

ICP-FORESTS

1st Needle/Leaf Interlaboratory Test 1993/94

Discussion paper for the 2nd EP Foliage Analysis
Ås/Norway 8-9.3.1994

Annex 2.

Laboratories ringtest, 1993-94

The ringtest was run on two samples (B = beech leaves, and S = spruce needles), with certificated values for the content of several elements, provided by BCR. Analysis were to be done with three replicates, for the elements N, S, P, Ca, K, and it was recommended also for Na, Zn, Mn, Fe, Cu, F, Cl, Cd, Pb, Al and B. The following countries (laboratories) participated in the ring test (sorted alphabetically):

Austria
Belgium
Britain
Croatia
Czech Republic
Denmark
Estonia
Finland
France
Germany
Greece
Hungary
Ireland
Italy 1 (Linea Ambiente Firenze)
Italy 2 (Inst. for Plant Nutrition - Roma)
Italy 3 (Land- und Forstwirtschaftliches Versuchszentrum, Laimburg)
Netherlands
Norway
Portugal
Slovenia
Spain
Sweden
Switzerland

The results showed for most laboratories good to excellent results (less than 10% deviation from the certified values). The deviations that were found, in some cases too big, seems to be linked with three factors:

1. Elements. In general N and K showed best results, Ca, Mg and P intermediate, and S is the most difficult element. See figs. 1.a-f, and Tables 1.a-h and 2.a-d.

2. Methods. Different methods have been used (Tables 3.a-k), and for some elements some methods seems better than others (Tables 4.a-k). The comparisons between methods were difficult because some methods were used by only one laboratory.

N. H₂SO₄ only and titration is not recommended.

Sulphur.

Generally dry ashing with Mg(NO₃)₂ and turbidimetry is not recommended.

Further comments:

A - Organic matter oxydation

1. Dry ashing: without stabilizing agent.

Leads to losses of an important part of Sulphur under organic form (losses as SO₂ gas during

6

Lab number	N		S		P		Ca		Mg	
	mg/g		mg/g		mg/g		mg/g		mg/g	
B.C.R. Mean	26.29		2.69		1.55		5.30		0.878	
Conf.interval	26.04	26.54	2.65	2.73	1.51	1.59	5.25	5.35	0.861	0.895
1	24.5		--		1.63		5.80		1.22	
	24.2	25.1			1.60	1.70	5.7	5.9	1.20	1.26
2	25.5		2.73		1.70		5.37		0.93	
	25.0	25.7	2.67	2.79	1.69	1.71	5.33	5.43	0.923	0.930
3	26.0		2.67		1.60		5.10		0.90	
	25.7	26.2	2.63	2.69	1.60	1.60	5.0	5.2	0.9	0.9
4	24.3		2.55		1.48		5.00		0.90	
	--	--	2.49	2.60	1.40	1.57	4.8	5.2	--	--
5	26.0		1.42		1.22		4.50		0.90	
	25.9	26.1	1.29	1.52	1.08	1.40	4.5	4.5	0.9	0.9
6	25.4		1.98		1.58		5.26		0.83	
	25.1	25.8	1.97	1.99	1.57	1.59	5.17	5.30	0.82	0.84
7	24.7		2.41		1.48		4.39		0.74	
	24.5	24.7	2.38	2.42	1.46	1.50	4.35	4.42	0.73	0.74
8	26.5		2.45		1.61		5.33		0.91	
	--	--	--	--	1.58	1.62	5.31	5.35	0.90	0.92
9	23;8		2.39		1.49		3.98		0.85	
	23.4	24.3	2.34	2.45	1.45	1.51	3.82	3.95	0.84	0.87
10	29.7		4.60		2.51		7.56		0.72	
	28.3	31.1	4.5	4.7	2.46	2.56	7.23	7.88	--	--
11	18.5		1.49		1.26		3.67		1.07	
	18.2	18.8	1.40	1.55	1.23	1.29	3.52	3.75	0.99	1.27
12	27.1		2.86		1.90		4.98		0.82	
	26.7	27.5	2.83	2.89	1.76	2.00	4.88	5.08	0.81	0.85
13	22.1		3.00		1.32		5.27		0.82	
	18.4	24.0	2.93	3.09	1.30	1.34	4.73	5.92	0.78	0.87
14	23.7		2.47		1.52		3.95		0.768	
	22.3	24.7	2.42	2.57	1.51	1.54	3.85	4.11	0.73	0.79
15	24.0		--		1.81		9.42		1.14	
	23.8	24.1			1.70	2.08	8.86	10.22	1.07	1.22
16	26.0		2.84		1.54		5.12		0.854	
	26.0	26.0	2.80	2.88	1.49	1.58	5.01	5.233	0.85	0.85
17	24.0		2.66		1.55		5.00		0.869	
	23.5	24.3	2.58	2.74	1.54	1.56	4.99	5.03	0.86	0.88
18	26.0		--		1.54		4.99		0.997	
	25.7	26.3			1.51	1.56	4.70	5.30	0.92	1.10
19	25.7		2.91		1.42		4.71		0.647	
	25.2	26.4	2.88	2.96	1.41	1.42	4.56	4.80	0.59	0.69
20	26.8		2.76		1.60		5.17		0.910	
	26.5	26.9	2.73	2.79	1.54	1.67	5.05	5.33	0.90	0.92
21	25.9		--		1.51		4.55		0.851	
	25.03	26.91			1.51	1.51	4.50	4.59	0.850	0.854
22	25.8		2.31		1.42		4.77		0.823	
	25.6	25.9	2.27	2.39	1.37	1.45	4.74	4.81	0.817	0.829
Table 1Ba Sample B Lab 1 to 22 _Elements N,S,P,Ca,Mg.										

Lab number	K	Na	Zn	Mn	Fe
	mg/g	mg/kg	mg/kg	mg/kg	mg/kg
B.C;R; Mean	9.94	245	69	1333	549
<i>Conf. interval</i>	9.74 10.14				
1	8.86	—	59.3	953	525
	8.60 9.00		59 60	944 958	520 528
2	9.87	224	67.9	1404	501
	9.73 9.97	221.3 226.8	66.9 68.4	1397 1411	484 526
3	9.60	—	—	1335	554
	9.60 9.60			1322 1351	543 560
4	9.62	300	61.7	1253	477
	9.29 9.95	300 300	58.0 65.4	1216 1290	442 513
5	10.0	220	—	1333	455
	10.0 10.0	220 220		1300 1400	433 466
6	9.39	206	60.1	1270	514
	9.20 9.54	199 211	59.2 61.1	1260 1290	509 524
7	7.85	177	55.4	1118	435
	7.76 7.92	176 179	54.8 56.0	1110 1124	432 439
8	10.16	238	67.6	1398	591
	10.06 10.29	236 241	67.4 67.9	1386 1418	585 599
9	9.39	294	57.6	1205	569
	9.34 9.44	282 305	56.1 58.9	1193 1231	566 570
10	8.87	515	112.7	1294	610
	8.85 8.90	515 515	91.4 124.0	1292 1296	607 613
11	4.74	—	—	—	—
	4.65 4.90				
12	9.42	223	—	1293	—
	9.26 9.53	210 240		1290 1300	
13	8.87	—	68.3	1302	506
	8.66 9.07		66.0 71.0	1273 1324	494 515
14	7.13	—	56.8	—	328
	7.03 7.53		53.8 65.9		312 359
15	9.42	—	—	—	—
	9.26 9.52				
16	9.49	320	65.7	1368	534
	9.39 9.60	320 320	65.4 65.9	1366 1370	533 536
17	9.38	242	68.3	1313	558
	9.18 9.56	231 254	64.0 73.0	1303 1330	556 562
18	10.06	—	—	—	—
	9.88 10.14				
19	10.10	—	—	2213	885
	10.1 10.1			2190 2230	862 911
20	9.46	270	67.9	1405	576
	9.36 9.61	254 289	59.8 78.9	1396 1413	562 583
21	9.52	283	54.1	976	213
	9.48 9.56	271 281	53.9 54.1	857 1110	211 215
22	7.00	203	75.0	1363	526
	6.54 7.46	201 207	74.0 76.0	1350 1390	519 531

Table 1Bb_Sample B_Lab 1 to 22_Elements K, Na,Zn,Mn, Fe.

AFinterctb1Bc

	A	B	C	D	E	F
1	Lab. number	Cu	F	Cl	Cd	Pb
2		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
3	B.C.R. Mean	11.8	14.3	1490	0.34	16.4
4	Conf. interval	—	—	1430 1550	—	—
5						
6	1	—	—	—	—	—
7						
8	2	10.74	—	—	<1.1	14.57
9		10.4 11.1	—	—	—	13.9 14.9
10	3	—	17.3	1520	—	—
11			16.2 18.0	1500 1540	—	—
12	4	6.90	—	1463	—	20.8
13		—	—	1326 1600	—	—
14	5	9.77	—	—	—	—
15		9.3 10.0	—	—	—	—
16	6	5.48	3.57	1613	—	6.15
17		5.25 5.65	3.2 3.9	1600 1620	—	4.54 7.23
18	7	8.87	—	—	0.23	—
19		8.80 9.00	—	—	0.23 0.23	—
20	8	10.23	—	1251	—	—
21		9.91 10.80	—	—	—	—
22	9	7.95	18.4	—	0.20	6.64
23		7.87 8.07	—	—	0.20 0.20	6.51 6.79
24	10	42.9	—	—	—	66.2
25		35.8 50.0	—	—	—	66.1 66.3
26	11	—	—	—	—	—
27						
28	12	—	—	—	—	—
29						
30	13	—	—	—	0.37	—
31					0.35 0.39	—
32	14	—	—	—	—	—
33						
34	15	—	—	—	—	—
35						
36	16	11,12	22.0	1630	0.23	8.73
37		11.09 11.18	—	—	0.227 0.231	8.42 9.05
38	17	10.60	—	—	0.40	17.17
39		10.50 10.70	—	—	—	15.90 18.40
40	18	—	—	700	—	—
41						
42	19	—	—	—	—	—
43						
44	20	9.93	—	—	—	—
45		9.87 9.97	—	—	—	—
46	21	6.44	—	—	0.12	6.25
47		6.40 6.51	—	—	0.102 0.133	5.53 7.61
48	22	9.67	—	—	—	—
49		9.0 10.0	—	—	—	—
50						

Table 1Bc_Sample B_Lab 1 to 22_Elements Cu,F,Cl,Cd,Pb.

AFInterctb1Bd

	A	B	C	D	E	F
1	Lab. number	Al	B			
2		mg/kg	mg/kg			
3	B.C.R. Mean	450	27			
4	Conf. interval	446 454				
5						
6	1	—	—			
7						
8	2	197	28.1			
9		192 205	27.4 28.9			
10	3	—	—			
11						
12	4	395	—			
13		— —				
14	5	—	—			
15						
16	6	—	24.0			
17			23.4 24.8			
18	7	193	—			
19		193 194				
20	8	402	29.7			
21		398 408	29.4 30.0			
22	9	196	38.5			
23		186.3 206.0	— —			
24	10	595	39			
25		519 671	— —			
26	11	—	—			
27						
28	12	—	—			
29						
30	13	—	—			
31						
32	14	—	—			
33						
34	15	—	—			
35						
36	16	237	28.8			
37		— —	28.6 29.0			
38	17	426	—			
39		415 431				
40	18	—	—			
41						
42	19	—	—			
43						
44	20	—	—			
45						
46	21	188	24.3			
47		186.6 190.0	23.8 24.8			
48	22	209	17.0			
49		204.0 216.0	17.0 17.0			
50						

Table 1Bd_Sample B_Lab 1 to 22_Elements Al,B.

