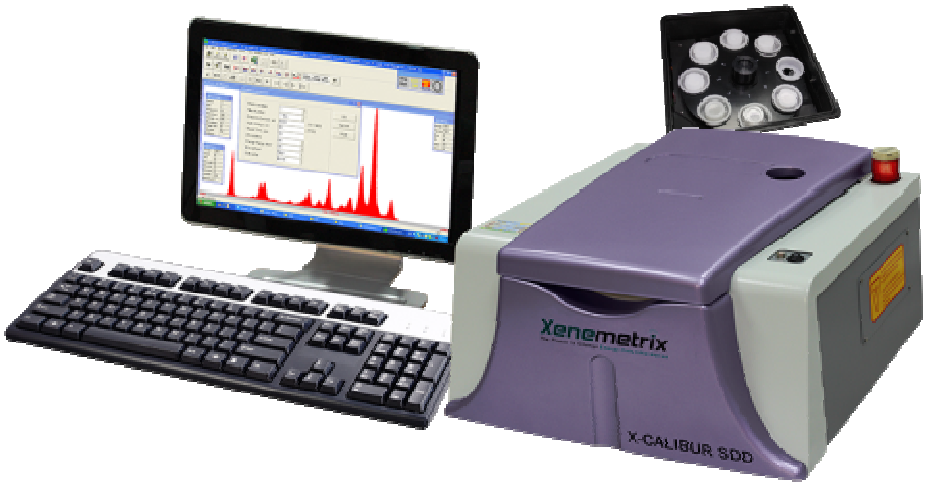
APPLICATION NOTE
XE-2012-3180

Xenemetrix
The Power to Change Energy Into Information

Quantitative analysis of Na, Mg, Al, Si, P, S, K, Ca, Ti, and Fe in Geological samples using X-Calibur EDXRF equipped with SDD detector with specialized window for light elements



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ABSTRACT

Quantitative analysis of defined elements in geological samples was performed using Xenemetrix EDXRF analyzer, model X-Calibur equipped with a high resolution and high performance Silicon Drift Detector (SDD) with specialized window for low Z elements. Repeatability studies were conducted to show the robustness of the EDXRF analyzer.

GOALS

1. To develop quantitative methods for analysis of Na, Mg, Al, Si, P, S, K, Ca, Ti, Fe in geological samples, and use the method to analyze unknown samples.
2. Evaluate the instrument performance in repeated analysis of the same sample.

BACKGROUND

Energy Dispersive X-ray Fluorescence (EDXRF) is a fast and non-destructive and non invasive, that can quantify any type of sample in solid, powder and liquid forms. EDXRF is an ideal method for quick and simple elemental analysis for industrial control purposes offering the following advantages: 1) Fast and minimal sample preparation, 2) Automated analysis process, 3) Limited or no exposure to corrosive reagents used by other analytical techniques, 4) Easy to operate by non-technical or non-specialized personnel. These advantages have made XRF the method of choice in diverse industries such as Geology, Mining, Petrochemical and Chemicals.

ANALYTICAL CONFIGURATION

Table 1: Analytical configuration of X-Calibur SDD

Instrument	X-Calibur SDD EDXRF Bench top Spectrometer System.
Excitation	Rh-Anode X-ray Tube 50KV, 50W
Detector	High Performance Silicon Drift Detector with specialized window for light Elements.
Analysis Time	300 seconds for all elements, 600 seconds for Na and Mg
Type of analysis	Quantitative linear regression analysis
Excitation	Direct excitation. In few cases titanium filter was used selectively to reduce the background (K and Ca).
Environment	Vacuum
Sample Preparation	All samples were analyzed as received in pressed pellet form as obtained from the customer. Pressed pellets were made using a hydraulic laboratory press.

EXPERIMENTALS

A set of 23 geological standards were provided for the analysis of K_2O and SO_3. From these, 12 standards were used for the analysis of Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, SO_3, K2O, CaO, TiO_2, and Fe_2O_2. The samples were analyzed in pressed pellets form as obtained from the customer. The acquisition parameters were optimized specifically for group of elements: Ti filter was used selectively to reduce the background noise and enhance the signal to noise for K, Ca. Al, Si and Ca also be analyzed in this manner. Direct excitation (without filters) was used for the rest of the elements. Special care was done with, Na and Mg were where low excitation energies was required in order to avoid inter element influence by heavier (higher Z) elements.

