The XRF facility

The XRF facility at CESS consists of a Bruker (formerly Siemens) model S4 Pioneer sequential wavelength-dispersive x-ray spectrometer and sample preparation units. XRF is equipped with a goniometer (which holds seven analyzing crystals: OVO-55, PET, LiF 200, LiF 220, Ge, ADP and InSb), 60 sample automatic loading system, 4 kW Rh X-ray tube, 0.23 and 0.46 collimators and latest (July 2006) SPECTRA^{plus} software for qualitative and quantitative determination of elements. The detector consists of an argon/methane flow proportional counter and a scintillation counter.

A view of CESS XRF Lab

Analysis of Geological Samples:

Hydraulic Press

Analysis are performed on pressed pellets for trace elements and fusion glass disks for major elements.

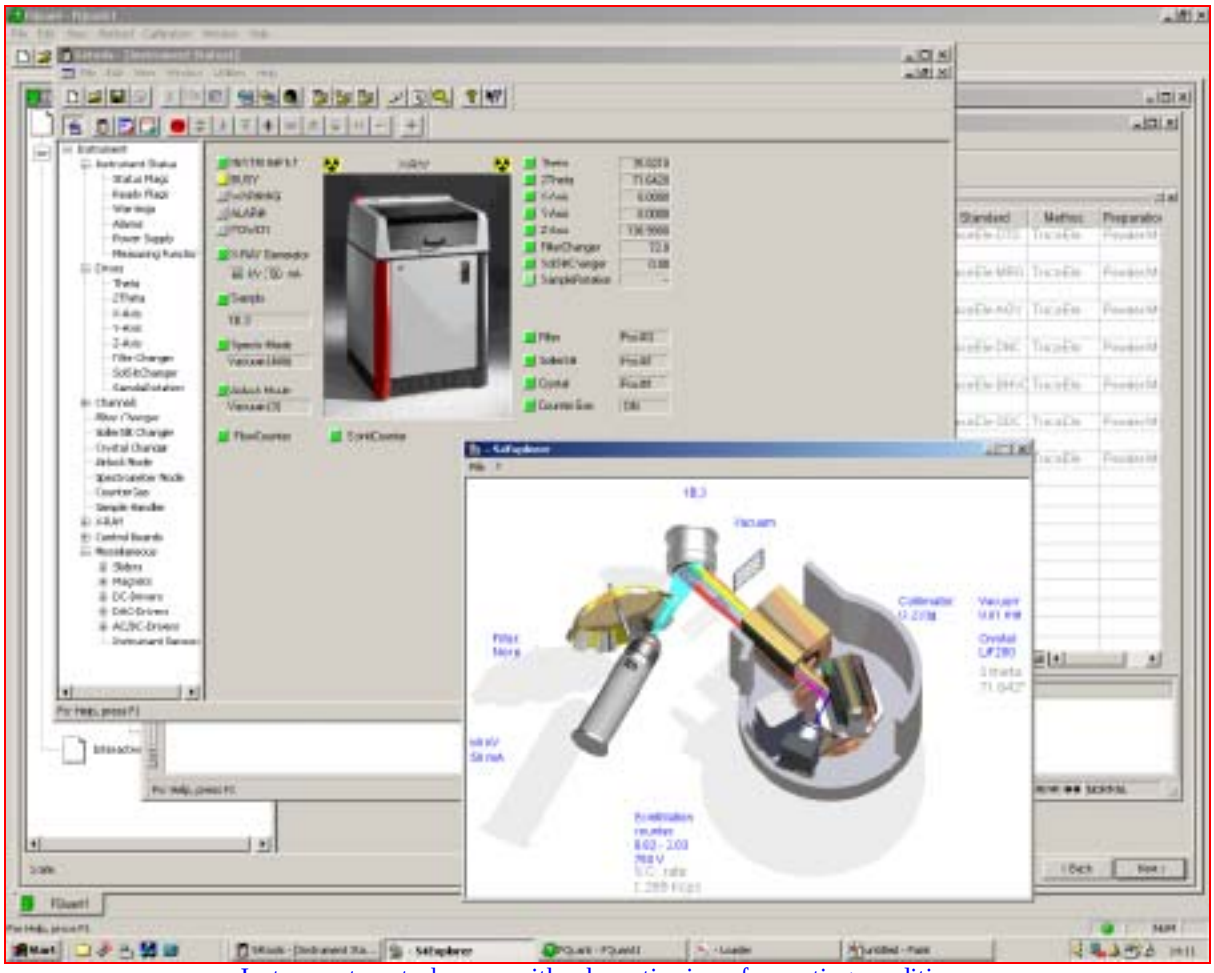
Pressed pellets are prepared using 40 mm aluminium cups filled with Boric acid crystals as binder. Finely powdered sample (-300 mesh) is sprinkled over boric acid and pressed in a 40 ton hydraulic press to produce a circular 40 mm disk.

