

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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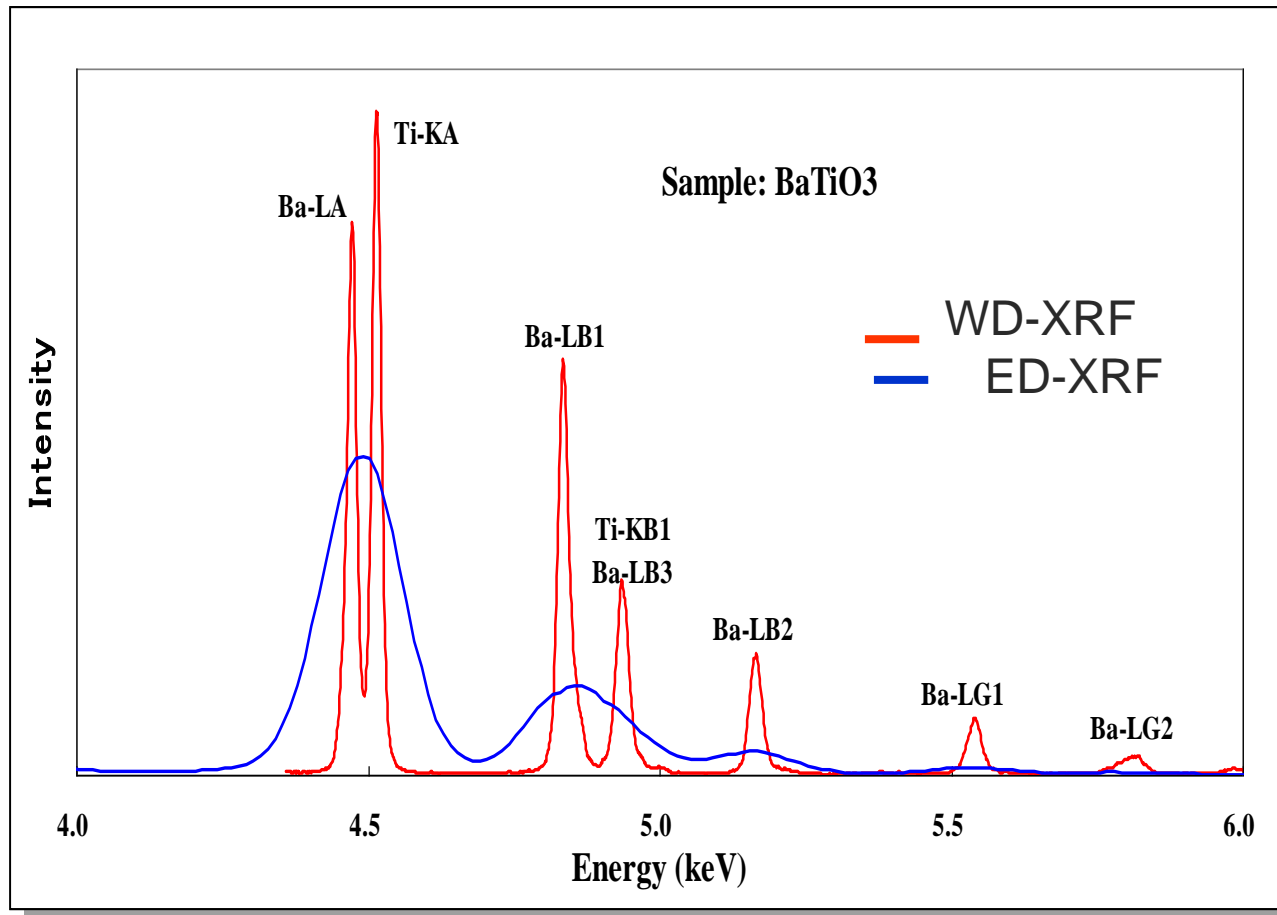
Topics

- 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.

