Online monitoring of trace chlorinated benzenes in flue gas of municipal solid waste incinerator by windowless VUV lamp single photon ionization TOFMS coupled with automatic enrichment system

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ABSTRACT

Chlorinated benzenes are typical precursors and indicators for polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) emissions from waste incinerators. Online and real-time monitoring of chlorobenzenes is a challenge due to their low concentration and complex nature of the flue gas. In this work, a continuous online monitoring system was built for detection of trace chlorinated benzenes based on a time-of-flight mass spectrometer (TOFMS). A single photon ionization (SPI) source based on a radiofrequency-excited windowless vacuum ultraviolet (VUV) lamp was developed for the first time to eliminate the signal attenuation resulting from the contamination of magnesium fluoride windows and to avoid the fragment ions. An automatic enrichment system including three parallel Tenax TA adsorption tubes was designed and coupled to the TOFMS to achieve the required ultrahigh sensitivity. The limits of quantitation at 7.65, 5.37 and 6.77 pptv were obtained for monochlorobenzene (MCBz), dichlorobenzene (DCBz) and trichlorobenzene (TrCBz), respectively, within a 29-min analytical period. Moreover, this apparatus was applied to continuously online monitor the actual flue gas from a waste incinerator for three months. During this period, the concentrations of MCBz, DCBz and TrCBz detected in the flue gas were in the range of 100~1200, 50~800 and 50~300 pptv, respectively. The relative standard deviation (RSD) of the sensitivity for the windowless VUV lamp ion source was 9.71% evaluated by the internal standard benzene over the 3-months flue gas monitoring. These results demonstrated the capability of this method in long-term analysis of the trace chlorinated benzenes in the flue gas.

Keywords: windowless VUV lamp; automatic enrichment; chlorinated benzenes; online monitoring; TOFMS

1. Introduction

Incineration has become one of the key treatment processes for municipal solid waste (MSW). However, polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), generated during the incineration process, may induce environmental pollution and cause serious social problems [1-3]. To evaluate the influence of the exhausted PCDD/Fs to organisms, the criterion of international toxic equivalence quantity (I-TEQ) was proposed via employing the concentrations of 17 toxic PCDD/Fs congeners [4]. Since the concentrations of PCDD/Fs in the flue gas are typically on the order of parts per quadrillion volume (ppqv) [5, 6], direct sampling and online measurement of PCDD/Fs is currently infeasible. So far, detecting the PCDD/Fs emissions from waste incinerators typically requires a multi-hour sample extraction, followed by 2-4 weeks of tedious analytical work to determine their concentrations in a laboratory [7, 8]. However, this time lag between the analytical results and the

operation conditions of incinerator prevents the plant from linking emissions to waste characteristics and plant operation in a timely fashion, so that it cannot guarantee the public safety. Therefore, it is desirable to be able to continuously online measure the PCDD/Fs concentration to control its emissions by adjusting the operation conditions for the incinerator. For this purpose, the dioxin precursor correlation method was developed in recent years, and the correlations between the PCDD/Fs and probable dioxin precursors were investigated [9, 10]. In these studies, the I-TEQ of the PCDD/Fs could be indirectly calculated through online monitoring of the concentrations for the dioxin precursors. The typical precursors mainly included polychlorobenzenes (PCBz) [11], polychlorophenols (PCPh) [12], polycyclic aromatic hydrocarbons (PAHs) [13], polychlorinated biphenyls (PCBs) [14], and so on. In fact, the concentrations of the precursors are generally over 1000 times higher than that of the PCDD/Fs [15], and correlated well with that of the PCDD/Fs [16, 17]. Blumenstock et al. [16] and Zimmermann et al. [17] used MCBz as the PCDD/Fs indicator, where a determination coefficient of $R^2 = 0.8200$ between the MCBz and the PCDD/Fs I-TEQ was obtained in both studies for a municipal waste incinerator. These works were consistent with other works [18, 19], where PCBz concentrations had been confirmed to have a strong correlation with the PCDD/Fs. Among all of the six chlorobenzenes, the low chlorinated benzenes, such as MCBz, DCBz and TrCBz, have lower boiling point and simpler structure, which had been proven to be easier for the online monitoring [20].

