Hitachi's X-Supreme8000 for rapid, cost-effective quality control analysis of cement and cement-making material

Instrument Package 10011620

Complies with ASTM C114*

INTRODUCTION

Routine chemical analysis is an essential part in controlling the manufacture of cement, from the full analysis of raw materials to testing each stage of the process. In a traditional system, natural minerals like limestone and clay form the raw mix that goes into the kiln for firing by coal, oil or natural gas to produce clinker. Control of the basic reaction requires accurate analysis for at least calcium, silicon, aluminium and iron in the raw meal. Calculations using these four elements (sometimes including sulfur) provide the required production control parameters such as lime saturation factor (LSF) and silica ratio (SR). Analysis of the clinker requires the same elements as for the raw meal, but control of the addition of gypsum during the final milling stage only requires the measurement of sulfur content.

Waste materials are increasingly being used in the cement-making process, bringing about many changes. When they contain the main cement-making components, waste materials can replace some of the natural raw materials and combustible wastes can help fire the kiln. This means more testing of the incoming raw materials, both during the process and in the final product. Thus, for a cement plant to compete in today's cost-conscious market its analytical capabilities must be extensive, cost-effective and flexible.

It is important that any new analytical methods required for this type of analysis fit easily into existing procedures. X-ray fluorescence (XRF) spectrometry is one of the simplest instrumental techniques for analysis in a cement works because the sample preparation is simple. For many years, benchtop energy-dispersive XRF (EDXRF) spectrometers have been used successfully as a quality control tool in cement plants to control incoming material as well as production samples.

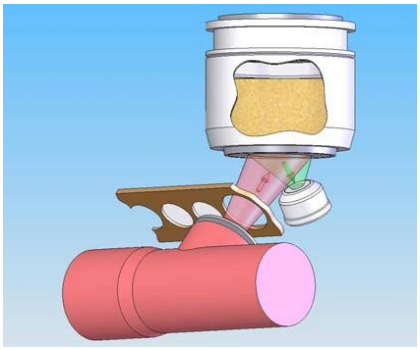
Hitachi have a long and highly respected reputation within the cement industry with instruments such as the LAB-X and Twin-X providing simple to use, accurate, cost-effective and dependable 24/7 analysis.

Hitachi's X-Supreme is a high-performance EDXRF spectrometer that successfully performs a wider range of elemental analyses required in the cement-making industry. The X-Supreme is the perfect analyzer for the rapid multi-element determination of cement making materials, including sodium, with the flexibility for additional elements such as chlorine in raw meals etc. This new level of performance has been achieved using Hitachi's unique "Focus SD" technology.

*Meets the precision requirement of ASTM C114 (Standard test method for chemical analysis of hydraulic cement).

INSTRUMENT

Hitachi have focused on the particular requirements of the cement industry to produce a dedicated analyzer optimized for the analysis of raw meals, cement, clinker, raw materials, etc whilst retaining many of the critically important features for the cement industry such as minimal dust ingress, high reliability and stability, and "operation by anyone" principles.



Hitachi's "Focus SD" technology obtains the highest level of performance from low atomic number elements such as sodium to high atomic number elements such as strontium. It combines a field-proven tungsten-target X-ray tube and associated Silicon Drift Detector (SDD) which provides high spectral resolution. "Focus SD" allows optimum speed of analysis and low detection limits. This delivers supreme performance for all elements of interest, including sodium.

FIGURE 1: HITACHI'S "FOCUS SD" TECHNOLOGY

All control of the instrument is through the X-Supreme's integrated PC and software which provides sophisticated calibration models that handle a wide variability of samples, while remaining easy to use. The software features easy data manipulation and storage, a report writing facility and data export.

With an enviable reputation for attention to detail on the cement industries' principle requirement of "minimal dust ingress", the X-Supreme was designed with this in mind. A unique "wind tunnel" arrangement draws external air into a section of the X-Supreme which provides a heat transfer. This section is completely isolated from the main components thereby preventing dust ingress ensuring long term reliability (see figure below).

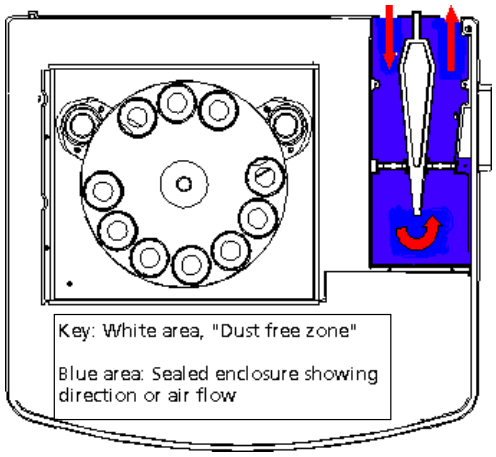


FIGURE 2: X-SUPREME: CUTAWAY PLAN VIEW SHOWING THE EXTERNAL AIR FLOW

The X-Supreme's compactness and robustness make it ideal for location either in laboratories or in production sites for twenty-four-hour operation. The X-Supreme includes a ten-position autosampler to enable simple and unattended multi-sample analysis.

