

For determination of the precision and accuracy of the HH-XRF, a number of chalk core samples were measured by both HH-XRF and ICP-MS on various cores and sections of the Danish Basin and the North Sea. Solid chalk core samples were measured at 3 different places (clean level flat surface of core sample) by HH-XRF with 60 s on each beam (Table A1). The core samples were then powdered using an agate mortar. ICP-MS was carried out as in Lenniger et al. (2014), where about 0.1 g of sample powder were digested in a mixture of 1 ml 65% nitric acid and 5 ml 40% hydrofluoric acid and placed in a closed Savillex vessel (polytetrafluorethylene polymer) on a hotplate at 130°C for 24h. Samples were then dried in the vessel on the hotplate, treated with 1 ml 65% nitric acid and evaporated to dryness again. This process was repeated, then 2.5 ml 65% nitric acid and Milli-Q was added and the closed vessel was placed on the hotplate at 130°C. After at least 12 h on the hotplate the sample was diluted with Milli-Q to 50 ml. Prior to the analyses this solution was further diluted (11 times) and measured using a PerkinElmer Elan 6100DRC ICP-MS at the Geological Survey of Denmark and Greenland. Measurements of the certified USGS standard BHVO-2 yielded accuracies (Al <0.1%, Fe <0.8%) that are within the accepted analytical error.

Core/ Section	Sample ID	Fe (ICP- MS) (ppm)	XRF 1 (ppm)	XRF2 (ppm)	XRF3 (ppm)	Avg of XRF	STDEV of XRF	Deviation from ICP- MS (%)	Absolute value of deviation (%)
E5X	#6	811	940	850	890	893	37	10	10
E5X	#3	4 279	3380	2790	3750	3307	395	-23	23
E5X	#23	1 322	1600	1980	1090	1557	365	18	18
E5X	#21	723	636	654	596	629	24	-13	13
N1XP	#9	1 216	1270	1730	1430	1477	191	21	21
N1XP	#(6-8)	675	850	880	790	840	37	24	24
Nykløv	NK2-L-16-17	6 834	7130	9100	6970	7733	969	13	13
Nykløv	NK2-N-10-12	5 229	5250	5390	5280	5307	60	1	1
Nykløv	NK2-J-10-11	904	1050	1130	1020	1067	46	18	18
Nykløv	NK2-O-7-9	2 304	2270	2480	2460	2403	95	4	4
Solrød	#15	4 491	5870	4470	4490	4943	655	10	10
Tune	#1	1 157	810	1110	870	930	130	-20	20
Tune	#2	729	590	630	680	633	37	-13	13
Tune	#3	560	515	520	497	511	10	-9	9
Tune	#4	1 425	1500	1390	1420	1437	46	1	1
Tune	#5	3 918	3490	3190	3630	3437	184	-12	12
Tune	#7	1 291	1440	1490	1340	1423	62	10	10
Tune	#12	5 579	6460	6170	6280	6303	120	13	13
Tune	#18	631	620	590	630	613	17	-3	3
Tune	#54	478	630	580	540	583	37	22	22
								14	7

Table A1: Comparison ICP-MS vs HH-XRF on various chalk samples of Danish Basin and North Sea sites.

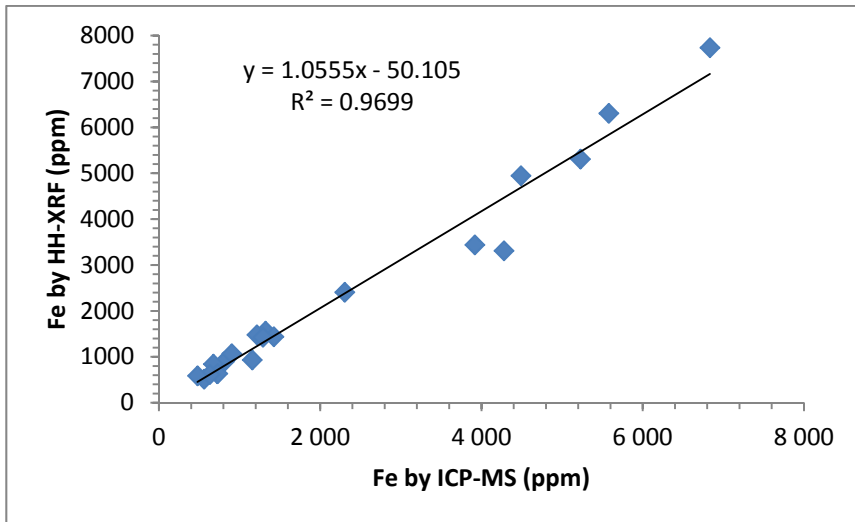


Figure A1: Cross-plot of Fe measurements by HH-XRF and ICP-MS derived from Table A1.

References

Lenniger, M., Nøhr-Hansen, H., Hills, L.V., Bjerrum, C.J., Arctic black shale formation during Cretaceous Oceanic Anoxic Event 2. *Geology* 42, 799-802.