Continuous Emission Monitoring for Clay Ceramic Manufacturing

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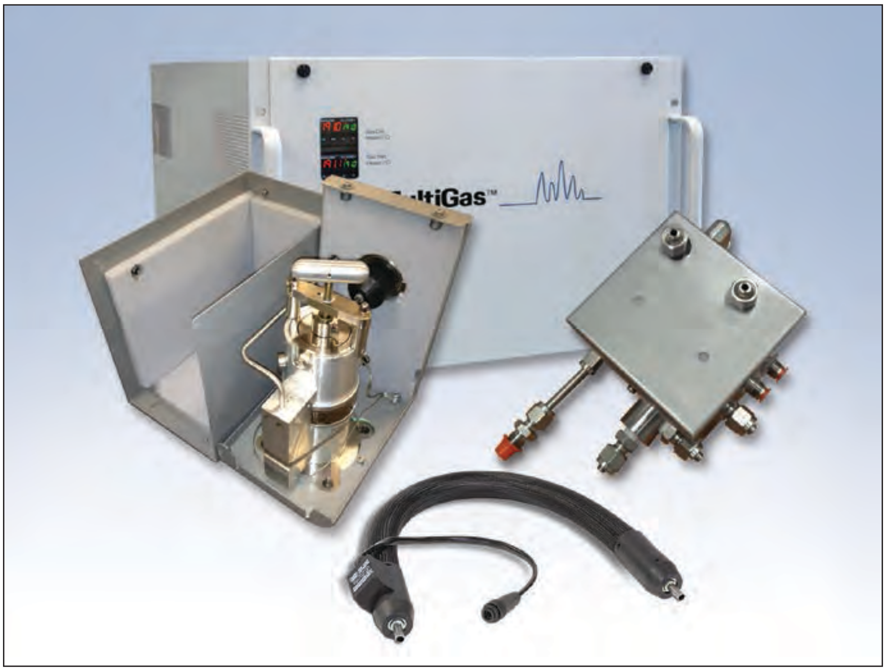

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A number of processing steps in ceramic manufacturing result in the emission of hazardous air pollutants (HAPs) such as acid gases (e.g., hydrofluoric acid, HF; and hydrochloric acid, HCl) that are released in the high-temperature firing steps of the manufacturing process. Table 1 (p. 20) provides estimates of the emission factor ratings for the HAPs emitted during the firing steps in ceramic products manufacturing.[1]

In September 2015, the U.S. Environmental Protection Agency (EPA) issued a final rule for the National Emission Standard for Hazardous Air Pollutants (NESHAP) for Brick and Structural Clay Products (BSCP) and Clay Ceramics Manufacturing.[2] The rule for clay ceramics applies to major HAP sources manufacturing vitreous plumbing fixtures (sanitaryware), including sinks, toilets, and pressed floor and wall tile. The new regulation limits the total emissions of HF, HCl and chlorine (Cl_2) to 140 lb/hr (HCl equivalent), where the limit applies to the sum of emissions from all kilns within a facility. Under the final Clay Ceramic NESHAP, HF and HCl emissions must be continuously monitored using one of the following: EPA Method 26A, EPA Method 26, EPA Method 320 or any other method approved under 40 CFR 63.7(f) of the EPA's General Provisions.

The new emission limits require that continuous emission monitoring systems (CEMS) for HF and HCl at ceramic manufacturers have certified detection limits for these gases at the sub-ppm level, since detection limits must be at least five times smaller than the regulated emissions level. Monitoring low concentrations of HF and HCl emissions in the harsh, corrosive and particle-laden gas streams typical of kiln exhausts is a challenging application for CEMS. Of the available methods, Fourier transform infrared (FTIR) spectrometry has proven to be best-suited to the measurement of compounds such as HF and HCl in effluent environments like those found in the ceramic industry. Instrumentation* is available to provide reliable, continu-

*Such as MKS Instruments MultiGas™ 2030 CEM FTIR gas analyzer; the MKS liquid nitrogen-cooled MultiGas 2030 CEM FTIR continuous gas analyzer is used by the EPA as the reference method anchor instrumentation by which all other CEM technologies are evaluated.

Table 1. Operating data and emission factors for the gaseous pollutant emissions from clay ceramic products manufacturing.[1]

Emission Component	Concentration
Dust	5-30 mg/m^3
NO_x (stated as NO_2)	5-150 mg/m^3
SO_x (stated as SO_2)	1-300 mg/m^3
CO	1-15 mg/m^3
Fluorine compounds (stated as HF)	5-60 mg/m^3
Chlorine compounds (stated as HCl)	20-150 mg/m^3
CO_2	1.5-4.0 vol%

ous monitoring and to deliver highly precise, accurate, and sensitive measurements of ultra-low levels of these compounds in a variety of kiln exhaust environments.