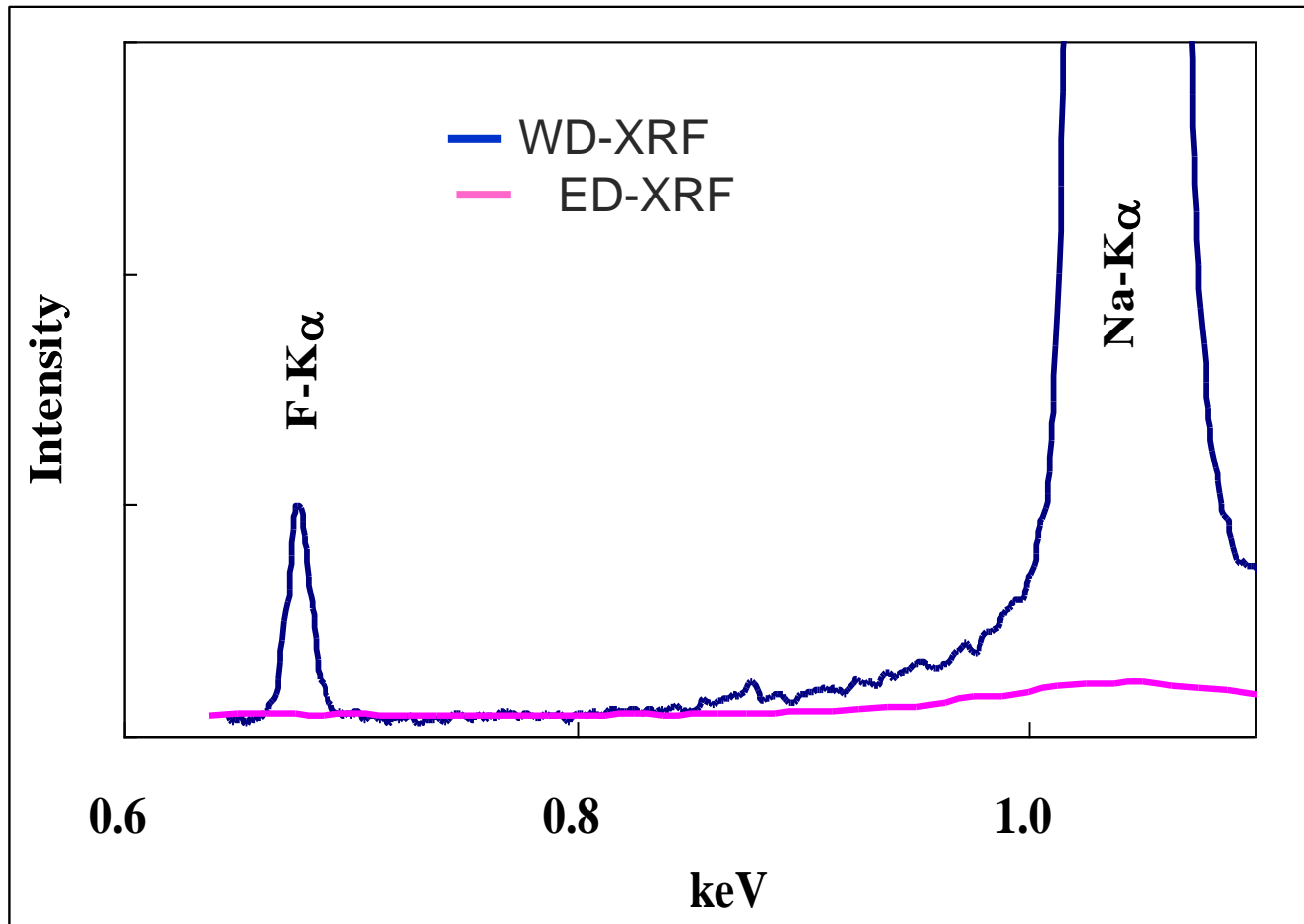
High resolution



Sample : BaTiO₃

WD-XRF technique has enough resolution to separate Ti-K α and Ba-L α .

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

PERIODIC TABLE OF THE ELEMENTS

<https://www.kj-soft.com/periodic-table/>

GROUP	PERIODIC TABLE OF THE ELEMENTS																18													
1											13	14	15	16	17	18														
1A											IIIA	IVA	VA	VIA	VIIA	VIIIA														
1	1.008											5.011	6.011	7.007	8.009	9.009	10.100													
1	H											B	C	N	O	F	Ne													
	HYDROGEN											BORON	CARBON	NITROGEN	OXYGEN	FLUORINE	NEON													
2	3.041	4.002											13.003	14.008	15.003	16.005	17.003	18.004												
2	Li	Be											Al	Si	P	S	Cl	Ar												
	LITHIUM	BERYLLIUM											ALUMINUM	SILICON	PHOSPHORUS	SULFUR	CHLORINE	ARGON												
3	11.009	12.011											26.982	28.086	30.974	32.065	35.453	39.948												
3	Na	Mg											K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
	SODIUM	MAGNESIUM											POTASSIUM	CALCIUM	SCANDIUM	TITANIUM	Vanadium	CHROMIUM	MANGANESE	IRON	COBALT	NICKEL	COPPER	ZINC	GALLIUM	GERMANIUM	ARSENIC	SELENIUM	BROMINE	KRYPTON
4	19.000	20.019	21.028	22.017	23.004	24.010	25.009	26.005	27.001	28.006	29.009	30.006	31.002	32.006	33.004	34.008	35.004	36.000												
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr												
	POTASSIUM	CALCIUM	SCANDIUM	TITANIUM	Vanadium	CHROMIUM	MANGANESE	IRON	COBALT	NICKEL	COPPER	ZINC	GALLIUM	GERMANIUM	ARSENIC	SELENIUM	BROMINE	KRYPTON												
5	37.000	38.081	39.098	40.078	41.008	42.010	43.000	44.010	45.002	46.005	47.003	48.003	49.002	50.009	51.008	52.007	53.004	54.006												
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe												
	RUBIDIUM	STRONTIUM	YTIUM	ZIRCONIUM	NIOBIUM	MOLYBDENUM	Technetium	RUTHENIUM	RHODIUM	PALLADIUM	SILVER	CADMIUM	INDIUM	TIN	ANTIMONY	TELLURIUM	IODINE	XENON												
6	55.000	56.005	57-71	72.044	73.021	74.025	75.023	76.024	77.023	78.024	79.022	80.021	81.024	82.022	83.024	84.026	85.022	86.022												
6	Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn												
	CAESIUM	BARIUM	Lanthanide	HAFNIUM	TANTALUM	TUNGSTEN	RHENIUM	OSMIUM	IRIDIUM	PLATINUM	GOLD	MERCURY	THALLIUM	LEAD	BISMUTH	POLONIUM	ASTATINE	RADON												
7	87.000	88.000	89-103	104.001	105.000	106.000	107.000	108.000	109.000	110.000	111.000	112.000																		
7	Fr	Ra	Ac-Lr	Rf	Db	Sg	Bh	Hs	Mt	Uub	Uuq																			
	FRANCIUM	RADIUM	Actinide	RUFORDIUM	DUBNIUM	SEBASTIUM	BORHVIUM	HASHEMITE	MITHRIUM	UNUNBIUM	UNUNTRIUM	UNUNQUADRIUM																		

