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A novel carbon trap sampling system for coal-fired flue gas mercury measurement

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Abstract: A novel carbon trap sampling system for gas-phase mercury measurement in flue gas is developed, including the high efficient sorbents made of modified biomass cokes and high precision sorbent traps for measuring particle-bound and total vapor-phase mercury in flue gas. A dedusting device is installed to collect fine fly ash for reducing the measurement errors. The thorough comparison test of mercury concentration in flue gas is conducted between the novel sampling system and the Ontario hydro method (OHM) in a 6 kW circulating fluidized bed combustor. Mercury mass balance rates of the OHM range from 95.47% to 104.72%. The mercury breakthrough rates for the second section of the sorbent trap are all below 2%. The relative deviations in the two test cases are in the range of 15.96% to 17.56% under different conditions. The verified data suggest that this novel carbon trap sampling system can meet the standards of quality assurance and quality control required by EPA Method 30B and can be applied to the coal-fired flue gas mercury sampling system.

Key words: mercury sorbent trap; coal-fired flue gas; mercury sampling unit

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Coal-fired power plants are the largest source of anthropogenic mercury emissions. According to the global mercury assessment[1], approximately 484 t of mercury in the air originated from coal-fired power plants in 2010, accounting for 24% of total anthropogenic mercury emissions. Mercury pollution has been of considerable concern due to its high toxicity, which is widely known to cause neurological, accumulative and permanent damage in humans[2].

Actually, research on the mechanism of mercury speciation and emission can help to effectively control mercury pollution from coal-fired flue gas. Therefore, it is necessary to develop novel sampling and monitoring technologies to measure mercury in flue gas with accuracy and expedience. The present monitoring technologies for industrial application can be divided into two categories[3]. They are the artificial sampling and analyzing method and the mercury continuous emission monitoring system (Hg-CEMS).

The Ontario hydro method (OHM) is recognized to be the standard and reference method for artificial mercury measurements in flue gas[4]. However, its operational complexity and errors tendency in solution preparation, digestion and analysis are not negligible. The Hg-CEMS can continuously sample the stack gases and provide an indication of mercury concentration in the flue gas. However, the high cost and difficult equipment maintenance have significantly restricted its wide application[5]. In recent years, a sorbent trap method known as EPA Method 30B has been gradually accepted internationally[6] for its easy operation, high precision and low cost. Nevertheless, the sorbent traps can be blocked by the ash in the flue gas easily. Another remarkable problem is the high cost of the activated carbons used in the sorbent traps. Therefore, it is highly imperative to develop a low cost and highly effective mercury sorbent to serve the carbon traps based on a broad potential utilization in coal-fired power plants. A novel self-developed carbon trap sampling system for gas-phase mercury measurements in flue gas based on the EPA Method 30B is introduced in this paper, focusing on the preparation of high efficient sorbents derived from modified biomass cokes and the innovative design of the dedusting device. Experimental tests for mercury measurement are conducted in a 6 kW circulating fluidized bed (CFB) combustor. The comparative results between the novel sampling system and the OHM were analyzed to evaluate the performance of this novel sampling system for flue gas mercury measurements.

1 The Mercury Carbon Trap Sampling System

The novel self-developed carbon trap sampling system adheres to the technical requirements of the quality accuracy and quality control (QA/QC) of EPA Method 30B. The entire sampling system consists of five parts (see Fig. 1), namely, the dedusting device, the carbon sorbent trap, water removal, the flow controller, and the temperature controller.

