ASTM C-114 accreditation for cement analysis by fusion

Introduction

Cement industries, as well as other types of factories that make products made of raw materials, need to meet more and more stringent quality controls. The physical properties of the final products can be influenced if the composition changes for any reason in the fabrication process. To ensure a maximum quality of the final product, there exist standards that help to ensure minimal variations in the analysis process.

What is ASTM C-114 ?

This standard is especially dedicated for the analysis of hydraulic cement. It gives limit values to respect, to ensure that the analytical process is fully controlled and yield minimal variations in results. It suggests reference test methods for every element of interest in the analysis of cement. But one can also use "rapid test method" if the variation in results respects the limitation proposed by this norm. We mean by "rapid test method" any method used to determine the concentration of analytes that complies with the ASTM C-114 validation requirements. This means that one can use fusion as rapid test method if the resulting variations are below the allowed values given by ASTM C-114 for the appropriate elements. The method needs to be validated with acceptable certified reference materials (CRMs) provided by NIST as suggested the ASTM C-114 standard. Here are the seven Portland cement CRMs available that contain all the elements of interest for the purpose of this study:

SRM 1880b

SRM 1881a

SRM 1884b

SRM 1886a

SRM 1887b

SRM 1888b

SRM 1889a

The certified values are available in annex 2

Sample preparation

We have used seven CRMs (certified reference materials) C-114 standards to demonstrate the performance of our rapid test method by fusion, using the Katanax K2 Prime fluxer. Those CRMs are Portland cement samples provided by the National Institute of Standard and Technology (NIST), and contain different concentration of elements in a certain range, according to the usual composition of Portland cement. (See the details of the CRMs in annex 2)

We used 0,8g of CRM sample mixed with 7g of flux 50/50 Lithium Tetraborate / Lithium Metaborate (LiT/LiM) and 30mg of LiBr as non-wetting agent to produce beads of 32mm in diameter. The components have been weighed with a Sartorius weighting cell WZ224-N with a precision of 0.1mg. All the products have been well mixed in a secondary container and then transferred into a platinum crucible. Here are the method parameters we used on the instrument:

Table1. Method used on the Katanax K2 Prime fluxer

Step	Temperature	Time	Ramp of temperature	Crucible mixing amplitude	Crucible mixing speed
1	1050°C	0:00	Fast	0°	0%
2	1050°C	0:00	Fast	0°	0%
3	1050°C	4:00	Fast	20°	90%
4	1050°C	6:00	Fast	25°	5%
Pouring				120°	50%
1		1:00		120°	80%
2		5:00		90°	80%

An independent mineral laboratory (Corem) was commissioned to do the XRF analysis. The instrument used by the laboratory was a WDXRF spectrometer with an Rh X-ray tube of 2.4 kW, multi crystals (LiF, Ge) and a scintillation detector.

To meet the requirement of the ASTM C-114, one has to run seven standards in duplicate on two different days. The accuracy results are based on the average of those duplicates. The values need to reach the ASTM C-114 limits in terms of precision and accuracy for all the elements that we want to analyse by XRF. The table shows the allowed values given by ASTM in term of precision and accuracy for each element of interest in the analysis of Portland cement. This table also contains the results we obtained for the standards we used to make the test. We list the average of all the standard materials according to the precision and accuracy of the associated element. The details results of each standard are shown in annex 1.

Table 2. ASTM C-114 limits compared to the results of the CRMs samples by fusion

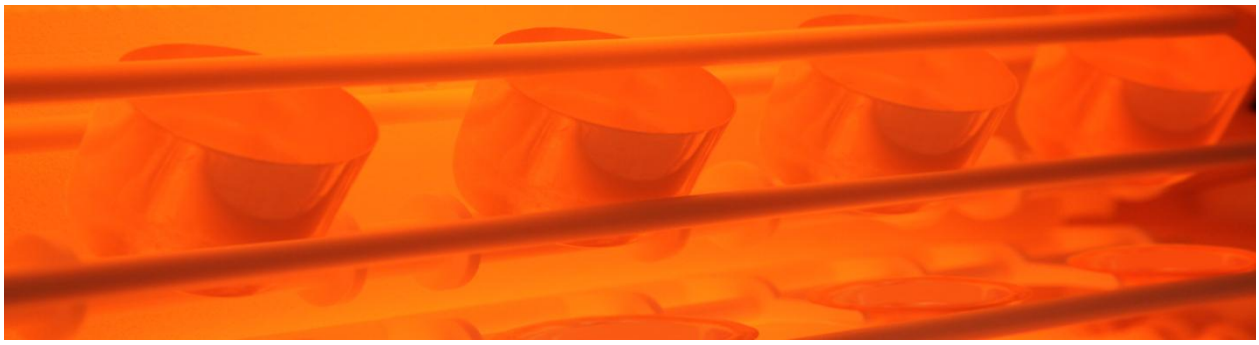
Elements	ASTM C-114 limits		Average of the seven standards by fusion	
	Precision	Accuracy	Precision	Accuracy
SiO2	0,16	0,2	0,047	0,054
Al2O3	0,2	0,2	0,038	0,059
Fe2O3	0,1	0,1	0,036	0,046
CaO	0,2	0,3	0,089	0,163
MgO	0,16	0,2	0,009	0,019
SO3	0,1	0,1	0,077	0,032
Na2O	0,03	0,05	0,014	0,006
K2O	0,03	0,05	0,008	0,018
TiO2	0,02	0,03	0,005	0,003
P2O5	0,03	0,03	0,002	0,008
ZnO	0,03	0,03	0,002	0,002
Mn2O3	0,03	0,03	0,003	0,011

All of the results lie within the limits proposed by ASTM C-114. This means that the rapid test method using fusion with the Katanax K2 Prime fluxer meets the ASTM C-114 requirements.