LANTHANIDE														
57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
LANTHANUM	CERIUM	PRASEODYMIUM	NEODYMIUM	PROMETHIUM	SAMARIUM	EUROPIUM	GADOLINIUM	TERBIUM	DYSPROSIUM	HOLMIUM	ERBIUM	THULIUM	YTERBIUM	LUTETIUM

ACTINIDE														
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
ACTINIUM	THORIUM	PROTACTINIUM	URANIUM	NEPTUNIUM	PLUTONIUM	AMERICIUM	CURIUM	BERKELIUM	CALIFORNIUM	FERMIUM	MENDELIUM	NOBELIUM	LAWRENCIUM	

(1) Pure Appl. Chem., 73, No. 4, 697-699 (2011)
 Relative atomic mass is shown with five significant figures. For elements with standard atomic weights, the values indicated in brackets indicate the range of values of the relative atomic mass of the element.
 Elements with such designations (B, P, A, and U) do not have a standard atomic weight because of isotopic composition, and their atomic weight is bracketed.
 Robert A. Johnson, rjohn@nd.edu



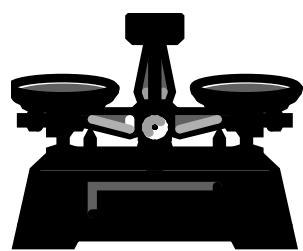
Certified values of standards

Unit : mass%

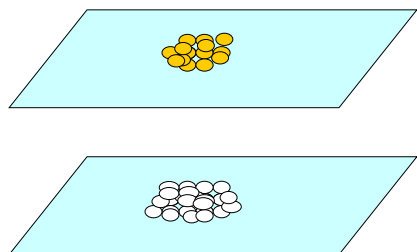
	SiO ₂	TiO ₂	Al ₂ O ₃	T-Fe ₂ O ₃	CaO	MgO	MnO	K ₂ O	Na ₂ O	P ₂ O ₅
JA-1	63.97	0.85	15.22	7.07	5.70	1.57	0.157	0.77	3.84	0.165
JA-2	56.42	0.66	15.41	6.21	6.29	7.60	0.108	1.81	3.11	0.146
JA-3	62.27	0.70	15.56	6.60	6.24	3.72	0.104	1.41	3.19	0.116
JB-1a	52.41	1.28	14.45	9.05	9.31	7.83	0.148	1.40	2.73	0.260
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

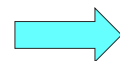


Sample 0.7g



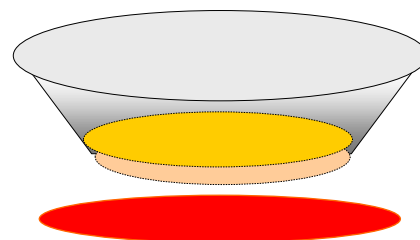
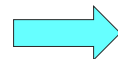
Flux : Lithium Tetraborate
($\text{Li}_2\text{B}_4\text{O}_7$) 3.5g

Dilution Ratio : 5
(flux/sample)