Lab number	N	S	P	Ca	Mg	K	Na	Zn
Mean	mg/g	mg/g	mg/g	mg/g	mg/g	mg/g	mg/kg	mg/kg
BCR mean	26.29	2.69	1.55	5.30	0.878	9.94	245	69
1	-8.0		+9.6	+11.3	+43.5	-14.5		
2	* -4.9	* +3.7	+10.3	* +2.5	+5.9	* -2.1	-9.7	* -3.0
3	* -2.3	* -2.2	* +3.2	-5.7	* +2.5	* -3.4		
4	-7.6	-7.4	-9.7	-9.4	* +2.5	-6.5	+22.4	-16.0
5	* -1.5	-52.1	-30.3	-5.1	* +2.5	* +0.6	-10.2	
6	* -4.5	-26.7	* +2.6	* -2.5	-6.6	-7.4	-18.8	-14.2
7	-6.8	-11.5	-5.8	-17.9	-16.9	-21.9	-28.2	-20.6
8	* +0.8	-8.9	* +4.5	* +0.9	* +4.8	* +3.5	* -3.7	* -2.3
9	-11.0	-13.0	-6.5	-27.9	* -4.3	-6.0	+24.5	-18.7
10	+18.3	+74.7	+65.2	+48.7	-18.0	-11.0	+110.2	+79.7
11	-30.8	-48.0	-20.6	-33.7	+44.6	-53.2		
12	* +4.6	+7.4	+29.0	-7.9	-7.7	-6.8	-14.3	
13	-30.0	+14.9	-16.1	+11.7	-11.2	-12.9		* -4.3
14	-15.2	-10.0	* -2.6	-21.1	-16.9	-30.3		-22.0
15	-9.5	-	+34.2	+92.8	+38.9	-6.8		
16	* -1.1	+7.1	* -3.9	-5.4	* -3.2	-5.5	+30.6	-5.2
17	-10.6	* -4.1	* +0.6	-5.9	* -2.1	-7.6	-5.7	-7.2
18	* -2.2	-	* -2.6	-11.3	+25.3	* +2.0		
19	* -4.1	+10.0	-9.0	-14.0	-32.8	* +1.6		
20	* +2.3	* +3.7	+7.7	* -4.7	* +4.8	-5.8	+17.9	-13.3
21	* -4.8		* -2.9	-15.2	* -3.2	* -4.6	+21.6	-21.9
22	* -2.6	-15.6	-11.6	-10.6	-6.9	-34.2	-18.0	+10.1

Table 5Ba_1 Sample B Max difference with BCR m mean In %. N, S, P, Ca, Mg, K, Na, Zn.

AFintc**tb5Bb**[illegible]

Lab number	N		S		P		Ca		Mg	
	mg/g		mg/g		mg/g		mg/g		mg/g	
B.C.R. Mean	18.89		1.70		1.69		4.28		0.619	
<i>Conf. interval</i>	18.71	19.07	1.66	1.74	1.66	1.73	4.20	4.36	0.610	0.628
1	17.6		—		1.75		5.70		1.080	
	17.4	17.9			1.57	1.88	5.70	5.70	1.02	1.14
2	18.3		1.74		1.90		4.74		0.670	
	18.0	18.6	1.69	1.78	1.82	1.95	4.53	4.84	0.66	0.68
3	18.9		1.74		1.77		4.40		0.600	
	18.1	18.9	1.72	1.76	1.70	1.80	4.40	4.40	0.60	0.60
4	18.2		1.79		1.73		4.45		0.600	
	—	—	1.67	1.90	1.56	1.90	4.40	4.50	—	—
5	18.9		0.84		1.30		3.88		0.650	
	18.8	19.0	0.75	0.88	1.20	1.50	3.75	4.00	0.65	0.65
6	18.3		1.24		1.79		4.74		0.619	
	18.2	18.4	1.21	1.27	1.77	1.80	4.65	4.80	0.61	0.62
7	17.9		1.59		1.66		3.86		0.544	
	17.9	18.1	1.57	1.62	1.63	1.69	3.80	3.93	0.53	0.55
8	19.0		1.59		1.77		4.59		0.669	
	—	—	—	—	1.76	1.78	4.57	4.61	0.67	0.67
9	16.7		1.47		1.65		3.40		0.597	
	15.3	17.1	1.37	1.59	1.60	1.69	3.36	3.45	0.58	0.61
10	19.5		3.65		2.71		5.68		0.500	
	19.2	19.8	3.50	3.80	2.71	2.72	5.46	5.91	—	—
11	13.4		1.01		1.51		4.48		0.735	
	13.3	13.5	0.94	1.10	1.49	1.53	4.39	4.62	0.69	0.79
12	19.4		1.87		2.07		4.32		0.576	
	19.1	19.7	1.80	1.94	2.01	2.13	4.28	4.36	0.56	0.60
13	17.6		2.05		1.58		5.51		0.574	
	17.5	17.8	2.04	2.06	1.57	1.59	4.98	5.80	0.57	0.58
14	19.3		1.53		1.68		4.26		0.612	
	18.3	20.7	0.81	2.42	1.67	1.69	4.18	4.38	0.58	0.65
15	17.4		—		0.74		7.96		0.984	
	17.2	17.6			0.66	0.80	7.52	8.40	0.93	1.07
16	18.5		1.95		1.67		4.39		0.613	
	18.5	18.6	1.93	1.98	1.65	1.71	4.34	4.44	0.61	0.61
17	18.1		1.70		1.73		4.29		0.626	
	18.0	18.2	1.63	1.76	1.71	1.76	4.24	4.36	0.61	0.65
18	17.6		—		1.68		4.21		0.627	
	17.3	17.9			1.67	1.70	3.94	4.44	0.61	0.63
19	18.4		1.85		1.46		4.08		0.403	
	18.0	18.7	1.77	1.90	1.43	1.48	3.99	4.13	0.40	0.41
20	18.8		1.72		1.77		4.63		0.616	
	18.3	19.1	1.71	1.74	1.76	1.80	4.62	4.67	0.61	0.63
21	18.0		—		1.70		3.63		0.667	
	17.8	18.3			1.69	1.71	3.57	3.70	0.66	0.67
22	18.0		1.65		1.68		4.27		0.591	
	17.9	18.1	1.59	1.69	1.63	1.70	4.16	4.37	0.52	0.608

Table 1Sa_Sample S_Lab 1 to 22_ Elements N,S,P,Ca,Mg.

A.F.Incaltab1Sb

Lab number	K	Na	Zn	Mn	Fe
	mg/g	mg/kg	mg/kg	mg/kg	mg/kg
B.C.R. Mean	6.20	60	35.3	915	151
Conf. interval	—	—	33.0 37.6	904 926	—
1	5.93	—	23.6	696	129
	5.80 6.00		23.0 25.0	692 705	128 132
2	6.53	54	34.1	985	150
	6.26 6.69	52 55	33.1 34.8	963 1001	148 152
3	6.20	38	33.0	933	157
	6.20 6.20	35.4 41.0	32.5 33.4	928 942	156 158
4	6.22	100	36.2	955	132
	5.17 6.30	—	34.4 38.0	911 999	120 145
5	6.66	70	—	917	161
	6.50 7.00	70 70		900 950	150 166
6	6.17	45	35.4	975	145
	6.16 6.18	44 47	34.6 36.3	968 981	139 154
7	5.22	38	28.8	801	131
	5.17 5.31	36.8 40.7	28.3 29.2	788 816	129 133
8	6.59	49	34.4	979	157
	6.53 6.68	48.9 49.9	34.3 34.5	963 987	154 160
9	5.77	104	30.9	893	160
	5.73 5.82	99 111	30.7 31.1	889 894	157 164
10	5.65	217	80.2	903	168
	5.57 5.72	97 337	39.4 121.0	899 908	159 177
11	4.31	—	—	—	—
	4.04 4.52				
12	6.10	53	—	906	—
	6.03 6.15	50 60		899 909	
13	5.83	—	40.4	863	184
	5.76 5.97		39.6 41.5	830 918	167 207
14	6.03	—	38.4	—	154
	5.98 6.09		37.7 38.8		135 171
15	6.15	—	—	—	—
	6.14 6.16				
16	6.13	106	33.3	944	141
	6.13 6.13	106 106	33.3 33.4	942 945	141 141
17	6.11	60	36.6	912	151
	6.06 6.19	55 66	36.0 37.1	906 915	142 160
18	6.23	—	—	—	—
	6.05 6.33				
19	6.33	—	—	1567	353
	6.20 6.50			1550 1580	320 399
20	6.21	20	29.8	972	166
	6.12 6.26	15 25	24.8 34.8	968 976	159 169
21	6.20	101	33.4	604	87
	6.18 6.21	9.9 1.11	32.7 34.3	568 624	83 91
22	5.22	55	36.7	914	149
	5.06 5.31	5.4 5.6	36.0 37.0	900 940	146 150
Table 1Sb_Samples_Lab 1 to 22_Elements K,Na,Zn,Mn,Fe.					

AFintrectb1Sc

	A	B	C	D	E	F
1	Lab. number	Cu	F	Cl	Cd	Pb
2		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
3	B.C.R. Mean	4.9	5.0	688	0.34	2.6
4	Conf. Interval	—	—	665 711	—	—
5						
6	1	—	—	—	—	—
7						
8	2	4.8	—	—	<1.12	<5.6
9						
10	3	4.1	6.3	700	0.36	2.6
11		3.9 4.2	5.7 6.9	690 710	0.35 0.36	2.5 2.6
12	4	4.2	—	654	—	2.4
13		—	—	609 700	—	—
14	5	5.0	—	—	—	—
15		4.7 5.3	—	—	—	—
16	6	3.8	<2.5	726	—	—
17		3.8 3.9	—	701 751	—	—
18	7	4.5	—	—	0.24	—
19		3.50 6.22	—	—	0.24 0.24	—
20	8	4.4	—	645	—	—
21		4.12 4.64	—	—	—	—
22	9	4.6	4.8	—	0.29	1.43
23		4.57 4.60	—	—	0.28 0.30	1.33 1.51
24	10	2.7	—	—	—	6.6
25		26.7 26.9	—	—	—	66 66
26	11	—	—	—	—	—
27						
28	12	—	—	—	—	—
29						
30	13	—	—	—	0.34	—
31					0.33 0.36	—
32	14	5.6	—	—	—	—
33		5.12 6.22	—	—	—	—
34	15	—	—	—	—	—
35						
36	16	4.7	3.59	698	0.22	1.27
37		4.54 4.70	—	—	0.21 0.23	1.24 1.31
38	17	4.5	—	—	0.31	2.57
39		4.04 4.80	—	—	0.29 0.34	2.50 2.60
40	18	—	—	800	—	—
41						
42	19	—	—	—	—	—
43						
44	20	5.0	—	—	—	—
45		4.94 4.98	—	—	—	—
46	21	6.3	—	—	0.33	1.00
47		6.16 6.51	—	—	0.322 0.334	0.94 1.09
48	22	4.0	—	—	—	—
49		4.0 4.0	—	—	—	—
50						

Table 1Sc_Sample S_Lab 1to 22_Elements Cu,F,Cl,Cd,Pb.