The pressed powder pellets allows trace element determinations, with limits of detection up to 1 ppm for selected elements. The elements determined presently in our lab are K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Ba, Ce, Pb, Th. Light elements like Si, Al, Mg and Na are less precise by this method. All major and trace elements are determined on sample pellets for which fused glass disk can not be made (for e.g. river and marine sediments, soils etc.).

Fused glass Disk is prepared on a Claisse Fluxy instrument in the sample preparation lab of CESS. One gram of finely powdered sample is mixed with 5 gram of flux (LiT/LiM/LiBR 49.75/49.75/0.50, Pure) and fused in a platinum crucible. The fluxer is microprocessor controlled and uses LPG and in controlled manner raises the temperature up to 1000 C. It has built in programmes for different sample types. Rotating and stirring of crucible for uniform mixing and pouring the fused liquid on to a platinum mold to produce 30 mm glass disk is done automatically. It is also possible to create need based programmes with different gas flow, crucible tilt, mixing speed and length of each step

Claisse Fluxy

Fused disks are excellent for analysing major elements as it reduces matrix effects; eliminates particle size effects; and provides a homogeneous specimen. A very accurate and precise analysis of light major elements in geological materials are obtained by this method (CESS XRF results for USGS standards are tabulated in the following page). Samples which contain higher than normal concentrations of elements like lead, tin, arsenic and/or antimony (as they can seriously damage the platinum ware) and samples which contain organic matter are not suitable for this method of sample preparation. Elements determined by this method are Na, Mg, Al, Si, P, K, Ca, Ti, Mn, and Fe.Due to large dilution of original sample during bead preparation by this method trace elements are not determined.



Instrument control screen with schematic view of operating conditions

Calibration

Instrument is loaded with software containing theoretical elemental line library. By this software qualitative (identification of major and minor elements) and semi-quantitative analysis of elements (>0.5%) by standardless method for unknown sample is possible. Standardless method has elemental lines calibrated and calibration coefficients stored in the line library. However, for precise and accurate quantitative determination, instrument has to be calibrated taking into consideration our specific needs, sample types and instrument configuration.

Calibration involves identification of optimum conditions of several variable factors for each element, like identifying correct elemental peak and back ground(s), power settings (kV and mA) for excitation of the line spectrum, crystal selection, detector type (scintillation or flow proportional), pulse height, collimator mask, counting time, dead time etc., followed by matrix and inter-element interference corrections. This is achieved by repeated analysis of standard samples with known certified values and correcting the variables to yield elemental concentration close to the certified reference values for standards.

Methods & Results

In preparing measurement programmes CESS XRF uses reliable calibration standards which are representative of the matrix and target element concentration ranges to be analyzed. Measuring arrangement follows empirical method based on the analysis of standards with known elemental compositions. Sample preparation method is same for a given measurement method. When standards are few (for eg. zircon, ilmenite, rutile, clays etc.) alternative standardless techniques is adopted using typical composition of the sample. The standardless calibration model is verified and optimized against single standard sample. Following is the list of International reference standards currently used in our lab.

