DEVELOPMENT OF A FUSED GLASS DISC XRF FACILITY AND COMPARISON WITH THE PRESSED POWDER PELLET TECHNIQUE AT INSTITUTO DE GEOCIÊNCIAS, SAO PAULO UNIVERSITY

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RESUMO DESENVOLVIMENTO DE MÉTODO DE FRX POR DISCO DE VIDRO POR FUSÃO E COMPARAÇÃO COM A TÉCNICA DE PASTILHA DE PÓ PRENSADO NO INSTITUTO DE GEOCIÊNCIAS, UNIVERSIDADE DE SÃO PAULO A técnica de pastilha de pó prensado (PPP) atualmente em uso no Laboratório de Fluorescência de Raios-X do Instituto de Geociências da Universidade de São Paulo (IG-USP) está sendo ampliada para incluir elementos adicionais e complementada por uma calibração para elementos maiores e traços usando pastilhas fundidas (FGD). Um total de 38 elementos maiores e traços são acessíveis (F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Co, Fe, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Mo, Sn, Sb, Ba, Pb, Bi, La, Ce, Nd, Th e U) com limites de detecção variáveis, geralmente abaixo de 10 ppm para elementos traço. A perda ao fogo é determinada por diferença de peso, permitindo o cálculo dos totais e consequentemente um excelente controle de qualidade dos dados. Uma análise completa, incluindo contagem de *background*, correção de matriz e todas as correções importantes pode ser obtida automaticamente em menos de 60 minutos. *A priori* qualquer matriz de amostra pode ser ajustada. Os dados confirmam que as técnicas de pastilha prensada e fundida são complementares e juntas fornecem em definitivo uma análise precisa. Entretanto, quando o objetivo é a análise simultânea de um grande número de elementos, ambas técnicas demandam considerável atenção aos detalhes, pois na técnica de fusão há uma tendência de perda de voláteis como F e S e o limite de detecção é maior. Na técnica de pó prensado é necessária uma excelente micronização e cuidados com os elementos leves como Al e Si principalmente. O artigo inclui, para todos os elementos de matriz corrigidos, um novo conjunto de coeficientes Alfa empíricos, não publicados anteriormente, baseados no sistema de metaborato de lítio e contrastam com os coeficientes teóricos fornecidos para os elementos considerados pela Philips.

Palavras-chaves: FRX, multi-elementos, pastilhas de pó prensado, discos de vidro fundido, alfas experimentais

ABSTRACT An X-ray fluorescence pressed powder pellet technique (PPP) currently in use at the X-Ray facility of the Institute de Geociências, Sao Paulo University (IG-USP) has been extended to include additional elements and complemented by a full major and trace element calibration by fused glass disc (FGD) X-ray fluorescence. A total of 38 major and trace elements are available (F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Mo, Sn, Sb, Ba, Pb, Bi, La, Ce, Nd, Th and U) with variable detection limits, but generally below 10 ppm for trace elements. Loss-on-ignitions determined by weight difference and totals provide extremely good control on data quality. A full analysis, including background, matrix correction and all relevant corrections can be achieved automatically in less than 60 minutes. Virtually any sample matrix can be accommodated. The data support the view that the fused disc and powder pellet techniques are complementary and together provide a definitive, rigorous XRF analysis. However, both techniques require considerable attention to details, with the glass disc technique prone to losses of F and S and increase detection limits for certain elements. The powder pellet technique requires fine micronising and caution when dealing with the light elements Si and Al. Additionally, the paper presents a new, previously unpublished experimentally determined Alpha coefficients for all matrix-corrected elements, which are based on the lithium metaborate system and contrast with the Philips theoretical alpha coefficients.

Keywords: XRF, multi-element, pressed powder pellet, fused glass disc, experimental alphas.

INTRODUCTION X-ray fluorescence spectrometry is one of the most widely used instrumental routine of elemental analysis of rocks, cements, metallurgical samples, paint samples, and virtually any substance that can be adequately presented to the X-ray beam. The technique is capable of extremely good precision in a wide range of sample matrices and has a dynamic range from a few ppm up to 100%.

The X-Ray facility at IG-USP houses full sample preparation facilities, including jaw crushing, hydraulic press, agate and tungsten carbide TEMA mills, a vibratory rod mill or microniser, and a modern (1996) wavelength dispersive Philips PW2400 XRF spectrometer. X-rays are generated using a Rh-anode X-ray tube, diffracted using a choice of 8 analyzing crystals (LiF200, UF220, LiF420, PET, Ge (III), PX1, PX2 and PX3), and detected by an argon-methane (P10) flow counter detector, a NaI scintillation detector, a Xe-sealed detector, or a combination of these. Collimators of sizes 150µm, 550µm and 4000µm are available. The equipment is capable of measuring elements above atomic number 8 with detection limits generally of the order of 1-10 ppm for trace elements. Multiple samples can be run overnight, and up to 102 samples can be analyzed in a single run.

Two methods of sample preparation dominate in XRF analysis, i.e., the pressed powder pellet (PPP) and the fused glass disc (FGD), each having specific advantages over the other. The sample preparation technique used at the IG-USP consists of pressed powder pellets with a wax binding agent. Inherent in any PPP technique are limitations imposed by mineralogical effects, which are pronounced for the lighter elements. As fluorescent X-rays are significantly attenuated within a sample there is a critical depth beyond which the X-ray can no longer penetrate to be detected by the spectrometer (the critical penetration depth). This depth varies amongst the elements and depend on the X-ray photon energy and the sample composition. Mineralogical effects become more intense as the critical penetration depth decreases (i.e. for light elements where specimen heterogeneity is of the same order as the X-ray penetration depth, Potts 1987). For this reason, elements such as F, Na, Mg, Al and Si are expected to have poor precision and accuracy in PPP relative to FGD.