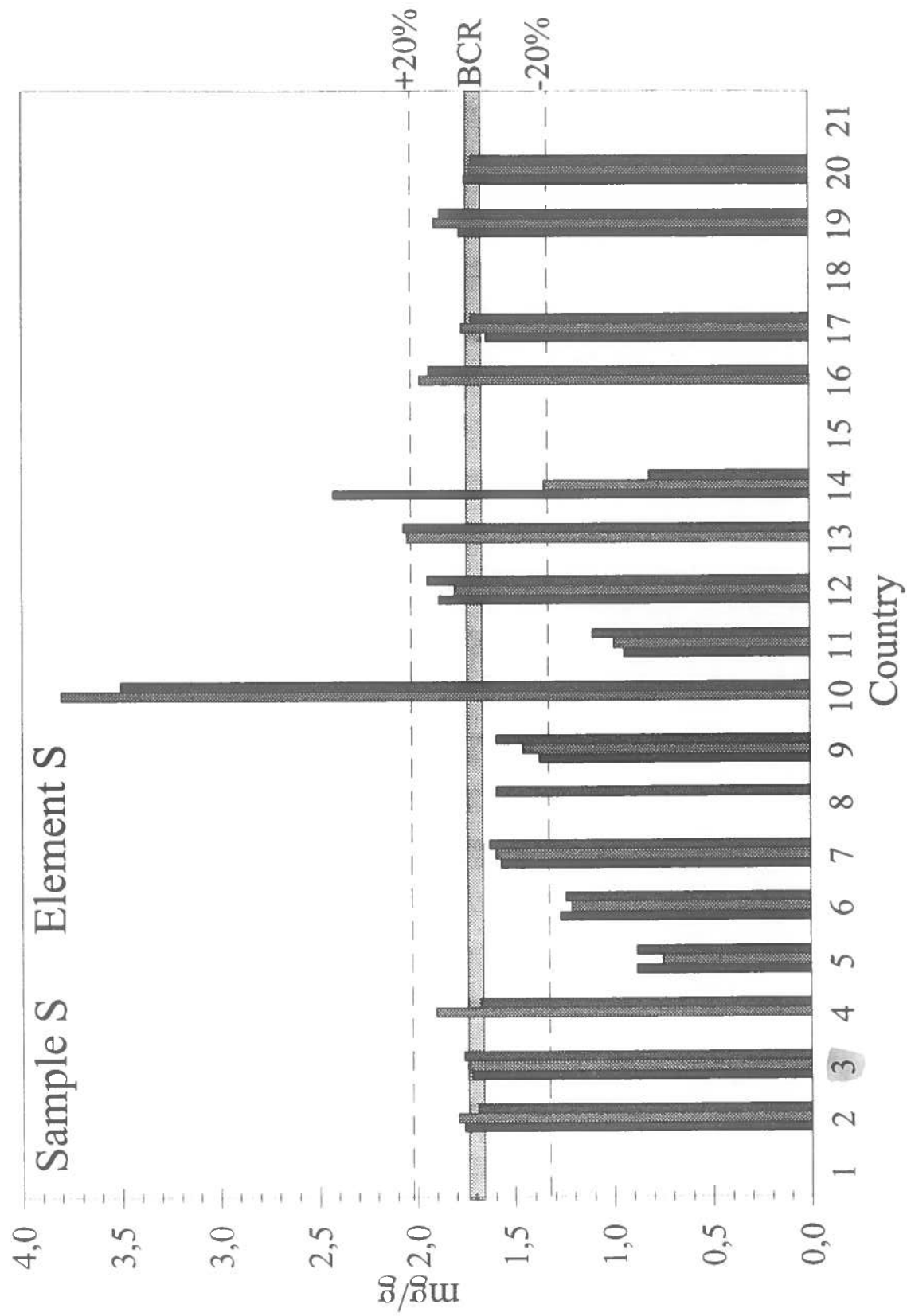
AFintcaltb1Sd

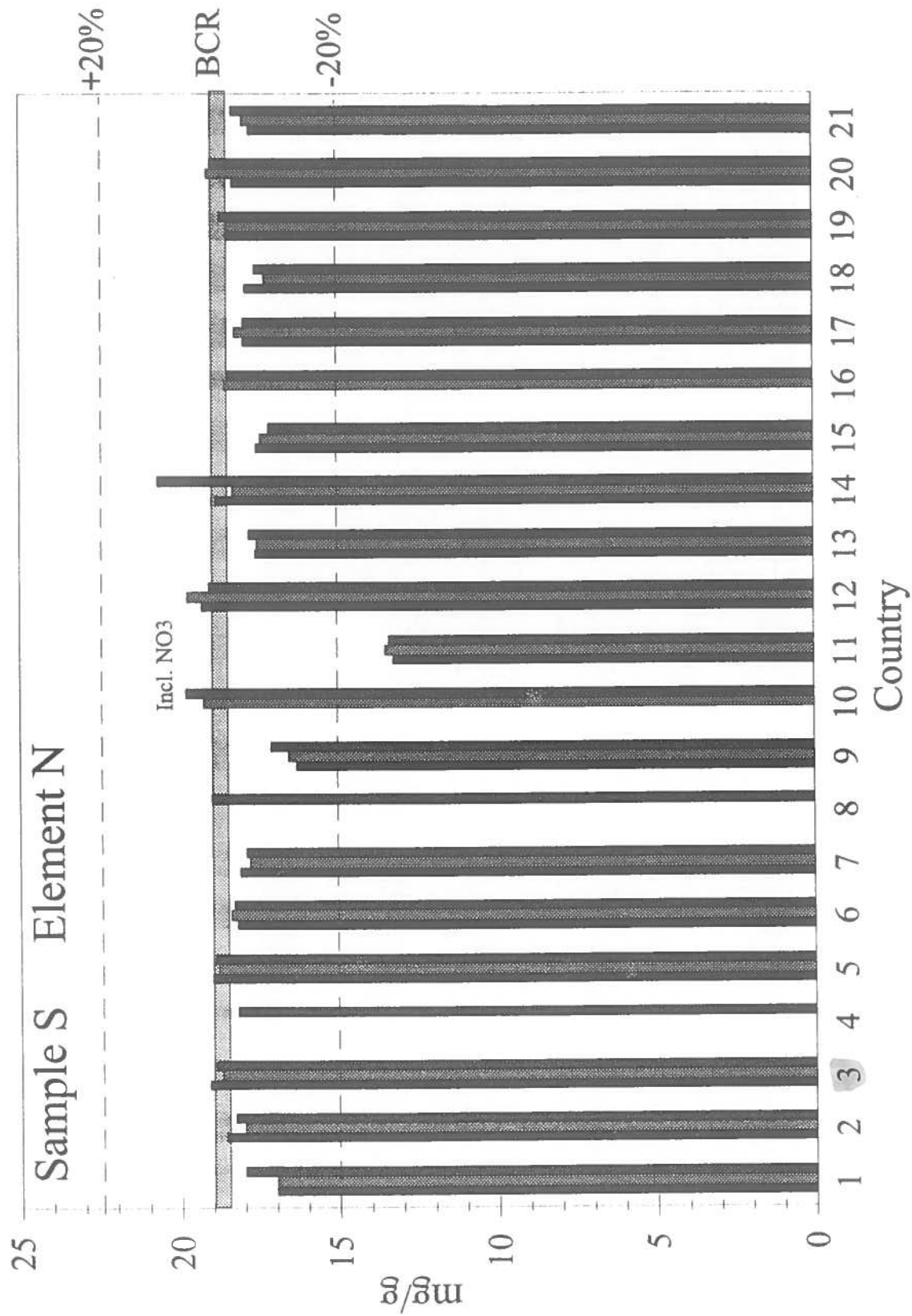
	A	B	C	D	E	F
1	Lab. number	Al	B			
2		mg/kg	mg/kg			
3	B.C.R. Mean	173	23			
4	Conf. Interval	168 178	— —			
5						
6	1	—	—			
7						
8	2	127	11.0			
9		124 129	10.6 11.4			
10	3	—	25.5			
11			25.0 26.4			
12	4	112	—			
13		—	—			
14	5	—	—			
15						
16	6	—	18.6			
17			18.5 18.6			
18	7	114	—			
19		112.3 116.7				
20	8	160	24.3			
21		158.6 164.2	24.2 24.6			
22	9	128	31.9			
23		127.0 128.8	— —			
24	10	237	38.1			
25		159 315	— —			
26	11	—	—			
27						
28	12	—	—			
29						
30	13	—	—			
31						
32	14	—	—			
33						
34	15	—	—			
35						
36	16	124	25.3			
37		— —	25.1 25.5			
38	17	144	—			
39		136 157				
40	18	—	—			
41						
42	19	—	—			
43						
44	20	—	—			
45						
46	21	129	21.2			
47		124.8 132.7	21.1 21.3			
48	22	119	14.3			
49		117 120	13 16			
50						

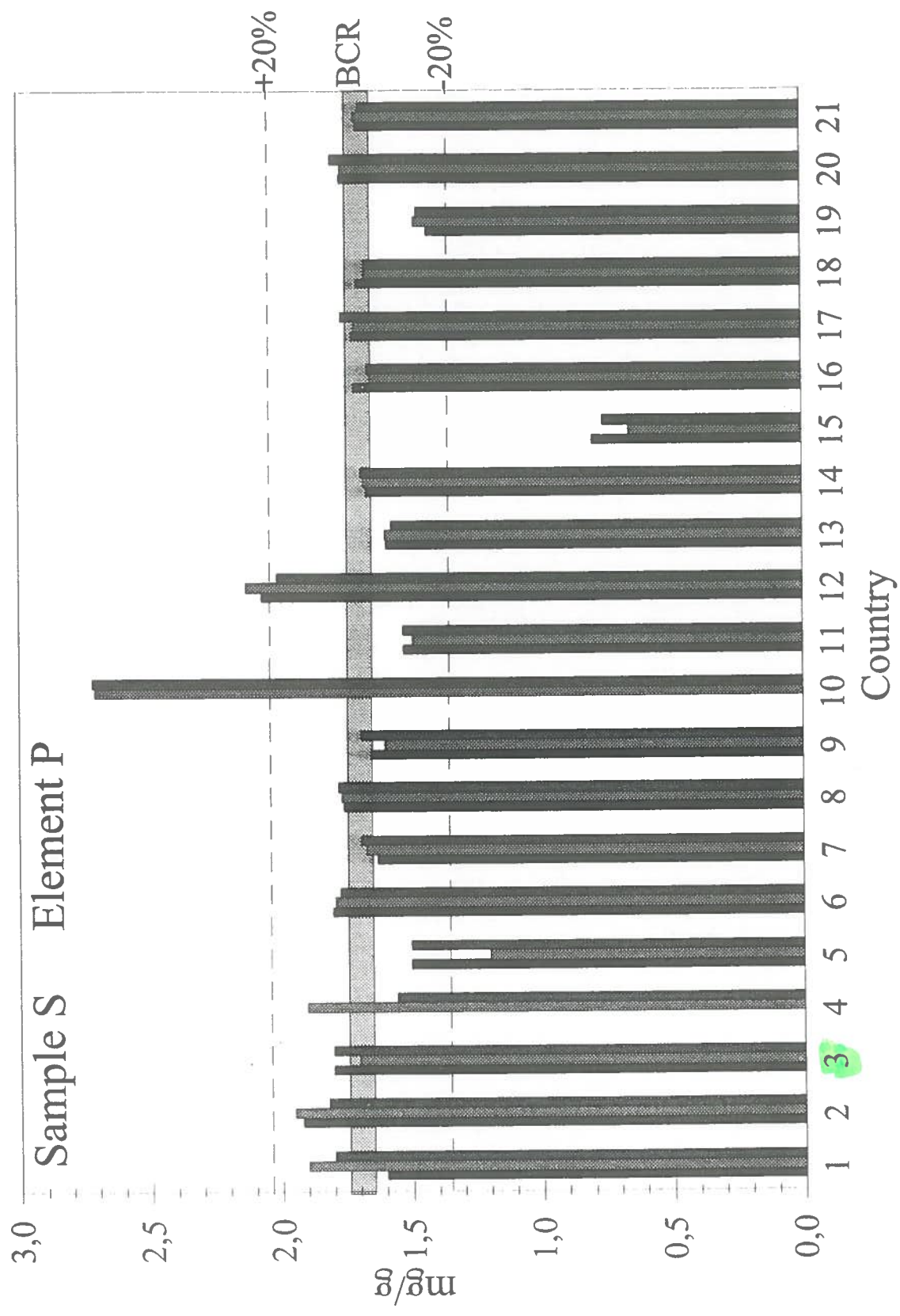
Table 1Sd_Sample S_Lab 1 to 22_Elements AL,B.