SAMPLE PREPARATION AND PRESENTATION

For precise and accurate multi-element analysis, it is essential to prepare the samples to give the high standards of production control that are the norm in the cement industry. This means grinding a powder sample in a swing mill with a grinding additive, to prevent the sample clogging the mill and to help it bind into a pellet. The best type of additive is one available as tablets of precise weight so that only the sample needs weighing. Hitachi supply one that has been used in the cement industry for many years. The resultant fine mixture is formed into a strong pellet (usually 35 or 40 mm diameter) by compression in a die using a hydraulic press. This pellet then fits into the Hitachi sample holder.

Note: For some cement plant operations an automated sample preparation system is used and sometimes the cement sample is retained in a steel ring (Polysius) of diameter 51.5 mm (2"). An optional sample tray is available for these types of samples.

After placing the samples on the instrument tray, entering their identification and selecting their tray position and method, measurement can be started by simply pressing the Start key on the integrated keypad. Preliminary results are available after only a few seconds (Simultaneous mode) or after the first condition (Sequential mode) and are updated until the end of the measurement. Results can be displayed in user-defined order and format, printed on an external USB printer, as well as electronically transmitted using USB or Ethernet as required.

CALIBRATION

Each X-Supreme comes pre-programmed with operating parameters that are optimized for each application included in this package. It is then simply a matter of following the relevant Hitachi method sheet and running at least six standards with known analyte concentrations.

Note: An optional Standardless (Fundamental parameter) method is available on the X-Supreme and this allows for elemental measurements when no standards are available.

QUALITY CONTROL AND INSTRUMENT CORRECTION

Setting-up-samples (SUSs) are provided by Hitachi and are measured at the time of calibration. They act as long term reference for the sensitivity of each element's X-rays.

From time to time, the instrument needs restandardizing by measuring the setting-up-samples. Capitalizing on the excellent stability of the X-Supreme, the best strategy is regular measurement of a quality control (QC) sample and only to restandardize when a result exceeds control limits. This is an easy process on the X-Supreme when using the QC check sample routine. This routine displays the QC check sample's results over time, in both graphical and numerical format, allowing a rapid assessment to be made. If the results are inside customer specified tolerances then routine analysis can proceed but if outside then restandardisation is necessary.

PERFORMANCE AND RESULTS

The optimized "Focus SD" technology in this package enables unprecedented determination of sodium in cement. **Figure 3** illustrates a typical sodium calibration for finished cement.

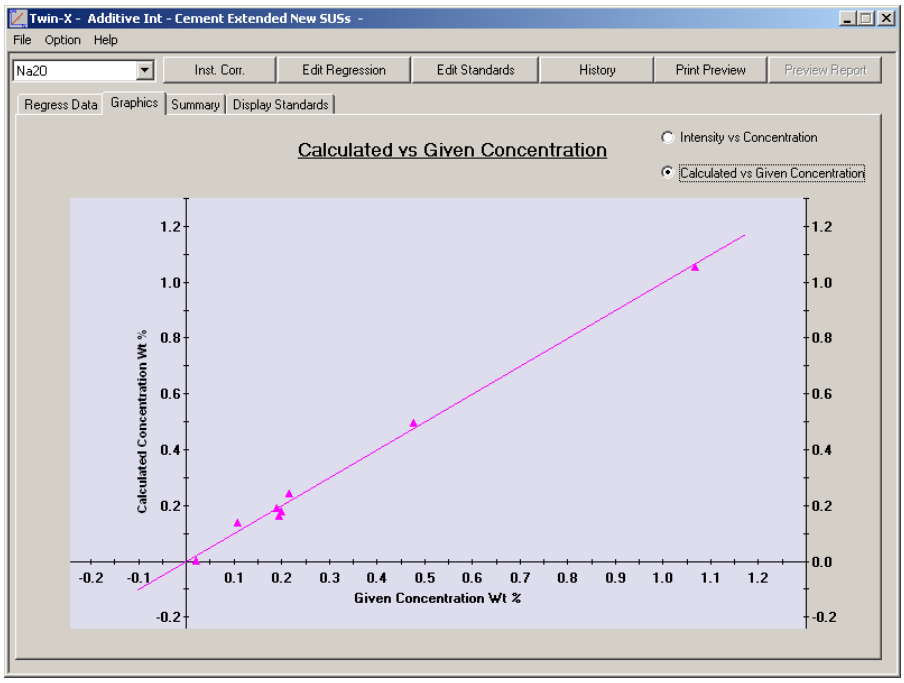


FIGURE 3: NA_2O CALIBRATION GRAPH FOR CEMENT

Tables 1 to 4 show typical calibration performance that illustrates how the X-Supreme can accurately and precisely analyse cement and cement-making material.