Infrared Spectrometry

Infrared (IR) spectroscopy directs a beam of broadband infrared energy (light) through a sample and measures the absorption of that energy at different frequencies. Each molecular bond in the chemical compounds within the sample absorbs infrared energy at a unique frequency, and most molecules exhibit a characteristic "fingerprint spectrum" of infrared absorbances. An unknown sample's infrared absorption pattern over a pre-defined frequency bandwidth (its IR spectrum) is the sum of the characteristic patterns for all of the chemical species contained in the sample.

In IR spectrometry, the strength of a sample's infrared transmission is measured over a selected frequency bandwidth and compared to a known background spectrum for the same frequencies. An inverse log of each transmission data point frequency is then performed to create the linear absorbance spectrum. Quantitative analysis is then performed using the Beer-Lambert law (Beer's law) to determine the concentration of the species of interest in the sample.

In an FTIR spectrometer, a broadband beam of IR radiation (typically from a silicon carbide "globar") is introduced to a Michelson interferometer (consisting of a beam splitter and two mirror assemblies, one fixed and one moving). In the interferometer, the beam splitter reflects approximately half of the IR light to the moving mirror and transmits approximately half to the fixed mirror. The light reflected by the two mirrors then recombines at the beam splitter, where wave interference occurs.

Constructive and destructive interference resulting from the action of the moving mirror leads to the sequential constructive and destructive interference of each of the different wavelengths of light in the beam, and the creation of an interferogram (see Figure 1a). The continuous modulation of the IR light takes place at different rates and encodes each wavelength with a new frequency. The x-axis of the interferogram recorded by the spectrometer is in the distance domain. Applying a Fourier transform to the interferogram converts the data from the time domain to the frequency domain, producing a single beam spectrum in which the x-axis represents wavenumbers (cm^{-1}), another measure of frequency. Applying a background spectrum (cell filled with nitrogen gas) ratio to the single beam spectrum and multiplying by the inverse log of each point produces a linearized absorption spectrum (see Figure 1b).

Resolution

The spectral resolution of an FTIR-based CEMS is a critical factor in determining its ability to accurately measure the concentration of an emission gas

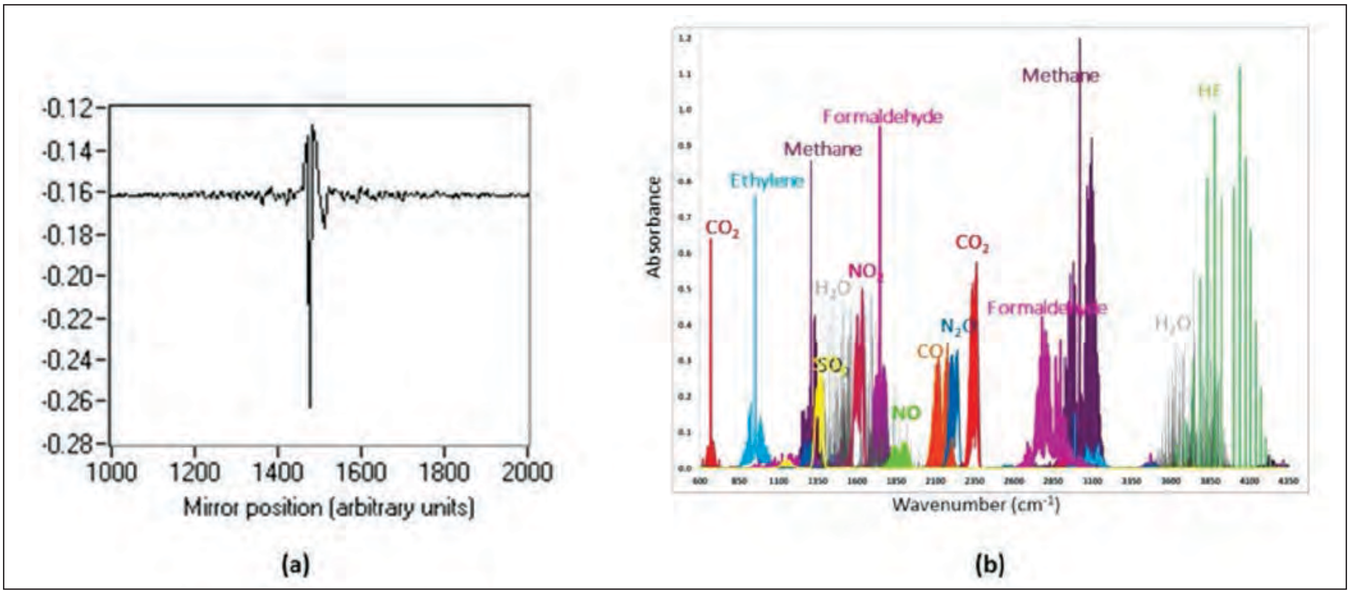

Figure 1. In the FTIR interferogram, the x-axis is in the time or distance domain (a), while the x-axis is in the wavenumber (frequency) domain for the absorption spectrum (b).