X-ray fluorescence analysis is a comparative technique and all matrix correction methods assume that the absorbed X-rays pass through a region of the sample that represents its average composition. Therefore, heterogeneous samples such as rocks must be finely ground prior to analysis. It is generally considered that it is not possible to grind beyond a grain size to avoid the particle size effects in PPP (Potts 1987). For PPP, calculated attenuation coefficients may not be appropriate for light elements because if attenuation occurs in discrete mineral phases then the results are not representative of the bulk composition of the sample. This is because, regardless of the grain size of the powder, minerals such as micas, may align preferably parallel to the pellet surface during compression. While devices such as the vibrating rod mill (McCrone microniser), designed to grind samples to ultrafine levels (<5 micron), may minimize these problems, it is important to establish the limitations of both techniques. Due particularly to these effects that the fused glass disc technique was developed using lithium metaborate or tetraborate fluxes to produce amorphous discs (Potts 1987, and references therein). Enzweiler and Webb (1996) compared the accuracy and precision of 1:5 glass discs with the pressed powder pellets using only the Compton corrections for 7 trace elements. They conclude that precision based on repeating the analysis of reference materials, and detection limits were both superior in pressed powder pellets while accuracy was higher in the fused glass discs. In the current study, both major and trace elements were analyzed (38 elements) and a broader approach was taken. Precision was based on the average standard deviation for all standards over their entire range and therefore assesses both general reproducibility over the dynamic range but also the relative stability of the two techniques.

The current work was conducted (i) to establish a fully calibrated fused glass disc (FGD) technique in order to substantially reduce mineralogical effects and to ensure sample homogeneity, incorporating loss-on-ignition (LOI) to calculate complete oxide and trace element 'totals' and to provide a high level of quality control on data; (ii) to extend the range of analyzed elements to 38 major and trace elements; (iii) to evaluate the mineralogical effects via PPP for light

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Table 1 - Instrumental conditions and overlap corrections used in PPP and FGD analytical techniques.

Element	Line	X-tal	Collimator	Detector	kV	mA	PPP Angle (°2T)	FGD Angle (°2T)	PPP Offset °2T	PPP Offset °2T	FGD Offset °2T	FGD Offset °2T	PPP PHD1 LL	PPP PHD1 UL	FGD PHD1 LL	FGD PHD1 UL	Counting time (s)	Line Overlaps	Correction Method
Al	KA	PE 002	550 µm	Flow	22	50	145,059	145,084					25	75	25	75	30	Br La1,2	Alpha
As	KB	LiF 200	150 µm	Scint.	60	50	30,405	30,397	-0,555	0,725	0,670	-0,637	29	72	29	72	120		Compton
Ba	LA	LiF 200	150 µm	Flow	40	50	87,177	87,156	0,873		0,887		39	63	39	63	60	Ti Ka	Alpha
Bi	LA	LiF 200	150 µm	Scint.	60	50	32,949	32,941	-0,639		-0,576		25	71	25	71	60		Compton
Ca	KA	LiF 200	550 µm	Flow	22	50	113,113	113,127					32	66	38	66	30		Alpha
Ce	LB1	LiF 200	150 µm	Flow	40	50	71,629	71,604	0,752		0,683		41	62	41	62	60		Alpha
Cl	KA	PE 002	550 µm	Flow	22	50	65,516	65,558			0,979		38	68	38	68	60		Alpha
Co	KA	LiF 200	150 µm	Flow	40	50	52,779	52,783	0,806		0,847		38	64	38	64	60	Fe Kb1,3	Alpha
Cr	KA	LiF 200	550 µm	Flow	40	50	69,357	69,342	-1,010	0,969	0,925		37	62	37	62	60	V Kb1,3, Ce Lb3	Alpha
Cu	KA	LiF 200	150 µm	Scint.	40	50	44,968	44,971	0,894		0,770		22	73	22	73	60	Ni Ka	Alpha
F	KA	PX1	550 µm	Flow	22	50	44,410	44,428			1,725		30	82	30	82	120	P Ka1,2, Co L1	Alpha
Fe	KA	LiF 200	550 µm	Flow	22	50	57,501	57,502					37	62	37	62	30		Alpha
Ga	KA	LiF 200	150 µm	Scint.	60	50	38,868	38,871	0,836		0,707		24	73	24	73	60		Alpha
K	KA	LiF 200	550 µm	Flow	22	50	136,709	136,711					31	67	31	67	30		Alpha
La	LA	LiF 200	150 µm	Flow	40	50	82,908	82,882	-0,681		-0,681		40	62	40	62	60		Alpha
Mg	KA	PX1	550 µm	Flow	22	50	23,422	23,418					34	77	34	77	60		Alpha
Mn	KA	LiF 200	550 µm	Flow	40	50	62,947	62,962					37	62	37	62	30		Alpha
Mo	KA	LiF 200	150 µm	Scint.	60	50	20,243	20,240			0,530		27	73	27	73	60	Zr Kb1, ULb3	Compton
Na	KA	PX1	550 µm	Flow	22	50	28,355	28,349					34	80	34	80	60		Alpha
Nb	KA	LiF 200	150 µm	Scint.	60	50	21,282	21,305			0,633		29	68	29	68	60	Y Kb1,3, U Lb2	Compton
Nd	LA	LiF 200	150 µm	Flow	40	50	72,092	72,099	0,788		0,536		39	63	39	63	60	Ce Lb1	Alpha
Ni	KA	LiF 200	150 µm	Scint.	40	50	48,614	48,624	-0,820		-0,791		22	74	22	74	60	Co Kb1,3	Alpha
P	KA	PE 002	150 µm	Flow	22	50	89,620	89,582					34	71	34	71	60		Alpha
Pb	LB1	LiF 200	150 µm	Scint.	60	50	28,182	28,182	0,520		0,572		25	72	25	72	60		Compton
Rb	KA	LiF 200	150 µm	Scint.	60	50	26,545	26,614	-0,663		-0,648		26	71	26	71	60	U La, Br Kb1,3	Compton
Rh	KA-C	LiF 200	150 µm	Scint.	40	50	18,257	18,260					29	68	29	68	20		Alpha
S	KA	PE 002	550 µm	Flow	22	50	75,882	75,840					36	69	36	69	60		Alpha
Sb	LA	LiF 200	150 µm	Flow	22	50	117,338	117,357			-0,563		36	65	36	65	120	K Kb1,3	Alpha
Sc	KA	LiF 200	150 µm	Flow	40	50	97,696	97,700	0,919		-0,656		37	65	37	65	60		Alpha
Si	KA	PE 002	550 µm	Flow	22	50	109,235	109,236					29	71	29	71	30		Alpha
Sn	LA	LiF 200	150 µm	Flow	40	50	126,764	126,760	-0,674		0,925	-0,633	37	65	37	65	60		Alpha
Sr	KA	LiF 200	150 µm	Scint.	60	50	25,070	25,073	0,847		0,637		26	69	26	69	60		Compton
Th	LA	LiF 200	150 µm	Scint.	60	50	27,402	27,401	-0,389		0,578		26	71	26	71	60		Compton
Ti	KA	LiF 200	550 µm	Flow	40	50	86,152	86,155					32	66	32	66	30		Alpha
U	LA	LiF 200	150 µm	Scint.	60	50	26,069	26,073	-0,484		-0,470		27	70	27	70	60	Rb Ka1	Compton
V	KA	LiF 220	150 µm	Flow	40	60	123,107	123,240	-0,785		-0,792		15	78	37	72	60	Ti Kb1,3	Alpha
Y	KA	LiF 200	150 µm	Scint.	60	50	23,714	23,711	0,781		0,768		26	71	26	71	60	Rb Kb 1,2,3	Compton
Zn	KA	LiF 200	150 µm	Scint.	40	50	41,745	41,747	0,827		0,721		22	74	22	74	60	Cu Kb1,3	Alpha
Zr	KA	LiF 200	150 µm	Scint.	60	50	22,458	22,463	-0,579		0,715		26	70	26	70	28	Sr Kb1,2,3	Compton