TABLE 1: TYPICAL CALIBRATION PERFORMANCE FOR CEMENT ANALYSIS (AIR PATH) (XSMET-03A)

Analyte	Range (% $^m/_m$)	Standard error of calibration (% $^m/_m$)	Guaranteed limit of detection (3σ) (%$^m/_m$)	Precision (95% confidence) (% $^m/_m$)	Measurement time (minutes)
Al_2O_3	3.9 - 7.1	0.2	n/a	0.13	~ 5
SiO_2	18.6 - 22.4	0.3	n/a	0.13	
CaO	57.6 - 67.9	0.5	n/a	0.05	
Fe_2O_3	0.2 - 3.1	0.04	0.008	0.01	

The precision was calculated from 10 repeat measurements of a standard containing 4.3% Al_2O_3, 20.6% SiO_2, 62.3% CaO, and 2.7% Fe_2O_3.

TABLE 2: TYPICAL CALIBRATION PERFORMANCE FOR FULL CEMENT ANALYSIS (XSMET-03B)

Analyte	Range (% $^{m}/_{m}$)	Standard error of calibration (% $^{m}/_{m}$)	Guaranteed limit of detection (3σ) (%$^{m}/_{m}$)	Precision (95% confidence) (% $^{m}/_{m}$)	Measurement time (minutes)
Na_2O	0.02 - 1.07	0.04	0.021	0.012	~ 7
MgO	0.81 - 4.48	0.06	0.015	0.03	
Al_2O_3	3.9 - 7.1	0.1	n/a	0.03	
SiO_2	18.6 - 22.4	0.2	n/a	0.07	
P_2O5	0.02 - 0.31	0.009	0.005	0.003	
SO_3	2.1 - 4.6	0.1	n/a	0.011	
K_2O	0.09 - 1.23	0.04	0.005	0.011	
CaO	57.6 - 67.9	0.5	n/a	0.08	
TiO_2	0.08 - 0.37	0.006	0.003	0.004	
Cr_2O_3	0.002 - 0.06	0.003	0.001	0.001	
Mn_2O_3	0.007 - 0.26	0.006	0.001	0.002	
Fe_2O_3	0.15 - 3.1	0.06	0.003	0.008	
ZnO	0.001 - 0.11	0.001	0.0006	0.001	
SrO	0.02 - 0.64	0.004	0.002	0.001	

The precision was calculated from 10 repeat measurements of NIST standards. The standards were chosen so that the analytes' concentration matches the calibration mid-range.

TABLE 3: TYPICAL CALIBRATION PERFORMANCE FOR HIGH-CALCIUM LIMESTONE (XSMET-03C)

Analyte	Range (% $^{m}/_{m}$)	Standard error of calibration (% $^{m}/_{m}$)	Guaranteed limit of detection (3σ) (%$^{m}/_{m}$)	Precision (95% confidence) (% $^{m}/_{m}$)	Measurement time (minutes)
MgO	1 - 4.1	0.05	0.04	0.02	~ 5
Al_2O_3	0.6 - 3.3	0.04	0.02	0.02	
SiO_2	2.3 -10.4	0.08	0.05	0.03	
K_2O	0.1 - 0.8	0.008	0.02	< 0.01	
CaO	42.3 - 52.6	0.4	n/a	0.05	
Fe_2O_3	0.4 - 1.3	0.006	0.02	0.01	

The precision was calculated from 10 repeat measurements of a standard containing 1% MgO, 2.2% Al_2O_3, 6.3% SiO_2, 0.5% K_2O, 48.2% CaO and 0.9% Fe_2O_3.

TABLE 4: TYPICAL CALIBRATION PERFORMANCE FO R DOLOMITIC LIMESTONE ANALYSIS (XSMET-03D)

Analyte	Range (% $^{m}/_{m}$)	Standard error of calibration (% $^{m}/_{m}$)	Guaranteed limit of detection (3σ) (%$^{m}/_{m}$)	Precision (95% confidence) (% $^{m}/_{m}$)	Measurement time (minutes)
MgO	18.8 - 21.2	0.21	0.16	0.14	~ 5
Al_2O_3	0.2 - 0.4	0.01	0.013	0.009	
SiO_2	0.3 - 2.2	0.12	0.04	0.02	
CaO	30.0 - 32.9	0.22	n/a	0.05	
Fe_2O_3	0.1 - 0.6	0.02	0.002	0.002	

The precision was calculated from 10 repeat measurements of a standard containing 20.3% MgO, 0.3% Al_2O_3, 1.2% SiO_2, 31.3% CaO, and 0.2% Fe_2O_3**.**

ROUTINE ANALYSIS

Pressed pellets are placed in Hitachi pellet holders, and placed on the X-Supreme sample tray. Their labels are entered on the routine analysis screen, and the analysis run is started.

The X-Supreme "Live result update" function displays preliminary results after only a few seconds (Simultaneous mode) for each sample. This offers the potential to spot production or sample issues very quickly and respond adequately.

INSTRUMENT SPECIFICATION

The X-Supreme instrument package for the analysis of cement making materials is 10011620. This includes the pre-loaded analytical methods (XSMET-03), associated method sheets, setting-up samples and other accessories, e.g. sample holders …etc required for the complete operation.