The 16th Norwegian X ray Conference in Kristiansand

X-ray fluorescence analysis of rocks by fusion method using a benchtop WD-XRF

13th September 2010

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Rigaku

Topics

- Purpose of this study
- Samples
- Sample preparations
- Apparatus
- Measurement & results
- Productivity of measurements
- Summary

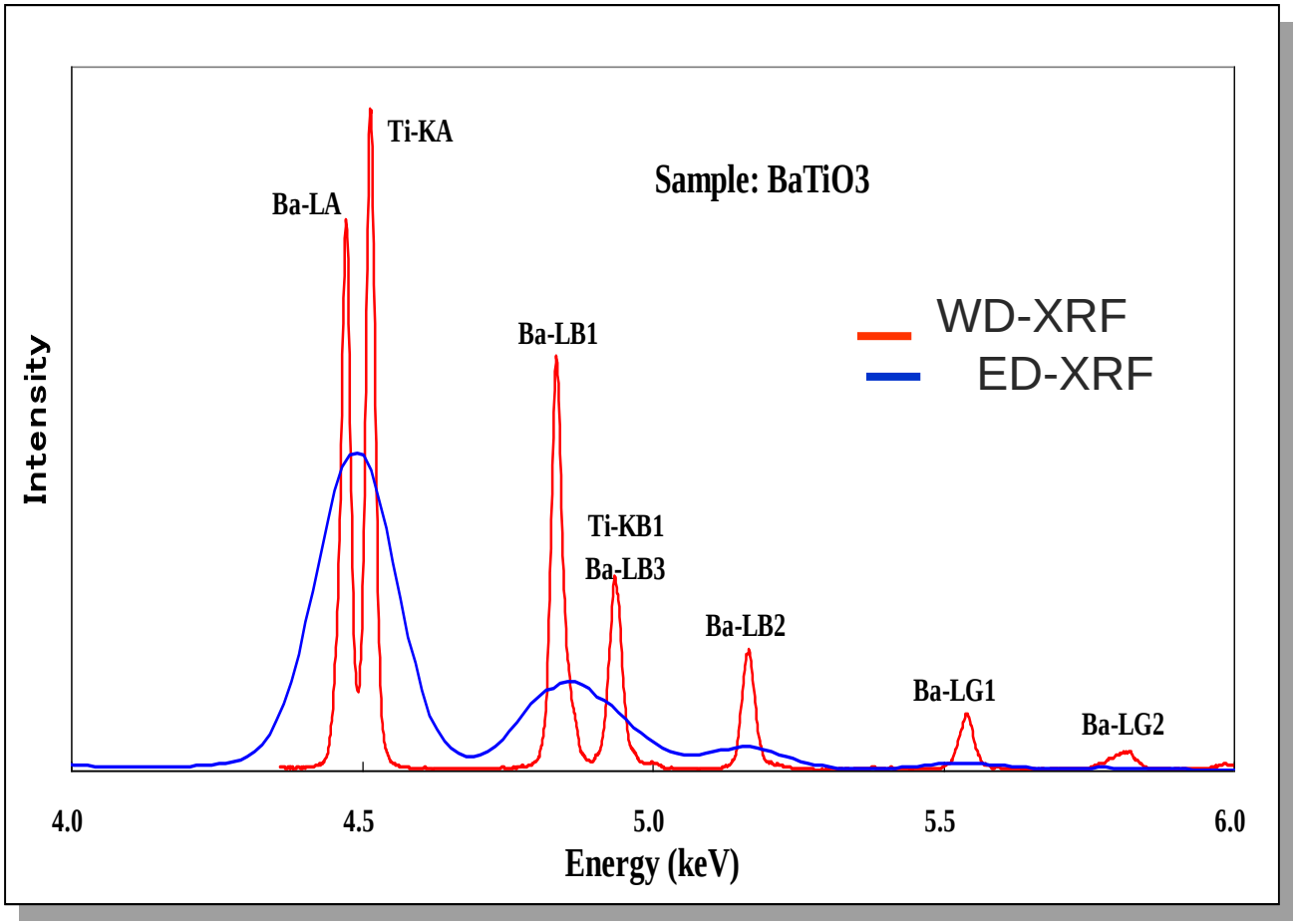
Purpose of this study

- From growing demands for mineral resources around the world,
- Rapid and accurate elemental analysis is required at small satellite laboratories on mining sites and geological resource survey, etc.

- Benchtop ED-XRF is widely used for this field,
- But WD-XRF is more suitable for analysis of rocks and minerals,
- Because of its superior spectral resolution and light-element sensitivity.

- We have used a benchtop WD-XRF to measure the feasibility of geological survey at small satellite laboratories.