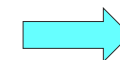


Fusing

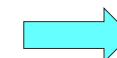
Pt crucible



@ 1200 deg C



Bead



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	K α									
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										
	SiO ₂	TiO ₂	Al ₂ O ₃	T-Fe ₂ O ₃	CaO	MgO	MnO	K ₂ O	Na ₂ O	P ₂ O ₅	
Component to apply corrections	SiO ₂	2.63067	8.32648	2.24037	8.83817	7.66251	2.07262	8.74517	7.48860	1.95555	6.70749
	TiO ₂	3.32931	8.04665	3.27340	29.3818	3.63445	0.320699	28.4337	3.40173	3.13119	3.38402
	Al ₂ O ₃	5.89495	7.38258	2.17161	7.73531	6.84241	1.88899	7.67308	6.72149	1.77394	6.12329
	T-Fe ₂ O ₃	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
	K ₂ O	2.65099	25.4027	2.60242	29.4233	26.6280	2.54297	28.5590	6.42215	2.46941	2.69666
	Na ₂ O	5.14022	6.07817	5.03889	6.21994	5.61787	4.91761	6.20548	5.54395	1.21709	5.23442
	P ₂ O ₅	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

$$Accuracy(\sigma_d) = \sqrt{\frac{\sum_i (c_i - \hat{W}_i)^2}{n - m}} \quad (\text{mass}\%)$$

C_i : certified concentration of sample i

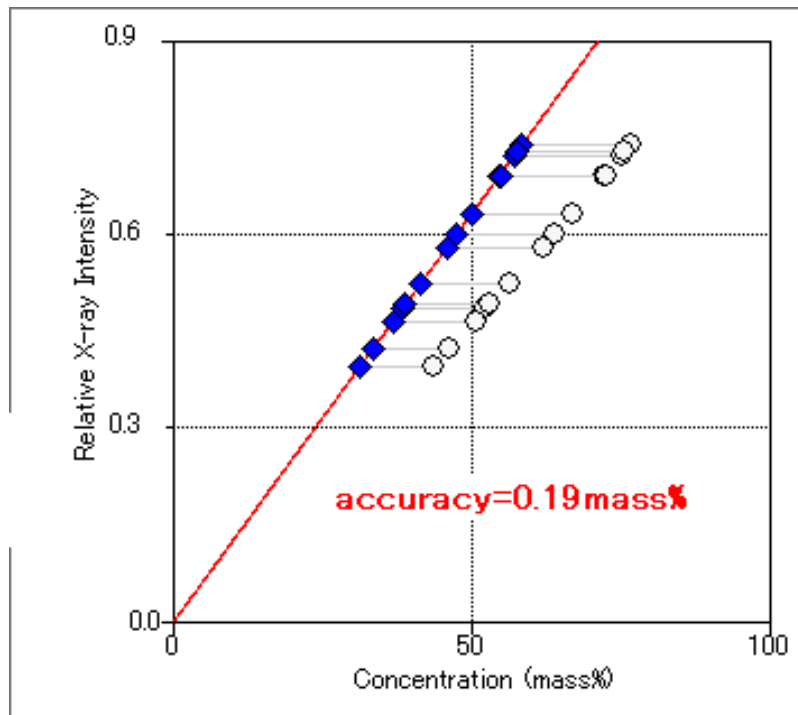
\hat{W}_i : calculated concentration

n : number of samples

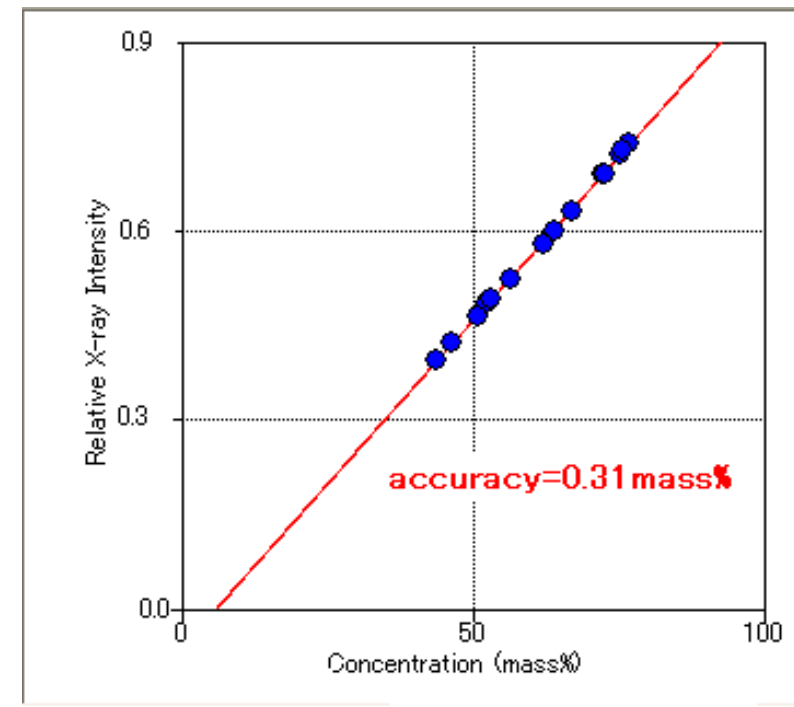
m : degree of freedom

(2 for linear, 3 for quadratic calibration)

