Establishing an Advanced Technique to Analyze Ultra Trace Dioxin Pollutants from an Integrated Steel Plant

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An isotope dilution method was applied to quantify the amount of seventeen 2,3,7,8-substituted polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). The total method detection limits (MDLs) of measuring seventeen 2,3,7,8-substituted PCDD/Fs congeners was evaluated at 1.80 pg I-TEQ, an excellent sensitivity for PCDD/F analysis in stack emission samples. To verify the reliability of analyzing PCDD/Fs in stack emission samples from the sintering plants, the China Steel Corporation (CSC) dioxin analysis laboratory carried out an inter-laboratory comparison with the testing laboratory of the National Central University (NCU). The relative variations of the inter-laboratory comparison study ranged from 3% to 17% among 9 stack emission samples from sintering plants. The CSC dioxin analysis laboratory has been approved and accredited by the Environmental Protection Administration, Taiwan. Currently, this laboratory is a qualified laboratory that can provide the services of dioxin testing for stack emissions, related to the purpose of surveillance of emission regulations.

1. INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are formally known as dioxins and furans; however, both these groups of congener are generally called “dioxins” by the general public. PCDDs and PCDFs are listed among the twelve most persistent organic pollutants (POPs) under the Stockholm Convention due to their environmental persistence and their high accumulativity in biological tissues. The group of dioxins/furans comprise 75 PCDDs and 135 PCDFs congeners in total, but only seventeen 2,3,7,8-substituted PCDD/Fs are classified as highly toxic substances.

The sintering process is a pre-treatment step in the steel making process. Iron ore sinter plants have been identified as a major source of PCDD/Fs to air in some countries [(1)]. Extensive studies into formation of PCDD/Fs in the sintering process have shown that they are formed within the sinter bed itself, and re-synthesized through *de novo* reaction in the gas collectors. For sintering plants with high use of waste, including cutting oils or other chlorinated contaminants, and low technology control may have higher dioxin emission than well-controlled plants with low waste use[(2)]. A steel industry sintering plant dioxin control and emission standard has been promulgated by the Environmental Protection Administration in 2004 in Taiwan. The current emission standard value for an existing sintering plant built before the date of promulgation is 1.0 ng-TEQ/Nm^3 on the 15% standard oxygen basis. A newly established sintering plant, however, is subject to a more stringent emission standard of 0.5 ng-TEQ/Nm^3 [(3)].

2. MAIN LAYOUT AND INSTALLATION

China Steel Corporation (CSC) began to establish a dioxin analysis laboratory and to develop the technique of analyzing ultra low PCDD/Fs in stack emission gas in November 2006. The goal of this laboratory is to provide a superior service of PCDD/Fs analysis to the CSC group, and to elevate its research abilities on the issue of dioxin emission reduction in sintering plants. Currently, four members, including 2 engineers and 2 technicians, are involved in this laboratory and able to handle approximately 600 samples for dioxin analysis per year. This laboratory is basically divided into two separate spaces: one is for the purpose of sample pretreatment, such as extraction or clean-up or concentration; and the other one is the instrument room. Figure 1 illustrates the layout of the CSC dioxin analysis laboratory. An Agilent 6890N high resolution gas chromatograph coupled with a Waters AutoSpec Premier high

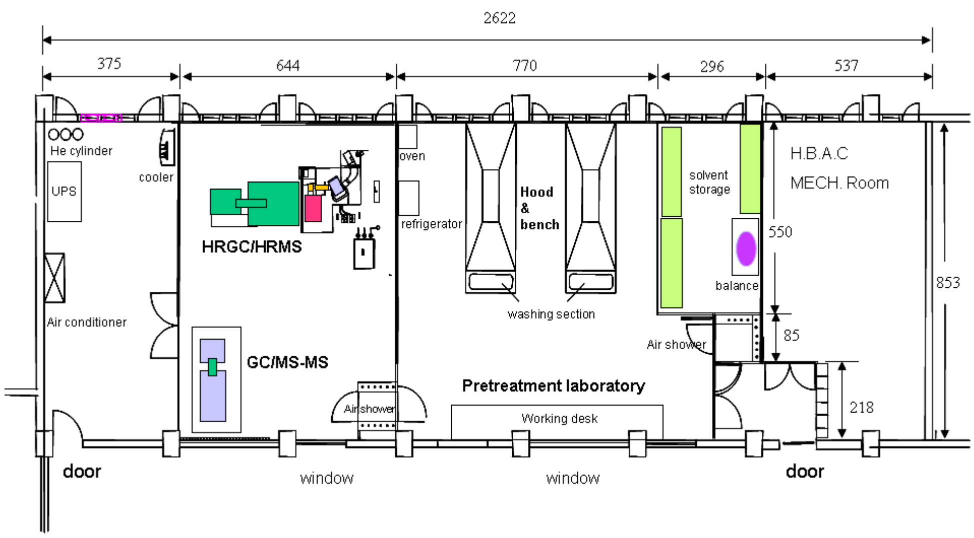

Fig. 1. Layout of CSC dioxin analysis laboratory.

resolution mass spectrometer (HRGC/HRMS) is used to detect and analyze the seventeen 2,3,7,8-substituted PCDD/Fs. The standard delivery time for dioxin analysis of one batch containing a maximum of ten real samples is 5 days; however, this time can be shortened to 3 days for meet an urgent analytical requirement.