Conclusion

ASTM C-114 requirements are a standard measure of performance. The ASTM C-114 method can be validated by the use of fusion and in this case the data shows that the Katanax K2 Prime meets these requirements.

We have shown that it is possible to use the Katanax K2 Prime fusion instrument as a part of an analytical method that meets the ASTM C-114 accreditation. An independent laboratory provided the analyses of the beads and they satisfied the requirements for C-114 analysis. One can conclude that the use of fusion with the Katanax K2 Prime instrument will successfully produce both precise and accurate results.



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References:

(1) ASTM C114-11b Standard Test Methods for Chemical Analysis of Hydraulic Cement

(2) Physics and Chemistry of Borate Fusion

(3) International Standard ISO 12677 Chemical analysis of refractory products by XRF – Fused cast bead method

(4) Corem (Mineral laboratory) 1180 Rue de la Minéralogie, Québec, Qc. G1N 1X7 418-527-8211

Annex 1

Table 3. Precision and accuracy results for the seven CRMs used for the accreditation

	Limits		SRM 1880b		SRM 1881a		SRM 1884b		SRM 1886a		SRM 1887b		SRM 1888b		SRM 1889a	
Element	Precision	Accuracy	Precision	Accuracy	Precision	Accuracy	Precision	Accuracy	Precision	Accuracy	Precision	Accuracy	Precision	Accuracy	Precision	Accuracy
SiO2	0,16	0,2	0,08	0	0,002	0,06	0,04	0,02	0,05	0,02	0,01	0,04	0,12	0,13	0,03	0,11
Al2O3	0,2	0,2	0	0,09	0,003	0,07	0,07	0,04	0,11	0,1	0,001	0,03	0,004	0,08	0,08	0,00008
Fe2O3	0,1	0,1	0,01	0,03	0,004	0,08	0,02	0,01	0,0002	0,05	0,001	0,05	0,2**	0,08	0,02	0,02
CaO	0,2	0,3	0,02	0,17	0,09	0,16	0,16	0,22	0,05	0,23	0,06	0,14	0,14	0,18	0,1	0,04
MgO	0,16	0,2	0,016	0,02	0,004	0,01	0,0008	0,02	0,02	0,002	0,01	0,03	0,006	0,02	0,005	0,03
SO3	0,1	0,1	0,05	0,02	0,18	0,02	0,09	0,001	0,04	0,05	0,09	0,06	0,05	0,01	0,04	0,06
Na2O	0,03	0,05	0,01	0,005	0,02	0,001	0,01	0,0007	0,01	0,02	0,04	0,01	0,01	0,0002	0,001	0,007
K2O	0,03	0,05	0,008	0,02	0,01	0,05	0,003	0,007	0,01	0,003	0,01	0,01	0,01	0,005	0,004	0,03
TiO2	0,02	0,03	0	0,003	0,0003	0,004	0,002	0,003	0,01	0,008	0,0004	0,001	0,01	0,004	0,01	0,0003
P2O5	0,03	0,03	0	0,01	0,0006	0,02	0,0006	0,006	0,00007	0,002	0,01	0,008	0,00008	0,002	0,0006	0,009
ZnO	0,03	0,03	0	0,0005	0,0002	0,001	0	0,004	0	0,001	0,01	0,0005	0,00003	0,002	0	0,005
Mn2O3	0,03	0,03	0,001	0,02	0,0004	0,01	0,01	0,009	0	0,007	0,00001	0,005	0,00006	0,004	0,009	0,02
Cl	0,003	NA	0*	0,02	0*	NA	0*	0,007	0*	0,004	0*	0,01	0*	0,01	0*	0,002
Final results	→		Passed		Passed		Passed		Passed		Passed		Passed		Passed	

Passed

Failed (but remain under twice permissible value, so acceptable)

* Detection limit of the instrumentation is over the value of chlorine in the sample.