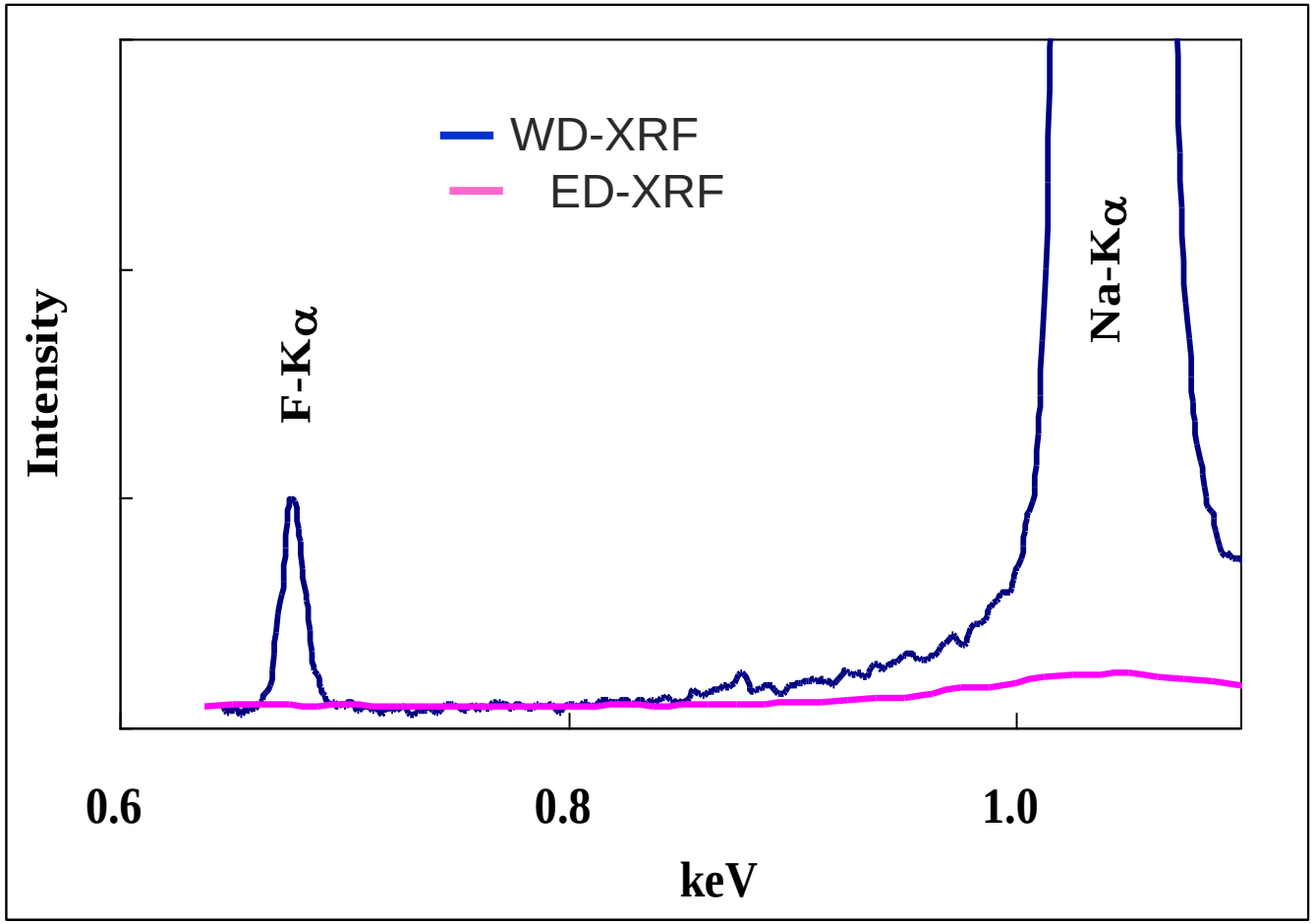
High resolution



Sample : BaTiO3

WD-XRF technique has enough resolution to separate Ti-Kα and Ba-Lα.

Light element sensitivity



Sample : Opal glass

F : 5.73 mass%
Na : 2.40 mass%

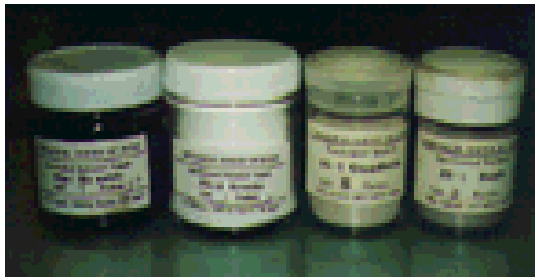
ED-XRF is unable to detect F and Na peaks clearly due to lack of sensitivity.

Samples

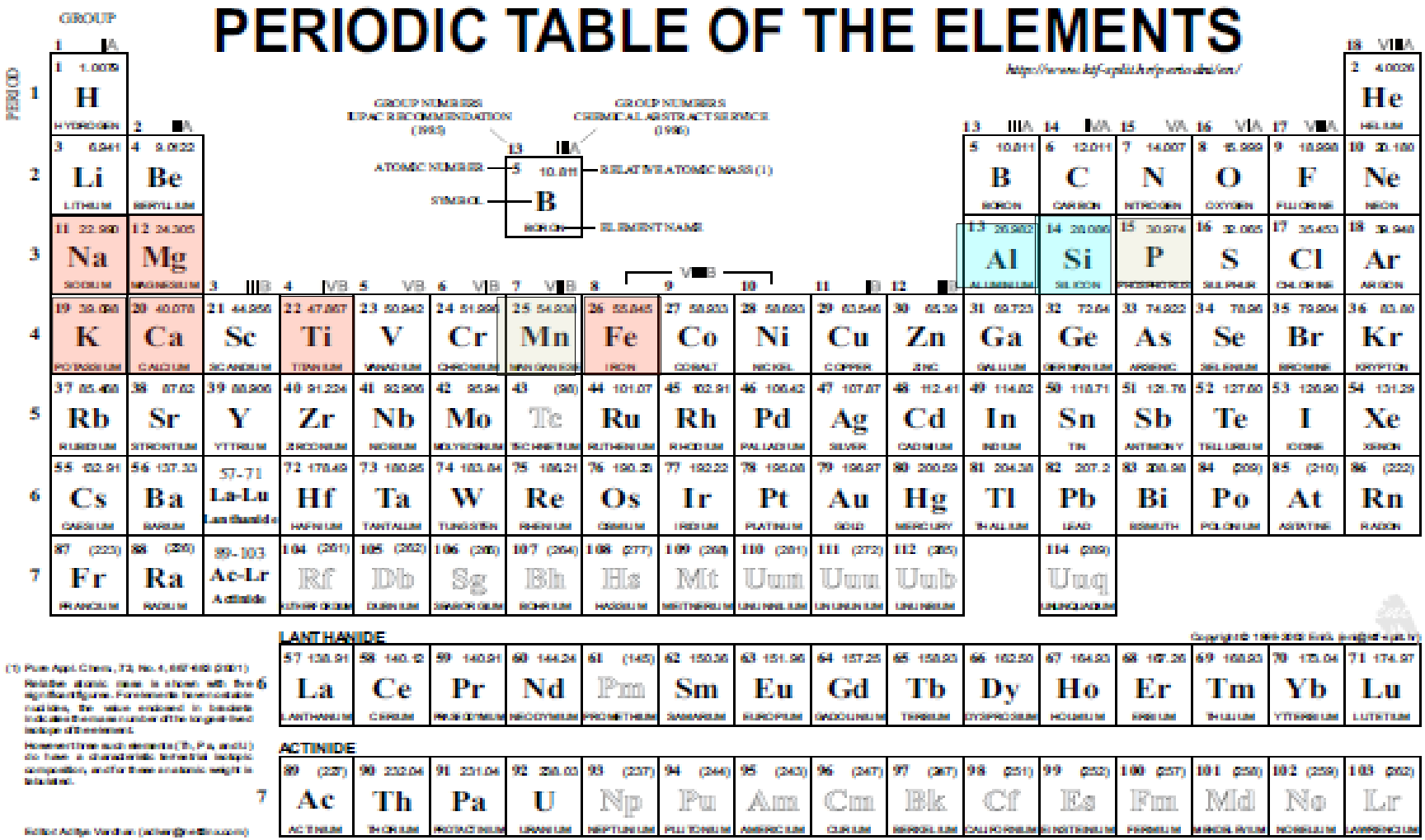
Geological reference materials, Igneous rocks, from AIST