1.1 Mercury carbon trap

The whole carbon sorbent trap is made of Pyrex, which

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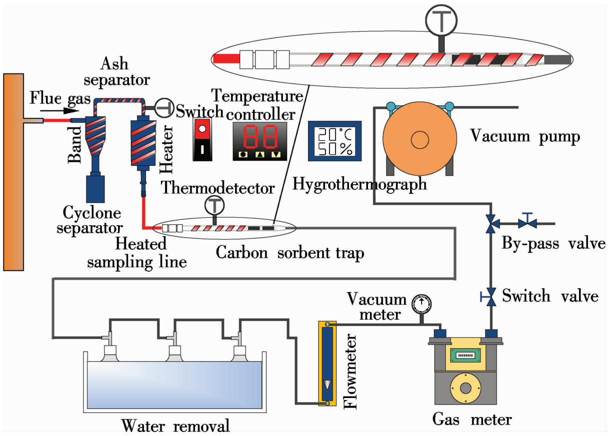


Fig. 1 Schematic diagram of carbon trap sampling system

is a type of heat resisting glass and has mercury adsorption free on the tube surface. The standard size of 200-mm length and 10-mm outside diameter of the sorbent trap is adapted, as shown in Fig. 2. For easy installation and disassembly, a connector made of Teflon is used between the carbon sorbent trap and the front sampling nozzle.

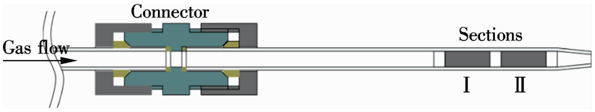


Fig. 2 Carbon sorbent trap for mercury measurement

This sorbent trap consists of two separated sorbent sections which are insulated by the fiberglass. Section Ⅰ represents the absorption part and Section Ⅱ is the breakthrough part. Each section is loaded with 500 mg sorbents.

1.2 Dedusting device

The sorbent traps can be blocked by the ash in the flue gas[7]. A dedusting device is equipped to prevent the ash from jamming the sorbent traps so that the sampling can be conducted in flue gas with the ash concentration. As illustrated in Fig. 3, the dedusting device contains a cyclone separator and filter. During the sampling, the large particle ash (PM 10) in the flue gas is separated by the cyclone, while the remaining ash (PM 2.5) is screened by the filter. This preprocessed gas guarantees a measurement which is accurate and reliable.

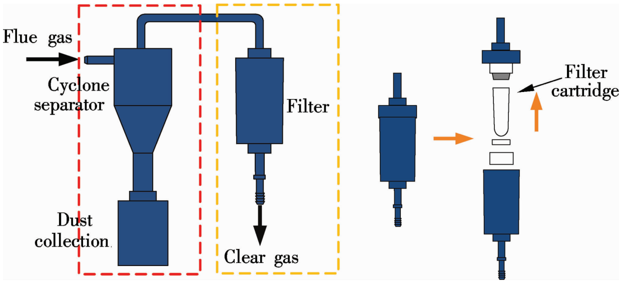


Fig. 3 Schematic diagram of dedusting device

1.3 Control of temperature and flow rate

The sampling line is heated electrically and coupled with the PID temperature control ensuring that the entire dedusting, sampling and adsorption process are conducted under a stable temperature around 120 ℃ for preventing the steam and gas-phase mercury in the flue gas from condensing. The isokinetic sampling and flow regulation are operated by the flow meter, gas meter and vacuum pump, restricting the sampling flow error within 2%[6].

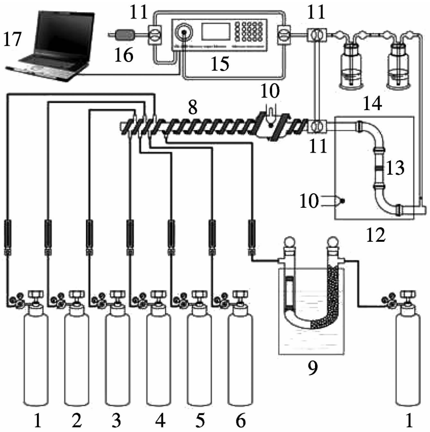
2 Quality Accuracy and Quality Control

In order to ensure the precision of sampling results, strict adherence is required to the EPA standard regulations of QA/QC[6]. The gas tightness should be checked before and after the sampling test. The negative pressure of the leak check must be 50.662 kPa[8] minimum. In detail, before sampling, the gas leak flow should be less than 4% of the setting flow, while after sampling, the gas leak flow should be less than 4% of the average flow.