** At least six of the seven CRM are within the prescribed limits for iron, so acceptable (according to ASTM-C114 requirement)

Annex2

Table 1. Certified Values for SRM 1880b

Constituent	Mass Fraction [a] (%)
SiO_2	20.42 ± 0.36
Al_2O_3	5.183 ± 0.073
Fe_2O_3	3.681 ± 0.023
CaO	64.16 ± 0.40
MgO	1.176 ± 0.020
SO_3 [b]	2.710 ± 0.099
Na_2O	0.0914 ± 0.0052
K_2O	0.646 ± 0.014
TiO_2	0.236 ± 0.012
P_2O_5	0.2443 ± 0.0027
Mn_2O_3	0.1981 ± 0.0020
Cl	0.01830 ± 0.00057
Cr_2O_3 [b]	0.01927 ± 0.00042

Table 1. Certified Values for SRM 1881a

Constituent	Mass Fraction (%)	Constituent	Mass Fraction (%)
SiO_2	22.26 ± 0.15	K_2O	1.228 ± 0.029
Al_2O_3	7.060 ± 0.081	TiO_2	0.3663 ± 0.0030
Fe_2O_3	3.09 ± 0.11	P_2O_5	0.1459 ± 0.0057
CaO	57.58 ± 0.34	Mn_2O_3	0.1042 ± 0.0016
MgO	2.981 ± 0.077	SrO	0.036 ± 0.004
SO_3 [a]	3.366 ± 0.069	Cr_2O_3	0.0588 ± 0.0020
Na_2O	0.199 ± 0.007	ZnO	0.0489 ± 0.0028

Table 2. Reference Values for SRM 1881a

Constituent	Mass Fraction (%)
Cl	0.013 ± 0.001

Table 1. Certified Values for SRM 1884b

Constituent	Mass Fraction [a] (%)
SiO_2	19.30 ± 0.18
Al_2O_3	4.851 ± 0.021
Fe_2O_3	2.937 ± 0.020
CaO	61.31 ± 0.36
MgO	4.74 ± 0.13
SO_3	4.034 ± 0.067
Na_2O	0.278 ± 0.010
K_2O	0.957 ± 0.018
TiO_2	0.2651 ± 0.0084
P_2O_5	0.0965 ± 0.0033
Mn_2O_3	0.0750 ± 0.0013
Cr_2O_3	0.00791 ± 0.00070
SrO	0.0258 ± 0.0038

Table 1. Certified Values for SRM 1886a

Constituent	Mass Fraction (%)	Constituent	Mass Fraction (%)
SiO_2	22.38 ± 0.27	Na_2O	0.021 ± 0.003
Al_2O_3	3.875 ± 0.035	K_2O	0.093 ± 0.004
Fe_2O_3	0.152 ± 0.013	TiO_2	0.084 ± 0.009
CaO	67.87 ± 0.26	P_2O_5	0.022 ± 0.004
MgO	1.932 ± 0.040	Mn_2O_3	0.0073 ± 0.0004
SO_3	2.086 ± 0.080	Cr_2O_3	0.0024 ± 0.0008

Table 2. Reference Values for SRM 1886a

Constituent	Mass Fraction (%)	Constituent	Mass Fraction (%)
SrO	0.018 ± 0.006	Cl	0.0042 ± 0.0004

Table 1. Certified Mass Fraction Values (As-Received Basis) for SRM 1887b

Constituent	Mass Fraction (%)		
SiO_2	19.59	±	0.29
Al_2O_3	4.911	±	0.043
Fe_2O_3	2.471	±	0.019
CaO	61.15	±	0.61
MgO	3.624	±	0.077
SO_3	4.599	±	0.020
Na_2O	0.288	±	0.014
K_2O	0.961	±	0.012
TiO_2	0.203 4	±	0.005 5
P_2O_5	0.154 0	±	0.006 6
ZnO	0.015 60	±	0.000 65
Mn_2O_3	0.095 7	±	0.001 4
Cl	0.010 01	±	0.000 55
Cr_2O_3	0.015 51	±	0.000 89
SrO	0.262 5	±	0.008 1

Table 1. Certified Mass Fraction Values for SRM 1888b

Constituent	Mass Fraction[(a)] (%)		
SiO_2	20.42	±	0.23
Al_2O_3	4.277	±	0.036
Fe_2O_3	3.062	±	0.053
CaO	63.13	±	0.29
MgO	3.562	±	0.057
SO_3	2.634	±	0.017
Na_2O	0.1364	±	0.0044
K_2O	0.658	±	0.017
TiO_2	0.2316	±	0.0076
P_2O_5	0.07307	±	0.00081
Mn_2O_3	0.0652	±	0.0022
Cl	0.0143	±	0.0015
SrO	0.1009	±	0.0030

Table 1. Certified Values for SRM 1889a

Constituent	Mass Fraction (%)			Constituent	Mass Fraction (%)		
SiO_2	20.66	±	0.16	K_2O	0.605	±	0.015
Al_2O_3	3.89	±	0.12	TiO_2	0.227	±	0.010
Fe_2O_3	1.937	±	0.054	P_2O_5	0.110	±	0.004
CaO	65.34	±	0.33	Mn_2O_3	0.2588	±	0.0073
MgO	0.814	±	0.028	SrO	0.042	±	0.004
SO_3	2.69	±	0.11	Cr_2O_3	0.0072	±	0.0005
Na_2O	0.195	±	0.010	ZnO	0.0048	±	0.0003

Table 2. Reference Values for SRM 1889a

Constituent	Mass Fraction (%)		
Cl	0.0019	±	0.0003