International Rock standards Currently used for Calibration

Basic rock Composition

BCR2[*], BIR1[*], DNC1[*], BE-N, W2a[*], AGV2[*], BHVO2[*], ANG[#], BR[*], DR-N[#], PM-S[#], WS-E[#], JA-1A[+], JA-2[+], JA-3[+], JB-1B[+], JB-2[+], JB-3[+], JGB-1, JGB-2

Granitic composition

G2[*], GSP2[*], STM1[*], SARM1[@], SARM2[@], SY3[@], RGM[*], GA[#], GH[#], GS-N[#], AC-E[#], MDOG[#], ISHG[#], VS-N[#], JG-1[+], JG-2[+], JG-3[+], JR-3[+], JSY-1[+]

Sediments

SCO1[*], SDC1[*], SO1[@], MAG1[*], SGR1[*], BX-N[#], MESS3, PACS2, HISS1, JD-1[+], JLK-1[+], JSD-1[+], JSD-2[+], JSD3[+], JMS-1[+], JMS-2[+]

Laterites

VL1[’], VL2[’], SO1[@], BX-N[#], SLB’, JSO-1[+]

Mineral Analysis

Minerals (ilmenite, rutile, zircon etc) are analysed by standardless method, which is verified and tested against certified mineral standards like SARM 59 (Ilmenite), SARM 61(rutile) and SARM 62 (zircon). Results are well within the confidence limits for all major elements by this method.

Standard samples Sources: [*]USGS, USA; [#]CNRS, France; [@]NRCAN, Canada; [’]Venezuela; [+]Geological survey of Japan