Figure 1 - Diagram of peak counts per second of PPP divided by peak counts per second of FGD versus increasing atomic number of the analyzed elements.

Table 2 - Standards and certified reference and recommended values used in the PPP and FGL methods.

Standard LD.	SiO ₂ (%)	TiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	MnO (%)	MgO (%)	CaO (%)	Na ₂ O (%)	K ₂ O (%)	P ₂ O ₅ (%)	SO ₃ (%)	As (ppm)	Ba (ppm)	Bi (ppm)	Ce (ppm)	Cl (ppm)	Co (ppm)	Cr (ppm)	Cs (ppm)	Cu (ppm)	F (%)
100Al ₂ O ₃	0	0	100	0	0	0	0	0	0	0	0.000	0	0	0	0	0	0	0	0	0	0
100SiO ₂	100	0	0	0	0	0	0	0	0	0	0.000	0	0	0	0	0	0	0	0	0	0
ACE	70,35	0,11	14,7	2,53	0,058	0,03	0,34	6,54	4,49	0,014	0,017	2,3	55	0,4	154	180	0,2	3,4	3	4	0,21
AL1	69,34	0,012	18,59	0,075	0,004	0,035	0,384	10,59	0,14	0,038	0,022	0,8	85	0,03	21	110	0,2	2	0,34	3	0,0045
ANG	46,3	0,22	29,8	3,36	0,04	1,8	15,9	1,63	0,13	0,01	0,035	0,2	34	0	4,7	300	25	50	0,05	19	0,012
BEN	38,2	2,61	10,07	12,84	0,2	13,15	13,87	3,18	1,39	1,05	0,075	1,8	1025	0	152	200	60	360	0,8	72	0,1
BR	38,2	2,6	10,2	12,88	0,2	13,28	13,8	3,05	1,4	1,04	0,097	2	1050	0	151	350	52	380	0,8	72	0,1
BXN	7,4	2,37	54,21	23,17	0,05	0,11	0,17	0,04	0,05	0,13	0,000	115	30	1,7	520	0	30	280	0,4	18	0,09
DRN	52,85	1,09	17,52	9,7	0,22	4,4	7,05	2,99	1,7	0,25	0,087	3	385	0,5	46	400	35	40	6,3	50	0,05
DTN	36,45	1,4	59,2	0,66	0,008	0,04	0,04	0,04	0,12	0,09	0,000	0,2	130	0,06	134	30	15	260	0,13	7	0,004
GA	69,9	0,38	14,5	2,83	0,09	0,95	2,45	3,55	4,03	0,12	0,020	1,7	840	0	76	250	5	12	6	16	0,05
GH	75,8	0,08	12,5	1,34	0,05	0,03	0,69	3,85	4,76	0,01	0,017	0,4	20	0	60	100	0,3	3	2,5	3	0,35
GSN	65,8	0,68	14,67	3,75	0,056	2,3	2,5	3,77	4,63	0,28	0,035	1,6	1400	0,18	135	450	65	55	5,4	20	0,105
JA1	64,06	0,87	14,98	6,95	0,15	1,61	5,68	3,86	0,78	0,16	0,005	2,92	307	0,009	13,5	35	11,8	7,3	0,64	42,2	0,018
JA2	56,18	0,67	15,32	6,14	0,11	7,68	6,48	3,08	1,8	0,15	0,002	0,77	317	0	32,7	0	30	465	4,2	28,6	0,0485
JA3	62,26	0,68	15,57	6,59	0,106	3,65	6,28	3,17	1,41	0,11	0,057	4,5	318	0	23,3	0	21	67,5	2,2	45,3	0,028
JG1A	72,19	0,25	14,22	2,05	0,06	0,69	2,13	3,41	4,01	0,08	0,002	0,39	458	0	45,2	0	5,7	18,6	11,4	1,3	0,045
JG2	76,95	0,04	12,41	0,92	0,015	0,04	0,8	3,55	4,72	0,002	0,002	0,8	67	0	49,5	0	4,3	7,6	7,5	0,4	0,096
JG3	67,1	0,48	15,52	3,73	0,072	1,79	3,76	4,03	2,63	0,12	0,012	0,37	453	0	40,1	0	11,4	23,6	1,9	6	0,0335
JGB1	43,44	1,62	17,66	15,16	0,17	7,83	11,98	1,23	0,24	0,05	0,487	1,11	63	0,014	7,86	0	61,6	59,3	0,27	86,8	0,015
JR1	75,41	0,1	12,89	0,96	0,1	0,09	0,63	4,1	4,41	0,02	0,002	15,9	40	0,51	47,1	920	0,65	2,3	20,2	1,4	0,0942
JR2	75,65	0,09	12,82	0,86	0,11	0,05	0,45	4,03	4,45	0,01	0,002	19,5	39	0,65	38,8	730	0,4	2,6	26	1,4	0,1087
LKSD1	40,1	0,5	7,8	4,11	0,09	1,73	10,8	2	1,14	0,16	3,921	40	430	0	27	11	31	1,5	44	0,03	
MAN	66,6	0,01	17,62	0,47	0,04	0,04	0,59	5,84	3,18	1,39	0,025	13	42	0	0,9	140	0,5	3	640	140	1,7
MICAF _e	34,4	2,5	19,5	25,65	0,35	4,55	0,43	0,3	8,75	0,45	0,017	3	150	1,9	420	500	23	90	180	5	1,6
MICAMg	38,3	1,63	15,2	9,46	0,26	20,4	0,08	0,12	10	0,01	0,032	0	4000	0	0,35	800	24	100	55	4	2,85
NIMD	38,96	0,02	0,3	16,96	0,22	43,51	0,28	0,04	0,01	0,01	0,000	0	10	0	0	400	210	2900	0	10	0
NIMG	75,7	0,09	12,08	2,02	0,021	0,6	0,78	3,36	4,99	0,01	0,000	1,5	120	0	195	170	4	12	1	12	0
NIML	52,4	0,48	13,64	9,96	0,77	0,28	3,22	8,37	5,51	0,06	0,000	0	450	0	240	1200	8	10	4	13	0
NIMN	52,64	0,2	16,5	8,91	0,18	7,5	11,5	2,46	0,25	0,03	0,000	0	100	0	6	100	58	30	0	14	0
NIMP	51,1	0,2	4,18	12,76	0,22	25,33	2,66	0,37	0,09	0,02	0,000	0	46	0	0	100	110	24000	0	18	0
NIST2709	63,45	0,57	14,17	5	0,069	2,5	2,64	1,56	2,45	0,142	0,222	17,7	968	0	13,4	130	5,3	34,6			
STSD1	42,5	0,75	9	6,48	0,5	2,21	3,6	1,75	1,25	0,38	0,449	23	630	0	51	17	67	1,8	36	0,095	
SY3	59,68	0,15	11,76	6,49	0,32	2,67	8,25	4,12	4,23	0,54	0,127	18,8	450	0,8	2230	150	8,8	11	2,5	17	0,696
TILL1	60,9	1	13,8	6,6	0,2	2,1	2,8	2,6	2,3	0,2			720		83	18	67	1	42		
UBN	39,43	0,11	2,9	8,34	0,12	35,21	1,2	0,1	0,02	0,04	0,050	10	27	0,1	0,8	800	100	2300	10	28	0,0095
VSN	55,57	1,08	13,44	4,14	0,1	4,51	4,53	5,95	8,12	0	0,000	0	1000	1000	800	0	700	700	900	800	0