2.1 Performance of sorbents

Since the commonly used sorbent trap is of high cost due to the consumption of the activated carbons, it is nessary to develop highly efficient but low cost sorbents. An innovative carbon sorbent made of modified biomass coke is proposed in this study for replacing the activated carbons, which performs as efficiently as commercial activated carbon[9].

Three kinds of modified biomass sorbents are tested on the fixed bed adsorption systems to verify their adsorption capacity for mercury (see Fig. 4). The performance test is conducted in the simulated flue gas at 150 ℃, which has similar components to the coal fired flue gas. The tested sorbents are placed on the adsorption column homogeneously. The gas-phase mercury can be adsorbed by the sorbents when the simulated flue gas passes through.



1 to 6—Simulated flue gas; 7—Flow meter; 8—Electrical heating belts; 9—Mercury permeation device; 10—Thermocouple; 11—Teflon triple valve; 12—Hot box; 13—Adsorption column; 14—Absorption liquid; 15—Mercury analyzer; 16—Activated carbon column; 17—Computer

Fig. 4 Fixed-bed Hg adsorption system

The mercury mass balance rate $R^{\mathrm{f}}_{\mathrm{Hg}}$ and breakthrough rate $B^{\mathrm{f}}_{\mathrm{Hg}}$ of mercury on the fixed bed is introduced to evaluate the mercury adsorption performance of these prepared sorbents. $R^{\mathrm{f}}_{\mathrm{Hg}}$ is the mercury absorption accuracy of the sorbents, and $B^{\mathrm{f}}_{\mathrm{Hg}}$ is the mercury adsorption efficiency of the sorbents. Both $R^{\mathrm{f}}_{\mathrm{Hg}} \leqslant 120\%$ and $B^{\mathrm{f}}_{\mathrm{Hg}} \leqslant 5\%$ [10-11] are required by necessity by QA/QC, $R^{\mathrm{f}}_{\mathrm{Hg}}$ and $B^{\mathrm{f}}_{\mathrm{Hg}}$ can be, respectively, calculated by

$$R^{\mathrm{f}}_{\mathrm{Hg}} = \frac{m^{\mathrm{s}}_{\mathrm{Hg}}}{m^{\mathrm{f}}_{\mathrm{Hg}}} \times 100\% \tag{1}$$

where $m^{\mathrm{s}}_{\mathrm{Hg}}$ is the total mass of Hg adsorbed by sorbents, μg; $m^{\mathrm{f}}_{\mathrm{Hg}}$ is the total mass of Hg flowing through the fixed bed reactor, μg.

$$B^{\mathrm{f}}_{\mathrm{Hg}} = \frac{m^{\mathrm{2nd}}_{\mathrm{Hg}}}{m^{\mathrm{T}}_{\mathrm{Hg}}} \times 100\% \tag{2}$$

where $m^{\mathrm{2nd}}_{\mathrm{Hg}}$ is the mass of Hg adsorbed by sorbents in the second layer of the fixed bed reactor, μg; $m^{\mathrm{T}}_{\mathrm{Hg}}$ is the total mass of Hg captured by the fixed bed reactor, μg.

2.2 Quantity of adsorbed Hg mass

Fig. 5 indicates the definition of mercury mass in each section of the trap. According to the protocols[12] of EPA Method 30B, the mass of mercury adsorbed in Section Ⅰ (m_1) should be the sum of P_1, S_1 and P_2, and mercury in Section Ⅱ (m_2) should be the sum of S_2 and P_3. S_1 and S_2 mean the sorbents while P_1, P_2 and P_3 represent the interval layers of fabric filter.

$$m_1 = m_{\mathrm{P}_1} + m_{\mathrm{S}_1} + m_{\mathrm{P}_2} \tag{3}$$

$$m_2 = m_{\mathrm{S}_2} + m_{\mathrm{P}_2} \tag{4}$$

Based on the former definition, the mercury concentration $C^{\mathrm{T}}_{\mathrm{Hg}}$ measured in the flue gas can be calculated by

$$C^{\mathrm{T}}_{\mathrm{Hg}} = \frac{m_1 - m_2}{V^{\mathrm{s}}_{\mathrm{m}}} \times 100\% \tag{5}$$

where $V^{\mathrm{s}}_{\mathrm{m}}$ is the volume of dry flue gas under the standard condition, m^3.