(National Institute of Advanced Industrial Science and Technology, JAPAN)

	Sample name	Calibration curve	Reproducibility test	Type of mineral
1	JA-1	x	x	Andesite
2	JA-2	x		Andesite
3	JA-3	x		Andesite
4	JB-1a	x		Basalt
5	JB-2	x		Basalt
6	JB-3	x		Basalt
7	JG-1a	x	x	Granodiorite
8	JG-2	x		Granite
9	JG-3	x		Granodiorite
10	JGb-1	x	x	Gabbro
11	JGb-2	x		Gabbro
12	JR-1	x		Rhyolite
13	JR-2	x		Rhyolite
14	JR-3	x		Rhyolite



Measured Elements



Certified values of standards

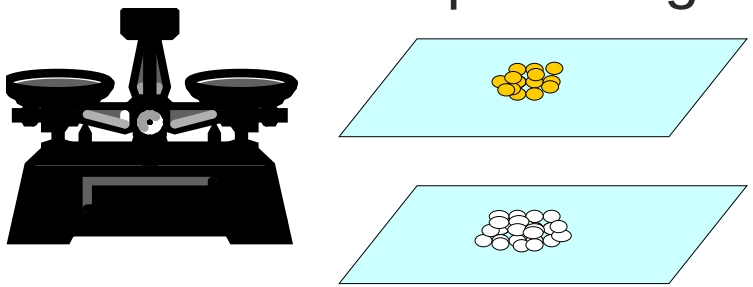
Unit : mass%

	SiO_2	TiO_2	Al_2O_3	T-Fe_2O_3	CaO	MgO	MnO	K_2O	Na_2O	P_2O_5
JA-1	63.97	0.85	15.22	7.07	5.70	1.57	0.157	0.77	3.84	0.165
JA-2	56.42	0.66	15.41	6.21	6.29	7.60	0.108	1.81	3.11	0.146
JA-3	62.27	0.70	15.56	6.60	6.24	3.72	0.104	1.41	3.19	0.116
JB-1a	52.41	1.28	14.45	9.05	9.31	7.83	0.148	1.40	2.73	0.260
JB-2	53.25	1.19	14.64	14.25	9.82	4.62	**0.218**	0.42	2.04	0.101
JB-3	50.96	1.44	17.20	11.82	9.79	5.19	0.177	0.78	2.73	**0.294**
JG-1a	72.30	0.25	14.30	2.00	2.13	0.69	0.057	3.96	3.39	0.083
JG-2	**76.83**	0.044	12.47	0.97	0.70	0.037	**0.016**	**4.71**	3.54	**0.002**
JG-3	67.29	0.48	15.48	3.69	3.69	1.79	0.071	2.64	3.96	0.122
JGb-1	**43.66**	**1.60**	17.49	**15.06**	11.90	**7.85**	0.189	0.24	1.20	0.056
JGb-2	46.47	0.56	**23.48**	6.69	**14.10**	6.18	0.130	**0.059**	**0.92**	0.017
JR-1	75.45	0.11	12.83	0.89	0.67	0.12	0.099	4.41	4.02	0.021
JR-2	75.69	**0.07**	12.72	**0.77**	0.50	0.04	0.112	4.45	3.99	0.012
JR-3	72.76	0.21	**11.90**	4.72	**0.093**	**0.05**	0.083	4.29	**4.69**	0.017

Sample Preparations

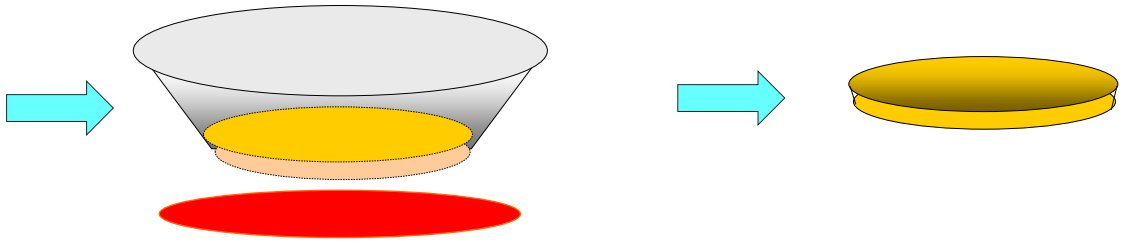
Weighing → Fusing → Bead

Sample 0.7g



Flux : Lithium Tetraborate ($Li_2B_4O_7$) 3.5g

Pt crucible



@ 1200 deg C

Dilution Ratio : 5 (flux/sample) → Ordinary Dilution Ratio is 10

Sample Preparations

Why the dilution ratio is 5?