Table 2. FTIR span, range and uncertainty results.

Gas	TÜV-Certified Range	Supplemental Range 1	Supplemental Range 2	Emission Limit Value	U/C %	U/C Requirement %
HF*	0-3 mg/m^3 (0-4 ppmv)	0-10 mg/m^3 (0-12 ppmv)	-	1 mg/m^3	19.3	30.0
HCl**	0-15 mg/m^3 (0-10 ppmv)	0-90 mg/m^3 (0-60 ppmv)	0-200 mg/m^3	10 mg/m^3	8.1	30.0
CO	0-75 mg/m^3	0-300 mg/m^3	0-1,500 mg/m^3	50 mg/m^3	6.2	7.5
SO_2	0-75 mg/m^3	0-300 mg/m^3	0-2,000 mg/m^3	50 mg/m^3	7.0	15.0
NO	0-200 mg/m^3	0-400 mg/m^3	0-1,500 mg/m^3	130 mg/m^3	6.8	15.0
NO_2	0-50 mg/m^3	0-100 mg/m^3	0-1,000 mg/m^3	50 mg/m^3	4.1	15.0
N_2O	0-50 mg/m^3	0-100 mg/m^3	0-500 mg/m^3	50 mg/m^3	4.5	15.0
NH_3	0-10 mg/m^3	0-75 mg/m^3	-	10 mg/m^3	6.2	30.0
CH_4	0-15 mg/m^3	0-50 mg/m^3	0-500 mg/m^3	10 mg/m^3	7.0	22.5
H_2O	0-40%	-	-	0-40%	3.4	7.5
CO_2	0-25%	-	-	0-25%	4.5	7.5

*HF: 1 mg/m^3= 1.22 ppmv @ 25°C **HCl: 1 mg/m^3 = 0.67 ppmv @ 25°C

species in the presence of other potentially interfering components that may absorb near the same frequency as the target compound. Resolution is specified in units of wavenumbers and is determined by the maximum distance travelled by the moving mirror inside the interferometer. Because resolution is essentially the reciprocal of the distance travelled by the mirror, a 0.5 cm^{-1} resolution would require the mirror to travel a distance of 2 cm in a perfectly straight line. This presents significant mechanical challenges, which are addressed through the use of corner-cube mirrors to ensure that incident and reflected IR light paths are parallel, irrespective of the orientation of the mirror to the perpendicular light beam.

Ceramic kiln CEM applications require stack gas analyses in exhaust streams that have significant levels of water vapor (up to 40%). In addition, spectral interferences due to the presence of nitric oxide (NO), nitrogen dioxide (NO_2), and sulphur dioxide (SO_2) may also be present in the region of interest (note the H_2O overlapping absorption in the HF region of the spectrum in Figure 1b). This situation is exacerbated by the fact that acid gases of interest in clay manufacturing CEM require relatively low emission limit values (ELVs) and therefore require monitoring at low composition ranges (the ELV for HF is 1 mg/m^3). In these circumstances, instrument resolution and the careful selection of interference-free or low interference regions for monitoring minor components, combined with the masking of high interference regions, are important factors in ensuring that cross-interference effects are minimized.

Software algorithms combined with high-resolution instruments become critical to successful low detection level success. High-resolution systems (0.5 cm^{-1} FWHH) are capable of resolving the spectral features of a target compound from those of other, interfering spectral features due to additional compounds present in the gas mixture being analyzed. Systems undergo extensive testing to ensure that accuracy is optimized and cross-correlation is minimized. The library of application-specific analytical methods for various industries allows users to simply hook up the system and turn it on for emissions information concerning regulatory compliance.

FTIR-Based CEM Instrumentation

The recently issued NESHAP for the clay ceramic industry requires the use of a CEMS to simultaneously monitor HF and HCl in plant kiln emissions. EPA Method 320/321[3] and EPA Performance Specifications PS-15[4] and PS-18[5] define the acceptable methodologies and equipment for HAP measurements using FTIR-based CEMs. The reference method specified for this application uses a patented high-optical-throughput sampling cell, application-specific analysis software, and an instrument-independent quantitative spectral library. The version of the instrumentation employed for CEMS incorporates a novel, long wavelength, thermoelectrically (TE) cooled detector that eliminates the need for liquid nitrogen while retaining as much as 85% of the performance of a detector requiring liquid nitrogen.