Calibration curve



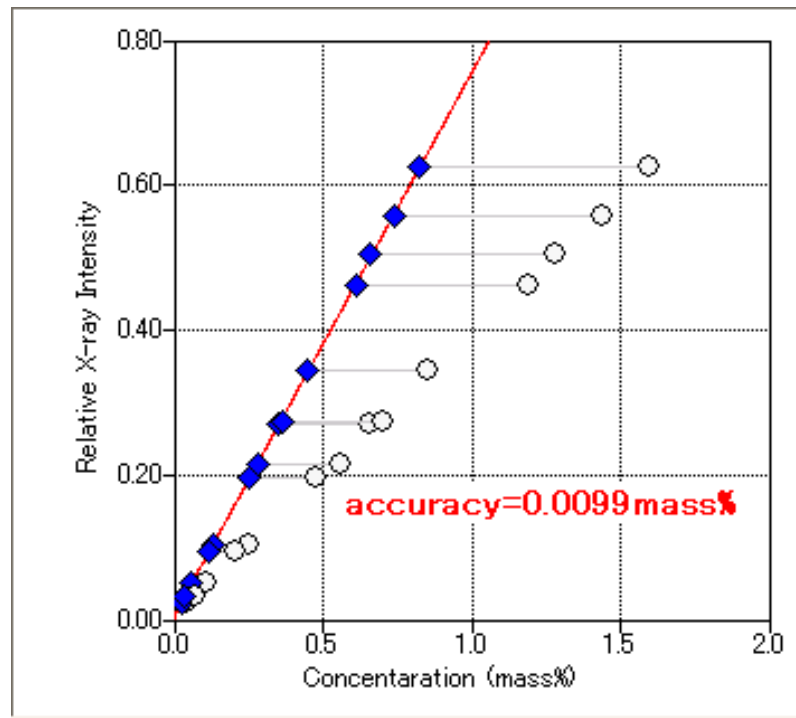
Corrected Calibration curve



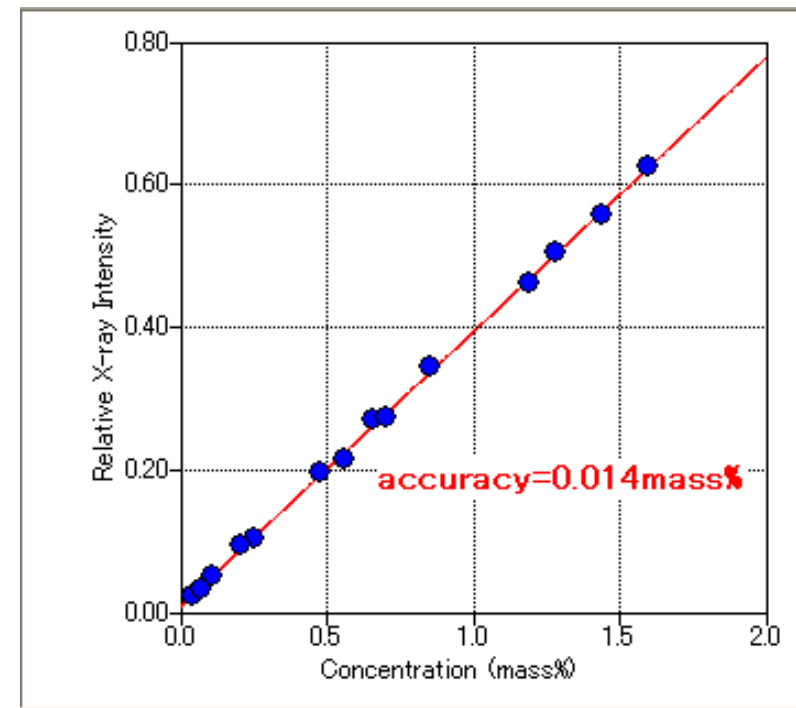
Uncorrected Calibration curve

Calibration curve

TiO₂

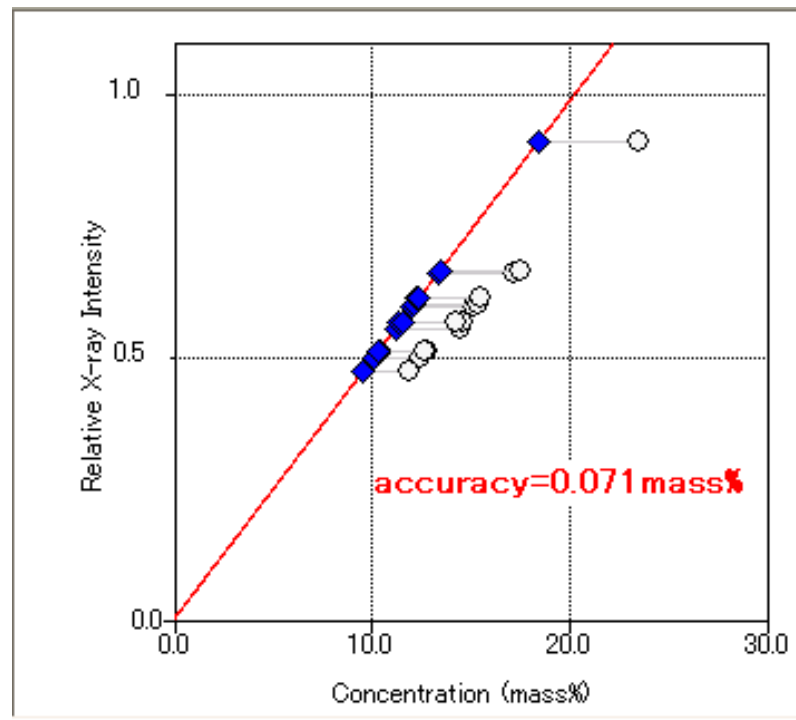


Corrected Calibration curve

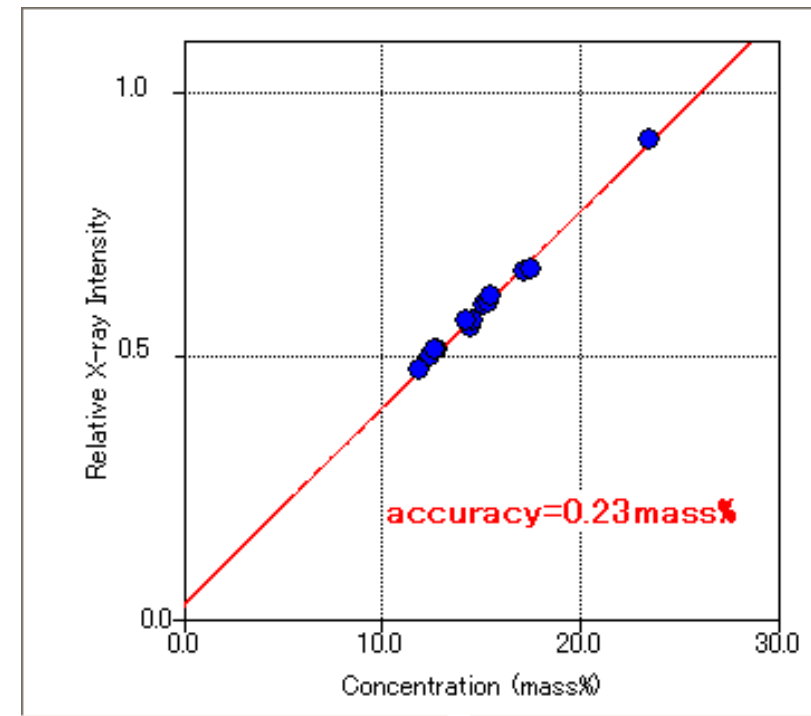


Uncorrected Calibration curve

Calibration curve

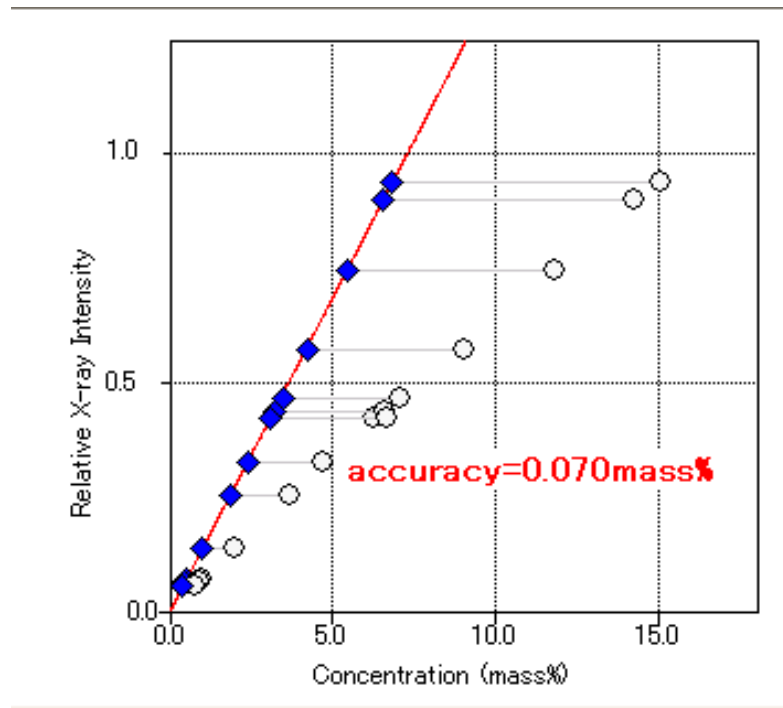


Corrected Calibration curve

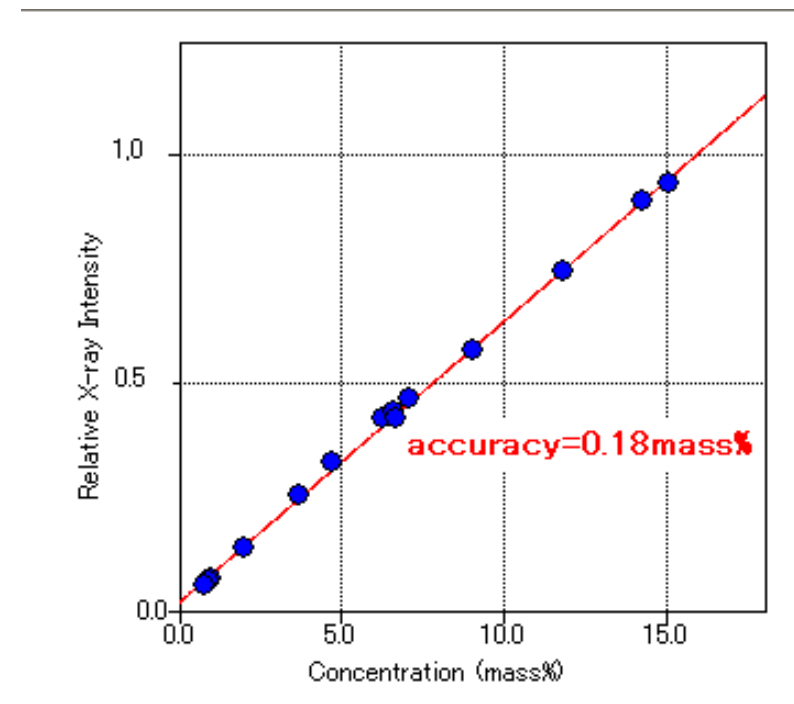


Uncorrected Calibration curve

Calibration curve



Corrected Calibration curve



Uncorrected Calibration curve

Results of the regression calculation

Unit : mass%

	SiO ₂	TiO ₂	Al ₂ O ₃	T- Fe ₂ O ₃	CaO	MgO	MnO	K ₂ O	Na ₂ O	P ₂ O ₅
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%

	SiO ₂	TiO ₂	Al ₂ O ₃	T- Fe ₂ O ₃	CaO	MgO	MnO	K ₂ O	Na ₂ O	P ₂ O ₅
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%

	SiO ₂	TiO ₂	Al ₂ O ₃	T- Fe ₂ O ₃	CaO	MgO	MnO	K ₂ O	Na ₂ O	P ₂ O ₅
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