The spectra acquisition for all samples was performed in vacuum in order to eliminate the oxygen in the X-ray beam path since otherwise the oxygen absorbs the low energy signal emitted by the light elements as Na, Mg, Si, P and S.

The SDD detector of X-Calibur analyzer was equipped with Light Element window, to enhance the signal of light elements such as Na, Mg and Al. Since this detector window is characterized by low absorbance of signals of low Z elements, emission peaks of sodium and magnesium are clearly observed in the spectrum and their detection limit is significantly improved. Summary of all standards with their element content are listed in table 2.

Table 2: Calibration standards for all elements in the pressed pellets; concentration in w/w%.

Standard ID	K2O	SO3	Na2O	MgO	Al2O3	SiO2	P2O5	SO3	K2O	CaO	TiO2	Fe2O3	lg-loss	Sum
Standard #1	0.1096	0.1329	0.0707	0.0009	12.878	82.162	0.0405	0.1329	0.1096	0.0029	0.4866	0.0778	3.0900	99.294
Standard #2	0.0566	0.1537	0.0759	0.0013	15.361	79.574	0.0755	0.1537	0.0566	0.0039	0.4029	0.0868	3.3000	99.302
Standard #3	0.0753	0.1721	0.0834	0.0012	16.665	78.256	0.0853	0.1721	0.0753	0.0151	0.4592	0.1648	3.5700	99.795
Standard #4	0.0530	0.1475	0.0859	0.0006	18.325	76.480	0.0789	0.1475	0.0530	0.0050	0.4166	0.0528	3.8100	99.656
Standard #5	Not provided													
Standard #6	0.1227	0.1276	0.0895	0.0001	19.002	75.844	0.0373	0.1276	0.1227	0.0106	0.4043	0.0291	3.9200	99.838
Standard #7	0.1278	0.1315	0.0949	0.0007	19.378	75.341	0.0634	0.1315	0.1278	0.0256	0.4701	0.0449	4.0300	99.967
Standard #8	0.0437	0.1562	0.0949	0.0033	21.719	73.091	0.0327	0.1562	0.0437	0.0115	0.4171	0.0806	4.4900	100.340
Standard #9	0.0714	0.1304	0.1047	0.0085	23.337	71.277	0.0480	0.1304	0.0714	0.0066	0.5401	0.2373	4.8700	100.833
Standard#10	0.5571	0.1592	0.0917	0.0033	18.258	76.406	0.1072	0.1592	0.5571	0.0218	0.4556	0.0527	3.7200	100.549
Standard#11	0.2363	0.1541	0.0939	0.0064	19.179	75.534	0.0612	0.1541	0.2363	0.0086	0.4562	0.2134	3.9400	100.274
Standard#12	0.1503	0.1459	0.0576	0.0027	8.809	86.345	0.0427	0.1459	0.1503	0.0112	0.4560	0.0376	2.4600	98.8142
Standard#13	0.2760	0.1023												
Standard#14	Not provided													
Standard #15	1.1133	0.0207												
Standard #16	Not provided													
Standard #17	0.3297	0.3820												
Standard #18	0.8378	0.3783												
Standard #19	0.2949	1.4730												
Standard #20	0.5024	2.8590												
Standard #21	0.1286	0.8220												
Standard #22	0.2077	1.0020												
Standard #25	0.4677	3.6877												
Standard #26	0.3109	2.5233												

RESULTS and DISCUSSION

QUANTITATIVE METHOD FOR K_2O, SO_3 Al_2O_3, Si_2O_3 and CaO

X-Calibur SDD was calibrated for K_2O and SO_3 using 23 standards; the Calibration data is listed in Table 3. Out of these standards, 3 standards were spared for analysis as unknowns (Table 5). Therefore second calibration was done with exclusion of these 3 standards from the quantitative method, ie: using 20 standards. The results for these standards could be used as validation of the method.
The same spectra acquired for standards 1-12 was also used to analyze Al2O3, Si2O3 and CaO (table 4). Again, 2 standards were speared for analysis as unknowns (Table 5).