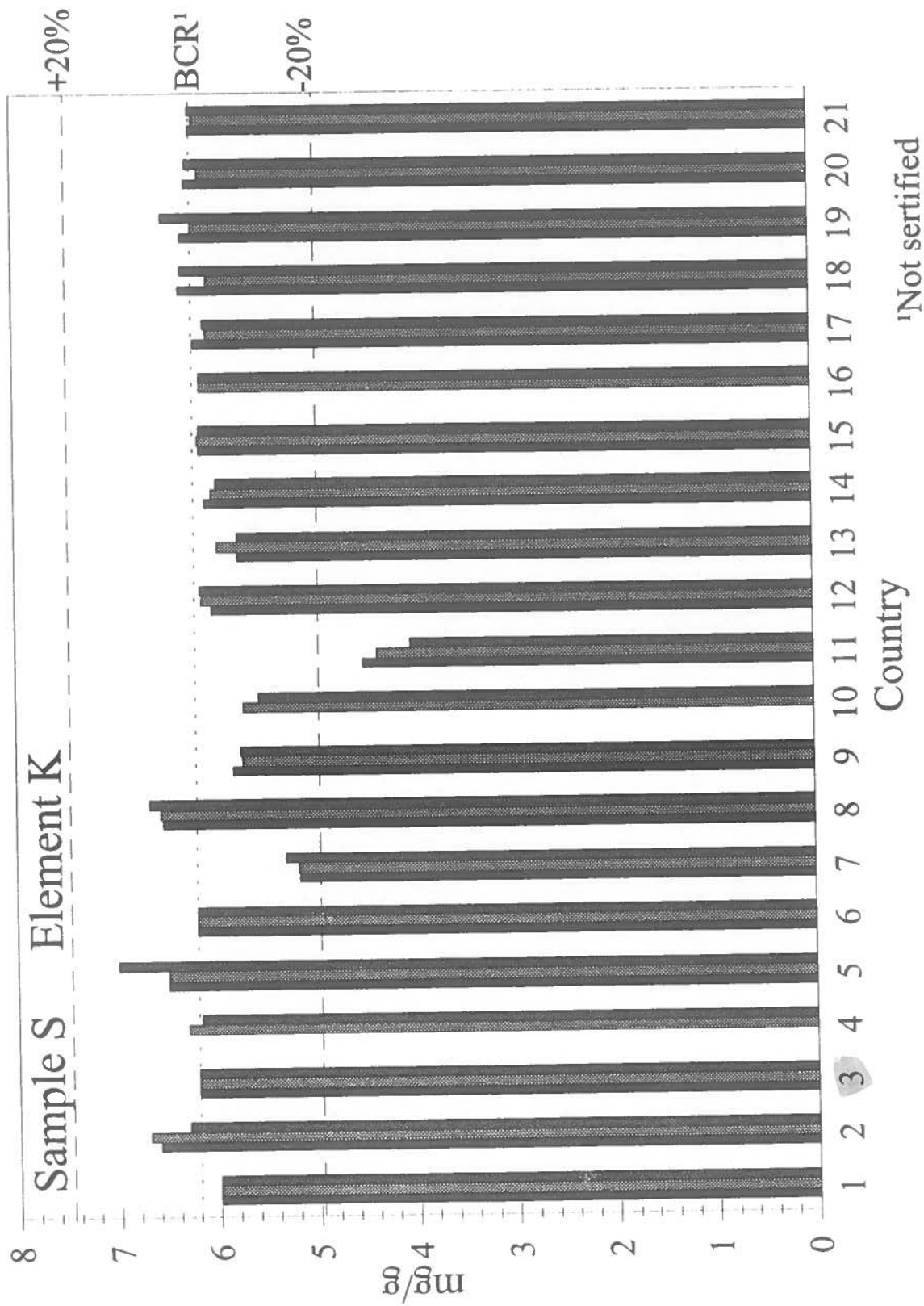
Lab number	Mn	Fe	Cu	F	Cl	Cd	Pb	Al	B
Mean	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
BCR mean	915	151	4.9	5.0	688	0.34	2.6	173	23
1	-24.4	-15.2							
2	+9.4	* -2.0	*				+115.4	-28.3	-53.9
3	* +2.9	* +4.6	-20.4	+38.0	* +3.2	+5.9	* +0.9		+14.8
4	+9.2	-20.5	-15.3		-11.5		-7.7	-35.6	
5	* +3.8	+9.9	+8.2						
6	+7.2	-7.9	-22.4	-50.0	+9.1				-19.6
7	-13.9	-14.6	-28.6			-29.4		-35.1	
8	+7.9	+6.0	-13.9		-6.3			-8.3	+7.0
9	* -2.9	+8.6	-6.7	* -4.0		-17.6	-48.8	-26.6	+38.7
10	* -1.8	+17.2	+449.0					+82.1	+65.7
11									
12	* -1.8								
13	+9.3	+37.1				+5.3			
14		+13.2	+26.9						
15									
16	* +3.3	-6.6	-7.3	-28.2	+14.5	-38.2	-52.3	-22.3	+10.9
17	* -1.0	+6.0	-17.5			-14.7	* -3.8	-21.4	
18					+16.3				
19	+72.7	+164.2							
20	+6.7	+11.9	* +1.6						
21	-37.9	-45.0	+32.9			*	-63.8	-27.9	-8.3
22	* -1.6	* -3.3	-18.4					-32.4	-43.5

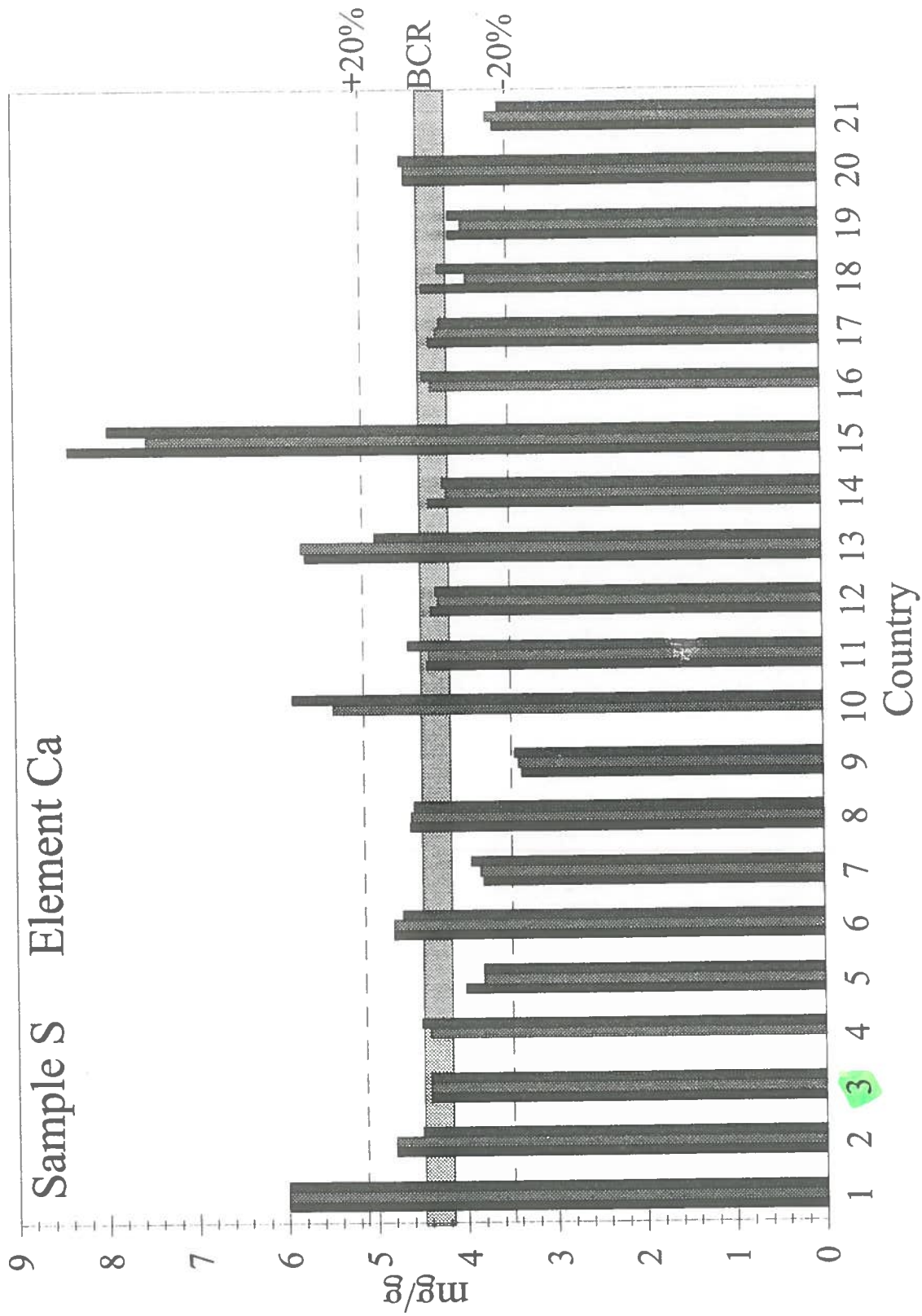
Table 5Sb Sample S Max difference with BCR R mean % Mn, Fe, Cu, F, Cl, Cd, Pb, Al, B.