- To analyze both major and minor elements by a single fusion bead.
- To avoid making powder pressed pellets for minor elements.
- To reduce the sample preparation time at satellite laboratories.

Apparatus
Benchtop WD-XRF

- Rigaku/Supermini
- Portable & Benchtop
- Air-cooled 200 W X-ray tube
- Single phase AC 100-240V

Measurement Conditions

	Si	Ti	Al	Fe	Ca	Mg	Mn	K	Na	P
X-ray line	Kα									
X-ray tube	End-window Pd tube									
KV & mA	50 kV and 4 mA									
Filter	Out									
Analysis Diameter	30 mm									
Analyzing crystal	PET	LiF200	PET	LiF200	PET	RX25*	LiF200	PET	RX25*	PET
Detector	F-PC	SC	F-PC	SC	F-PC	F-PC	SC	F-PC	F-PC	F-PC
PHA	Differential method									
Measurement time (s)	40	100	40	20	40	100	100	40	100	100
Atmosphere	Vacuum									

* Synthetic multilayer

Theoretical matrix correction coefficients

Analyzing oxide components

($x10^{-3}$)

Component to apply corrections

	SiO2	TiO2	Al2O3	T-Fe2O3	CaO	MgO	MnO	K2O	Na2O	P2O5
SiO2	2.63067	8.32648	2.24037	8.83817	7.66251	2.07262	8.74517	7.48860	1.95555	6.70749
TiO2	3.32931	8.04665	3.27340	29.3818	3.63445	0.320699	28.4337	3.40173	3.13119	3.38402
Al2O3	5.89495	7.38258	2.17161	7.73531	6.84241	1.88899	7.67308	6.72149	1.77394	6.12329
T-Fe2O3	5.08775	4.165887	4.94681	14.9180	4.30761	4.77664	11.4384	4.46715	4.57535	5.21112
CaO	2.92832	2.61327	2.88601	29.7106	6.95320	2.83816	28.9270	3.67402	2.78859	2.96961
MgO	5.79771	6.85846	5.60121	7.10738	6.47934	1.78125	7.07105	6.39179	1.58388	5.96095
MnO	4.74169	3.97533	4.62285	14.2443	3.92944	4.47315	14.1285	4.05343	4.28834	4.84366
K2O	2.65099	25.4027	2.60242	29.4233	26.6280	2.;54297	28.5590	6.42215	2.46941	2.69666
Na2O	5.14022	6.07817	5.03889	6.21994	5.61787	4.91761	6.20548	5.54395	1.21709	5.23442
P2O5	2.60556	8.92780	2.37759	9.63647	8.40969	2.21184	9.50222	8.20914	2.10235	3.14150

Ignition loss is set as the balance component

Accuracy

$$Accuracy(\sigma_d) = \sqrt{\frac{\sum_i (ci - \hat{W}i)}{n - m}} \quad (mass\%)$$