Various instruments based on mass spectrometry were developed for monitoring the chlorobenzenes. Kuribayashi et al. [21] constructed a vacuum ultraviolet single photon ionization ion trap time-of-flight mass spectrometry (VUV-SPI-IT-TOFMS) for online detection of TrCBz at a waste incinerator. Their results showed 10 pptv detection limits with 18 s response time. Even though SPI is a soft ionization process that can avoid fragmentation during the ionization process [22-24], the contamination on the MgF_2 window surface of the VUV lamp would gradually decay its detection sensitivity for a long-term measurement. They actually prepared eight windows working in turn to reduce this attenuation effect. However it would lead to some more complicated construction and operation problems. Additionally, other measurement method [6] based on a resonance-enhanced multiphoton ionization time-of-flight mass spectrometry (GC-REMPI-TOFMS) coupled with a gas chromatography was proposed to monitor the PCDD/Fs by using PCBz as the indicators. A correlation of $R = 0.850$ was established between 40 pairs of simultaneous 5-min GC-REMPI-TOFMS measurements of 1,2,4-TrCBz and 5 min conventional sampling and analysis for the PCDD/Fs I-TEQ. And the correlation between 1,2,4-TrCBz and total measures of PCDD/Fs was 0.890. However, this method involved a laser system that was bulky, expensive and sophisticated, which made it difficult for this method to be readily applicable. Hence, it is necessary to develop other innovative and inexpensive instruments and methods to achieve long-term stability and high sensitivity.

The VUV lamp is a kind of compact and solvent free SPI source. And SPI-MS system based on the VUV lamp had been widely applied to online analyzing organic species in recent years [24-26]. However, the attenuation of the sensitivity caused by the contamination of the light window during continuous work [21, 27] makes it unsuitable for the direct long-term monitoring. Furthermore, the low photon flux (10^{11} photons/s) limits its sensitivity at the level of several parts per billion volume (ppbv) [28-30], which makes this kind of VUV lamp SPI-MS system cannot detect the MCBz, DCBz and TrCBz at pptv level in the flue gas [15].

In this study, we developed a windowless VUV lamp single photon ionization TOFMS coupled with an automatic enrichment system for the online/real-time monitoring of MCBz, DCBz and TrCBz in the flue gas at an actual municipal solid waste incinerator (MSWI). The whole system had been used to continuously online monitor the concentrations of MCBz, DCBz and TrCBz at an actual MSWI for three months with an unattended operation.

2. Material and Methods

2.1. Instrumentation

The apparatus for online monitoring of the PCBz consisted of an automatic enrichment system and a home-built

reflection TOFMS, as shown in Figure 1. The TOFMS system included a windowless VUV lamp ion source, a radiofrequency-only (rf-only) quadrupole, a set of electrostatic ion optics lens and an orthogonal acceleration TOF (oaTOF) mass analyzer, as illustrated in Figure 1b.

The windowless VUV lamp ion source was composed of a commercial available windowless VUV lamp (EUV-X-L, Resonance Ltd., Ontario, Canada) with the photon flux about 10^{15} photons/sec/str and an ionization region. The windowless VUV lamp (178.66×113.39×96.65 mm) is a radiofrequency-excited discharge lamp and was installed on the top of the ionization region. Pure krypton was chosen as the discharge gas which was introduced into the discharge glass tube from a 8 L gas cylinder and controlled by a mass flow controller (MFC3). The acquired photon energies are 10.0 eV and 10.6 eV, which are high enough to ionize MCBz, 1,3-DCBz and 1,2,4-TrCBz with the ionization energies (IEs) of 9.07 eV, 9.10 eV and 9.04 eV, respectively. The ionization region was constituted of six circular stainless steel electrodes separated by five 1 mm thick insulator rings: a repelling electrode (6 mm thickness, 16 mm i.d., 28 mm o.d., and a 8 mm central hole in the front panel), four transmission electrodes (5 mm thickness, 16 mm i.d., 28 mm o.d.) and an orifice electrode (with a central hole 1mm in diameter). All of the electrodes were connected with 1 MΩ resistors in sequence. DC voltages of 17 V and 13 V were applied onto the repelling electrode and the orifice electrode, respectively.