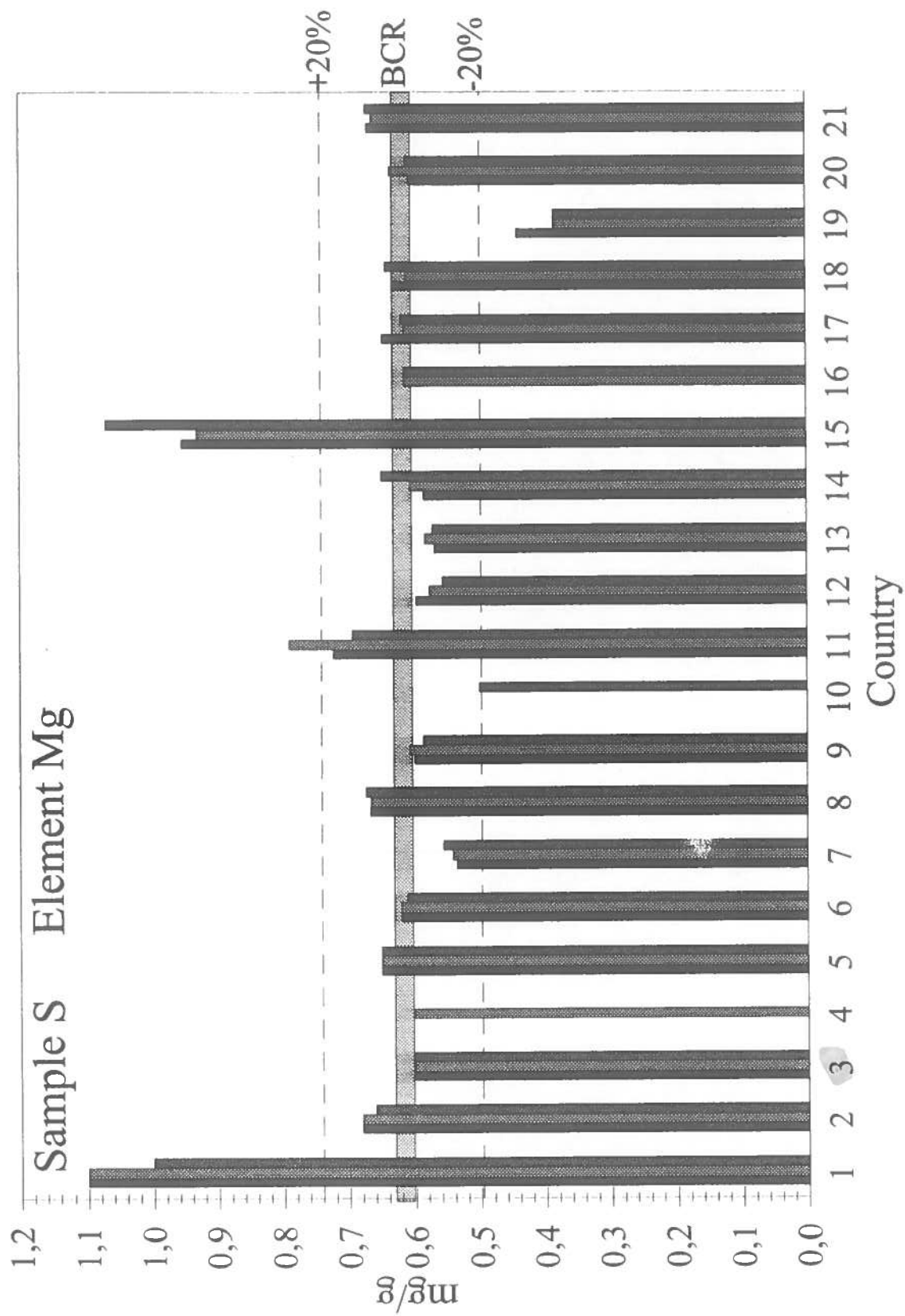


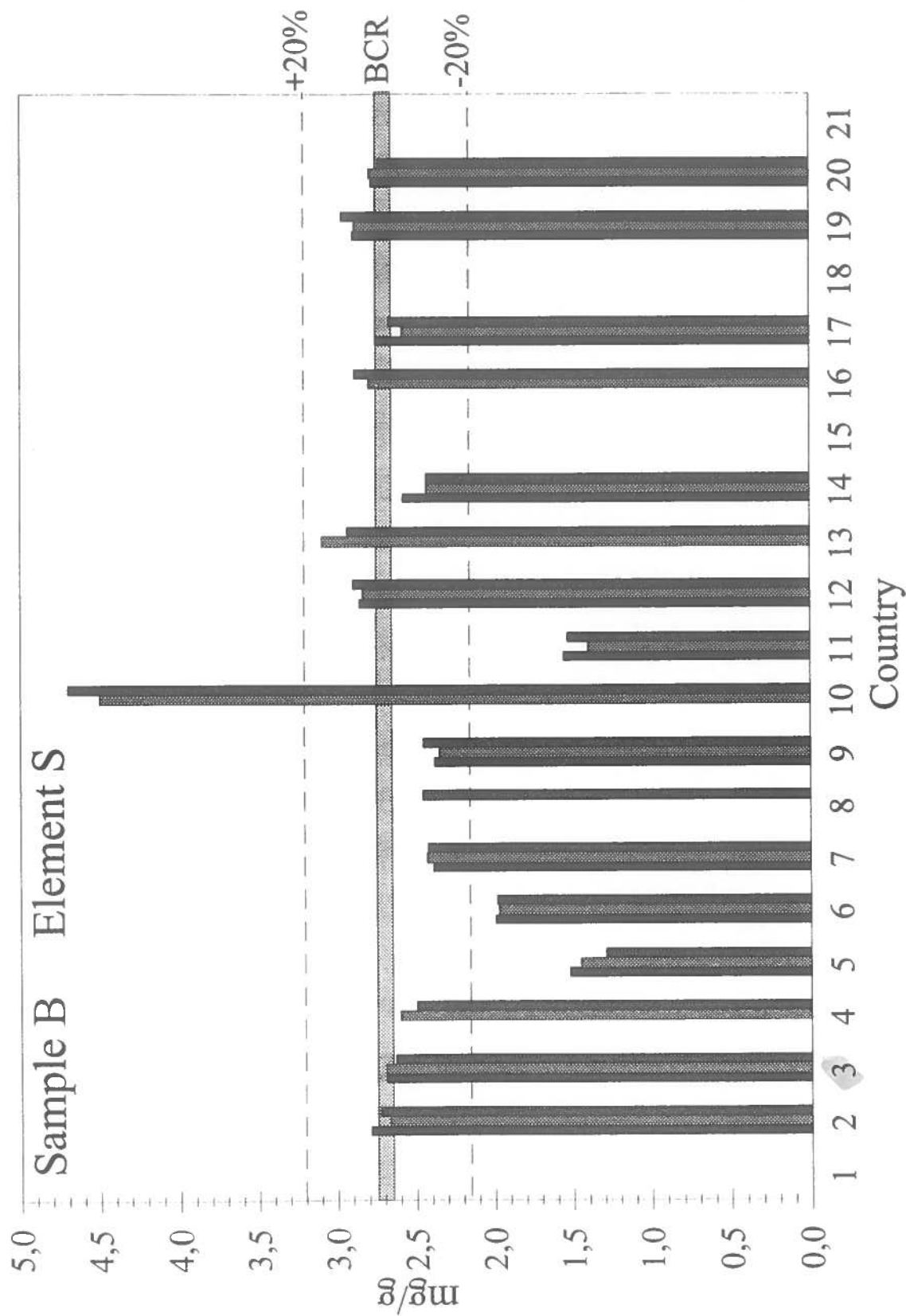


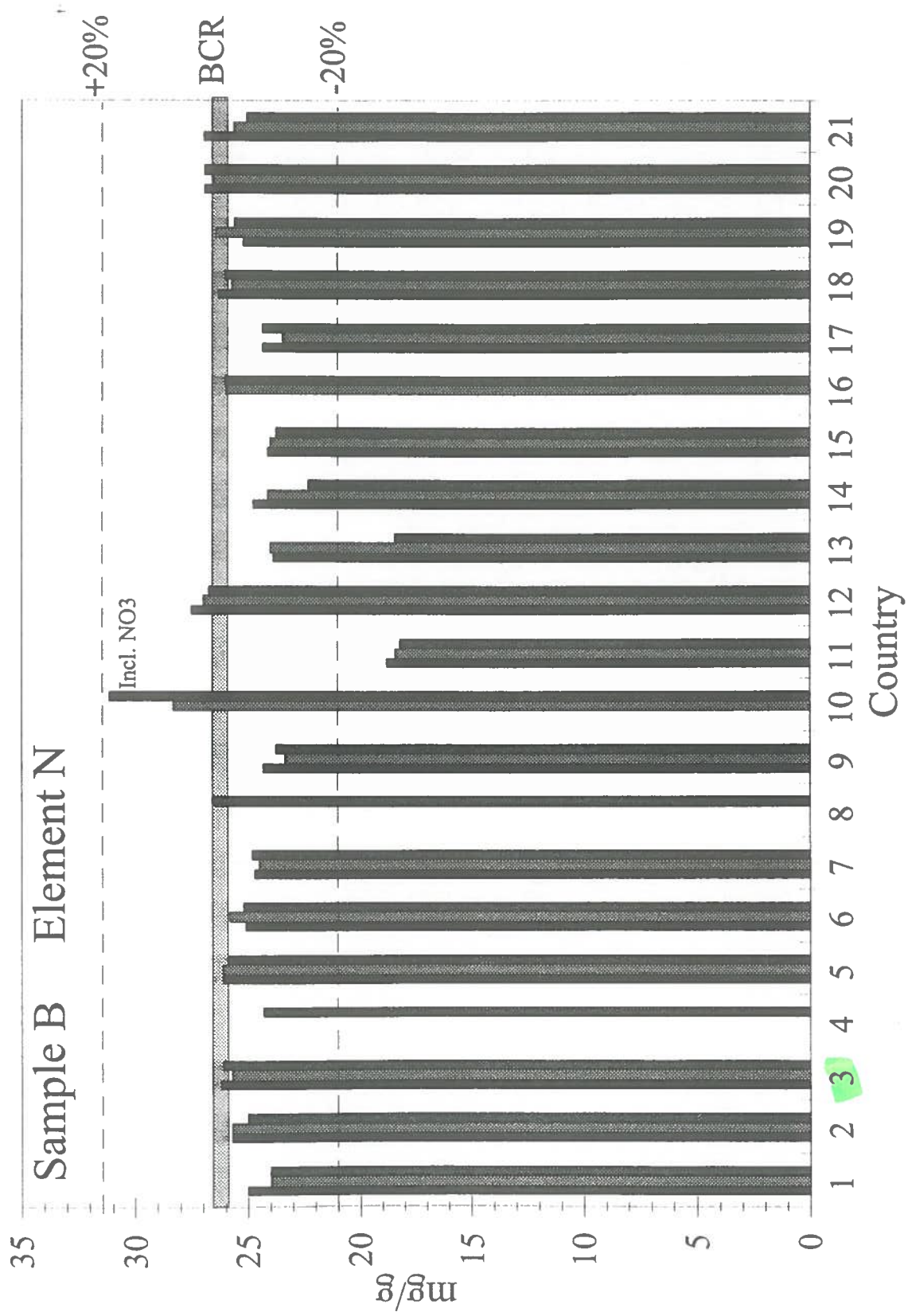


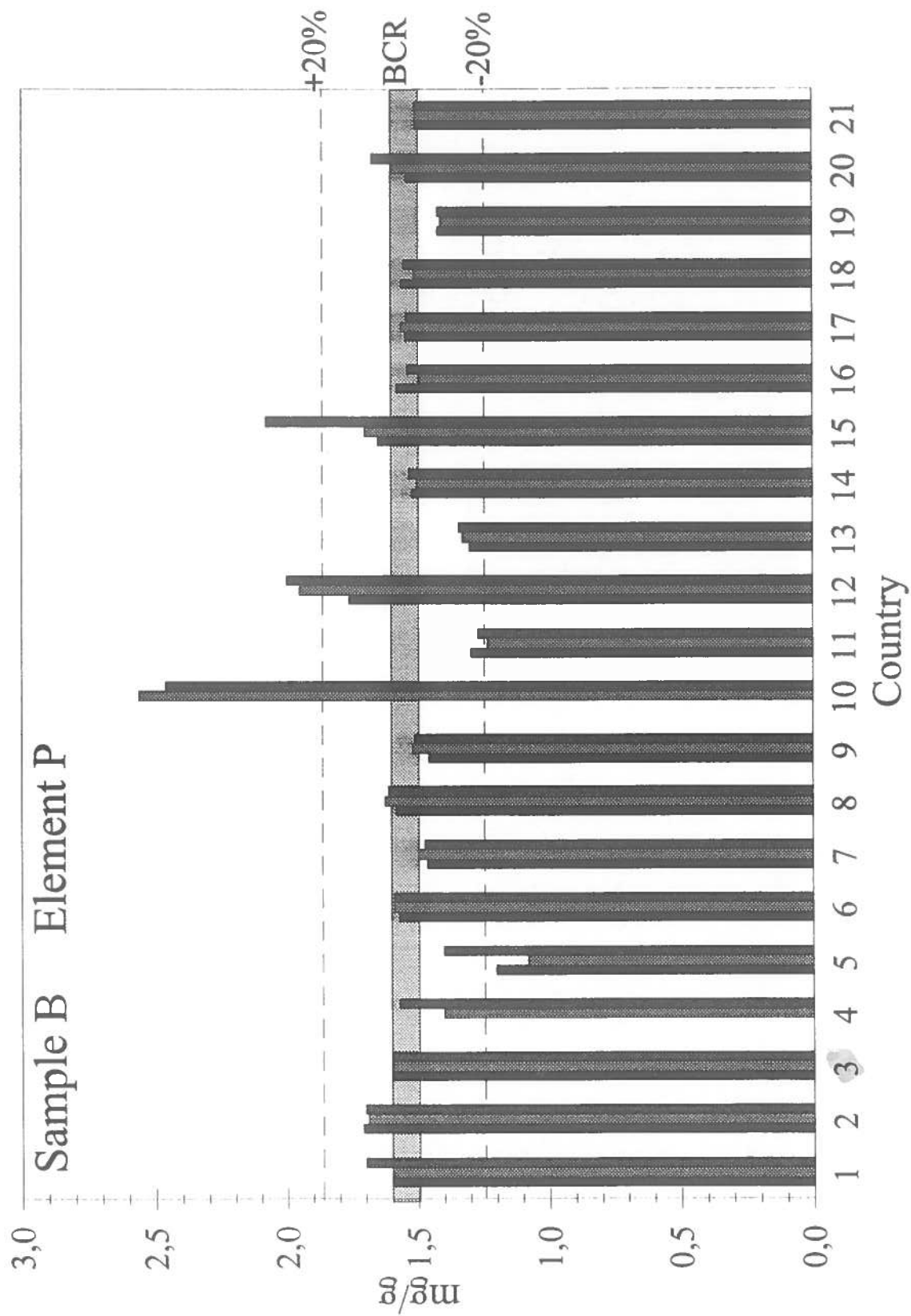


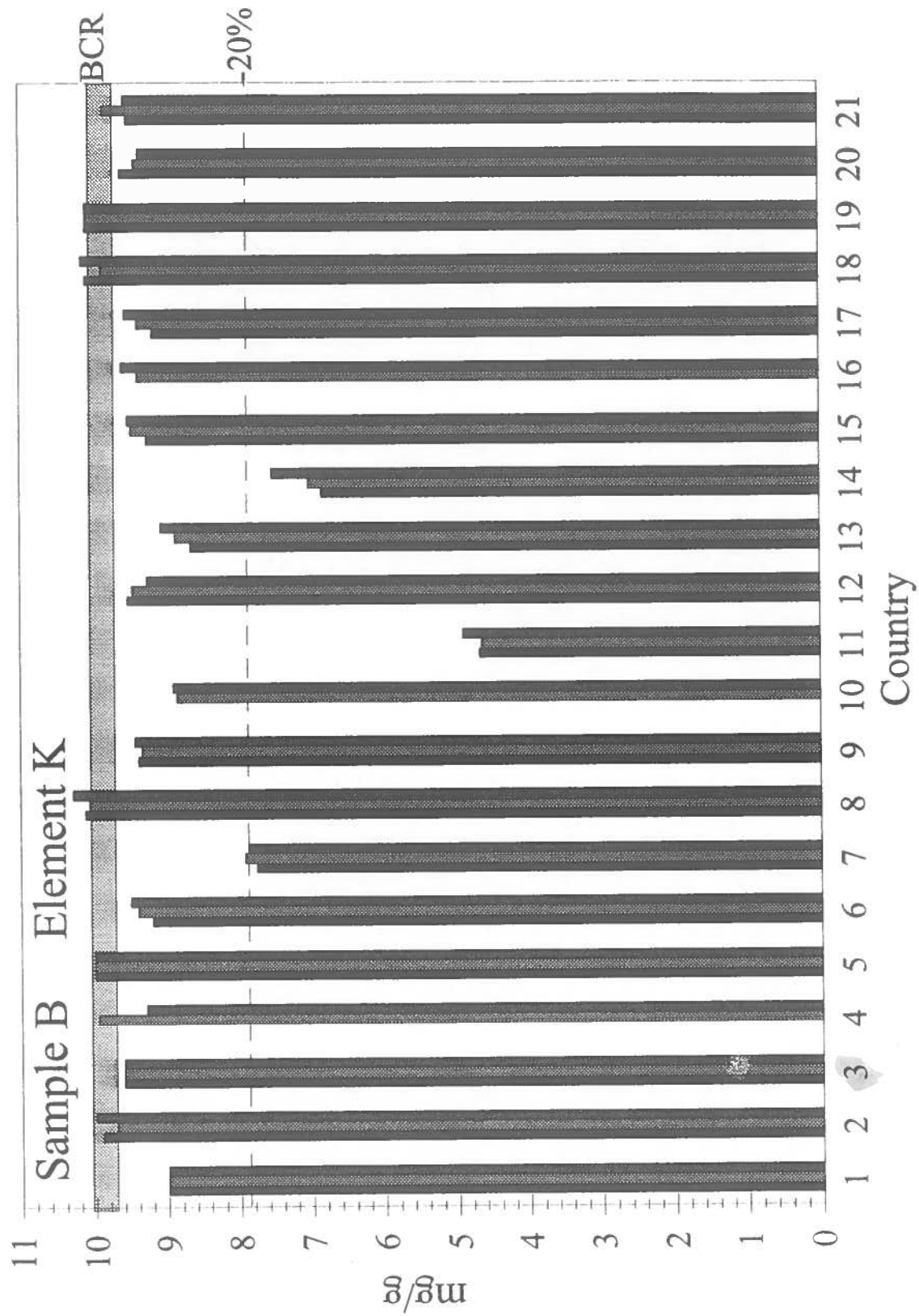


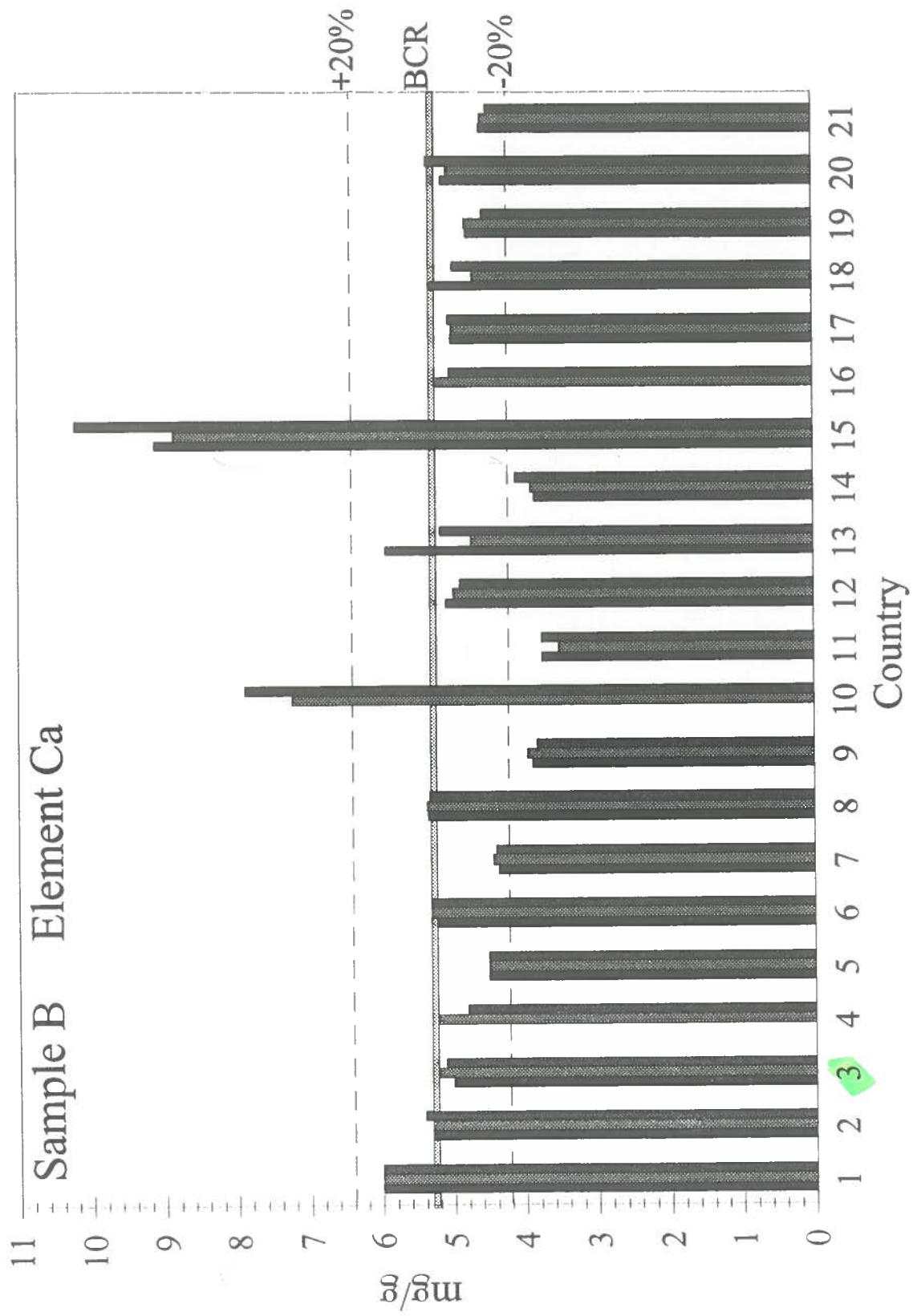


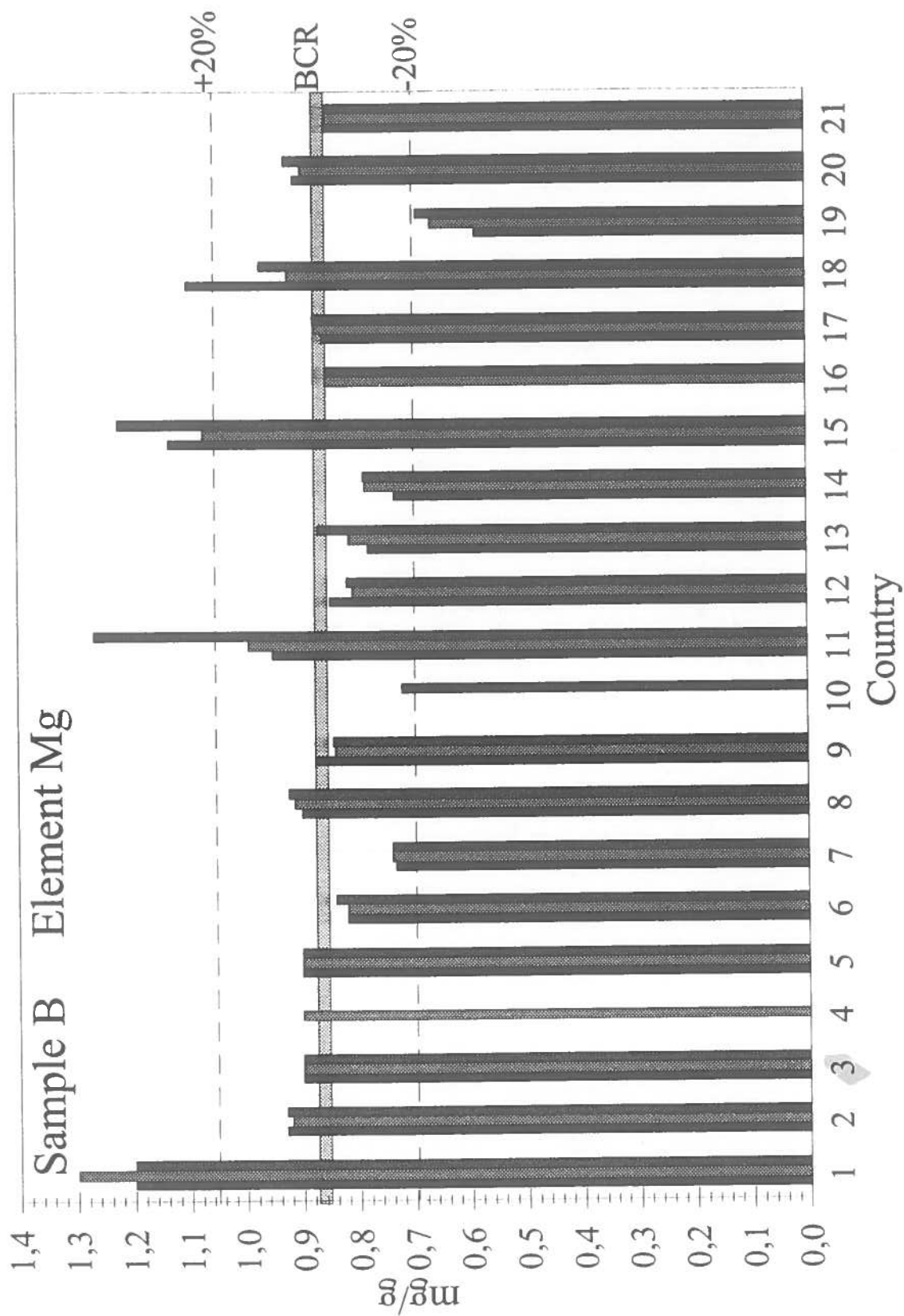












Lab	Method		B	S
1	Kjeldahl	Dist.	G -	G -
2	Kjeldahl	F I A	E	E
3	Kjeldahl	Tit.	E	E
4	Kjeldahl	Tit.	G -	E
5	Kjeldahl	Tit.	E	E
6	CHN		E	E
7	CHN		G -	G -
8	Kjeldahl	Tit.	E	E
9	H ₂ SO ₄	Tit.	g -	p -
10	Kjeldahl		p +	E
11	H ₂ SO ₄	Tit.	p -	p -
12	CHN		E	E
13	Kjeldahl	Tit.	p -	G -
14	Kjeldahl	Spec. electr.	p -	G+
15	Kjeldahl	Tit.	G -	G -
16	Kjeldahl	Tit.	E	E
17	Kjeldahl	Colorim.	p -	E
18	H ₂ SO ₄ + H ₂ O ₂	Colorim.	E	G -
19	CHN		E	E
20	CHN		E	E
21	Kjeldahl	Tit.	E	G -
22	CHN		E	G-

Table 6N

E ; <+ 5% from BCR mean ; G : < 10% ;
g : < 15% : p : > 15%

Lab	Method	B	S
1	—	—	—
2	HNO ₃ + HClO ₄ I C P	E	E
3	Integr. comb. -determ. C_S	E	E
4	X - Ray determination	G -	g +
5	Ashing with MgNO ₃ Turbid.	p -	p -
6	HNO ₃ microw. oven I C P	p -	p -
7	HNO ₃ + H ₂ O ₂ I C P	g -	G -
8	HNO ₃ +HClO ₄ I C P	G -	G -
9	Ashing with AgO ₂ +NaHCO ₃ Ion chrom.	g -	p -
10	Ashing MgNO ₃ ?	p +	p +
11	Ashing Colorimetry	p -	p -