Ci : *certified concentaration of sample i*

$\hat{W}i$: *calculated concentration*

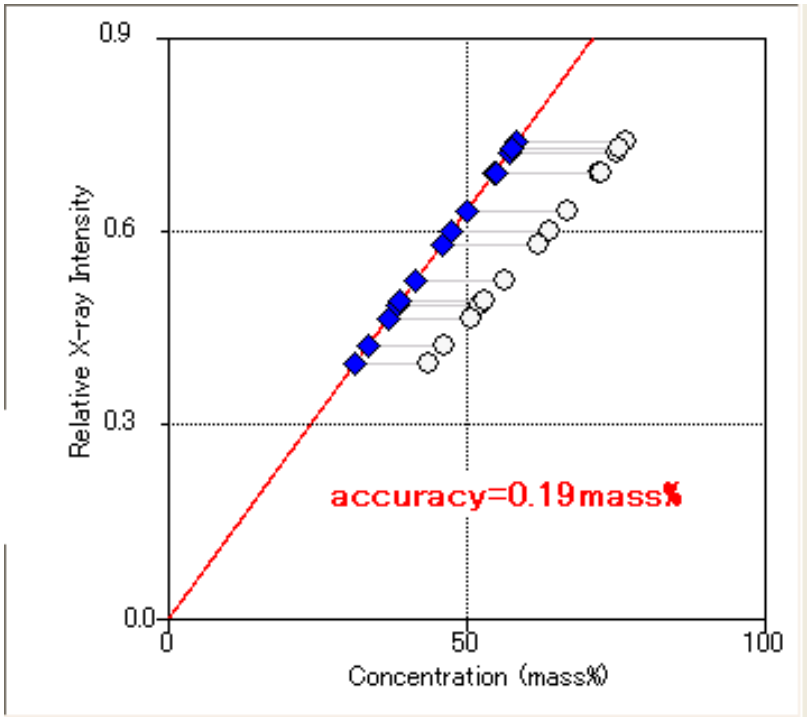
n : *number of samples*

m : *degree of freedom*

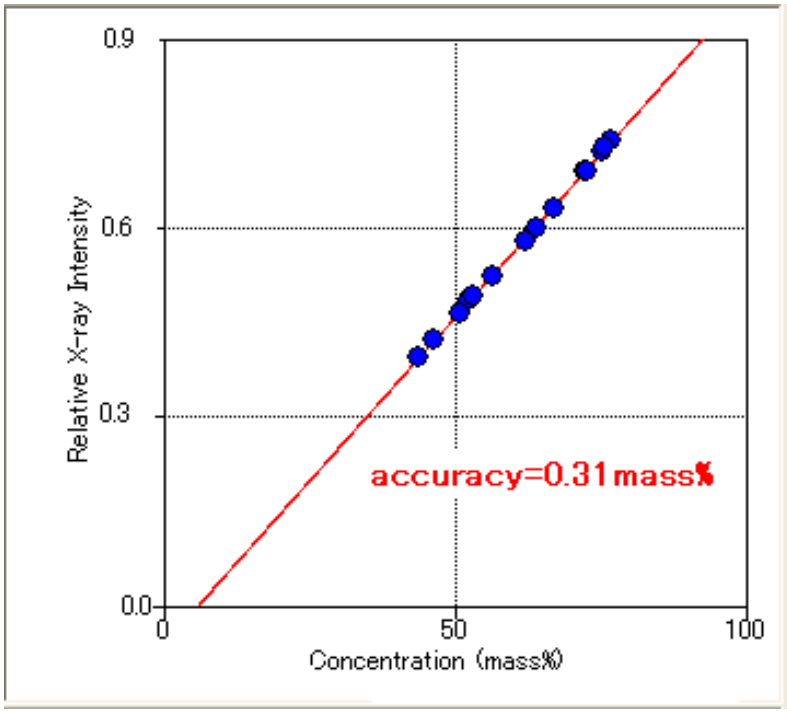
(2 *for linear*, 3 *for quardratic calibration*)