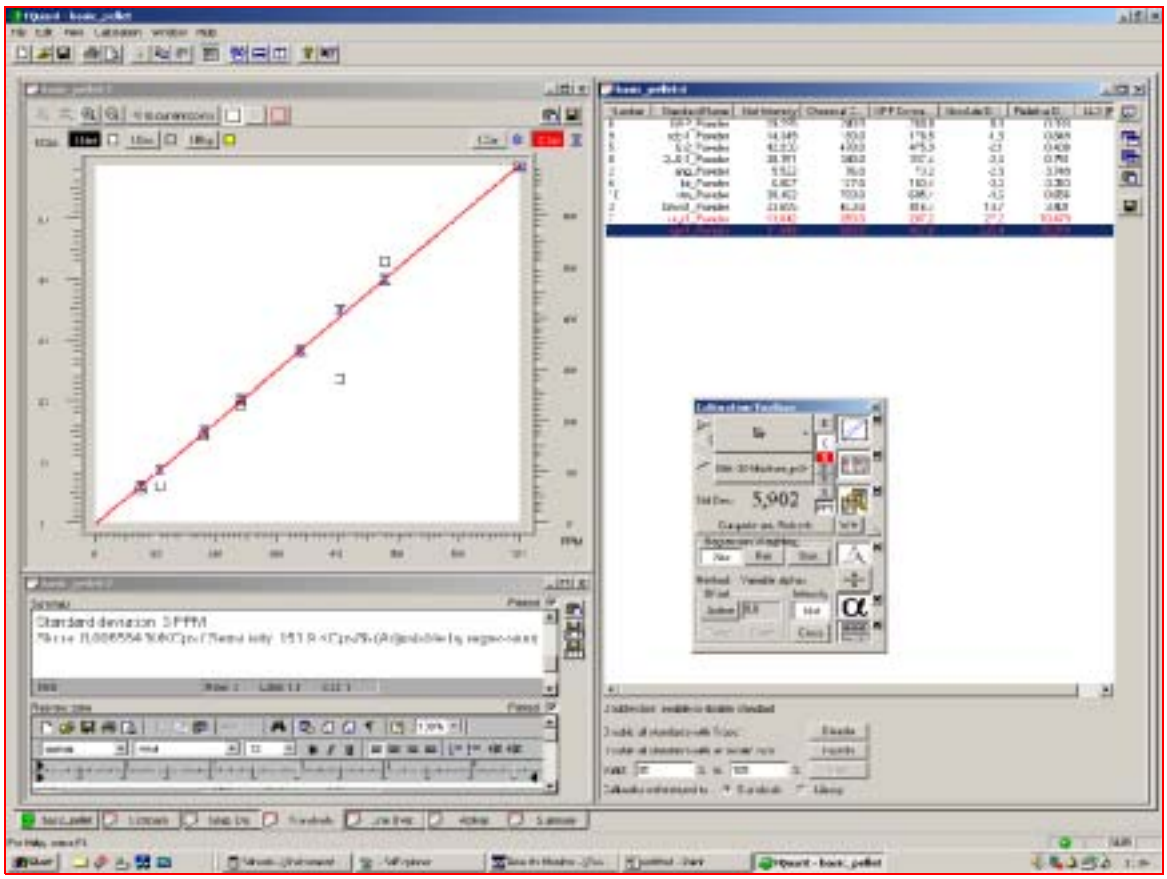
Accuracy and Reliability

Accuracy and reliability of results on unknown depend on good calibration (measuring arrangement). We have achieved good agreement with standard reference materials. With each sample batch a reference standard is included as a check on reproducibility. These data are provided with analytical results to the user. At present we can analyse complete major and trace element analysis of silicates, oxide rocks and sediments (Si, Al, Mg, Na, K, Ca, Ti, P, Sc, V, Cr, Mn, Fe, Ni, Cu, Co, Zn, Ga, Rb, Sr, Y, Zr, Nb, Ba, Ce, La, Nd, Sm, Pb, Th). Major element results on our XRF for International standards are compared with recommended values in the following table.

Results on Powder Pellets*						Results on Fused Glass Disks						
	USGS		CESS XRF			USGS		CESS XRF			CNRS	CESS
Sample	STM		STM	STM	STM	G2		G2	G2	G2	GA	GA
Analysis Date	Recommended Values	–	16/11/07 09:49	01/11/07 14:15	17/09/07 13:46	Recommended Values	–	06/11/07 15:56	07/11/07 09:46	07/11/07 09:54	Recommended Values	–	06/11/07 11:14
SiO2	59.6	0.49	58.68	58.79	58.33	69.14	0.3	68.93	68.82	68.78	69.9	0.14	69.09
TiO2	0.14	0.23	0.14	0.14	0.11	0.48	0.03	0.49	0.49	0.49	0.38	0.01	0.36
Al2O3	18.4	0.02	18.35	18.35	18.36	15.39	0.3	15.41	15.4	15.42	14.5	0.09	14.73
MnO	T		0.26	0.27	0.27	0.03	0.01	0.03	0.02	0.02	0.09	0	0.09
Fe2O3	5.22	0.1	5.68	5.72	5.73	2.66	0.17	2.78	2.77	2.77	2.83	0.06	2.49
CaO	1.09	0.06	1.12	1.12	1.1	1.96	0.08	1.94	1.93	1.93	2.45	0.03	2.43
MgO	0.1	0.02	0.19	0.19	0.04	0.75	0.03	0.76	0.76	0.76	0.95	0.04	0.92
Na2O	8.94	0.2	8.91	8.94	8.87	4.08	0.13	4.18	4.17	4.17	3.55	0.03	3.53
K2O	4.28	0.07	4.16	4.16	4.19	4.48	0.13	4.53	4.52	4.52	4.03	0.03	4.04
P2O5	0.16		0.15	0.15	0.13	0.14	0.01	0.13	0.14	0.14	0.12	0.01	0.12
Total	97.93		97.65	97.83	97.13	99.11		99.16	99.01	99.00	98.80		97.80

**Note analysis were carried out on different dates & time, and good correlations for lighter elements like Si, Al , Na on Powder pellets. Standards STM & G2 are from US Geological Survey, USA; GA from CNRS: France*

We have recently added 21 reference standards from the Geological Survey of Japan, extending numbers of standards used to 64, to improve the accuracy and cover wide concentration range of elements in different types of geological samples.