12	Integr? comb. _ determ. C_S	G+	g +
13	Ashing Conductimetry	g +	p +
14	Ashing with MgNO ₃ Turbidimetry	G -	p -
15	—	—	—
16	HClO ₄ +HNO ₃ + CaCl ₂ Colorimetry	G+	p +
17	Acid digest., microw. ov. I C P	E	E
18	—	—	—
19	Integr. comb. determ. C_S	G+	g +
20	Integr. comb. - determ. C_S	E	E
21	—	—	—
22	HNO ₃ + HClO ₄ I C P	p -	G -

Table 6 S E :< 5% from BCR mean ; G <10% ;
g : <15% ; p : > 15% .

Lab	Method	B	S
1	H ₂ SO ₄ +HClO ₄ Colorimetry	G+	g+
2	HNO ₃ + HClO ₄ I C P	g+	p+
3	HNO ₃ + H ₂ SO ₄ I C P	E	G+
4	X - Ray determination	G-	g+
5	Ashing Colorimetry	p -	p -
6	Ashing I C P	E	G+
7	HNO ₃ + H ₂ O ₂ I C P	G-	G-
8	Ashing, SiO ₂ elimin. I C P	E	G+
9	Ashing Colorimetry	G-	G-
10	Ashing +digestion Colorimetry	p+	p+
11	Ashing Colorimetry	p -	g -
12	HNO ₃ microw. oven Colorimetry	p+	p+
13	HNO ₃ +HClO ₄ Colorimetry	p -	G-
14	Ashing Colorimetry	E	E
15	HNO ₃ +H ₂ O ₂ Colorimetry	p+	p -
16	H ₂ SO ₄ +H ₂ O ₂ Colorimetry	E	E
17	Acid digest., microw. ov. I C P	E	E
18	H ₂ SO ₄ +H ₂ O ₂ Colorimetry	E	E
19	HNO ₃ +H ₂ O ₂ microw. oven Colorimetry	G-	p -
20	HNO ₃ microw. oven Colorimetry	G+	G+
21	Ashing D C P	E	E
22	HNO ₃ + HClO ₄ I C P	g -	G-

Table 6P E : < 5% from BCR mean ; G : < 10% ;

g : <15% ; p : > 15% .