Gaseous analytes were introduced into the ion source through two 127 μm i.d. and 7 cm in length stainless steel sampling capillaries (SSC1 and SSC2), one introducing the desorbed analytes and the other introducing 1 ppmv benzene standard gas. The analytes were ionized by the photons generated by the windowless VUV lamp, and then passed through the rf-only quadrupole region and the electrostatic ion optics lens region. The transmitted ions finally pulsed into the TOF mass analyzer and detected by the microchannel plate (MCP) detector. The signals were recorded by a 100-ps time-to-digital converter (TDC) (model 9353, Ametec Inc., Oak Ridge, U.S.A.). A mass resolution of ~3000 was achieved at m/z 78.

2.2. Automatic enrichment system

The automatic enrichment system, as shown in Figure 1a, included a standard gas preparation device which was kept at 200 °C, five two-way solenoid valves (VAL1-5), an adsorption and thermal desorption device, two MFCs, a sampling pump and a set of flue gas sampling and purification device. The adsorption and thermal desorption device consisted of three parallel Tenax TA adsorption tubes (Beijing Hua Rui Xin Yi Technology Ltd, Beijing, China) which were used for sample enrichment. Each Tenax TA adsorption tube was 5 mm i.d., 6 mm o.d., 150 mm in length and filled with 200 mg Tenax TA adsorbent.

The automatic enrichment process included the following three steps:

Adsorption: The temperature of the Tenax TA adsorption tubes was set at 35 °C, while the VAL2 and VAL4 were kept open, and the flow rate of the gas sampling pump was adjusted at 2 L/min by a rotameter. The gaseous analytes were then adsorbed by the Tenax TA adsorption tubes for 10 min along the green line. When analyzing standard samples, the VAL5 was kept open. While analyzing actual flue gas, the VAL5 was closed.

In addition, the 1ppmv benzene standard gas was introduced into the ionization region via SSC2 at 15 mL/min flow rate controlled by MFC4 during the adsorption process. The benzene signals were recorded for online assessing the stability of the windowless VUV lamp ion source.

Thermal desorption: After the adsorption step finished, the VAL1, VAL2 and VAL3 were kept open, the temperature of the Tenax TA adsorption tubes was set at 250 °C, and the flow rate of the sweep gas, N₂, was controlled at 50 mL/min by MFC1, simultaneously. The temperature of the adsorption tubes could increase from 35 °C to 250 °C within 3.5 min, then the sample was desorbed at 250 °C and introduced into the ionization region through the SSC1 along the brown line. The entire thermal desorption process persisted for 15 min, during which the flue gas signals were recorded.

Cooling: After the thermal desorption step finished, the cooling device (See Fig.S1 of supplementary data) began to work. The temperature of the adsorption tubes was decreased to 35 °C within 4 min.

It's worth noting that, the pipelines connected with each part of the enrichment system and the SSC1 were all kept at 180 °C to prevent the target analytes from condensation and adsorption. In addition, all steps of the enrichment system were

automatically controlled by a multifunctional circuit board working with a specific timing sequence (See Fig. S2 of supplementary data).

Fig. 1. Schematic diagram of (a) the automatic enrichment system and, (b) the windowless VUV lamp SPI-TOFMS.