Fig. 5 Schematic diagram of sorbent trap

2.3 Breakthrough rate

To evaluate the precision of the carbon trap, the breakthrough rate (RB) of Section Ⅱ is defined by

$$\mathrm{RB} = \frac{m_2}{m_1} \times 100\% \tag{6}$$

A valid sample[13] conducted by the carbon trap requires that if the Hg concentration is more than 1 $\mu\mathrm{g/m}^3$, RB must be within 10%, and if the Hg concentration is less than or equal to 1 $\mu\mathrm{g/m}^3$, RB must be within 20%. Otherwise, the sample data are invalid.

2.4 Relative deviation

The relative deviation (RD) is evaluated by comparing the measuring results of sorbent traps with the simultaneous results obtained by the OHM, which is accepted as the reference method for mercury measurements in flue gas. RD is calculated by

$$\mathrm{RD} = \frac{C^{\mathrm{T}}_{\mathrm{Hg,OHM}} - C^{\mathrm{T}}_{\mathrm{Hg,30B}}}{C^{\mathrm{T}}_{\mathrm{Hg,OHM}}} \times 100\% \tag{7}$$

where $C^{\mathrm{T}}_{\mathrm{Hg,OHM}}$ is the mercury concentration in the flue gas measured by OHM, $\mu\mathrm{g/m}^3$; $C^{\mathrm{T}}_{\mathrm{Hg,30B}}$ is the mercury concentration in the flue gas measured by the sorbent trap, $\mu\mathrm{g/m}^3$.

According to the precision criterion required by QA/QC[11], if the Hg concentration is more than 1 $\mu\mathrm{g/m}^3$, the RD must be within 10%, and if the Hg concentration is less than or equal to 1 $\mu\mathrm{g/m}^3$, the RD must be within 20%. Since the $C^{\mathrm{T}}_{\mathrm{Hg,OHM}}$ is recognized as the standard value, the RD can reflect the measurement accuracy of the data measured by sorbent traps effectively.

3 Results and Discussion

3.1 Adsorption ability of sorbents

Three kinds of sorbents (AC-HBr, AC-KI and HC-PHBr) are selected for the adsorption ability test. AC-HBr and AC-KI are two kinds of activated carbons modified by HBr and KI, respectively, while RHC-PHBr is a kind of biomass (rice husk) coke chemically treated by phosphorus activation and HBr modification.

These sorbents are tested under simulated flue gas loaded with mercury containing 6% O_2, 12% CO_2, 0.12% SO_2 and 0.03% NO. The rest content is N_2. During the test, the total mercury mass in the entrance and the exit of the fixed bed reactor are recorded. The mass of mercury entering the adsorption column and absorbed by tested sorbents are compared for evaluating the performance of the sorbents, which are respectively defined as the theoretical adsorption capacity and actual adsorption capacity. The Hg balance rate $R^{\mathrm{f}}_{\mathrm{Hg}}$ and breakthrough rate $B^{\mathrm{f}}_{\mathrm{Hg}}$ are introduced to reflect the quantity of mercury that is adsorbed or breaks through.

The data in Tab. 1 suggest that these tested sorbents passed the restrictions of $R_{\mathrm{Hg}} \leqslant 120\%$ and $B_{\mathrm{Hg}} \leqslant 5\%$, indicating that when the simulated gas flows through the adsorption column, gas-phase mercury is adsorbed by the sorbents completely and immediately. Moreover, the modified biomass cokes perform perfectly as the activated carbons for mercury adsorption. The adsorption ability test suggests that the modified sorbents possess an outstanding mercury adsorption property and capacity, and are competent for the Method 30B sorbent traps measurement, which should be recognized for its significant contribution to reducing the high sampling cost.