Lab	Method	B	S
1	H ₂ SO ₄ + HClO ₄ Fl. emiss.	g+	p+
2	HNO ₃ + HClO ₄ I C P	E	g+
3	HNO ₃ + H ₂ SO ₄ I C P	G-	E
4	X - Ray determination	G-	G+
5	HNO ₃ +HClO ₄ A A S	G-	g -
6	Ashing I C P	E	g+
7	HNO ₃ + H ₂ O ₂ I C P	p -	g -
8	Ashing, SiO ₂ elimin. I C P	E	G+
9	Ashing Flame emission	p -	p -
10	Ashing + Digest. A A S	p+	p+
11	Ashing Titrimetry	p -	G+
12	HNO ₃ microw. oven A A S	G-	E
13	HNO ₃ +HClO ₄ A A S	g+	p+
14	Ashing A A S	p -	E
15	HNO ₃ +H ₂ O ₂ A A S	p+	p+
16	H ₂ SO ₄ + H ₂ O ₂ Fl. emiss.	G-	E
17	Acid digest., microw. ov. I C P	G-	E
18	H ₂ SO ₄ + H ₂ O ₂ D C P	g -	G-
19	HNO ₃ + H ₂ O ₂ microw. oven A A S	g -	G-
20	HNO ₃ microw. oven I C P	E	G+
21	Ashing D C P	p -	p -
22	HNO ₃ + HClO ₄ I C P	g -	E

Table 6Ca E : < 5% from BCR mean ; G : < 10% ;
g : < 15% ; p : > 15% .

Lab	Method	B	S
1	H ₂ SO ₄ +HClO ₄ A A S	p+	p+
2	HNO ₃ + HClO ₄ I C P	G+	G+
3	HNO ₃ + H ₂ SO ₄ I C P	E	E
4	X - Ray determination	E	E
5	HNO ₃ +HClO ₄ A A S	E	E
6	Ashing I C P	G-	E
7	HNO ₃ + H ₂ O ₂ I C P	p -	g -
8	Ashing, SiO ₂ elimin. I C P	E	G+
9	Ashing A A S	E	G-
10	Ashing + Digest. A A S	p -	p -
11	Ashing Titrimetry	p+	p+
12	HNO ₃ microw. oven A A S	G-	G-
13	HNO ₃ +HClO ₄ A A S	g -	G-
14	Ashing A A S	p -	G-
15	HNO ₃ +H ₂ O ₂ A A S	p+	p+
16	HNO ₃ +HClO ₄ + H ₂ SO ₄ A A S	E	E
17	Acid digest., microw. ov. I C P	E	E
18	H ₂ SO ₄ + H ₂ O ₂ D C P	p+	E
19	HNO ₃ + H ₂ O ₂ microw. oven A A S	p -	p -
20	HNO ₃ microw. oven I C P	E	E
21	Ashing D C P	E	G+
22	HNO ₃ + HClO ₄ I C P	G-	G-

Table 6Mg E : < 5% from BCR mean ; G : <10% ;
g : < 15% ; p : >15% .

Lab	Method	B	S
1	H2SO4 + HClO4 Fl. emiss.	g -	G -
2	HNO3 + HClO4 I C P	E	G+
3	HNO3 + H2SO4 I C P	E	E
4	X - Ray determination	G -	E
5	HNO3 + H2SO4 Fl. emiss.	E	g+
6	Ashing I C P	G -	E
7	HNO3 + H2O2 I C P	p -	p -
8	Ashing, SiO2 elimin. I C P	E	G+
9	Ashing AAS Fl. emiss.	G -	G -
10	Ashing + Digest. A A S	g -	g -
11	Ashing Fl. emiss.	p -	p -
12	HNO3 ,microw. ov. Fl. emiss.	G -	E
13	HNO3 + HClO4 Fl. emiss.	g -	G -
14	Ashing A A S	p -	E
15	HNO3 + H2O2 Fl. emiss.	G -	E
16	H2SO4 + H2O2 Fl. emiss.	G -	E
17	Acid digest., microw. ov. I C P	G -	E
18	H2SO4 + H2O2 D C P	E	E
19	HNO3 + H2O2 microw. ov. Fl. emiss.	E	E
20	HNO3 Fl. emiss.	G -	E
21	Ashing D C P	E	E
22	HNO3 + HClO4 I C P	p -	p -

Table 6K E : < 5% from BCR mean ; G : <10% ;
g : < 15% ; p : > 15% .

Lab	Method	B	S
1	—	—	—
2	HNO ₃ + HClO ₄ I C P	G-	g -
3	HNO ₃ + HF press. dig. I C P	—	p -
4	X - Ray determination	p+	p+
5	HNO ₃ + H ₂ SO ₄ Fl. emiss.	g -	p+
6	Ashing I C P	p -	p -
7	HNO ₃ + H ₂ O ₂ I C P	p -	p -
8	Ashing, SiO ₂ elimin. I C P	E	p -
9	Ashing Fl. emiss.	p+	p+
10	Ashing + Digest. A A S	p+	p+
11	—	—	—
12	HNO ₃ .microw. ov. Fl. emiss.	g -	p -
13	—	—	—
14	—	—	—
15	—	—	—
16	H ₂ SO ₄ + H ₂ O ₂ Fl. emiss.	p+	p+
17	Acid digest., microw. ov. I C P	G-	G+
18	—	—	—
19	—	—	—
20	HNO ₃ microwave oven Fl. emiss.	p+	p -
21	Ashing D C P	p+	p+
22	HNO ₃ + HClO ₄ I C P	p -	G-

Table 6 Na

E ; <+- 5% from BCR mean ;G : < 10% ;
g : < 15% : p :>15%

Lab	Method	B	S
1	—	—	—
2	—	—	—
3	HNO3 Titr. AgNO3	E	E
4	X - Ray determination	g -	g -
5	—	—	—
6	Shoniger comb. Ion chrom.	G+	G+
7	—	—	—
8	Ashing with MgO +KOH Titr. AgNO3	p -	G-
9	—	—	—
10	—	—	—
11	—	—	—
12	—	—	—
13	—	—	—
14	—	—	—
15	—	—	—
16	HNO3 K2SO4 and AG electr.	G+	g+
17	—	—	—
18	Cold H2O Ion electr.	p -	—
19	—	—	—
20	—	—	—
21	—	—	—
22	—	—	—

Table 6Cl E : < 5% from BCR mean ; G : < 10% ;
g. <15% ; p: > 15%

Table 6Fe

Lab	Method	B	S
1	H ₂ SO ₄ + HClO ₄ A A S	G-	p-
2	HNO ₃ HClO ₄ microw.oven I C P	g-	E
3	HNO ₃ + H ₂ SO ₄ I C P	E	E
4	X - Ray determination	p-	p-
5	HNO ₃ +HClO ₄ A A S	p-	G+
6	Ashing I C P	G-	G-
7	HNO ₃ + H ₂ O I C P	p-	g-
8	Ashing, SiO ₂ elimin. I C P	G+	G+
9	Ashing A A S	E	G+
10	Ashing + Digest. A A S	g+	p+
11	—	—	—
12	—	—	—
13	HNO ₃ +HClO ₄ A A S	G-	p+
14	Ashing A A S	p-	g+
15	—	—	—
16	HNO ₃ + HClO ₄ + H ₂ SO ₄ A A S	E	G-
17	Acid digest., microw. ov. I C P	E	G+
18	—	—	—
19	HNO ₃ + H ₂ O ₂ microw. oven A A S	p+	p+
20	HNO ₃ Microw. oven A A S	G+	g+
21	Ashing D C P	p-	p-
22	HNO ₃ + HClO ₄ I C P	E	E

Table 6 Fe E : < 54% from BCR mean ; G : <10 % ;
g : < 15% ; p : >15% .

Table 6Mn

Lab	Method	B	S
1	H ₂ SO ₄ + HClO ₄ A A S	p -	p -
2	HNO ₃ + HClO ₄ I C P	G -	G +
3	HNO ₃ + H ₂ SO ₄ I C P	E	E
4	X - Ray determination	G -	G +
5	HNO ₃ +HClO ₄ A A S	E	E
6	Ashing I C P	G -	G +
7	HNO ₃ + H ₂ O I C P	p -	g -
8	Ashing, SiO ₂ elimin. I C P	G +	G +
9	Ashing A A S	g -	E
10	Ashing + Digest. A A S	E	E
11	—	—	—
12	HNO ₃ microw. oven A A S	E	E
13	HNO ₃ +HClO ₄ A A S	E	G +
14	—	—	—
15	—	—	—
16	HNO ₃ + HClO ₄ + H ₂ SO ₄ A A S	E	E
17	Acid digest., microw. ov. I C P	E	E
18	—	—	—
19	HNO ₃ + H ₂ O ₂ microw. oven A A S	p +	p +
20	HNO ₃ Microw. oven A A S	G +	G +
21	Ashing D C P	p -	p -
22	HNO ₃ + HClO ₄ I C P	E	E

Table 6 Mn E : < 5% from BCR mean ; G : < 10% ;
g : < 15% ; p : > 15% .

Table 6Cu

Lab	Method	B	S
1	—	—	—
2	HNO ₃ HClO ₄ microw.oven I C P	g -	E
3	HNO ₃ + HF I C P	—	p -
4	X - Ray determination	p -	p -
5	HNO ₃ +HClO ₄ A A S	p -	G -
6	Ashing I C P	p -	p -
7	HNO ₃ + H ₂ O I C P	p -	p -
8	Ashing, SiO ₂ elimin. I C P	p -	g -
9	Ashing A A S	p -	G -
10	Ashing + Digest. A A S	p +	p +
11	—	—	—
12	—	—	—
13	—	—	—
14	Ashing A A S	—	p +
15	—	—	—
16	HNO ₃ + HClO ₄ + H ₂ SO ₄ A A S	G -	G -
17	Acid digest., microw. ov. I C P	g -	p -
18	—	—	—
19	—	—	—
20	HNO ₃ Microww. oven A A S	p -	E
21	Ashing D C P	p -	p +
22	HNO ₃ + HClO ₄ I C P	p -	p -

Table 6 Cu E : <5% from BCR mean; G : <10%;
g : <15%; p : >15% .

NITROGEN

E : excellent; **G** : good; **g** : fairly good; **p** : poor.

Method	Mark	Sample B	Sample S	B + S
Kjeldahl + catalyst + titration	E	5	5	10
	G	3	4	7
	g	0	0	0
	p	1	0	1
Kjeldahl + catalyst + FIA	E	1	1	2
	G	0	0	0
	g	0	0	0
	p	0	0	0
Kjeldahl + electroded	E	0	1	1
	G	0	0	0
	g	1	0	1
	p	0	0	0
Kjeldahl + colorimetry	E	0	1	1
	G	0	0	0
	g	1	0	1
	p	0	0	0
H ₂ SO ₄ + H ₂ O ₂ + colorimetry	E	1	0	1
	G	0	1	1
	g	0	0	0
	p	0	0	0
H ₂ SO ₄ only + titration	E	0	0	0
	G	0	0	0
	g	1	0	1
	p	1	2	3
Element analysis CHN	E	5	5	10
	G	1	1	2
	g	0	0	0
	p	0	0	0

- 1) Kjeldahl + catalyst or H₂O₂ : all methods are good (not always good by electroded);
- 2) H₂SO₄ alone : bad;
- 3) Integrated combustion and detection : very good.

TOTAL : 24 E, 1 G+, 11 G-, 1p+, 7 (g + p)-

S U L P H U R

Method		Sample B		B + S
Integrated combustion and determination C- S app.	E	2	2	4
	G	2	0	2
	g	0	2	2
	p	0	0	0
Acid digestion Room pressure	ICP	E	0	0
		G	1	3
		g	1	0
		p	1	0
	Spectrophotometry	E	0	0
		G	1	0
		g	0	0
		p	0	1
	Microwave oven HNO ₃ +HClO ₄	E	2	2
		G	0	0
		g	0	0
		p	0	0
	HNO ₃ only or not described	E	0	0
		G	0	0
		g	0	0
		p	1	1
Dry ashing with Mg(NO ₃) ₂	Turbidimetry	E	0	0
		G	1	0
		g	0	0
		p	2	3
	with AgO ₂ + NaHCO ₃ , Ion chrom.	E	0	0
		G	0	0
		g	1	0
		p	0	1
	without addition	E	0	0
		G	0	0
		g	1	0
		p	1	2
X-ray determination	E	0	0	0
	G	1	0	1
	g	0	1	1
	p	0	0	0

- C.S. apparatus and Acid digestion are better than dry ashing.

$$\text{CS/Acid dig./ashing, } 6(E+G) - 2(g+p) / 9(E+G) - 5(g+p) / 1(E+G) - 11(g+p) \\ = 75 - 25 / 64 - 36 / 8 - 92 \%$$

- Room pressure and microwave oven are not very different.