These analyzers produce accurate, highly sensitive measurements of most gases and vapors in high moisture stream (up to 40%) environments by producing high-resolution spectra (0.5 cm^{-1}) that enable the detection and measurement of HF and HCl without the need to remove the moisture. Two configurations of the instrument have been evaluated in EPA and TÜV certification field tests: standard and high sensitivity.** TÜV is one of the main European certification agencies for CEMS technology approval. Under TÜV testing, the CEM system is taken to a facility that is certified to measure compliance emissions and run for a full maintenance interval (six months, in this case). EPA tests conformed to PS-15, PS-18 and ASTM D6348-12;

***MultiGas™ 2030 CEM HiSens gas analyzer for low-level emissions monitoring*

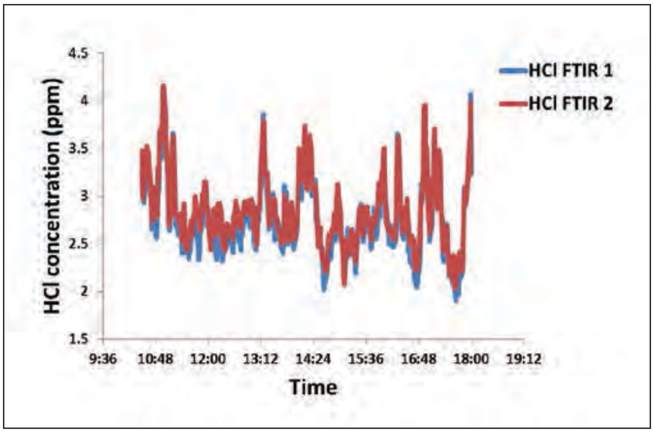

Figure 2. TÜV reproducibility test results for a CEM FTIR gas analyzer.

TÜV certification was carried out in compliance with DIN EN 15267 Part 3.

Table 2 (p. 21) shows the TÜV certified span, range and uncertainty results obtained for the standard unit in use for continuous emission monitoring. Minimum detectable levels (MDLs) for acid gases such as HF and HCl (3 × standard deviation) for the three system configurations were determined by ASTM D6348-12. The liquid nitrogen-cooled unit had an MDL of 76 ppbv; the CEMS configured analyzer had an MDL of 0.18 ppmv; and the standard unit had an MDL of 26 ppbv. The systems proved to be highly repeatable during TÜV certification testing, as evidenced by the reproducibility data for HCl shown in Figure 2. The average difference between readings for the two FTIR systems was only 0.1 ppm.

Other Infrared-Based Spectrometric Monitors

Infrared-based spectrometric analyzers can also be used to provide critical fuel quality monitoring in clay ceramic manufacturing facilities. One example is a hydrocarbon gas analyzer† that uses a proprietary tunable Fabry-Perot optical assembly to allow wavelength scanning in preselected regions of the spectrum, coupled with chemometric-based pattern recognition software to determine the composition and heating quality of the hydrocarbon fuel that heats the kilns. The analyzer provides measurement data for percentages of the following components in hydrocarbon fuel gas: methane (0-100%), ethane and propane (0-25%), iso- and n-butanes (0-10%), and nitrogen (calculated as balance). Software within the analyzer calculates the calorific value of the fuel in MJ/m^3 and the Wobbe Index of the fuel in MJ/m^3.

Effective Monitoring

FTIR gas analyzers are effective for continuous emission monitoring of the acid gases emitted by kilns firing in clay ceramic manufacturing facilities. FTIR CEM analyzers per-

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†MKS Instruments Precisive® 5 TFS™ tunable filter spectroscopy hydrocarbon gas analyzer

Tunable filter spectroscopy hydrocarbon gas analyzer.

form well with very low uncertainties, high accuracy and very long maintenance intervals. The newest FTIR analyzers have extremely low detection limits for HF and HCl in the presence of up to 40% H_2O and 30% CO_2 by volume, making them well-suited for the analysis of such emissions in ceramic firing operations.

EPA- and TÜV-certified FTIRs are reliable, accurate, precise, and repeatable CEMS that fulfill requirements of recent EPA NESHAP rules for HF and HCl emission monitoring in the clay ceramic manufacturing industry. Related, infrared-based instruments have been developed to provide accurate and precise monitoring of fuel gas feed quality for ceramic manufacturing facilities.

For additional information, contact the author at (978) 738-3058 or peter_zemek@mksinst.com, or visit www.mksinst.com.

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