CORRELATION BETWEEN CHLOROBENZENE AND DIOXIN TEQS IN FLUE GAS FROM MUNICIPAL SOLID WASTE INCINERATOR

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Introduction

2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-tetra-CDD) and the corresponding dibenzofuran analogue (2,3,7,8-tetra-CDF) appear is the most toxic isomers[1], and it toxicity can be cyanide 1000 times. Dioxins were identified as carcinogens by World Health Organization (WHO). Currently, the most possible to achieve online monitoring is REMPI-TOFMS (Resonance Enhanced Multiphoton Ionization-Time of Flight Mass) or VUV-TOFMS (Vacuum Ultraviolet Ionization-Time of Flight Mass)[2-4]. Both have efficient selection of organic compounds ionization function in a complex atmosphere, combined with TOF technology, with the ability to quickly detect. Tsytsik et al used TOFMS and thermal gravimetric to research chlorobenzene control generated in municipal solid waste incineration (MWI).[5]

Dioxins surrogate compounds selection is very important to realized dioxins real time detection. Incomplete combustion products have a causal relationship with dioxins generation in the flue gas, and the degree of correlation is very large. The transient, unstable combustion in combustion process can significantly induce incomplete combustion products and dioxin formation. Based on the research about the reaction mechanism of dioxins generated by precursors, chlorobenzen is generally considered a better indicator. Blumstock and Gullett et al respectively used low chlorinated chlorobnezene (four chlorinated or less) as an indicator, and real-time detected dioxins I-TEQ in a MWI and flue gas. The result shows that the respectively correlation coefficient R^2 between chlorobenzen concentration and I-TEQ were 0.91 and 0.94.[6,7]

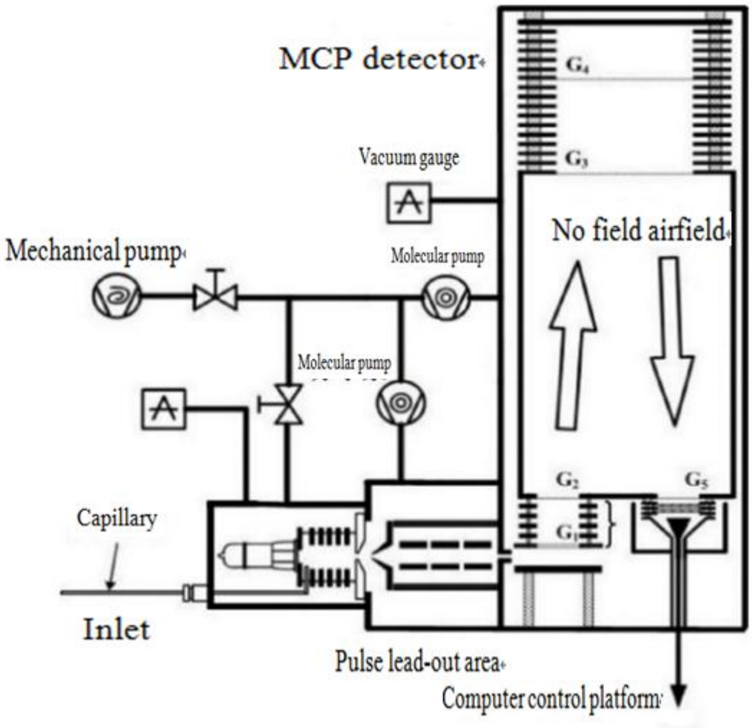
Materials and methods

Research data from fifteen typical domestic MWI incinerators, acquisition time focus on 2011~2012, daily disposal capacity 150~600t/d.

Based on the U.S. EPA 23 flue isokinetic sampling method, with the South Korean company's M5 flue gas sampler, sample volume control in about 2 m^3, while recording the oxygen content of the flue gas, samples need to be split, half offline analysis and half on-line detection.

In dioxins detection, pretreatment of flue gas samples using US EPA 23 method, analysis by JMS800D type High Resolution Gas Chromatography/ High Resolution Mass Spectrum (HRGC/HRMS) produced by Japan JEOL company, and instrument conditions in the relevant literature.[8] Chlorobenzen detection pretreatment is established by HJ 621-2011standard, analysis by Agilent 6890N GC.