3. DEVELOPING A PCDD/Fs ANALYTICAL TECHNIQUE

3.1 Testing Procedures

A flow chart that summarizes the procedures for PCDD/Fs analysis in stack emission gas is depicted in Figure 2. After a stack emission sample is withdrawn isokinetically from the gas stream, and is collected on a glass fiber filter and XAD-2 resin adsorbent material, the PCDD/Fs are extracted from the sample using a Soxhlet apparatus. The aliquots of the sample are then fortified with nine $^{13}C_{12}$ labeled PCDD/Fs congeners as internal standards and $^{13}C_{12}$-1,2,3,7,8,9-HxCDF as the alternative standard before extraction and clean-up, respectively. The extract is cleaned-up with a 40% sulfuric acid-impregnated silica gel column, followed with another acidic alumina column. Another carbon/ celite column is next applied to separate the PCDD/Fs and the Co-planar polychlorinated biphenyls (Co-PCBs) eluted from the acidic silica gel and acidic alumina columns. Next, $^{13}C_{12}$-1,2,3,4-TeCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD are spiked into the cleaned extract as recovery standards. The spiked concentrates are finally analyzed using an Agilent 6890N HRGC/Waters AutoSpec Premier HRMS equipped with an Agilent DB-5ms fused-silica capillary column (60m×0.25mm i.d.×0.25μm film). A minimum mass resolution of 10,000 (10% valley definition) should be maintained.

3.2 Detection Limit

The isotope dilution method, in which the test portions are fortified with $^{13}C_{12}$ labeled PCDD/Fs congeners as an internal standard before sample preparation, is applied to quantify the seventeen 2,3,7,8-substituted PCDD/Fs congeners. The method detection limits (MDLs) of dioxin analysis in stack emission samples were evaluated by "Guidance of Determination of the Method Detection Limit for Environmental Analysis"[(4)] promulgated by the Environmental Analysis Laboratory, Taiwan. The individual congener MDLs for tetra-chlorinated PCDD/Fs, penta~hepta-chlorinated PCDD/Fs, and octa-chlorinated PCDD/Fs were estimated at *ca.* 0.3 pg, 1.0 pg, and 2.5 pg, respectively, and the total MDLs of the seventeen 2,3,7,8-substituted PCDD/Fs congeners was calculated at 1.80 pg I-TEQ.

3.3 Certification of Real Plant Measured Reliability

To verify the reliability of the measured dioxin contents in stack emission samples from sintering plants, an inter-laboratory comparison between the CSC dioxin analysis laboratory and the testing laboratory of National Central University (NCU) was held in July 2007. Nine stack emission samples were collected from three sintering plants in CSC, and their extracts were equivalently separated into two aliquots, which were then distributed to the above two laboratories. Both laboratories used their own methods for sample preparation and instrumental analysis. Table 1 lists the results of this inter-laboratory comparison of dioxins in the real stack emission samples from the sintering plants. As shown in Table 1, the relative variations of determining dioxin contents in individual stack emission samples from sintering plants between the CSC laboratory and the NCU laboratory range from 3% to 17%. However, the relative variation can be further reduced down to 3%~4% if the comparison is based on the average dioxin concentration from each single sintering plant.