- Acid digestion with HClO₄ is better than without HClO₄.

- X-ray is not very good.

- The not excellent results are mainly lower than BCR : $16 < \text{BCR} / 11 > \text{BCR}$.

PHOSPHORUS

Method	Mark	Sample B	Sample S	B+S
Ashing + colorimetry + ICP or DCP	E	1	1	2
	G	1	1	2
	g	0	0	0
	p	1	1	2
	E	2	1	3
	G	1	2	3
	g	0	0	0
	p	0	0	0
Acid digestion + colorimetry + ICP	E	2	2	4 (1)
	G	2	1	3
	g	0	1	1
	p	5	5	10 (1)
	E	2	1	3
	G	2	4	6
	g	2	0	2
	p	0	1	1
X-Ray determination	E	0	0	0
	G	1	0	1
	g	0	1	1
	p	0	0	0

(1) : without HClO₄

CONCLUSION : Different methods are used, which have not very different qualities. Ashing and acid digestion seem equivalent. Colorimetry seems equivalent to ICP-DCP. In case of acid digestion without HClO₄ (HCl, HNO₃, HNO₃ + H₂O₂, H₂SO₄ + H₂O₂) several results by colorimetry are poor, but several others are excellent or good.

TOTAL : 13 E, 6 G +, 8 G -, 9 (g + p) +, 8 (g + p) -

CALCIUM

Method	Mark	Sample B	Sample S	B + S	
Acid digestion	ICP	E	2	2	4
		G	2	1	3
		g	2	2	4
		p	1	0	1
	AAS	E	1	1	2
		G	2	2	4
		g	2	1	3
		p	2	3	5
	Flame emission	E	0	1	1
		G	1	0	1
		g	1	0	1
		p	0	1	1
Dry Ashing	ICP	E	2	0	2
		G	0	1	1
		g	0	1	1
		p	1	1	2
	AAS	E	0	1	1
		G	0	0	0
		g	0	0	0
		p	1	0	1
	Flame emission + titration (t)	E	0	0	0
		G	0	1	1
		g	0	0	0
		p	2	1	3
X-Ray determination	G	1	1	2	

CONCLUSION : No clear differences between methods .

Ac. digestion/ashing : 15 (E + G), 15 (g + p), 4 (E + G), 6 (g + p)
= 50 - 50 / 40 - 60 %.

Ac. digestion with HClO_4 / Ac. digestion without HClO_4 :
3 (E + G), 7 (g + p) / 10 (E + G), 8 (g + p)
= 30 - 70 / 55 - 45 %.

ICP / AA / Fl. Em. :
10 (E + G), 8 (g + p) / 7 (E + G), 9 (g + p) / 2 (E + G), 4 (g + p)
= 56, 44 / 44, 56 / 35 - 65 %.

A weak advantage to ICP.

TOTAL : 10 E, 4 G +, 8 G -, 10 (g + p) +, 12 (g + p) -

MAGNESIUM

Method		Mark	Sample B	Sample S	B + S
Acid digestion	ICP	E	3	3	6
		G	2	3	5
		g	0	1	1
		p	2	0	2
	AAS	E	3	3	6
		G	1	2	3
		g	1	0	1
		p	2	2	4
	Fl. emiss.	E	0	0	0
		G	0	0	0
		g	0	0	0
		p	1	1	2
Dry ashing	ICP	E	2	1	3
		G	1	2	3
		g	0	0	0
		p	0	0	0
	AAS	E	1	0	1
		G	0	2	2
		g	0	0	0
		p	2	1	3
	Titration	p	1	1	2
X-Ray determination		E	1	1	2

CONCLUSION : The main difference is between ICP and AAS.

ICP / AAS : 17 (E + G), 3 (g + p) / 12 (E + G), 8 (g + p)
= 85, 15 / 60, 40 %.

- No difference between acid digestion and dry ashing.

Acid digestion / dry ashing : 18 (E + G), 10 (g + p)
/ 9 (E + G), 5 (g + p) = 65, 35 / 65, 35 %.

- Weak difference between digestion with HClO₄ and digestion without HClO₄.

with/without : 9 (E + G), 3 (g + p) / 9 (E + G), 7 (g + p)
= 75, 25 / 56, 44 %.

- X-Ray determination is very good.

TOTAL : 17 E, 4 G +, 8 G-, 7 (g + p) +, 8 (g + p) -.

POTASSIUM

Method	Mark	Sample B	Sample S	B + S
Acid digestion ICP	E	3	3	6
	G	1	1	2
	g	0	0	0
	p	2	2	4
	AAS	0	0	0
Dry ashing	Flame emission	E	5	7
		G	2	6
		g	1	3
		p	0	0
	ICP	E	2	4
		G	1	2
		g	0	0
		p	0	0
	AAS	E	1	1
		G	1	2
		g	1	2
		p	0	1
	Flame emission	E	0	0
		G	0	0
		g	0	0
		p	1	2
X-Ray determination	E	0	1	1
	G	1	0	1

CONCLUSION : Good results on the whole : $32(E + G) / 12(g + p)$.

- Flame emission and ICP are better than AAS.

$$\text{Fl. em. / ICP / AAS : } 13(E + G), 5(g + p) / 14(E + G), 4(g + p) / 3(E + G), 3(g + p) \\ = 72, 28 / 78, 22 / 50, 50 \%$$

- Without HClO_4 is better than with HClO_4

$$\text{without/with : } 16(E + G), 2(g + p) / 5(E + G), 5(g + p) \\ = 50, 50 / 89, 11 \%$$

- Not large difference between ashing and acid digestion (the latter is a little bit better).
- X-Ray determination is a good method.

TOTAL : 19 E, 2 +, 11 G -, 1 g +, 11 (g + p) - .

SODIUM

Method		Mark	Sample B	Sample S	B + S	
Acid digestion	ICP	E	0	0	0	
		G	2	2	4	
		g	0	1	1	
		p	3	3	6	
	AAS		0	0	0	
	Flame emission	E	0	0	0	
		G	0	0	0	
		g	2	0	2	
		p	2	4	6	
	Dry ashing	ICP	E	1	0	1
			G	0	0	0
			g	0	0	0
p			1	2	3	
AAS		E	0	0	0	
		G	0	0	0	
		g	0	0	0	
		p	1	1	2	
Flame emission		E	0	0	0	
		G	0	0	0	
		g	0	0	0	
		p	1	1	2	
X-Ray determination		p	1	1	2	

- . Results are poor : 5 (E + G) / 24 (g + p)
- . No difference between acid digestion and dry ashing
 Acid dig. / dry ashing : 4 (E + G), 15 (g + p) / 1 (E + G), 7 (g + p)
 = 20 - 80 / 12 - 88 %.
- . ICP is a little better than flame - emission
 ICP / Fl. emiss. : 5 (E + G) - 10 (g + p) / 0 (E + G) - 10 (g + p)
 = 33 - 67 / 0 - 100 %.
- . No difference between digestion with and without HClO₄ :
 with/without : 2 (E + G) - 5 (g + p) / 2 (E + G) - 9 (g + p)
 = 29 - 71 / 18 - 82 %.
- . TOTAL : 1 E, 1 G +, 3 G -, 12 (g + p) +, 12 (g + p) -

CHLORINE

		B	S	B + S
Schöniger Bomb ion chrome	E	0	0	0
	G	1	1	2 +
	g	0	0	0
	p	0	0	0
Room pressure acid extraction Titrimetry 3	E	1	1	2
	G	0	0	0
	g	0	0	0
	p	0	0	0
Ion electr. 16	E	0	0	0
	G	1	0	1 +
	g	0	1	1 +
	p	0	0	0
Water extraction Ion electr. 18	E	0	0	0
	G	0	0	0
	g	0	0	0
	p	1	0	1-
Ashing + MgO + KOH Titrimetry 8	E	0	0	0
	G	0	1	1-
	g	0	0	0
	p	1	0	1-
X-Ray determination : 4	E	0	0	0
	G	0	0	0
	g	1	1	2 -
	p	0	0	0

CONCLUSION : Difficult to compare methods as only one lab work by each method.

Schöniger bomb and room pressure acid extraction seem better than water extraction, ashing, or X-Ray determination. Titrimetry or ion chromatography seem better than ion electrode.

TOTAL : 2 E, 3 G +, 1 G -, 1 g +, 4 (g + p)-

Table 7 Mn

Manganese					
Solubllisation	Determination	Mark	Sample B	Sample S	B + S
Acid digestion	A A S	E	4	3	7
		G	1	2	3
		g	0	0	0
		p	2	2	4
	I C P	E	3	3	6
		G	1	1	2
		g	0	1	1
		p	1	0	1
Ashing	A A S	E	1	2	3
		G	0	0	0
		g	1	0	1
		p	0	0	0
	I C P	E	0	0	0
		G	2	2	4
		g	0	0	0
		p	1	1	2
X_Ray determination		E	0	0	0
		G	1	1	2
		g	0	0	0
		p	0	0	0

Acid digestion / Ashing : 13 E, 5 G , 6 (g + p) / 3 E, 4 G, 3 (g + p)
 54, 21, 25 / 30, 40, 30 %

Acid digestion is a little better than ashing.

A A S / I C P : 13(E + G), 5(g + p) / 12(E + G), 4(g + p)
 = 72, 28 / 75, 25 %

No difference

With HClO₄ /without HClO₄ : 10(E + G), 2(g + p) / 8(E + G), 4(g + p)
 = 83, 17 / 66, 33 %

Digestion with HClO₄ is a little better than without

X-Ray determination : good

TOTAL ; 16 E, 3 G-, 8 G+, 7 (g + p)-, 2 (g + p) +

Table 7Fe

Iron					
Solubillisation	Determination	Mark	Sample B	Sample S	B + S
Acid digestion	A A S	E	1	0	1
		G	3	2	5
		g	0	1	1
		p	2	3	5
	I C P	E	3	3	6
		G	0	1	1
		g	1	1	2
		p	1	0	1
Ashing	A A S	E	1	0	1
		G	0	1	1
		g	1	1	2
		p	1	1	2
	I C P	E	0	0	0
		G	2	2	4
		g	0	0	0
		p	1	1	2
X_Ray determination		E	0	0	0
		G	0	0	0
		g	0	0	0
		p	1	1	2

Acid digestion /Ashing : 7 E, 6 G, 9 (g + p) , /1 E, 5 G, 6 (g + p)
 = 32, 27, 41 / 8, 42 42, 50 %

Acid digestion is a little better than ashing.

A A s / I C P :8(E + G), 10(g + p), /11(E + G) , 5(g + p)
 = 44, 56 /69, 31 %

I C P is a little better than A A S

With HClO₄ /without HClO₄ : 8(E + G), 4(g + p) / 5(E + G), 5(g + p)
 = 67, 33 /50, 50 %

Digestion with HClO₄ is a little better than without

X_Ray determination give no good results

TOTAL :8E, 5G-, 6G+, 10(g + p)-, 7(g + p)+

Table 7Cu

Copper					
Solubillsation	Determination	Mark	Sample B	Sample S	B + S
Acid digestion	A A S	E	0	1	1
		G	1	1	2
		g	0	1	1
		p	2	0	2
	I C P	E	0	1	1
		G	0	0	0
		g	2	0	2
		p	2	4	6
Ashing	A A S	E	0	0	0
		G	0	1	1
		g	0	0	0
		p	2	2	4
	I C P	E	0	0	0
		G	0	0	0
		g	0	1	1
		p	3	2	5
X_Ray determination		E	0	0	0
		G	0	0	0
		g	0	0	0
		p	1	1	2

Acid digestion /Ashing :2E, 2G, 11(g + p) / 0E, 1G, 9(g + p)
 = 13, 13, 74 / 0, 10, 90 %

Acid digestion is better than ashing

A A S / I C P : 4(E + G), 7(g + p) / 1(E + G) / 14(g + p)
 = 36, 64 / 7, 93 %

A A S is better than I C P

With HClO₄ /Without HClO₄ :9(E + G), 5(g + p) /1(E + G), 6(g + p)
 = 64, 36 / 14, 86 %

Digestion with HClO₄ is better than without

X-Ray determination give no good results

TOTAL : 2 E, 4 G-, 0 G+, 18 (g + p)-, 4 (g + p)+