VUV-TOFMS



Structure: ionization region; pulse lead out area, no fiel air field, microchannel plate detector (MCP)
Conditions: ion source voltage:50V; pulse voltage:391V; accelerating area voltage: -2513V; resolution: 500; mass range: 1~500; organic detection limit: 1ng/m^3; ionization source: 10.6 eV miniature vacuum ultraviolet light;

Results and discussion

Off-line

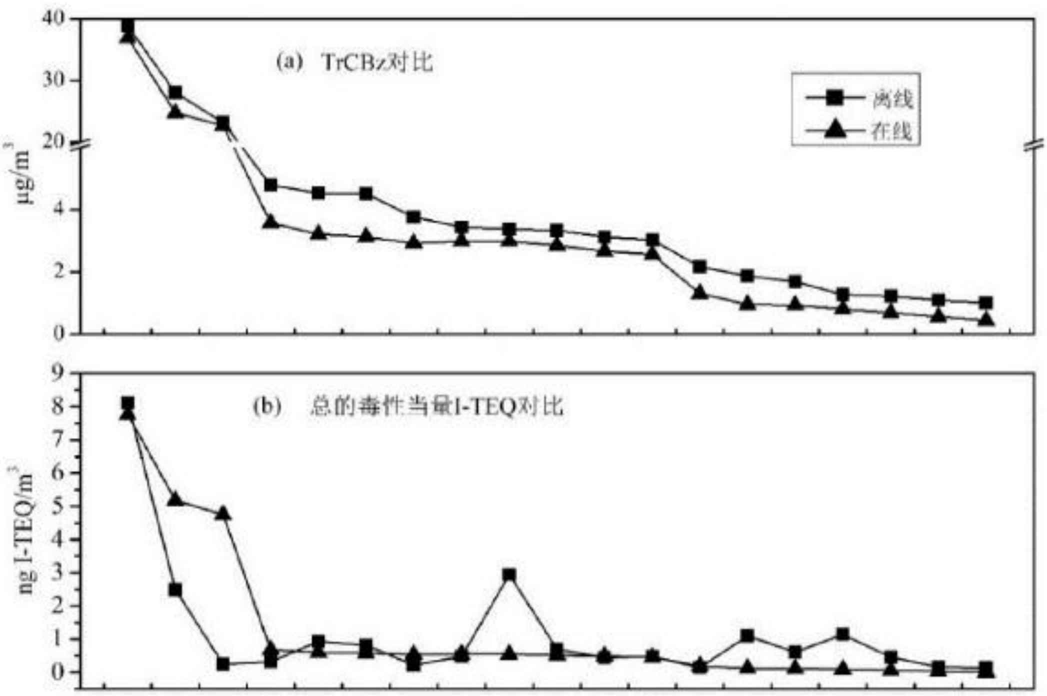
Precursors like chlorobenzenes are always* employed as indicators for online monitoring of dioxins and furans in flue gas. In order to construct a correlation model, chlorobenzenes (CBzs) and dioxins and furans in flue gas of a municipal solid waste incinerator (MSWI) were measured and investigated. The correlation coefficient between kinds of chlorobenzens indicators and PCDD/FS, I-TEQ were analysis by means of linear regression, which is based on the Pearson correlation coefficient generated by the principle of least squares.
The correlation coefficients (R^2) between trichlorobenzene (TrCBz), Tetrachlorobenzene (TeCBz), pentachlorobenzene (PeCBz), Hexachlorobenzene (HxCBz) and dioxin Toxic Equivalent (TEQ) are all above 0.8. TrCBz correlation coefficient (R^2) is 0.81, while PeCBz has the strongest correlation coefficient (R^2) 0.89**

	Indicators (Y)	Correlative equation	R^2
I-TEQ (X)	TrCBz	0.3907+4.6989X	0.8055
	TeCBz	0.0142+2.7633X	0.8606
	PeCBz	-1.9187+10.0904X	0.8964
	HxCBz	-0.0146+2.7812X	0.8298
	TrCBz	0.8625+0.1520X	0.8506

PCDD/Fs (X)	TeCBz	0.2858+0.0900X	0.9150
	PeCBz	-0.9412+0.3302X	0.9575
	HxCBz	0.2532+0.0912	0.8881

On-line

In practical applications, compared to high chlorinated chlorobenzenes, low chlorinated chlorobenzenes have advantages in instrument detection, which reflected in the smaller molecular weight and easily ionized. Take into account the practical application and characteristics of VUV-TOFMS instrument itself (VUV-TOFMS can 't distinguish three trichlorobenzens isomers), even if TeCBz, PeCBz and HxCBz correlation have advantages, TrCBz was used as an indicator for on-line experimental analysis.[9-11]



Compareation of offline and online

VUV-TOFMS was used to online detect TrCBz in a simulated gas stream. A very good linear relationship exists between signal strength and trichlorobenzene concentrations. The target substance detection was not interference by fragment ion peak. Online results compared with offline results, overall trends showed consistency. However, in offline low I-TEQ concentration region, the relative standard deviation is large. In high offline concentration region, can get a better online detection.If we use the constructed correlation model between TrCBz and TEQ value, a continuing online data for TEQs of dioxins and furans in flue gas can be easily calculated and visualized for guidance of combustion operating adjustment.

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