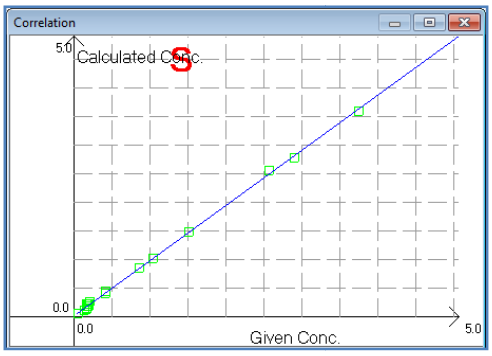
Table 3: Calibration results for K_2O, SO_3

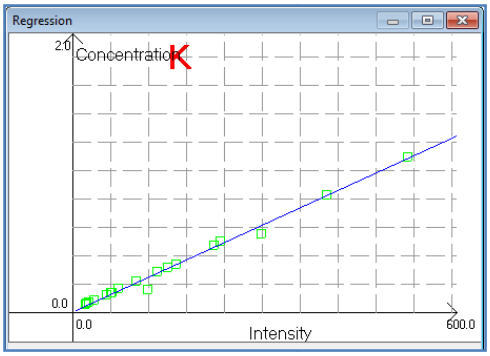
Sample ID	K_2O Standard deviation=0.0275 correlation =0. 9947			SO_3 pressed beads Standard deviation=0.039 correlation =0.9995		
	Given conc. w/w%	calc. conc. w/w%	Relative error	Given conc. w/w	Calc. conc. w/w	Relative error
Standard #1	0.1096	0.1060	0.0265	0.1329	0.1452	0.0775
Standard #2	0.0566	0.0479	0.1608	0.1537	0.1810	0.1653
Standard #3	0.0753	0.0655	0.1301	0.1721	0.2290	0.3196
Standard #4	0.0530	0.0419	0.2189	0.1475	0.1528	0.0231
Standard #6	0.1227	0.1195	0.0179	0.1276	0.0905	0.3056
Standard #7	0.1278	0.1243	0.0188	0.1315	0.1221	0.0859
Standard #8	0.0437	0.0377	0.1510	0.1562	0.1859	0.1780
Standard #9	0.0714	0.0642	0.1022	0.1304	0.1075	0.1902
Standard#10	0.5571	0.5868	0.1149	0.1592	0.1940	0.2067
Standard#11	0.2363	0.1443	0.3834	0.1541	0.1484	0.0500
Standard#12	0.1503	0.2385	0.6081	0.1460	0.1881	0.2884
Standard#13	0.2760	0.2704	0.0065	0.1023	0.0802	0.2346
Standard #15	1.1133	1.0874	0.0061	0.0207	0.0186	0.0730
Standard #17	0.3297	0.3312	0.0194	0.3820	0.3772	0.0175
Standard #18	0.8378	0.8360	0.0026	0.3783	0.4120	0.0841
Standard #19	0.2949	0.2997	0.0162	1.4730	1.4878	0.0109
Standard #20	0.5024	0.4830	0.0386	2.8590	2.8262	0.0120
Standard #21	0.1286	0.1260	0.0202	0.8220	0.8418	0.0219
Standard #22	0.2077	0.2060	0.0091	1.0020	1.0119	0.0082
Standard #25	0.4677	0.4650	0.0058	3.6877	3.6597	0.0079
Standard #26	0.3119	0.3100	0.0083	2.5330	2.5937	0.0234

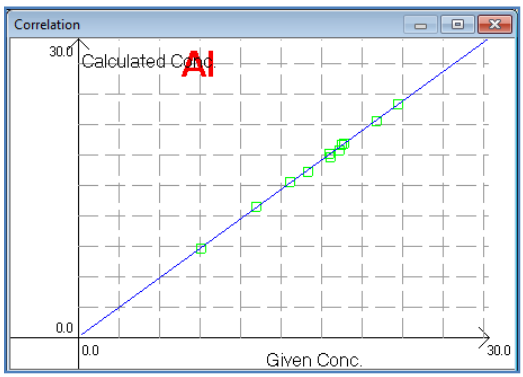
Table 4: Calibration results for Al_2O_3, Si_2O_3 and CaO