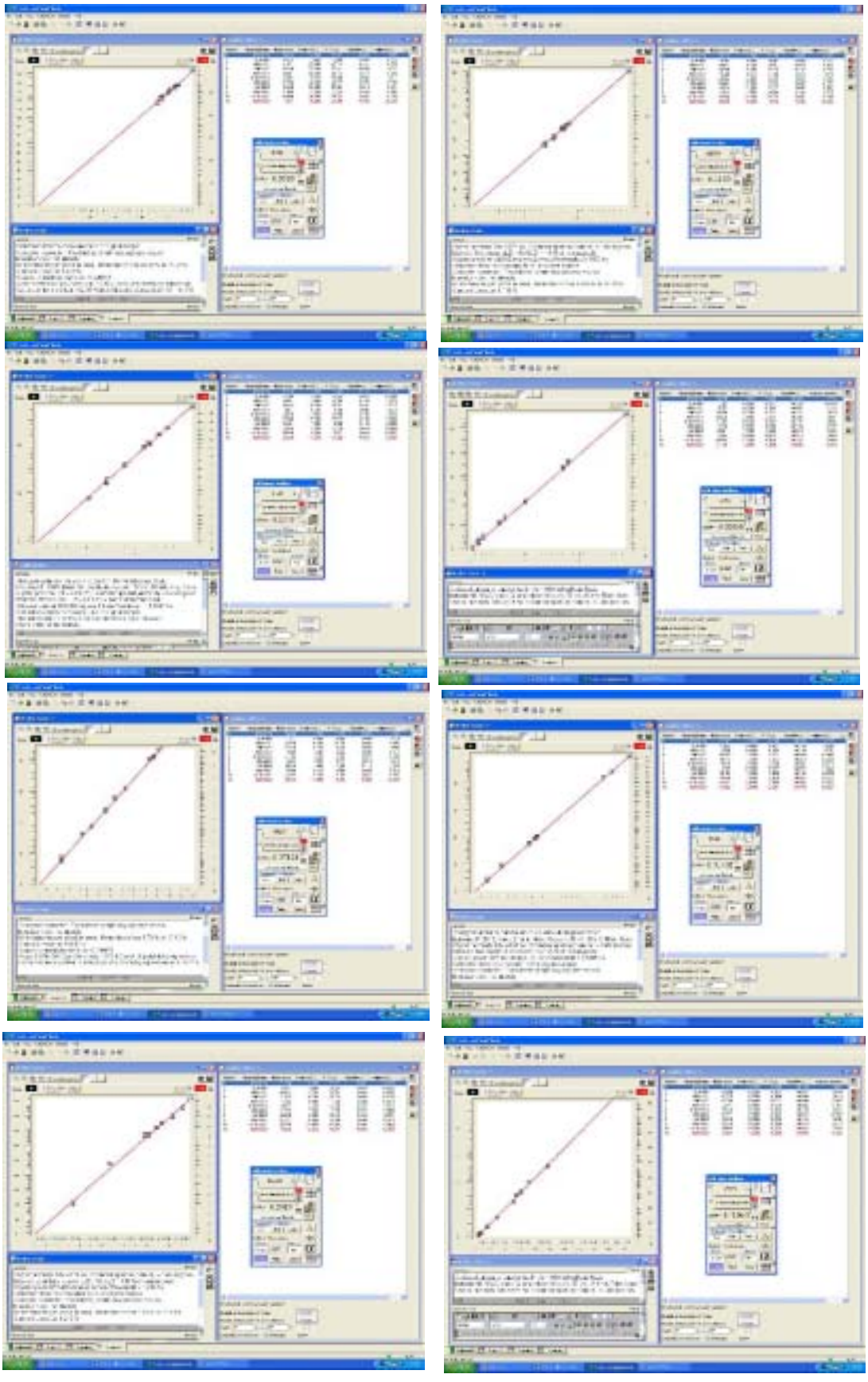
Our lab is presently extending free analytical support to all academic Institutes and universities in the state. Due to diverse fields of research at CESS and other research organisation, XRF lab receives requests to analyse widest possible range of geological materials for a very wide range of compositions, presenting special problems. We are continuously enlarging our International standards in the calibration to cover a wide range of sample types and compositions. We have put in considerable amount of time in successfully analysing unusual sample types and unusual compositions in soils, river and beach sediments, clay, ilmenite, waste composite etc.