2.3. The flue gas sampling

The flue gas was sampled by a sampling probe, then passed through a metal sintering filter, a condensation filter and a nafion tube. The flue gas finally arrived at the enrichment system, while a high temperature resistant pump was used as the driven power. Water moisture, hydrogen chloride and particulate matter were removed by this treatment. All of the flue gas transmission pipelines were kept at 180 °C during sampling procedure.

2.4. Sample preparation

A 1 ppmv standard benzene gas in nitrogen (Dalian Special Gas Company, Dalian, China) was used for online stability assessment of the ion source. MCBz, 1,3-DCBz, 1,2,4-TrCBz and methanol were all analytical grade (Tianjin kemiu chemical reagent Ltd, Tianjin, China). Nitrogen (N₂) and krypton (Kr) with purity higher than 99.9993% were purchased from Dalian Special Gas Company, Dalian, China.

A concentration of 2.23×10^{-3} mol/L PCBz standard stock solution was prepared by adding 11.4 μ L of MCBz, 12.6 μ L of 1,3-DCBz and 13.9 μ L of 1,2,4-TrCBz to a 50 mL volumetric flask with purified methanol, simultaneously. Other lower concentration samples, e.g. 2.23×10^{-5} mol/L and 2.23×10^{-6} mol/L were prepared by stepwise dilution of the standard stock solution. The gaseous standard samples with desired concentrations were prepared by mixing the standard solutions with N₂ at different flow rates through the standard gas preparation device. For example, introducing 2.23×10^{-5} mol/L PCBz standard solution into the standard gas preparation device at a flow rate of 20 μ L/min controlled by a microsyringe pump, at the same time 2 L/min N₂ controlled by the MFC2 was introduced, and thus a concentration of 5ppbv of the three chlorobenzenes vapor were obtained.

3. Results and discussion

3.1. Typical mass spectrum of MCBz, 1,3-DCBz and 1,2,4-TrCBz

Figure 2 shows the typical mass spectrum of 5 ppbv MCBz, 1,3-DCBz and 1,2,4-TrCBz obtained after enrichment by this

system. The characteristic ions of the three chlorobenzenes were all molecular ions M^+ , showing the soft ionization feature of the windowless VUV lamp ion source. For the element chlorine (Cl), there are two isotopes of ^{35}Cl and ^{37}Cl with the abundance ratio of 1:0.32. Therefore, MCBz had two characteristic peaks m/z 112 and 114. For 1,3-DCBz the characteristic peaks were m/z 146 and 148. For 1,2,4-TrCBz the characteristic peaks were m/z 180, 182 and 184. As shown in Figure 2, the actual measurement intensity ratios of the characteristic peaks for MCBz, 1,3-DCBz and 1,2,4-TrCBz were 1:0.33, 1:0.65 and 1:0.93:0.30, respectively, which were in accordance with the values calculated from the theoretical abundance ratio of the Cl isotopes. It should be noted that the main peaks m/z 112, 146 and 180 were chosen for MCBz, 1,3-DCBz and 1,2,4-TrCBz for quantitative analysis, respectively.

Fig. 2. Typical mass spectrum of MCBz, 1,3-DCBz and 1,2,4-TrCBz obtained by the windowless VUV lamp SPI-TOFMS

3.2. Optimization the parameters of the windowless VUV lamp ion source

One ppmv MCBz, 1,3-DCBz and 1,2,4-TrCBz were used for the optimization of the windowless VUV lamp ion source without enrichment, which focused on the flow rate of discharging gas and the pressure of the ionization region. Figure 3a illustrated the intensity changes of the three chlorobenzenes with the pressure of the ionization region changed from 43 Pa to 157 Pa while the flow rate of Kr was maintained at 10 mL/min. The signal intensities shown in Figure 3a had a trend of increase while the pressure were under 105 Pa and then decreased between 105 Pa to 157 Pa. The increase of the intensities was mainly attributed to the increased density of the analytes, while the decrease was attributed to the deterioration of the discharge conditions for the windowless VUV lamp and the excessive ion-molecule collisions which reduced the ions transmission efficiency under higher pressures. The optimal pressure for the windowless VUV lamp ion source was thus found to be 105 Pa.