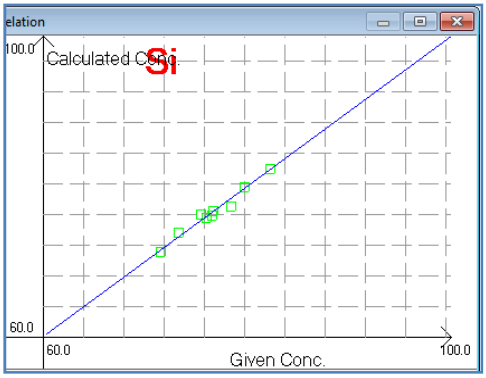
Sample ID	Al_2O_3 Standard deviation= 0.3028 correlation =0. 9948			SiO_3 Standard deviation=0.389 correlation =0.9994			CaO Standard deviation=0.0032 correlation =0.8971		
	Given conc. w/w%	calc. conc. w/w%	Relative error	Given conc. w/w	Calc. conc. w/w	Relative error	Given conc. w/w	calc. conc. w/w	Relative error
Standard #1	12.8780	13.0150	0.0106	82.1620	82.6469	0.0059	0.0030	0.0027	0.1000
Standard #2	15.3610	15.4919	0.0085	79.5740	79.5906	0.0002	0.0040	Not used	Not used
Standard #3	16.6650	16.5567	0.0065	78.2560	77.8169	0.0056	0.0150	0.0162	0.0800
Standard #4	18.3250	18.0241	0.0164	76.4800	76.0428	0.0057	0.0050	Not used	Not used
Standard #6	19.0020	18.7143	0.0151	75.8440	75.4356	0.0054	0.0110	0.0124	0.1273
Standard #7	19.3780	19.4184	0.0021	75.3410	75.3423	0.0000	0.0260	0.0234	0.1000
Standard #8	21.7190	21.7404	0.0010	73.0910	73.7179	0.0086	0.0120	0.0106	0.1166
Standard #9	23.3370	23.4382	0.0043	71.2770	71.2241	0.0007	0.0070	0.0098	0.4000
Standard#10	18.2580	18.4068	0.0081	76.4060	76.5340	0.0017	0.0220	0.0200	0.0909
Standard#11	19.1790	19.3120	0.0106	75.5340	Not used	Not used	0.0090	Not used	Not used
Standard#12	8.809	Not used	Not used	82.1620	Not used	Not used	0.0110	0.0089	0.1909

Figure 1: Calibration curves of K_2O, S_2O, Al_2O_3, SiO_2 and CaO in geological samples