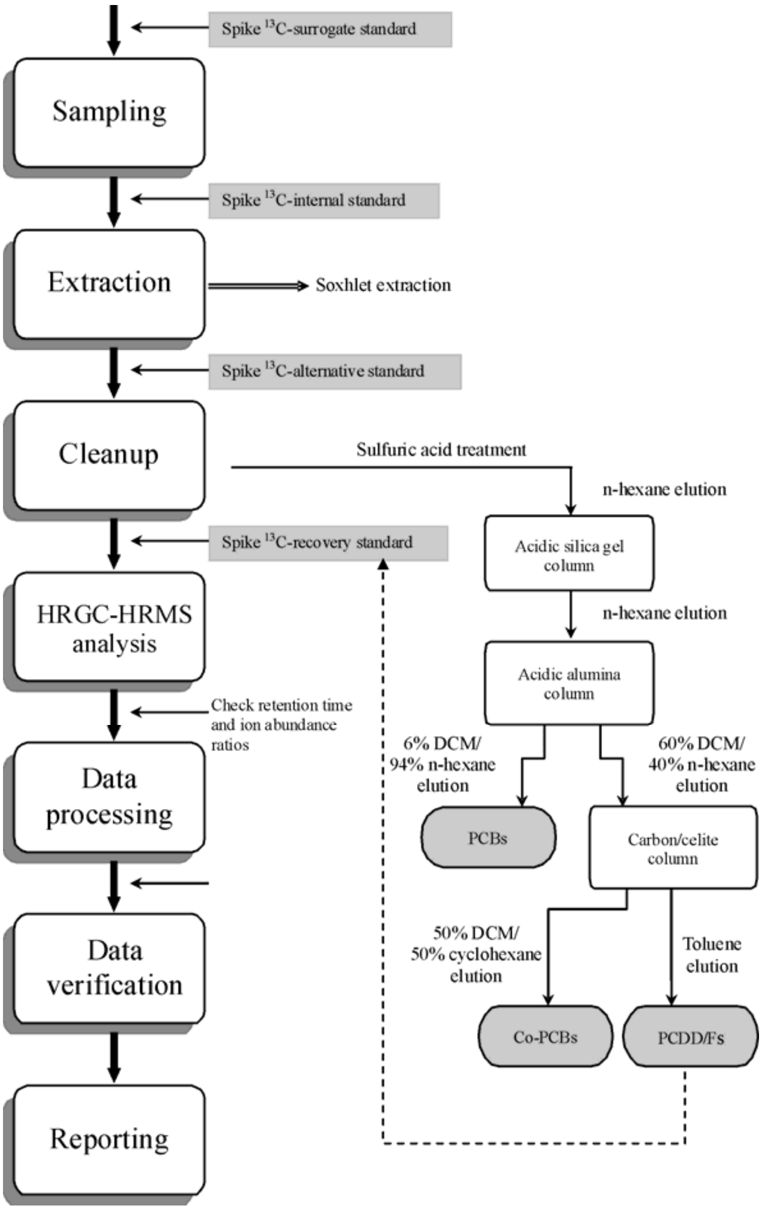

Fig. 2. Flow chart of PCDD/Fs analysis in stack emission gas.

Table 1 Results of inter-laboratory comparison of dioxins in real stack emission samples from sinter plants

Sampling site		Plant A			Plant B			Plant C		
Sample No.		1	2	3	4	5	6	7	8	9
CSC tested	Dioxin concentration (ng-I-TEQ/Nm^3)	0.434	0.462	0.244	0.510	0.799	0.500	0.356	0.314	0.555
	Average (ng-I-TEQ/Nm^3)		0.380			0.603			0.408	
NCU tested	Dioxin concentration (ng-I-TEQ/Nm^3)	0.395	0.496	0.289	0.532	0.721	0.483	0.346	0.298	0.634
	Average (ng-I-TEQ/Nm^3)		0.393			0.579			0.426	
Relative variation	Individual	9%	7%	17%	4%	10%	4%	3%	5%	13%
	Average		3%			4%			4%	

3.4 Characterization of Dioxin Congeners Profile from Real Plant

Figure 3 represents the individual dioxin congener TEQ profiles originating from the stack emissions of four CSC sintering plants. There are similar distributions of dioxin congeners in the stack emissions of the four sintering plants. In the CSC sintering plants, PCDFs are more dominant than PCDDs among the stack emission dioxins. Ten 2,3,7,8-substituted PCDFs contributed over 80% of the total I-TEQ, especially 2,3,4,7,8-PeCDF, which is the most dominant one making up more than half the total I-TEQ. Comparing the studies from British and Korean sintering plants [5-6], similar characterizations of dioxin congener profiles were also observed.

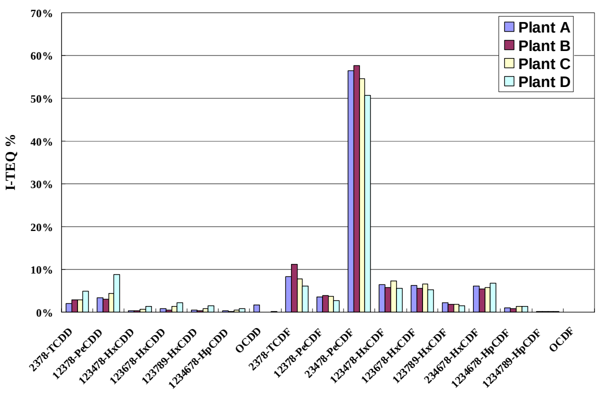

Fig. 3. Individual dioxin congener TEQ profiles originating from stack emissions from four CSC sinter plants.

4. SUMMARY

The CSC dioxin analysis laboratory has successfully developed the technique of analyzing dioxins, and started to provide comprehensive testing services on dioxins measurement since 2007. Up to September 2009, the laboratory has received approximately 1,200 samples for dioxin analysis from CSC's various plants. The sample types include stack emission, ambient air, ash, dust and zinc oxide. The validation results have shown that the CSC dioxin analysis laboratory has an excellent ability to analyze ultra trace PCDD/Fs in stack emission samples. To prove the reliability of the analytical data to the general public, the laboratory also submitted an accreditation application for testing dioxins in stack emission samples to the Environmental Protection Administration of Taiwan in June 2008. The laboratory was assessed by experts and gained approval from the technical committee of the Environmental Analysis Laboratory in October 2008, becoming a qualified laboratory that can provide the services of dioxin testing for stack emissions, related to the purpose of surveillance of emission regulations.

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