With the pressure fixed at 105 Pa, the Kr flow rate was optimized as following. As shown in Figure 3b, the signal intensities of the tested compounds increased as the flow rate increased from 7 mL/min to 11.5 mL/min initially and then kept decreasing from 11.5 mL/min to 20 mL/min. This phenomenon could be explained by two aspects, the number density of the photons and the dilution effect towards the sample gases. On the one hand, more photons were produced with the increasing of Kr flow rate, which promoted the ionization efficiency of the analytes. On the other hand, further increase of the Kr flow rate may dilute the sample significantly, which lowered the number density of the analytes and thus reduced the detection sensitivity.

Fig. 3. The optimization of the windowless VUV lamp ion source: (a) pressure of the ionization region and, (b) flow rate of Kr

3.3. Optimization the parameters of the automatic enrichment system

Five ppbv chlorobenzenes standard gas was used to optimize the automatic enrichment system, which mainly targeted for the following four aspects: the TOFMS sampling speed, the sampling flow rate, the time-delay between desorption and sampling and finally the data acquisition time.

The TOFMS sampling speed refers to the speed of introducing the desorbed gases into the ionization region, which was determined based on the size of SSC1. With the pressure of the ionization region fixed at 105 Pa, the TOFMS sampling speed was optimized. As depicted in Figure 4a, with the increase of the TOFMS sampling speed, the thermal desorption time was shortened while the detected signal intensities illustrated a trend of decline after the initial increase. The former phenomenon was attributed to the greater TOFMS sampling speed that signified the faster removal of the analytes around the Tenax TA adsorbent. This process was conducive to break the adsorption and desorption equilibrium process of the adsorbent, while accelerated the thermal desorption process. The latter observation was attributed to the feature of the TDC which can record only one count at each time, and cannot accumulate more signals in a shorter time range, resulting in excessive loss of the analyte ions. Therefore, 10 mL/min was selected as the optimal TOFMS sampling speed, where the signal intensity was the highest with acceptable 15 min desorption time.

The sampling flow rate refers to the total speed of sample gas passing through the Tenax TA adsorption tubes during the adsorption process, which depends on the pumping speed of the sampling pump. As shown in Figure 4b, with the decrease of the sampling flow rate, the detection sensitivity decreased gradually. The optimal sampling flow rate of our system was significantly higher than that of previous work [31], where the optimal sampling flow rate of a single Tenax TA adsorption tube was found to be 200 mL/min. The result was attributed to the design of three parallel adsorption tubes for our adsorption device, which increased the sampling flux as well as the detection sensitivity. Considering that the full speed of our sampling pump was 3 L/min and the requirements of the long-term stable operation without any damage for the pump, the sampling flow rate of 2 L/min was chosen with only 15% intensity reduction compared with the flow rate at 3 L/min.

The time-delay between desorption and sampling determined the appropriate time point for introducing the desorbed gases into the ionization region after the adsorption process, i.e. the waiting time after the heating process (from 35 °C) of the adsorption tubes begins, which was controlled by the VAL1. As clearly displayed in Figure 4c, the 0 min time-delay could get the highest sensitivity, indicating that the sampling step should be conducted immediately at the end of the adsorption process.

The data acquisition time refers to the time range needed for the sample collection. Its optimization was based on the thermal desorption curves. As shown in Figure 4d, although the three chlorobenzenes have different boiling point, the desorption temperature (250 °C) was high enough so that they were almost desorbed simultaneously. Therefore, the most suitable time for the data acquisition was from 230 s to 530 s, during which the signal intensities of the three chlorobenzenes were at the highest so that the best sensitivity were obtained.