Standard I.D.	Ga (ppm)	La (ppm)	LOI (%)	Mo (ppm)	Nb (ppm)	Nd (ppm)	Ni (ppm)	Pb (ppm)	Rb (ppm)	Sb (ppm)	Sc (ppm)	Sn (ppm)	Sr (ppm)	Th (ppm)	U (ppm)	V (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)	LOI (%)	Total (%)
100Al ₂ O ₃	0	0	0.00	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	100.00
100SiO ₂	0	0	0.00	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	100.00
ACE	39	59	0.37	2.5	110	92	1.5	39	152	0.4	0.11	13	3	18.5	4.6	3	184	224	780	0.37	99.96
AL1	20	9.7	0.40	0.1	1.6	10.4	2	4.5	5.8	0.2	1.75	0.4	80	9.5	5.8	2	6.8	8	43	0.4	99.66
ANG	18	2.2	0.65	0.2	0.7	2.4	35	2	1	0.1	10	1.4	76	0.04	0.12	70	7.5	20	11	0.65	99.94
BEN	17	82	2.45	2.8	105	67	267	4	47	0.26	22	2	1370	10.4	2.4	235	30	120	260	2.45	99.59
BR	19	82	3.00	2.4	98	65	260	5	47	0.2	25	2	1320	11	2.5	235	30	160	260	3	100.26
BXN	67	355	12.17	8.3	52	163	180	135	3.6	8	60	13.4	110	50	8.8	350	114	80	550	12.17	100.29
DRN	22	21.5	2.26	0.9	7	23.5	15	55	73	28	28	2	400	5	1.5	220	26	145	125	2.26	100.33
DTN	30	90	1.43	0.5	34	52	14	25	6	0.25	2.1	2.2	30	12	2.3	150	6.6	28	370	1.43	99.63
GA	16	40	1.00	0.5	12	27	7	30	175	0.2	7	2.7	310	17	5	38	21	80	150	1	100.07
GH	23	25	0.70	2	85	29	3	45	390	0	0.8	10	10	87	18	5	75	55	150	0.7	100.29
GSN	22	75	1.33	1.2	21	49	34	53	185	0.7	7.3	3	570	41	7.5	65	16	48	235	1.33	100.24
JA1	17.3	5.1	1.06	2	1.7	11	1.8	5.8	11.8	0.26	28.4	0.78	266	0.82	0.34	105	30.6	90.6	88.3	1.06	100.29
JA2	16.4	16.3	2.47	0.54	9.8	13.8	142	19.3	68	0.13	19.6	1.5	252	4.7	2.4	130	18.1	62.7	119	2.47	100.31
JA3	17	9	0.31	1.6	3	12.3	35.5	6.7	36	0.34	21.8	0.9	294	3.4	1.4	172	21.3	67.5	119	0.31	100.32
JG1A	17	21.8	0.68	0.67	12	21	6.4	27	180	0.06	6.31	4.2	185	12.1	4.7	23	31.6	38.8	121	0.68	99.94
JG2	19	20.1	0.38	0.23	15	25.8	2.1	32.8	297	0.06	2.47	2.5	16	29.7	12.5	3	88.2	12.7	101	0.38	100.01
JG3	17	20.7	0.88	0.44	5.6	16.8	13	12.3	66	0.07	8.93	1	372	8	2	73	17.2	44.8	143	0.88	100.29
JGB1	18.9	3.74	1.27	0.45	2.8	5.65	25.4	1.9	4	0.11	36.6	0.36	321	0.53	0.15	640	10.75	111	33.5	1.27	101.01
JR1	17.6	19.7	1.18	3.2	15.5	23.5	0.66	19.1	257	1.48	5.16	2.7	30	26.5	9		45.4	30	101	1.18	100.15
JR2	18.2	16.9	1.42	2.9	19.2	21.1	0.84	21.9	297	1.83	5.57	3.2	8	32.2	10.5		51.3	27.2	97.2	1.42	100.20
LKSD1	16	29.90	10	7	16	16	82	24	1.2	9	16	250	2.2	9.7	50	19	331	134	29.9	100.09	
MAN	59	0.5	1.82	0.3	173	3	29	3600	1.7	0.2	900	84	1.4	12.5	0.2	4	220	25	1.82	99.92	
MICAF _e	95	200	2.00	1.2	270	180	35	13	2200	0	14.8	70	5	150	80	135	48	1300	800	2	101.19
MICAMg	21	0.32	1.75	0.25	116	0.08	110	9	1300	0	1.2	5	27	0.1	0.15	90	0.04	290	16	1.75	100.77
NIMD	0	0.2	0.70	4	0	72	2050	7	0	0	7	2	3	0.8	0	40	0	90	20	0.7	101.59
NIMG	27	109	0.59	3	53	72	8	40	320	0.6	1	4	10	51	15	2	143	50	300	0.59	100.42
NIML	54	250	2.48	4	960	48	11	43	190	3	0.3	7	4600	66	14	81	22	400	11000	2.48	99.14
NIMN	16	3	0.43	5	2	3	120	7	6	0.4	38	8	260	0.6	0.6	220	7	68	23	0.43	100.71
NIMP	8	2	0.34	0	0	0	560	6	5	0.8	29	8	32	1	0.4	230	5	100	30	0.34	99.80
NIST2709	14	23	7.15	2		19	88	18.9	96	7.9	12		231	11	3	112	18	106	160	7.15	100.00
STSD1	30	31.60		5	28	24	35	30	3.3	14	4		170	3.7	8	98	42	178	218	31.6	100.47
SY3	27	1340	1.16	1	148	670	11	133	206	0.31	6.8	6.5	302	1003	650	50	718	244	320	1.16	101.05
TH.L1	29	7.30	2	12		20	21		8	15			229	6	2		37	91	518	7.3	99.99
UBN	3	0.35	12.06	0.55	0.05	0.6	2000	13	4	0.3	13	0	9	0.07	0.07	75	2.5	85	4	12.06	100.11
VSN	400	850	0.00	700	700	0	800	1000	800	800	300	800	700	0	0	600	800	800	700	0	99.11