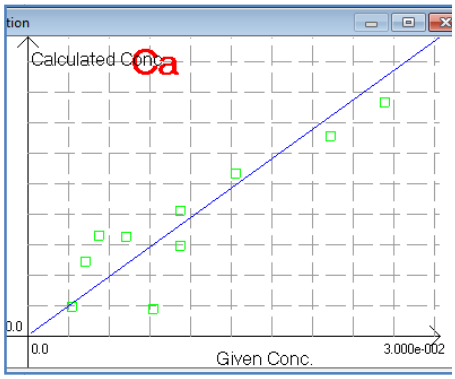


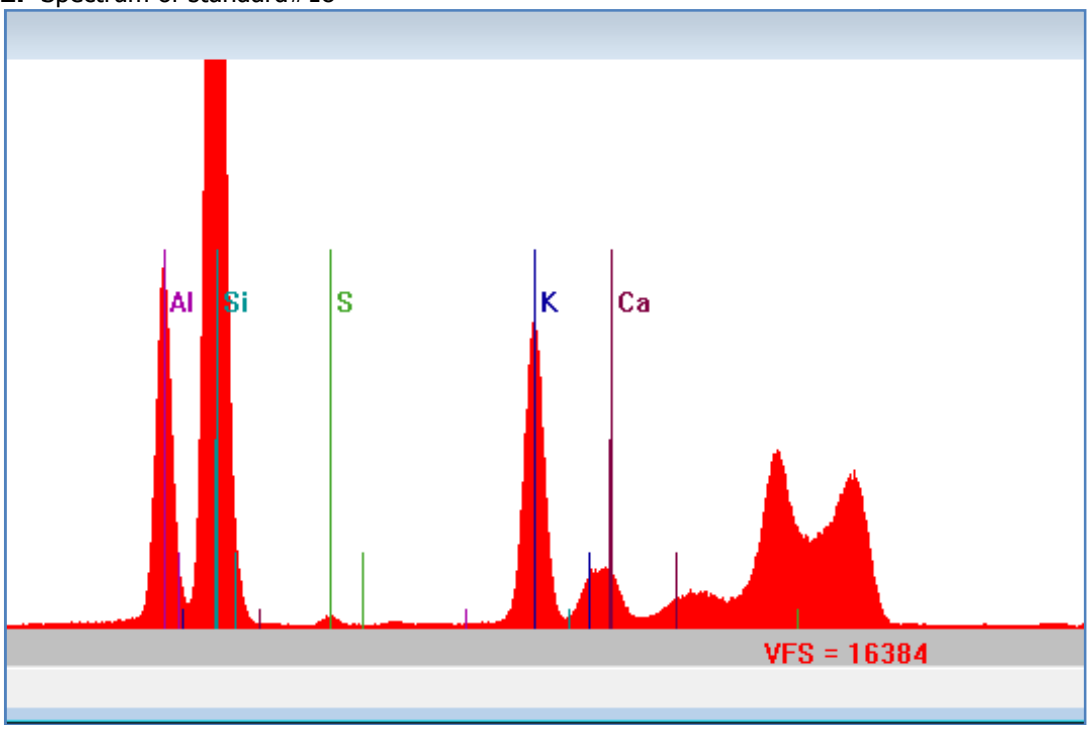
Table 5: Analysis of K_2O, S_2O, Al_2O_3, SiO_2 and CaO concentration in unknown samples

	S_2O			K_2O		
Spectrum ID	given	calculated	relative error	given	calculated	relative error
Standard #17	0.3820	0.3739	0.0212	0.3297	0.3312	0.0045
Standard #18	0.3783	0.4087	0.0803	0.8378	0.8214	0.0195
Standard #22	1.0020	1.0096	0.0075	0.2077	0.2033	0.0226

	Al_2O_3			SiO_2			CaO		
Spectrum ID	given	calculated	relative error	given	calculated	relative error	given	calculated	relative error
Standard #3	16.665	16.686	0.0013	78.256	77.094	0.0148	0.0151	0.0157	0.0397
Standard #10	18.258	17.926	0.0181	76.406	75.978	0.0055	0.0218	0.0192	0.1192

Standard#18 is a representative spectrum acquired with Ti filter specific for the analysis of K_2O, S_2O, Al2O3, SiO2 and CaO.

Figure 2: Spectrum of standard#18



QUANTITATIVE METHOD FOR TiO_2, Fe_2O_3, and P_2O_5.

Quantitative procedure for Ti, Fe and P was established with 10 of the 12 provided standards (table 6). The remaining standards were spared for analysis as unknowns (table 7).

Table 6: Calibration results for TiO_2, Fe_2O_3 and P_2O_5

Sample ID	TiO_2 Standard deviation= 0.0068 correlation =0. 9864			Fe_2O_3 Standard deviation=0.0096 correlation =0.9909			P_2O_5 Standard deviation=0.0098 correlation =0.8936		
	Given conc. w/w%	calc. conc. w/w%	Relative error	Given conc. w/w	Calc. conc. w/w	Relative error	Given conc. w/w	Calc. conc. w/w	Relative error
Standard #1	0.4866	0.479	0.0156	0.0778	0.0938	0.2057	0.0405	0.0443	0.0938
Standard #2	0.4029	0.3998	0.0077	0.0868	0.0926	0.0668	0.0755	0.0669	0.1139
Standard #3	0.4592	0.4672	0.0174	0.1648	0.1583	0.0394	0.0853	0.0855	0.0023
Standard #4	0.4166	0.4061	0.0252	0.0528	0.0481	0.0890	0.0789	0.0693	0.1217
Standard #6	0.4043	0.4128	0.0210	0.0291	0.0147	0.4948	0.0373	0.05	0.3405
Standard #7	0.4701	0.4725	0.0051	0.0449	0.0425	0.0535	0.0634	0.0693	0.0931
Standard #8	0.4171	0.4197	0.0062	0.0806	0.078	0.0323	0.0327	Not used	
Standard #9	0.5401	0.5357	0.0081	0.2373	0.2264	0.0459	0.0481	0.0796	0.6549
Standard#10	0.4556	0.4579	0.0050	0.0527	0.0595	0.1290	0.1072	0.0974	0.0914
Standard#11	0.4562	0.4561	0.0002	0.2134	0.2201	0.0314	0.0612	0.0771	0.2598
Standard#12	0.4561	0.4629	0.0149	0.0376	0.0517	0.3750	0.0427	0.0312	0.2693

