± 0.06
CaO	(32.7)	33.18 ± 0.06	31.14 ± 0.06	34.19 ± 0.06	32.85 ± 0.06
Fe	0.59 ± 0.05	0.495 ± 0.004	0.515 ± 0.004	0.623 ± 0.005	0.526 ± 0.004

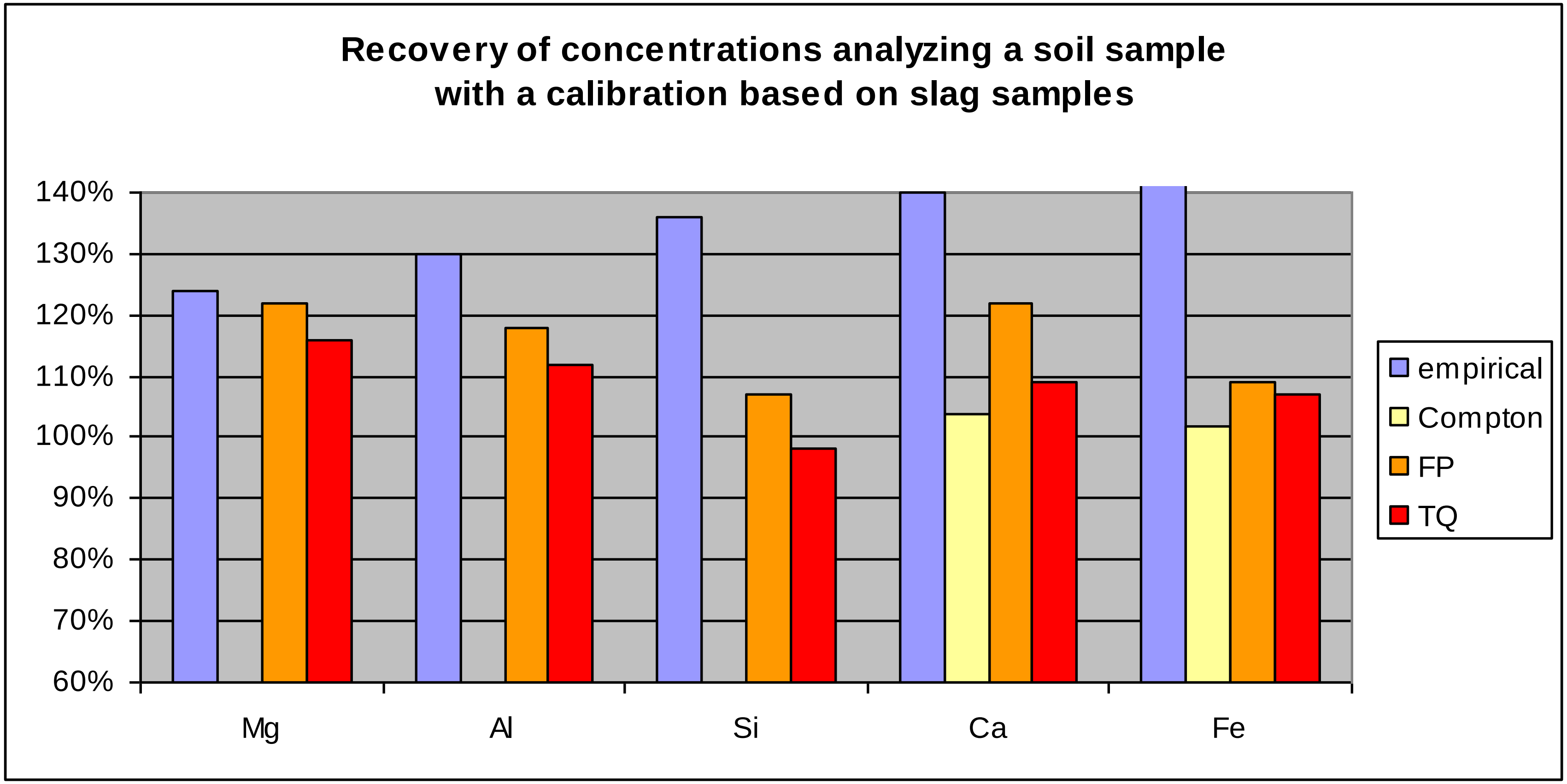
Comparison


Std. dev. of a repeated analysis for one slag sample using various calibration procedures
0,1
0,09
0,08
0,07
0,06
0,05
0,04
0,03
0,02
0,01
0
MgO
Al2O3
SiO2
CaO
Fe
empirical
Compton
FP
TQ

Comparison


Recovery of concentrations analyzing a cement sample
with a calibration based on slag samples
140%
130%
120%
110%
100%
90%
80%
70%
60%
Mg
Al
Si
Ca
Fe
empirical
Compton
FP
TQ

Comparison


Recovery of concentrations analyzing a soil sample
with a calibration based on slag samples
140%
130%
120%
110%
100%
90%
80%
70%
60%
Mg
Al
Si
Ca
Fe
empirical
Compton
FP
TQ

Summary

- The example measurements have confirmed that modern pre-calibrated FP based methods are very versatile for a wide range of matrices
- For some powder sample applications the physical corrections of these methods are (currently?) not sufficient to describe all sample effects satisfactory to achieve best results

- Calibrations based on empirical corrections can be applied to correct for such effects
- These applications certainly cannot meet the versatility of FP based methods