3.2 Hg mass balance by OHM

The OHM is adopted as the reference method during the comparison test. To ensure the validity, the Hg mass balance by the OHM is also examined under different conditions, as shown in Tab. 2.

Tab. 1 Hg equilibrium test for sorbent

Adsorbents	Total Hg mass/μg (Entrance)	Total Hg mass/μg (Exit)	Theoretical adsorption capacity/μg	Actual adsorption capacity/μg	$R_{\mathrm{Hg}}^{\mathrm{f}}$/%	$B_{\mathrm{Hg}}^{\mathrm{f}}$/%
AC-HBr	5.784	0	5.784	5.596	103.25	1.46
AC-KI	5.784	0	5.784	4.718	118.43	0.81
RHC-PHBr	5.760	0	5.760	5.205	109.64	1.03

Tab. 2 Measuring results by the OHM

Condition	$C_{\mathrm{Hg}}^{0}/(\mu g \cdot m^{-3})$	$C_{\mathrm{Hg}}^{2+}/(\mu g \cdot m^{-3})$	$C_{\mathrm{Hg}}^{\mathrm{P}}/(\mu g \cdot m^{-3})$	$C_{\mathrm{Hg}}^{\mathrm{T}}/(\mu g \cdot m^{-3})$	R_{Hg}^{0}/%	R_{Hg}^{2+}/%	$R_{\mathrm{Hg}}^{\mathrm{P}}$/%	Equilibrium rate of Hg mass/%
0.1% $CaCl_2$	2.276	2.572	14.766	19.614	11.60	13.11	75.28	95.47
0.2% $CaCl_2$	1.808	1.162	18.273	21.242	8.51	5.47	86.02	104.72
0.3% $CaCl_2$	0.424	0.604	25.629	26.657	1.59	2.27	96.14	128.98
0.1% $CaBr_2$	1.228	1.433	20.520	23.180	5.30	6.18	88.52	112.74

With respect to the measuring results under the four sampling runs by the OHM, Hg concentration varies with the addition of different additives to the coal (0.1% $CaCl_2$, 0.2% $CaCl_2$, 0.3% $CaCl_2$ and 0.1% $CaBr_2$). It is commonly found that particle mercury $C_{\mathrm{Hg}}^{\mathrm{P}}$ accounts for the overwhelming majority of total mercury in the flue gas, while elemental mercury and oxidized mercury are relatively lower. Besides, the Hg mass equilibrium rates of the OHM ranging from 95.47% to 128.98% meet the requirement (70% to 130%)[3], which indicates that the sampling data by the OHM are valid because the errors caused by the operation and measurement are verified as negligible. Thus, the mercury concentration can be treated as the standard value to evaluate the results measured by the sorbent trap measurement.

3.3 Comparison test between sorbent trap and OHM

In order to evaluate this novel mercury carbon trap sampling system, a thorough comparison test of measurements on mercury speciation concentration in flue gas is conducted between the carbon trap sampling system and the OHM in a 6 kW CFB combustor. Different types of coal are used in the four sampling runs. During the comparison test, great attention is paid to evaluating the practicability and precision of this novel sampling system.

Fig. 6 shows the variation trend of the Hg concentration under different sampling conditions. The fluctuations of measured mercury concentration $C_{\mathrm{Hg,OHM}}^{\mathrm{T}}$ and $C_{\mathrm{Hg,30B}}^{\mathrm{T}}$ are reasonable since the coal varies with the sampling conditions. It is expected that the measuring results by sorbent trap is consistent with those by the OHM. The sorbent traps are easily operational under field-testing. Each of the sorbent traps successfully passes the post-test leak check. The dedusting device, temperature and flow control are all in a perfect working order. The entire sampling system runs well without congestion and condensation trouble. As a result, the favorable operation practice guarantees the sample data comparable to the OHM reference results.