Fig. 4. Optimizations of the automatic enrichment system: (a) TOFMS sampling speed, (b) sampling flow rate, (c) time-delay between desorption and sampling, (d) data acquisition time from the thermal desorption curves

3.4. Performance

Under the optimal conditions described before, 5 ppbv standard samples for MCBz, 1,3-DCBz and 1,2,4-TrCBz were tested by this system for 8 cycles while the thermal desorption processes of each cycle were tracked. Clearly exhibited in Figure 5, the RSDs of the maximum signal intensities of the three compounds during each cycle were 4.9%, 5.6% and 8.1%, respectively. These results revealed that this system was stable enough for the actual flue gas measurement.

Fig. 5. Thermal desorption processes of 8 cycles of the whole system with 5 ppbv MCBz, 1,3-DCBz and 1,2,4-TrCBz

In addition, 10, 20, 50, 100, 200, 500, 1000, 2000, 5000, 10000 pptv mixed standard samples of the three chlorobenzenes and benzene, o-chlorophenol and 2,4-dichlorophenol were analyzed five times at each concentration, the RSDs for MCBz, 1,3-DCBz and 1,2,4-TrCBz were 4.4%, 5.1% and 7.8%, respectively. Among the six compounds, benzene, o-chlorophenol and 2,4-dichlorophenol were selected as the matrix to evaluate the matrix effect. As a result, a satisfactory linearity from 10 pptv to 10000 pptv for the MCBz, 1,3-DCBz and 1,2,4-TrCBz was obtained, and a good linearity for the benzene, o-chlorophenol and

2,4-dichlorophenol from 50 pptv to 10000 pptv was also obtained, which implied that the matrix effect on the single photon ionization efficiency is not serious. The calibration curves can be found in the supplementary data (See Fig. S3). As shown in Table 1, the determination coefficient (R^2) for MCBz, 1,3-DCBz and 1,2,4-TrCBz were 0.9841, 0.9899 and 0.9946, respectively. Based on the signal-to-noise (S/N) ratios and the calibration curves, the limits of detection (LODs, S/N=3) of the MCBz, 1,3-DCBz and 1,2,4-TrCBz were calculated as 2.63, 1.71 and 2.14 pptv, respectively; the limits of quantitation (LOQs, S/N=10) were calculated to be 7.65, 5.37 and 6.77 pptv for MCBz, 1,3-DCBz and 1,2,4-TrCBz.

Table 1

Linear ranges, Determination coefficient, Quantitative equations, LODs and LOQs

Compounds	Linear range (pptv)	Quantitative equations	Determination coefficient (R^2)	LODs (pptv)	LOQs (pptv)
MCBz	10-10000	$\lg(y^a) = 0.83 + 1.12 \lg(C_{\text{MCBz}})$	0.9841	2.63	7.65
1,3-DCBz	10-10000	$\lg(y^a) = 1.06 + 1.04 \lg(C_{\text{DCBz}})$	0.9899	1.71	5.37
1,2,4-TrCBz	10-10000	$\lg(y^a) = 0.96 + 1.03 \lg(C_{\text{TrCBz}})$	0.9946	2.14	6.77

^a Intensities of the three chlorobenzenes in mass spectra.

3.5. Applications

The whole system was used for the online monitoring of MCBz, DCBz and TrCBz in actual flue gas for three months from a MSWI in China with an unattended operation. The typical SPI mass spectrum of the actual flue gas was shown in Figure 6a. It could be seen that the flue gas was a complicated mixture which contained numerous compounds such as propionic acid, butyric acid, phenol, MCBz, DCBz and TrCBz [15]. Figure 6b showed the monitoring curve of the 1 ppmv benzene internal standard gas during the three months. During the entire monitoring process, the incinerator was shutdown four times for maintenance which were marked as 1, 2, 3 and 4 in Figure 6b. Excluding these four maintenance stages, the RSD for benzene intensities was 9.71%. The result indicated that the windowless VUV lamp could work steadily for a long period of time without any maintenance procedure comparing with the results from the conventional VUV lamp work, because this method avoided the contamination of the light window. In addition, the stability of the automatic enrichment system was also evaluated at the beginning of the monitoring process and the following labelled 2, 3, 4 incinerator shutdown periods, respectively. The result was shown in the supplementary data (See Fig. S4).