Calibration curve

SiO_2



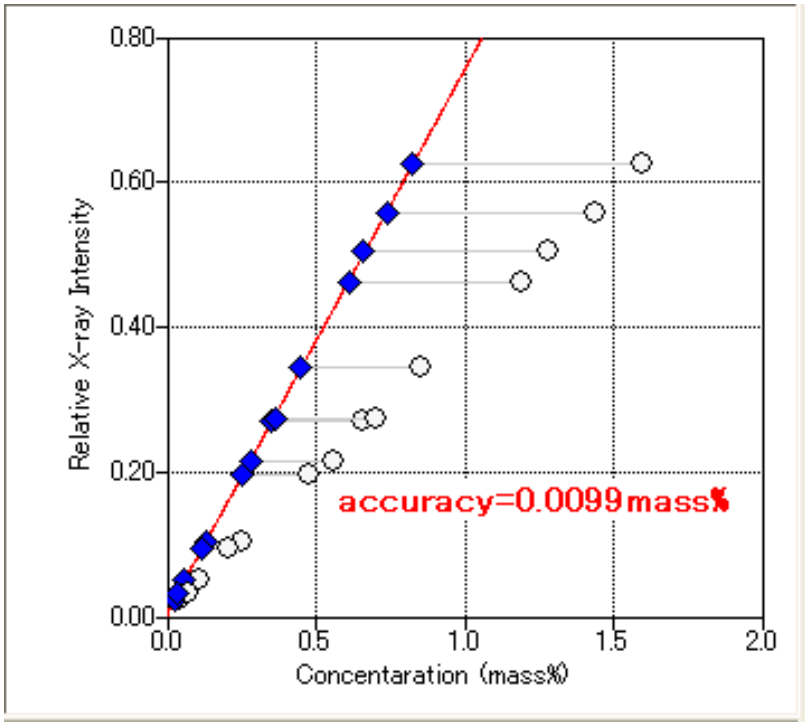
Corrected Calibration curve



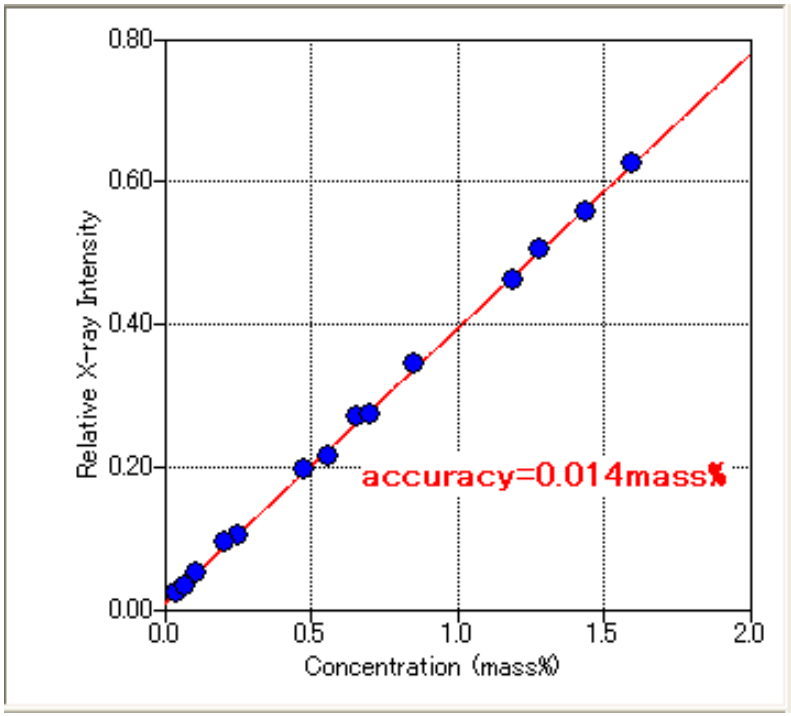
Uncorrected Calibration curve

Calibration curve

TiO_2



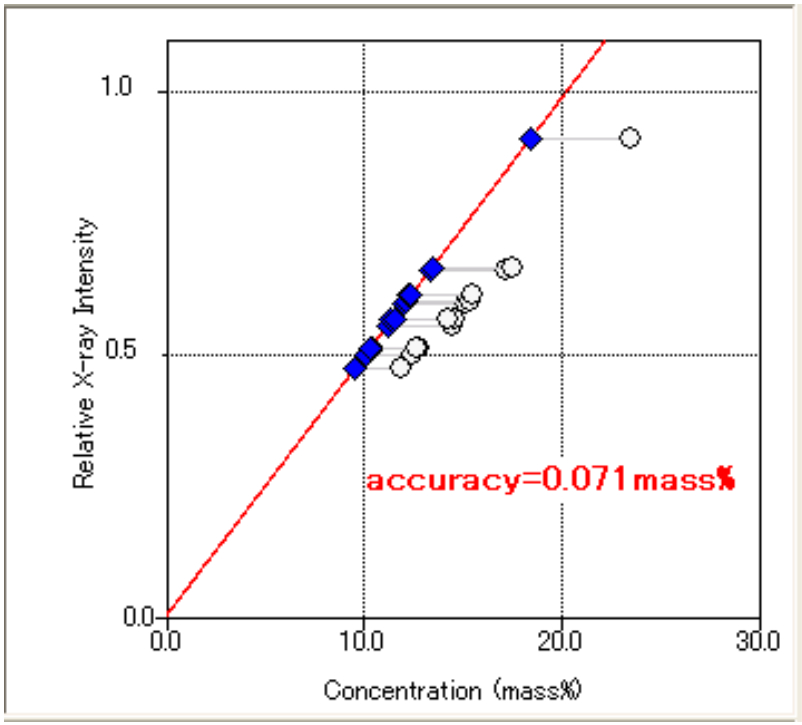
Corrected Calibration curve



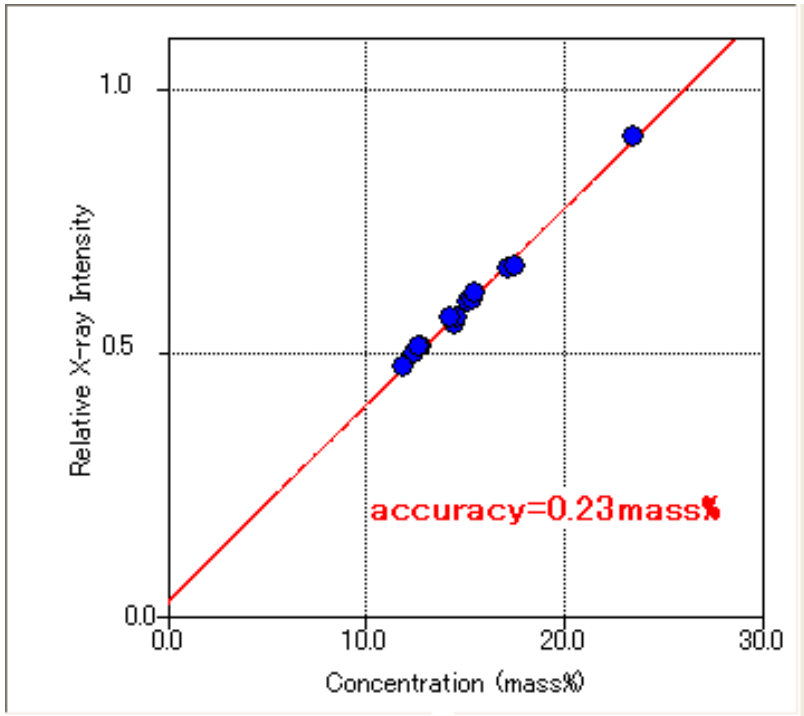
Uncorrected Calibration curve

Calibration curve

Al_2O_3



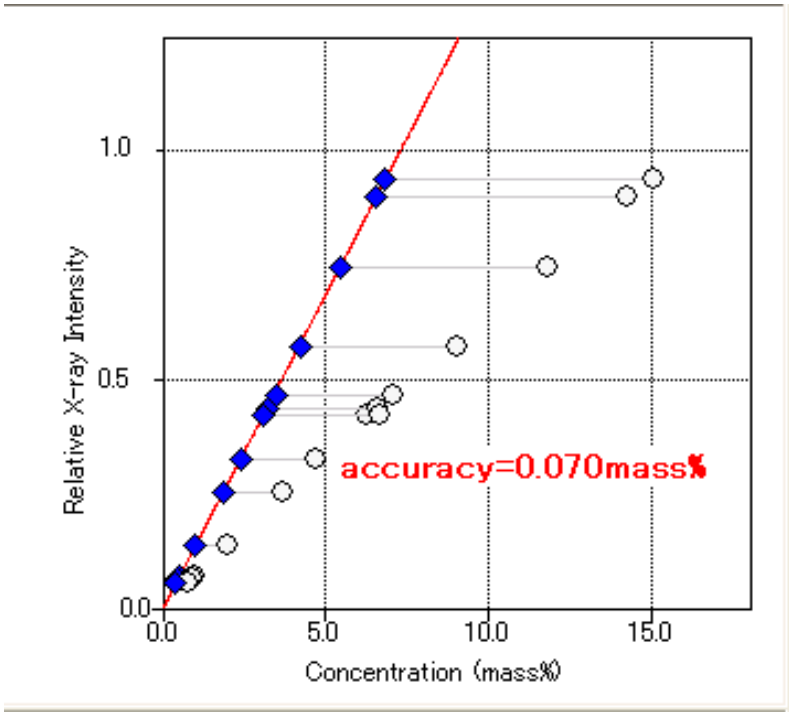
Corrected Calibration curve



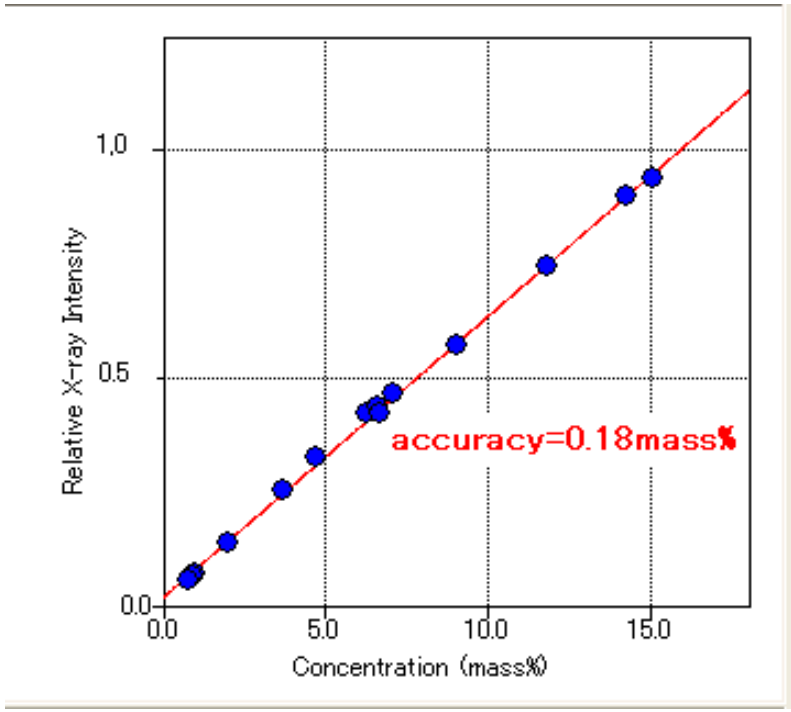
Uncorrected Calibration curve

Calibration curve

T-Fe_2O_3



Corrected Calibration curve



Uncorrected Calibration curve

Results of the regression calculation

Unit : mass%

	SiO2	TiO2	Al2O3	T-Fe2O3	CaO	MgO	MnO	K2O	Na2O	P2O5
Conc. Range Max. (%)	76.83	1.600	23.48	15.06	14.10	7.850	0.218	4.710	4.960	2.294
Conc. Range Min. (%)	43.66	0.070	11.90	0.770	0.093	0.005	0.016	0.059	0.920	0.002
Accuracy without correction (%)	0.31	0.015	0.23	0.18	0.049	0.081	0.0043	0.024	0.033	0.0045