Table 3 - Comparison of the LOD's and root mean square (RMS) calculated for the standards used in the FGD and PPP procedures.

	Limit of Determination		Root Mean Square (RMS)	
	PPP	FGD	PPP	FGD
Al	120	200	1.05	0.65
As	1	2	*	*
Ba	15	20	3.47	21.6
Bi	1	2	*	*
Ca	55	145	0.67	0.08
Ce	8	10	58.2	83.7
Cl	2	6	81.2	108
Co	2	3	4.05	4.67
Cr	1	2	66.0	22.9
Cu	1	2	4.26	11.1
F	115	110	0.09	#
Fe	15	15	0.44	0.10
Ga	1	1	3.47	3.12
K	20	20	0.11	0.17
La	8	15	21.1	22.3
Mg	30	80	0.49	0.13
Mn	4	7	0.02	0.01
Mo	1	1	*	*
Na	35	105	0.27	0.11
Nb	1	1	13.9	9.45
Nd	6	7	8.17	12.7
Ni	2	2	6.47	7.11
P	135	240	0.04	0.01
Pb	1	2	9.61	7.10
Rb	1	1	11.2	36.6
S	2	6	0.01	0.01
Sb	7	10	85.6	30.9
Sc	4	5	39.0	6.86
Si	100	105	1.88	0.67
Sn	10	15	34.5	21.1
Sr	1	1	41.9	23.9
Th	1	1	10.8	10.1
Ti	7	16	0.04	0.02
U	1	1	4.96	5.03
V	3	5	10.7	8.43
Y	1	1	5.61	23.8
Zn	1	2	11.3	6.35
Zr	1	1	45.1	16.3
* Poor Standard Variation. Unreliable precision calculation.				
# No clear linear relationship.				

nize. The powder is then reduced to less than 5 microns in a vibratory rod mill (McCrone Microniser) with ethanol.

Pressed Powder Pellet (PPP) Technique Samples and standards are dried overnight in disposable plastic cups at 60°C. A 7.000 ± 0.005 g of rock powder aliquot is weighted and stored in disposable plastic mixing bags containing 1.400 ± 0.005g Hoechst microgranular binding wax C₆H₈O₃N₂, followed by thoroughly homogenizing by hand rolling. The pressed powder pellet is produced in a Herzog powder tungsten carbide platen pellet machine for 60 seconds at 30 kPa, producing a 40-mm diameter pellet. Standards and samples are housed in a Nalgene Cat No. 5317 (0180) desiccator cabinet prior to analysis.

Fused Glass Disc Technique (FGD) The used technique is a modification of the described by Haukka and Thomas (1977) and Thomas and Haukka (1978). All glassware and crucibles are cleaned with de-ionized water and reagents are PA grade or better. In general, duplicate samples are run for every 15 unknowns to determine analytical precision, together with an in-house basalt or granite standard depending on the approximate composition of the unknown sample to determine accuracy. A synthetic monitor is run before each sample to correct for the machine drift.

Samples and standards are first dried in porcelain crucibles at 105°C for at least 2-3 hours. The sample is precisely weighed (2.0000 ±

0.0003 g of rock powder) into a glass vial with cap, followed by 10.0000 ± 0.0003 g of 4:1 lithium metaborate:lithium tetraborate commercial flux (Caisse eutectic mixture of 20% lithium tetraborate and 80% lithium metaborate), previously heated to 600°C. For sulfur analysis, a small amount (approximately 0.2-0.4g) of ammonium nitrate is added to the mixture to prevent loss of sulfur and the sample/flux mixture is homogenized by rolling the vial to collect this material. The mixture is then carefully poured into a pre-weighed platinum crucible, which is placed in a Caisse flux automatic melting machine. If the samples are electrostatically charged an unacceptable loss can occur, which can be prevented by adding more ammonium nitrate to the vial. A pre-programmed controller is then initialized such that the 3 crucibles are heated to 500°C for 15 minutes followed by ramping to 1000°C with gentle rolling. Samples are cooled to room temperature before re-weighing to determine loss of ignition. The crucibles are then returned to the furnace at 1000°C for 5-10 minutes. To facilitate non-wetting, one drop of lithium bromide solution (250 g/l) is added to the platinum crucible just prior to pouring, but note that Br overlap must now be considered for some elements. Pouring is conducted inside the furnace into platinum moulds. Slow overnight annealing of the disc at 300°C is essential to prevent shattering. This typically produces a 40 mm diameter and > 4 mm thick glass disc. Methods have been developed to cope with unusual sample matrices such as sulfides, carbonates and organic-rich samples. This method is applicable to any sample type, excluding waters and alloys. For very low Si samples, additional high-grade SiO₂ is added.