Figure 3: Calibration curves for TiO_2, Fe_2O_3 and P_2O_5

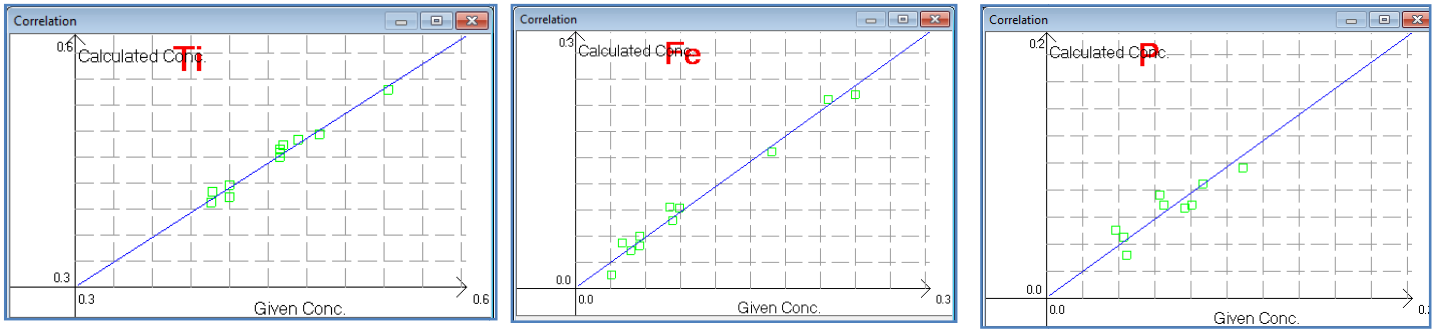
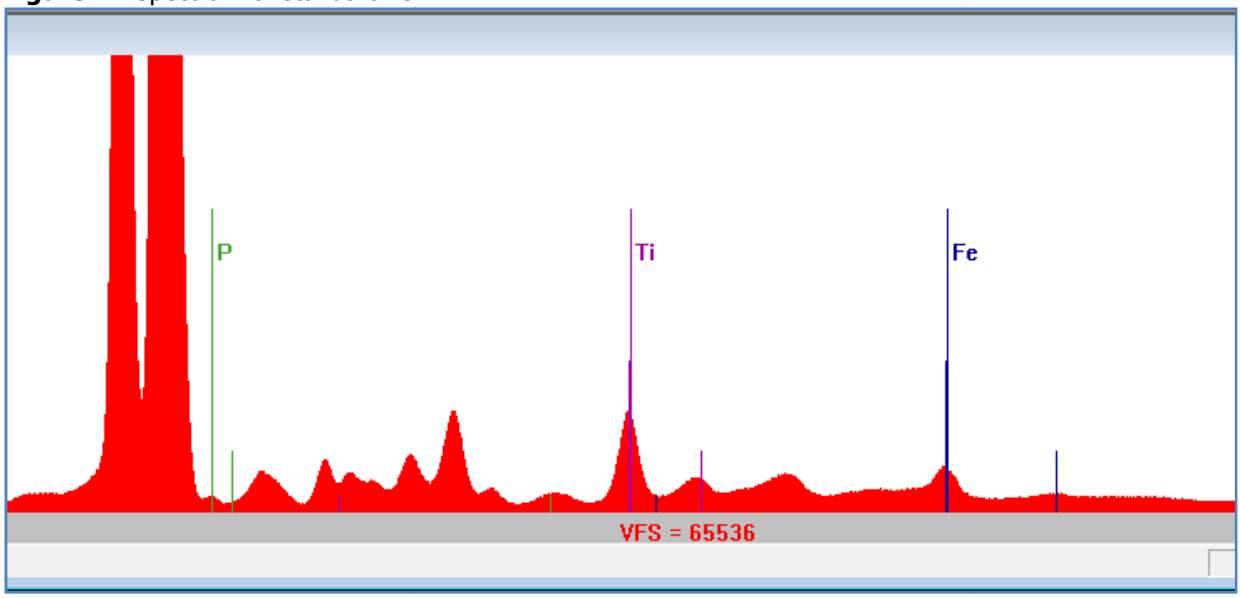