Accuracy with Correction (%)	**0.19**	**0.0099**	**0.07**	**0.07**	0.042	0.051	0.0035	0.023	0.033	0.0042

Reproducibility measurement result for sample JA-1

Unit : mass%

	SiO2	TiO2	Al2O3	T-Fe2O3	CaO	MgO	MnO	K2O	Na2O	P2O5
Standard Value	63.97	0.850	15.22	7.070	5.700	1.570	0.157	0.770	3.840	0.165
Average value	64.18	0.850	15.19	6.960	5.690	1.530	0.160	0.770	3.880	0.160
Standard deviation	0.081	0.0059	0.035	0.011	0.013	0.015	0.010	0.0060	0.045	0.0010
R.S.D. (%)	0.13	0.69	0.23	0.16	0.22	0.95	0.69	0.78	1.15	0.60

Reproducibility measurement result for Sample JG-1a

Unit : mass%

	SiO2	TiO2	Al2O3	T-Fe2O3	CaO	MgO	MnO	K2O	Na2O	P2O5
Standard Value	72.30	0.250	14.30	2.000	2.130	0.690	0.057	3.960	3.390	0.083
Average value	72.38	0.250	14.24	2.010	2.120	0.690	0.060	4.020	3.400	0.820
Standard deviation	0.11	0.0034	0.039	0.0062	0.011	0.012	0.0007	0.012	0.040	0.0014
R.S.D. (%)	0.15	1.38	0.27	0.27	0.52	1.74	1.23	0.29	1.18	1.67