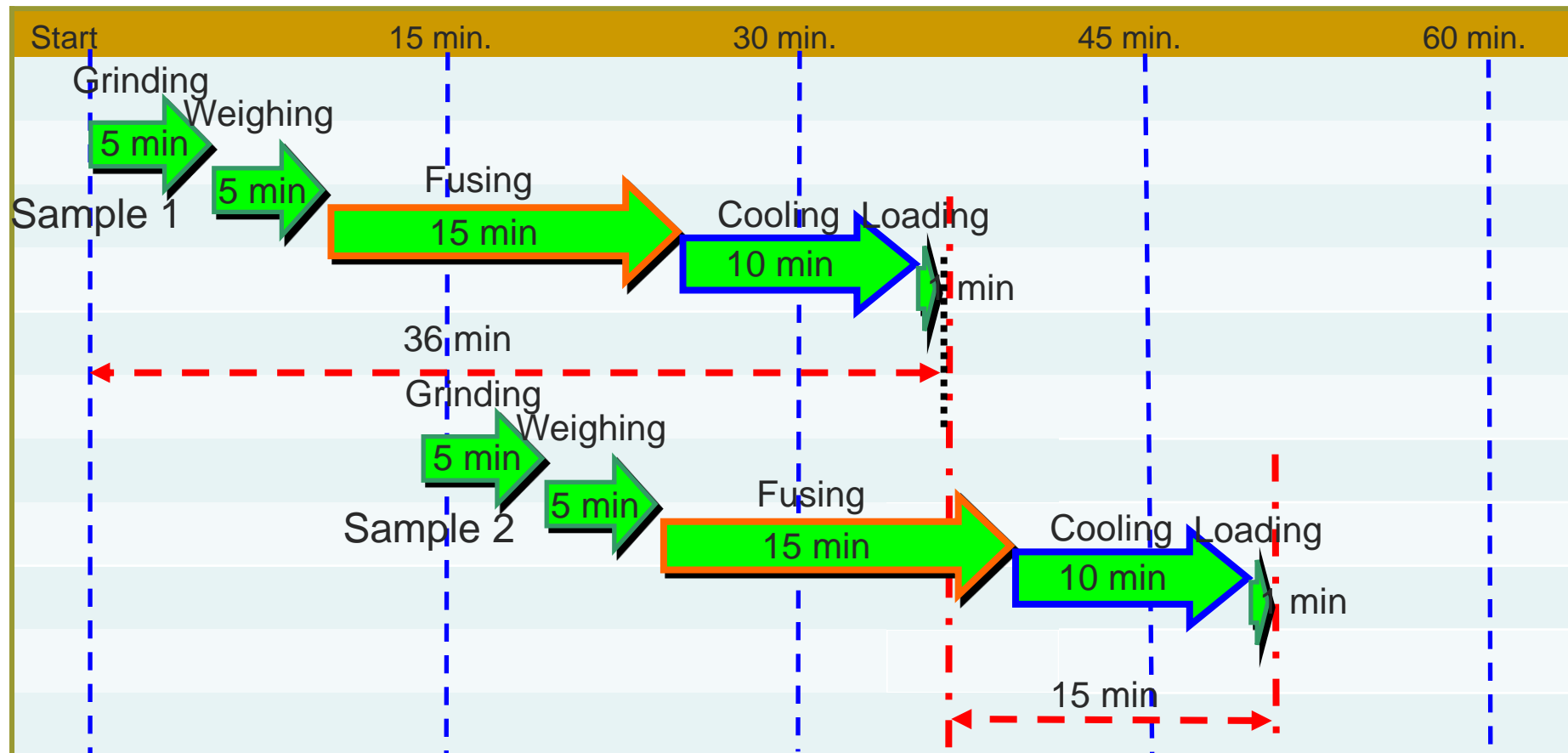
Unit : mass%

	SiO ₂	TiO ₂	Al ₂ O ₃	T- Fe ₂ O ₃	CaO	MgO	MnO	K ₂ O	Na ₂ O	P ₂ O ₅
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

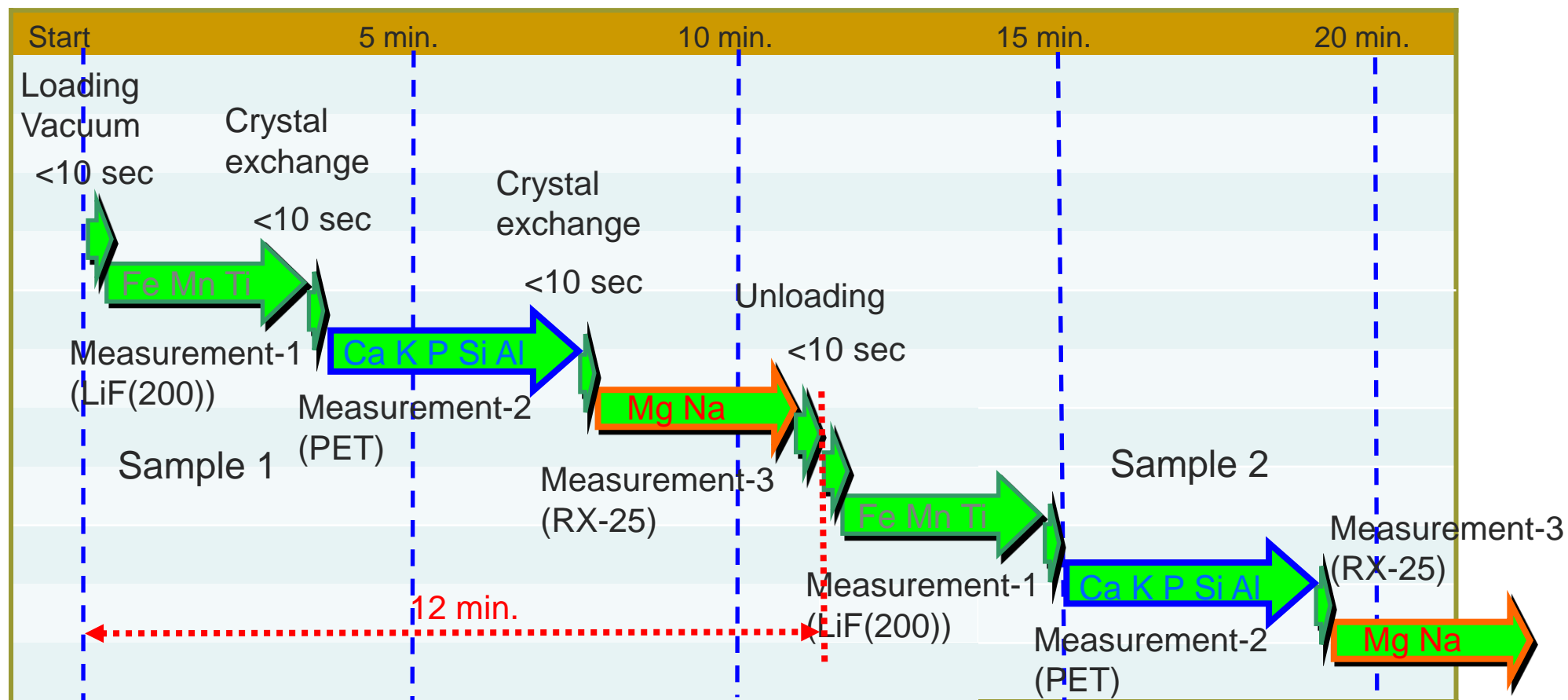
- Fast speed measurement is a big advantage of ED-XRF system.
- High through put is not required for satellite laboratories from their original purpose, but reasonable efficiency is required.

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.