RESULTS AND DISCUSSION In order to compare the two techniques (PPP and FGD), instrument conditions, overlap corrections, counting times and matrix corrections were equivalent whenever possible. Table 1 resumes the instrumental conditions and overlap corrections in both procedures. Apart from minor variations in peak and background positions, the conditions are identical. In general, two-theta angles, overlap corrections, and choice of diffracting crystals and detectors were selected based on modifications proposed by Chappell (1991) and Potts (1987). Analysis was conducted in vacuum with a 37-mm mask.

Standards used in both techniques were the same. The XRF facility at IG-USP houses an impressive array of certified rock, soil and mineral standards covering all ranges of rock types. Additionally, spec-pure reagents of all elements of interest are available to manufacture synthetic standards for unusual applications. An initial selection of 36 standards, including two synthetic end-member standards, was chosen to represent a broad compositional range of the samples. Table 2 details the used standards and their certified reference and recommended values. Daily monitoring of the XRF spectrometer is achieved by use of a commercial monitor designed to provide moderate level intensities of all the elements of interest.

Matrix correction procedures were the same in both the PPP and FGD methods. For Nb, Zr, Y, Sr, Rb, U, Pb, Th, As, Mo and Bi, a Rh-Compton correction was chosen for matrix correction. For major and trace elements the Philips Fundamental Parameter software was used to generate theoretical alphas. This was conducted to ensure results were comparable.

Due to the variation in the quality of the worldwide rock and mineral standards analysis, it is inevitable that some standards will be 'outliers' in any given calibration as a result of uncertainties of the data. Several standards were consistent outliers for several elements and were therefore excluded from both calibrations (e.g. NIML, STSD1).

Detection Limits and Precision The six-sigma limit of determination (LOD) of Potts (1987) was used to compare the two techniques. The LOD equation is as follows:

$$LDO = 6\sqrt{2R_b T_b} \cdot \frac{C}{R_p T_p}$$

where R_b is the background count rate, R_n is the peak count rate, T_b is the background count time, T_p is the peak count time and C is the concentration of the element in the standard. It should be stressed that LOD equation provides a theoretical limit of determination, which is in general much lower than the expected in real samples. It also depends on the matrix of the sample used to determine the LOD. However, in this study the same standards were used for the same elements in both the FGD and PPP techniques which allows valid comparisons to be made between the two techniques.

Table 4 - Experimentally determined alphas (Haukka, unpublished data) for the lithium metaborate system under the conditions presented in Table 1.

	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	Cl	Cr	Ba	Sc	Ce	
SiO ₂	0,847	0,031	0,128	0,494	0,373	0,343	0,425	0,075	0,350	0,012	0,030	0,040	-0,030	0,272	0,845	0,100	0,867
TiO ₂	0,919	0,008	0,042	-0,051	-0,110	-0,142	-0,112	1,336	-0,167	1,422	0,080	0,142	0,500	-0,196	0,642	0,372	0,642
Al ₂ O ₃	0,936	-0,010	0,170	-0,028	0,443	0,430	0,524	0,105	0,300	0,055	0,030	0,100	-0,030	0,342	0,762	0,842	0,839
Fe ₂ O ₃	0,848	0,001	1,350	-0,057	0,528	0,430	-0,096	1,401	-0,149	1,456	0,068	0,170	0,400	2,300	4,400	4,196	3,632
MnO	0,863	0,000	1,510	-0,046	0,352	0,420	-0,105	1,410	-0,166	1,460	0,062	0,108	0,400	0,342	3,318	3,118	2,618
MgO	0,948	0,000	0,226	-0,029	0,421	0,400	-0,050	0,135	0,431	0,090	0,025	0,100	-0,050	0,337	0,768	0,768	0,768
CaO	0,993	0,015	-0,213	-0,053	-0,183	-0,198	-0,080	-0,030	-0,191	1,528	0,090	0,135	0,500	-0,221	0,578	0,123	0,591
Na ₂ O	0,970	0,000	0,206	-0,014	0,389	0,363	-0,080	0,123	0,001	0,089	0,080	0,100	0,100	0,306	0,525	0,535	0,535
K ₂ O	1,040	0,002	-0,288	-0,044	-0,169	-0,189	-0,119	-0,268	-0,179	-0,075	0,096	0,235	0,500	-0,218	0,617	0,157	0,607
P ₂ O ₅	1,072	0,010	-0,330	-0,040	-0,160	-0,188	-0,100	-0,410	-0,183	-0,444	-0,370	-0,299	-0,420	-0,240	0,700	0,180	0,411
SO ₃	1,060	0,003	-0,200	-0,044	-0,143	-0,183	-0,113	-0,315	-0,153	-0,392	0,096	-0,294	-0,421	-0,220	0,300	0,259	0,259
Ba	0,949	-0,004	0,412	-0,045	-0,167	-0,190	-0,113	1,508	-0,173	1,604	0,150	0,200	0,500	-0,207	0,900	0,446	1,044
Ce	0,868	0,000	1,515	-0,045	-0,110	0,190	-0,105	1,360	-0,165	1,390	0,150	0,130	1,160	0,090	2,590	0,890	0,675
Cl	1,010	0,000	-0,200	-0,005	-0,020	0,000	-0,010	-0,300	-0,060	-0,310	0,295	0,550	1,000	-0,150	0,800	-0,100	0,500
Co	0,828	-0,010	1,475	-0,052	0,494	2,590	-0,115	1,390	-0,160	1,445	0,065	0,112	1,192	2,500	4,185	1,150	3,612
Cr	0,885	0,000	1,510	-0,080	-0,100	0,200	-0,100	1,600	-0,160	1,550	0,070	0,130	0,400	0,500	2,600	2,600	0,500
Cu	0,710	-0,010	1,290	-0,050	2,610	2,610	-0,100	1,160	-0,120	1,180	0,065	0,120	0,990	2,400	3,930	1,150	3,930
F	0,970	0,250	0,250	0,010	0,250	0,230	0,250	0,140	-0,235	0,090	0,200	0,250	0,000	0,250	0,525	0,100	0,535
Ga	0,730	0,000	1,280	-0,050	2,578	2,600	-0,040	1,170	-0,080	1,160	0,060	0,110	0,970	2,400	3,910	1,150	3,910
La	0,901	0,000	0,317	-0,046	-0,151	-0,110	-0,110	1,350	-0,150	1,400	0,075	0,110	0,400	-0,120	1,085	1,300	0,900
Nd	0,866	0,000	1,515	-0,045	0,315	0,315	-0,105	1,365	-0,165	1,425	0,150	0,115	1,195	0,315	3,415	3,115	0,915
Ni	0,845	0,000	1,313	-0,055	2,630	2,673	-0,070	1,170	-0,128	1,190	0,066	0,162	1,190	2,400	4,002	1,150	4,002
Pb	0,690	0,000	1,305	-0,020	3,110	2,750	-0,040	1,164	-0,060	1,172	0,060	0,113	0,974	2,039	4,062	1,200	4,062
Rb	0,726	0,004	1,319	-0,010	2,684	2,699	-0,020	1,160	-0,030	1,154	0,065	0,119	0,989	2,400	4,109	1,150	4,109
Sc	0,923	-0,004	0,350	-0,055	-0,170	-0,170	-0,116	1,650	-0,171	1,600	0,076	0,138	0,500	-0,200	0,638	0,368	0,368
Sr	0,726	0,004	1,319	-0,010	2,684	2,699	-0,020	1,160	-0,030	1,154	0,065	0,180	0,989	2,400	4,109	1,150	4,109
V	0,923	-0,004	0,258	-0,055	-0,126	-0,146	-0,116	1,332	-0,171	1,418	0,080	0,138	1,158	-0,200	0,638	0,368	0,368
Y	0,730	0,000	1,315	-0,015	2,680	2,695	-0,020	1,190	-0,030	1,150	0,065	0,115	0,985	2,400	4,105	1,150	2,729
Zn	0,773	0,017	1,310	-0,075	2,550	2,620	-0,080	1,170	-0,110	1,180	0,080	0,180	0,990	2,400	3,930	1,150	3,930
Zr	0,710	-0,005	1,315	-0,020	2,680	2,695	-0,030	1,250	-0,030	1,145	0,071	0,125	0,995	2,400	4,115	1,150	2,954