Reproducibility measurement result for Sample JGb-1

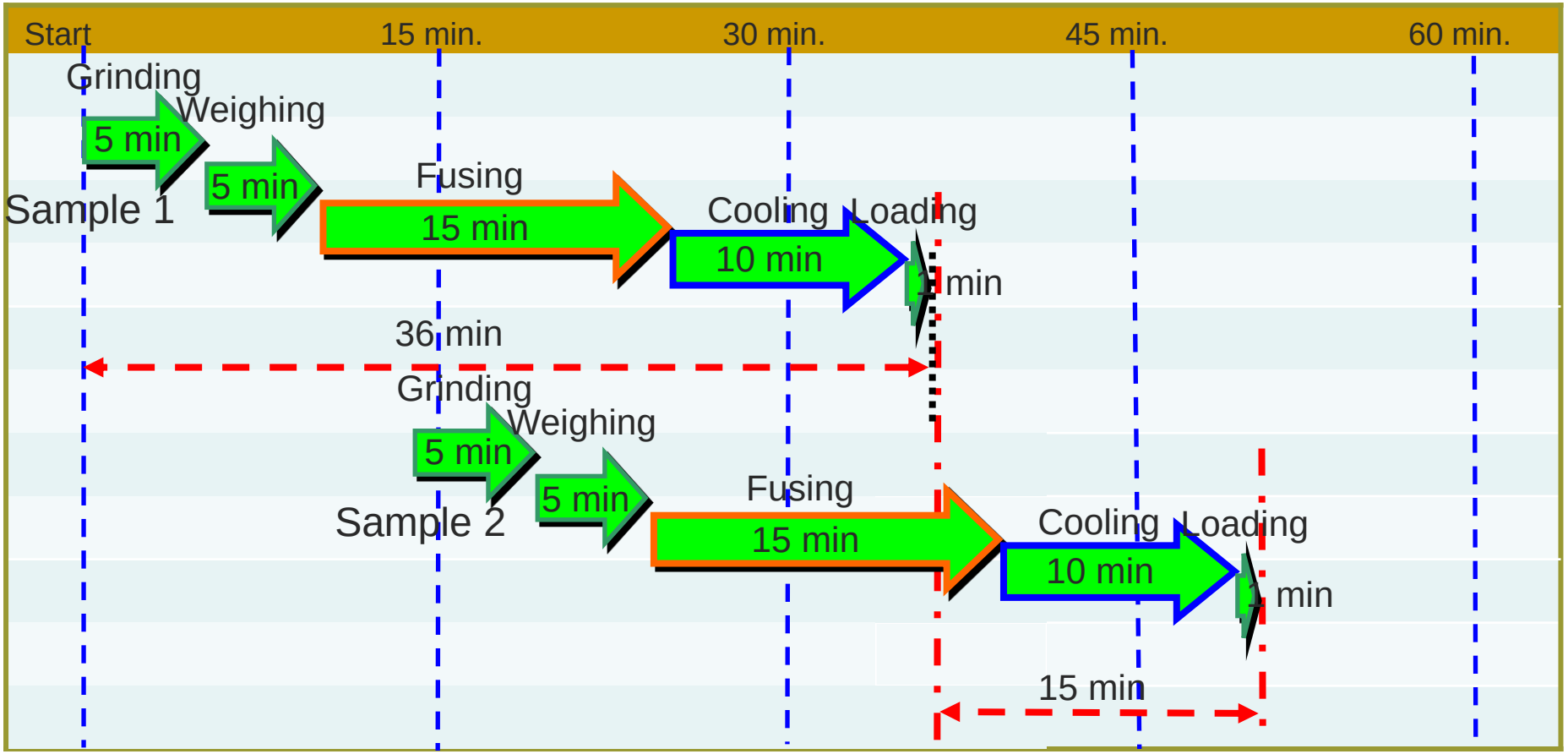
Unit : mass%

	SiO2	TiO2	Al2O3	T-Fe2O3	CaO	MgO	MnO	K2O	Na2O	P2O5
Standard Value	43.66	1.600	17.49	15.06	11.90	7.850	0.189	0.240	1.200	0.056
Average value	43.61	1.600	17.51	15.10	11.90	7.860	0.190	0.250	1.230	0.059
Standard deviation	0.072	0.0064	0.047	0.032	0.026	0.029	0.0015	0.0031	0.022	0.0011
R.S.D. (%)	0.17	0.40	0.27	0.21	0.37	0.37	0.79	1.26	1.75	1.81

Productivity of measurement

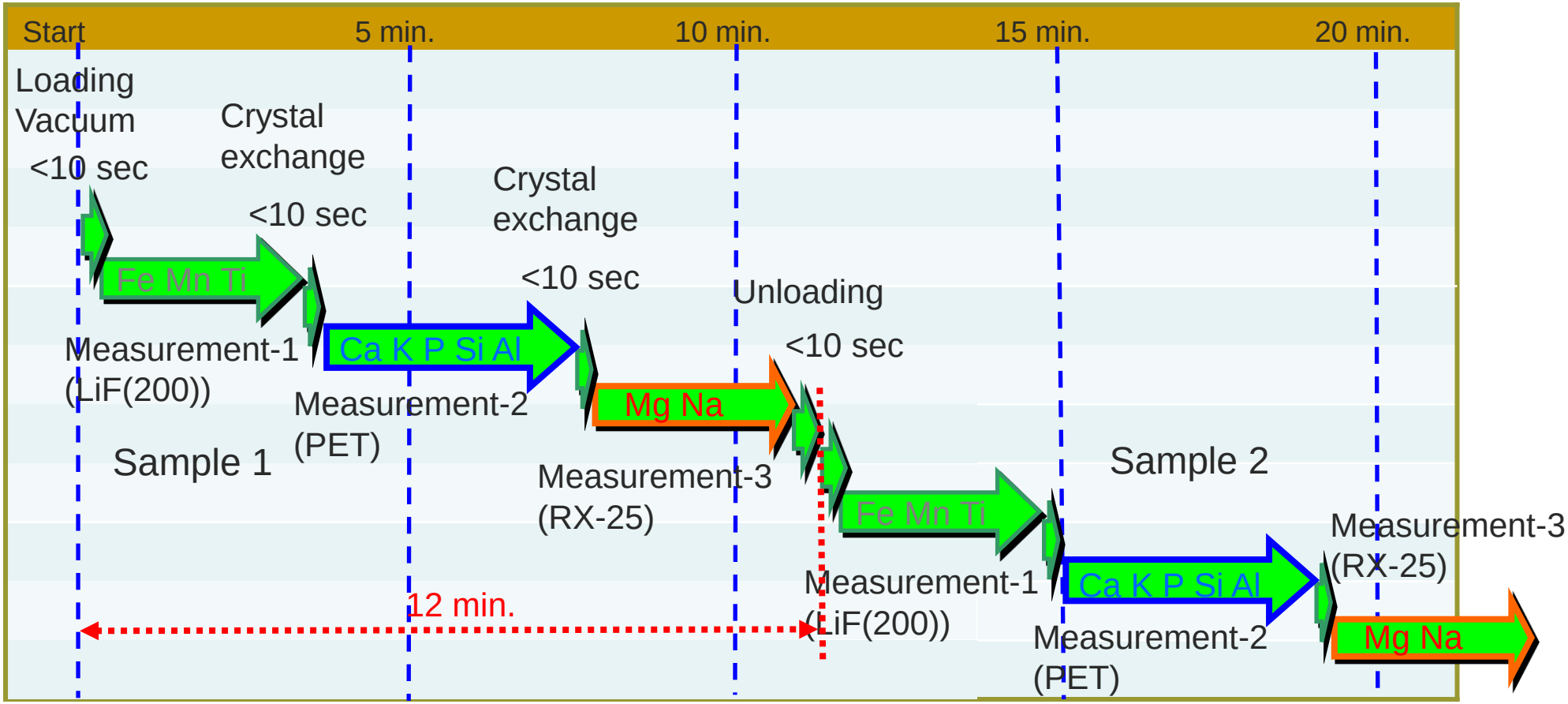
- Fast speed measurement is a big advantage of ED-XRF system.
- High through put is not required for satellite laboratories from their original purpose, but reasonable efficiency is required.

Sample Preparation Time Chart



A sample every 15 min.

Measurement Time Chart



Measurement Time does not impact to the productivity.

Summary

- The bench top WD-XRF is suitable for geological survey at small satellite laboratories on mining sites.
- The productivity (measurement speed) is not disadvantage for WD-XRF, when we consider the productivity of sample preparations at small satellite laboratories.
- The middle dilution ratio fused bead method is provided good results for major and minor elements analysis in Rock samples.

Thank you for your attention.