Fig. 6. (a) Typical SPI mass spectrum of the actual flue gas, (b) monitoring curve of the 1 ppmv benzene standard gas during the three months

Figure 7a displayed the change trends of the concentrations of MCBz, DCBz and TrCBz in the flue gas during the three months. From the monitoring curves, it could be observed that there was an initially significant increase of the concentrations of the three chlorobenzenes when the incinerator resumed again from the maintenances, which was consistent with the previous researches [32-34], where an increase of the PCDD/Fs emissions during combustor transients had been reported. After the star-

tup, the three chlorobenzenes had different behaviors, as shown in Figure 7b, the zoom in results of the change curves from 9/19/2014 to 9/26/2014. DCBz and TrCBz kept decreasing slowly monotonically while MCBz tended to be stable with a slight increase in the end. These phenomena suggested that rapid online monitoring of the trace chlorinated benzenes in flue gas is necessary to identify the reasons why the PCDD/Fs emissions would increase during the combustor transients. Furthermore, the concentrations of MCBz, DCBz and TrCBz in the flue gas in the range of 100-1200 pptv, 50-800 pptv and 50-300 pptv were quantified during the three months, respectively. Prospectively, these concentration information could be used to calculate the I-TEQ of PCDD/Fs once the relationship between the concentrations of chlorobenzenes and the I-TEQ of PCDD/Fs was established. The correlation will be studied in our following works.

Fig. 7. (a) Concentration change trends of MCBz, DCBz and TrCBz in the flue gas during the three months, (b) Zoom in of the change curves from 9/19/2014 to 9/26/2014.

Compared with other online methods, such as Kuribayashi et al. (VUV-SPI-IT-TOFMS) [21] and Zimmermann et al. (REMPI-TOFMS) [17], our system has its unique advantages. In the former study, a VUV lamp with MgF_2 window was act as the ion source and a quadrupole ion trap was used to accumulate the target ions to enhance the sensitivity. The LOD at 10 pptv for TrCBz was achieved. In the latter study, a 1 + 1 two-photon REMPI with laser wavelength at 269.82 nm was used to enhance the ionization efficiency of MCBz. The LOD for MCBz was better than 100 pptv. In our system, a windowless VUV lamp was proposed as the ion source to improve the long-term stability. Furthermore, three chlorobenzenes, i.e. MCBz, DCBz and TrCBz, could be detected simultaneously and an automatic enrichment system was developed to lower the LODs of them as low as 1.71-2.63 pptv. Additionally, the flue gas could be online monitored in long-term with unattended operation by our system, while both of the above quoted studies could not achieve.

4. Conclusions

In this study, the windowless VUV lamp SPI-TOFMS coupled with an automatic enrichment system had been developed to online monitor the pptv-level PCBz emissions from the waste incinerator. As a result, the attenuation and insufficient of the sensitivity with conventional VUV lamp were overcome. The LOQs for MCBz, DCBz and TrCBz were 7.65, 5.37 and 6.77 pptv within 29-min measurement period, respectively. The system was then applied for the online, real-time monitoring of MCBz, DCBz and TrCBz in actual waste incineration flue gas for three months with an unattended operation. During the three months, the concentrations of MCBz, DCBz and TrCBz obtained in the flue gas were in the range of 100~1200, 50~800 and 50~300 pptv, respectively. The RSD of the sensitivity for the windowless VUV lamp ion source was 9.71%. The results showed that this system had a robust performance and was able to achieve high sensitivity and stability in analyzing MCBz, DCBz and TrCBz in the flue gas for long-term autorun, which has important significance for controlling the PCDD/Fs emissions by real-time optimization of the incineration conditions.

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366