	Nd	V	Co	Cu	Zn	Ni	Ga	Zr	Y	Sr	Rb	F	Pb	La	LOI	
SiO ₂	0,847	0,994	0,237	0,550	0,600	0,695	0,588	0,927	0,300	0,262	0,290	0,250	0,150	0,630	0,829	-0,346
TiO ₂	0,919	0,642	0,200	0,472	0,202	0,172	0,022	0,400	1,012	0,972	0,972	0,972	-0,167	2,600	0,642	-0,620
Al ₂ O ₃	0,936	0,835	0,642	0,842	0,550	1,142	0,842	1,200	0,169	0,139	0,122	0,082	0,140	0,429	0,756	-0,360
Fe ₂ O ₃	0,848	3,525	4,623	0,350	0,170	0,190	0,150	0,311	1,197	1,168	1,143	1,143	-0,150	2,750	3,614	-0,597
MnO	0,863	0,618	4,518	0,618	0,098	0,138	0,098	0,350	1,018	1,018	1,018	1,018	-0,145	2,750	4,000	-0,570
MgO	0,948	0,768	0,518	0,868	0,668	0,568	0,200	0,198	0,168	0,138	0,108	0,160	0,160	0,367	0,750	-0,332
CaO	0,993	0,591	0,200	0,323	0,126	0,203	0,043	0,550	1,144	1,144	1,123	1,123	-0,160	2,447	0,596	-0,669
Na ₂ O	0,970	0,535	0,425	0,535	0,865	0,385	0,585	0,200	0,215	0,185	0,155	0,115	0,100	0,345	0,500	-0,290
K ₂ O	1,040	0,607	0,257	0,257	0,212	-0,013	-0,093	0,602	1,207	1,207	1,207	1,207	0,090	1,992	0,560	-0,690
P ₂ O ₅	1,072	0,411	0,080	0,280	0,080	0,180	-0,020	0,900	-0,211	-0,211	0,980	0,980	0,080	-0,029	0,411	-0,620
SO ₃	1,060	0,409	0,109	0,076	0,300	0,296	0,140	0,856	0,909	0,859	0,800	1,059	0,050	0,200	0,400	-0,516
Ba	0,949	1,044	0,200	0,581	0,146	0,200	0,111	0,396	1,044	1,014	1,000	1,231	-0,173	2,768	1,044	-0,560
Ce	0,868	0,775	0,200	0,590	-0,030	0,030	-0,020	0,400	1,020	0,990	0,990	0,990	-0,100	2,600	0,900	-0,260
Cl	1,010	0,500	0,000	0,000	0,000	0,000	0,000	0,300	1,190	1,190	1,190	1,190	0,020	1,300	0,500	-0,250
Co	0,828	3,212	1,800	0,670	0,112	0,212	0,608	0,290	1,182	1,152	1,132	1,132	-0,100	2,750	3,200	-0,320
Cr	0,885	0,700	0,200	0,600	0,000	0,050	0,000	0,350	1,000	1,000	1,000	1,000	-0,190	2,700	3,800	-0,320
Cu	0,710	4,570	1,800	4,330	0,600	0,820	0,920	0,320	0,930	0,930	0,930	0,930	-0,120	2,750	4,400	-0,140
F	0,970	0,535	0,425	0,535	0,585	0,180	0,585	0,200	0,215	0,185	0,155	0,115	-0,280	0,100	0,500	-0,210
Ga	0,730	4,610	1,800	3,400	3,900	0,910	3,710	1,500	0,910	0,910	0,910	0,910	-0,080	2,600	4,300	-0,120
La	0,901	0,900	-0,010	-0,040	-0,030	-0,040	0,040	0,400	1,020	1,020	1,000	1,000	-0,150	2,500	0,945	0,557
Nd	0,866	1,042	0,200	0,715	0,095	0,135	0,095	0,400	0,990	0,960	1,015	1,015	-0,165	2,600	0,832	-0,260
Ni	0,845	4,717	1,800	0,640	0,600	0,015	0,990	0,311	0,935	0,935	0,935	0,935	-0,128	2,750	4,400	-0,195
Pb	0,690	4,062	1,800	3,397	4,247	5,520	4,000	4,800	1,007	1,500	1,500	1,500	-0,060	5,646	4,062	-0,462
Rb	0,726	4,909	1,800	4,589	4,320	4,753	3,824	4,804	1,009	1,909	1,909	2,775	-0,030	9,100	4,600	-0,280
Sc	0,923	0,568	0,200	0,468	0,198	0,168	0,018	0,496	1,008	0,968	0,968	0,968	-0,171	2,447	0,550	-0,330
Sr	0,726	4,909	1,800	4,589	4,320	5,200	3,824	4,804	1,109	1,909	2,940	1,709	-0,030	9,100	4,600	-0,280
V	0,923	0,568	0,300	0,468	0,198	0,168	0,018	0,396	1,008	0,968	0,966	0,968	-0,150	2,980	5,600	-0,380
Y	0,730	2,729	1,800	4,585	4,296	4,749	3,820	4,800	0,473	1,529	1,905	1,705	-0,030	9,100	2,526	-0,230
Zn	0,773	4,630	1,800	4,330	0,910	0,880	3,730	0,320	0,930	0,930	0,930	0,930	-0,110	2,750	4,300	-0,180
Zr	0,710	3,492	1,800	4,595	4,296	4,759	3,830	4,810	3,550	1,674	1,515	10,015	-0,030	12,000	2,954	-0,260