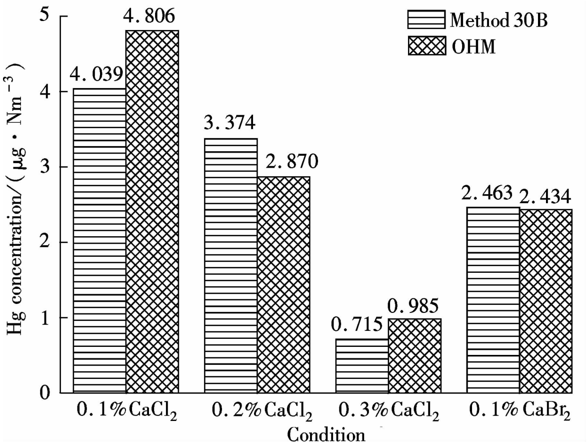


Fig. 6 Comparison of sorbent trap and OHM

The RB and RD were calculated for deep discussion on the measuring results by sorbent traps, as shown in Tab. 3.

The results presented in Tab. 3 suggest that when $C_{\mathrm{Hg,30B}}^{\mathrm{T}} > 1$ μg/m³, both RB and RD are within 10%; when $C_{\mathrm{Hg,30B}}^{\mathrm{T}} \leqslant 1$ μg/m³, RB and RD are also within 20%, conforming to the precision criterion required by QA/QC. In detail, the low RB value is consistent with

Tab. 3 Measuring results by sorbent trap

Condition	$C_{\mathrm{Hg,OHM}}^{\mathrm{T}}/(\mu g \cdot m^{-3})$	$C_{\mathrm{Hg,30B}}^{\mathrm{T}}/(\mu g \cdot m^{-3})$	m_1/μg	m_2/μg	RB/%	RD/%
AC-HBr	4.806	4.039	6.054	0.005	0.09	8.67
AC-HBr	2.870	3.374	5.056	0.005	0.09	8.07
AC-KI	0.985	0.715	1.056	0.017	1.65	15.90
RHC-PHBr	2.434	2.463	3.682	0.012	0.32	0.60

all the gas-phase mercury in the flue gas being completely absorbed by the sorbent traps. The high precision of the sorbent traps is verified by RD analysis in addition. Based on the excellent properties mentioned above, this novel sorbent traps sampling system has a high precision and reliability, which is suitable for industrial application.

4 Conclusions

1) The fixed-bed Hg adsorption tests indicate that the modified biomass cokes (RHC-PHBr) perform perfectly as the activated carbons (AC-HBr, AC-KI) for mercury adsorption. All the modified sorbents are feasible for Method 30B sorbent traps.

2) The gas-phase mercury is completely absorbed by the sorbent traps during the sampling. The novel sorbent traps have consistent results with the reference method OHM. Both the relative deviation and breakthrough rate of sorbent traps show negligible fluctuation with the variations of the mercury concentration in the flue gas and meet the requirements of QA/QC of EPA Method 30B.

3) This novel carbon sorbent trap sampling system possesses high precision and reliability and it can be applied to the coal-fired flue gas mercury sampling.

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碳管法燃煤烟气汞浓度取样装置研制

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摘要：自主研制了包括内置吸附剂和两段式碳吸附管在内的整套新型碳管法烟气汞浓度取样装置，以期实现燃煤烟气中颗粒汞和气相总汞浓度的精确测量. 在 6 kW 燃煤循环流化床装置上同时采用碳管法与安大略标准法(OHM)进行烟气中汞浓度取样. 结果表明，碳管法所得汞平衡率均处于 95.47% ~104.72% 之间. 不同工况下碳吸附管第 2 段穿透率始终低于 2%，且与相同工况下 OHM 测试结果的相对偏差在 15.96% ~17.56% 之间，均小于 20%. 结果表明，所研制的碳吸附管干法烟气汞浓度取样装置符合美国 EPA 质量保证和质量控制(QA/QC)标准，可应用于实际燃煤烟气汞浓度的取样测试.

关键词：汞吸附管；燃煤烟气；汞取样装置

中图分类号：X511