Table 7: Analysis of TiO_2, Fe_2O_3 and P_2O_5 concentration in unknown samples

Standard ID	TiO_2 given	TiO_2 calculated	TiO_2 error	Fe_2O_3 given	Fe_2O_3 calculated	Fe_2O_3 error	P_2O_5 given	P_2O_5 calculated	P_2O_5 relative error
Standard#7	0.4701	0.4725	0.0051	0.0449	0.0416	0.0734	0.0634	0.0693	0.0930
Standard#10	0.4556	0.4578	0.0048	0.0527	0.0587	0.1138	0.1072	0.0976	0.0896

Standard#3 is a representative spectrum acquired at 9KV without any filters suitable for the analysis of TiO_2, Fe_2O_3 and P_2O_5 (figure 4)

Figure 4: Spectrum of standard#3



QUANTITATIVE METHOD FOR Na_2O and MgO

Quantitative procedure for Na_2O was established with 11 of the 12 provided standards (table 8). The remaining standard were spared for analysis as unknowns (table 9). For MgO, only four standards could be used for calibration, since most standards had Mg at concentration below limit of quantitation, estimated as 45ppm. Yet, Mg peak could be detected in all standards except for standard#6: 1ppm mg. The calibration results and analysis of unknown samples are shown in table 8 and 9.

Table 8: Calibration results for Na_2O and MgO

Sample ID	Na_2O Standard deviation=0.0027 correlation =0.9719			MgO Standard deviation=0.0014 correlation =0.8186		
	Given conc. w/w %	Calc. conc. w/w %	Relative error	Given conc. w/w%	calc. conc. w/w%	Relative error
Standard #1	0.0710	0.0722	0.0170	Not detected	Not detected	Not detected
Standard #2	0.0760	0.0785	0.0330	Not detected	Not detected	Not detected
Standard #3	0.0830	0.0817	0.0161	Not detected	Not detected	Not detected
Standard #4	0.0860	0.0899	0.0438	Not detected	Not detected	Not detected
Standard #6	0.0890	0.0890	0.0000	Not detected	Not detected	Not detected
Standard #7	0.0950	0.0933	0.0174	Not detected	Not detected	Not detected
Standard #8	0.0950	0.0986	0.0377	Not detected	Not detected	Not detected
Standard #9	0.1050	0.1038	0.0116	0.0085	0.0092	0.0823
Standard#10	0.0920	0.0873	0.0510	0.0033	0.0057	0.7272
Standard#11	0.0940	0.0906	0.0361	0.0064	0.0052	0.1875
Standard#12	0.0580	0.0579	0.0018	0.0027	0.0033	0.2222