Unlike the PPP technique, the FGD procedure allows the determination of loss-on-ignition (LOI) by means of the weight difference of the sample pre- and post-fusion. The LOI must therefore be considered during calibration. As the Philips software does not recognize losses, the LOI was allowed to regress after the calculation of the theoretical alphas.

Table 3 compares the LOD's and root mean square (RMS) calculated for the standards used in the FGD and PPP procedures. In general, the LOD's by the FGD procedure are larger than by the PPP standards. This is hardly surprising as the FGD standards are diluted by a factor of 5. However, this dilution is not fully reflected in a five-fold loss in sensitivity for glass discs. In fact, glass disc LOD's are generally only a factor of 2-3 higher for FGD than those for PPP and this sensitivity reduction drops to a factor of less than 2 as the atomic number of the elements increase. This is strikingly illustrated in Figure 1, where the peak counts per second of PPP divided by peak counts per second of FGD is plotted against increasing atomic number. As the atomic number of the elements increase, the relative gain in sensitivity decreases in the PPP in opposite to the flux-diluted FGD. The diagram also illustrates the important feature that fluorine is a significant outlier due to its volatilization during fusion.

Table 3 emphasizes the value of the fused glass disc method over the pressed powder pellet technique for the light elements, such as Na, Mg, Al, Si, Ca and Fe, with the improvement in Si and Ca being particularly striking. Nonetheless, the error in the Si and Al analyses of FGD standards is greater than the expected and may reflect inadequate sample homogenization, which can be improved by mixing for a longer period of time in the fusion machine.

For certain heavier elements (e.g. Ba, Rb and Y) the PPP technique provides substantially better precision. Two of these elements (Rb and Y) are determined by using mass attenuation corrections based on Compton scatter. This method stems from the observation that the intensity of secondary fluorescent radiation is affected by absorption to the same degree as primary X-ray tube radiation scattered from the sample at an adjacent angle (Potts 1987). The ratio between the Rh-tube Compton and the X-ray line of the element of interest is therefore virtually independent of sample attenuation effects. This procedure is applicable provided no significant absorption edge intervenes between the Compton and the measured peak. Potts (1987) calculated that the infinite thickness for Rh Ka radiation is 12.4 mm in glass discs using a similar dilution and flux to that used in this study. As the glass discs produced at IG-USP are of the order of 4 mm thick, we believe that the Rh-Compton cannot be used for matrix correction, which might account for discrepancies between the PPP and FGD techniques for Compton-corrected elements. Haukka and Thomas (1978) recognized this potential problem but argued that errors would be cancelled provided that the standards and samples have similar mass absorption coefficients and thickness. This conclusion is supported as not all Compton corrected elements were affected and, indeed, the Philips Fundamental Parameter software was applied to the Compton corrected elements, with no improvement in precision.

Contrasting Philips Fundamental Alphas with Experimentally Determined Data The fluorescent X-ray count-rates observed in an analysis are not directly proportional to element concentration because of absorption-enhancement effects, which are due to the influence of all other elements in a sample. These so-called

Matrix Effects are caused largely by absorption and enhancement of both primary and fluorescent X-rays, with absorption being the dominant process. These effects must be corrected for major and trace elements in order to perform quantitative analysis. The Philips system uses alpha coefficients to correct the effect of one element over other elements that are calculated using theoretical considerations based on flux composition, fluorescent yield, etc., and then compared with standards from a linear regression. An alternative to this method is to use experimentally determined alphas. Systematic doping of single component systems with increasing amounts of other elements derives experimentally determined alpha corrections. This time-consuming procedure is rarely conducted these days but does, however, produce very rigorous alpha coefficients for a given system. Table 4 lists experimentally determined alphas (Haukka, unpublished data) for the lithium metaborate system under the conditions described in Table 1. A comparison of element precision obtained in the fused glass disc system for the fundamental parameters versus the experimentally determined alphas has demonstrated that the results are comparable for virtually all elements. It should be noted, however, that the experimental alphas are based on a 1:2 sample:lithium metaborate system using an ARL two-goniometer X-ray spectrometer. Therefore minor differences should be expected, but otherwise conditions are identical. Thomas and Haukka (1977) demonstrate that the major element alphas experimentally determined for this system were equally applicable to higher dilutions (up to 1:4).

CONCLUSIONS The FGD method clearly offers major advantages over the PPP method in terms of precision and accuracy, which is most striking in the light elements. The technique suffers from compromised limits of determination due to the 1:5 dilution, although not to the same extent as the magnitude of the dilution. The FGD technique is extremely rigorous and, with the added advantage of loss on ignition analysis, the quality of the analytical data is immediately obvious by observation of the oxide and trace element totals, and a high quality XRF analysis by this method should provide totals of between 99.25 and 100.75%. Importantly, the FGD technique cannot be used for the analysis of F and caution should be used when attempting to analyze potentially volatile elements such as S. The PPP method offers the advantage of ease of preparation and, as the technique is non-destructive, samples can be recovered for further study. It is clear that the ideal compromise for the modern XRF laboratory is the ability to offer both FGD and PPP techniques in order to extend and complement the offered services. It is essential that samples for PPP analysis be ground as fine as possible using the vibratory rod mill. Even so, it is likely that the harder compounds in a particular matrix will not be broken down, an effect that tends to fractionate the composition of a sample. This is clearly evidenced by the poor precision of Zr in the PPP calibration. Zirconium is likely to occur as zircon, which is a hard mineral that may enhance the nugget effect. Due to the severe lack of variation obtained in certified reference samples for the elements Mo, Bi and As, it is not possible to derive relative precision. For these elements synthetic samples must be produced.

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