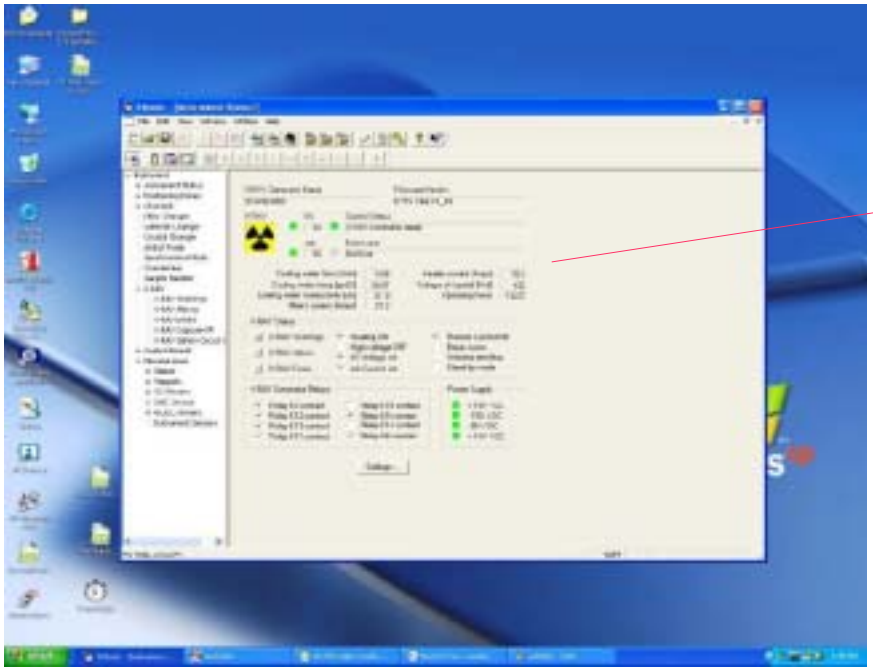
Recently we have calibrated a programme for measurement of major and trace element concentrations in Soil samples. Following is the result for Certified reference material SO-1 by this calibration. Please note that results for lighter elements (<Si) on pellets pose problems due to mineralogical and particle size effect.

Sample	Date	SiO2	Al2O3	TiO2	MnO	Fe2O3	CaO	MgO	Na2O	K2O	P2O5	V	Cr	Co	Ni	Cu	Zn	Rb	Sr	Zr	Nb	Ba	La	Ce	Pb
SO1	Recommended values	54.90	17.50	0.88	0.11	8.58	2.46	3.83	2.40	3.18	0.15	133	170	29	92	61	144	141	331	84	12	870	54	102	20
SO-1	28/11/07 17:02	55.10	16.47	0.82	0.11	8.05	2.18	3.69	2.30	3.10	0.14	134	143	28	91	62	141	109	322	82	9	840	49	131	18
SO-1	29/11/07 11:59	54.67	16.40	0.82	0.11	8.00	2.18	3.69	2.29	3.09	0.14	133	141	29	91	61	139	104	307	82	8	835	49	108	24
SO-1	26/11/07 15:16	55.19	16.47	0.82	0.11	8.08	2.18	3.69	2.30	3.10	0.14	133	145	29	90	61	142	105	328	81	8	852	48	106	18

Calibration curves for major elements based on 11 International standards of basic compositions are given below. Theses figures illustrate concentration vs intensity, which is, recommended versus obtained values.

Excellent correlation of Chemical vs XRF concentration, good linear calibration lines, lower standard deviation supports reliability of analysis and method of sample preparations! (Results for BE-N is bad for all elements due to bad sample storage and hence omitted from calibration).





- *XRF has logged more than 13,000 hours, including standby time till date (Nov 28, 2007)*

- *Till date (28th November 2007) CESS XRF has analysed over 2300 samples, including those of standards analysed for calibrations.*