Figure 5: Calibration curves for NaO_2 and MgO

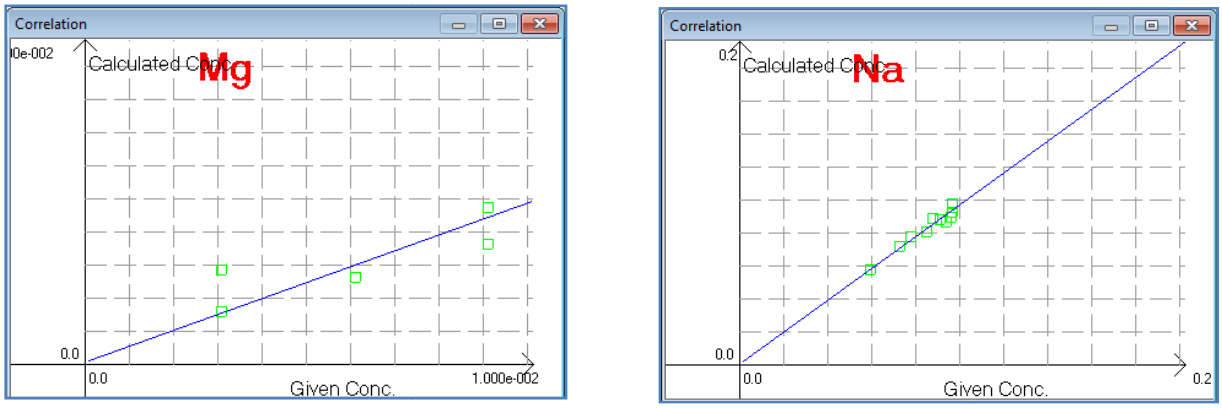


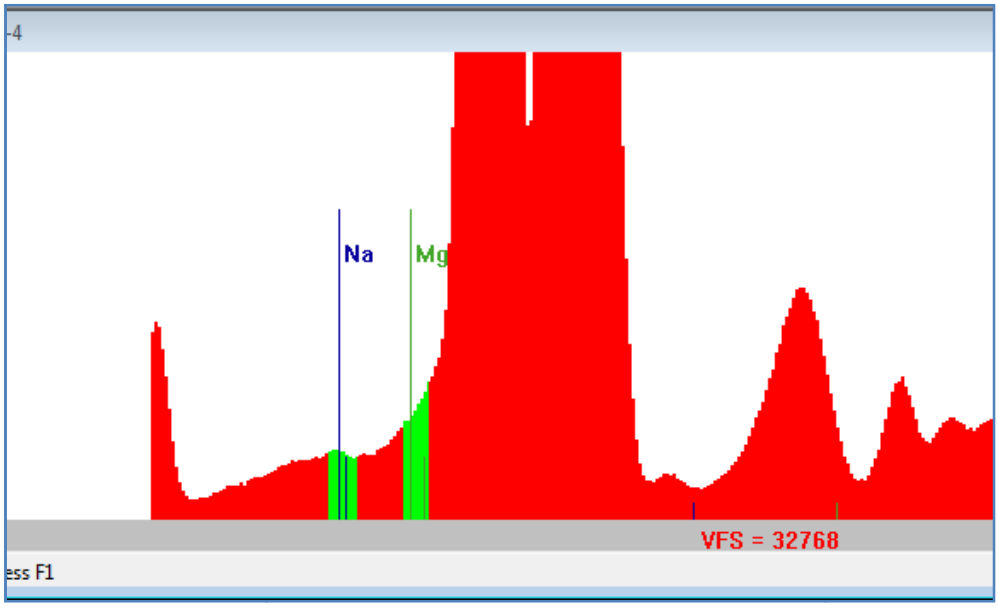
Table 9: Analysis of Na_2O and MgO

Element:	Na_2O			MgO		
Standard ID	given	calculated	Relative error	given	calculated	Relative error
STD9	0.1047	0.0994	0.0506	0.0085	0.0092	0.0823

It is advised to improve the quantitative method for Mg by addition of more standards.

Standard#9 is a representative spectrum acquired at low excitation energies suitable for the analysis of Na_2O and MgO.

Figure 6: Spectrum of standard#9



REPEATABILITY:
Static precision of K_2O and SO_3 in geological samples

Repeatability studies were performed to show the robustness of X-Calibur SDD. The analysis was performed for K_2O and SO_3 with 10 consecutive measurements of standard #19 without moving the sample between the acquisitions. The measured mean value with standard deviation and relative standard deviation were calculated for K_2O and SO_3 (Table 10).

Table 10: Repeatability results K_2O and SO_3 in geological samples

Standard ID	Element	Given value	Calculated mean value	Standard deviation	Relative standard deviation (%)
Standard #19	K_2O	0.295	0.293	0.004	1.35%
Standard #19	SO_3	1.473	1.500	0.028	1.84%

Based on the repeatability results, The X-Calibur analyzer with SDD detector is robust and provides reproducible results.

CONCLUSIONS

This report shows the excellent capability of Xenemetrix made X-Calibur-SDD with specialized window for low elements to analyze quantitatively Na, Mg, Al, Si, P, S, K, Ca, Ti and Fe in geological samples.
Although Mg was detected in all standards, most were below the limit of quantitation. More standards should be added to improve the quantitative method for Mg.
Repeatability studies proved that X-Calibur SDD is robust, precise and provides reproducible results.
In summary, the X-Calibur EDXRF analyzer provides the necessary tools to successfully perform reliable qualitative and quantitative analysis of all elements in geological samples.