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Chemical Looping Combustion Pretreatment of Fuel Gas for a Novel Mercury Continuous Emissions Monitor by Cold Vapor Atomic Absorption Spectrometry

Bi Zhang, Ping Xu, Jingjing Ma, Hui Wu, Guangqian Luo,* Minghou Xu, and Hong Yao*

State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan, Hubei 430074, People's Republic of China,

ABSTRACT: The cold vapor atomic absorption spectrometry (CVAAS) technique has been commercially used in a Hg continuous emissions monitor (CEM) for flue gas and ambient air; however, it fails in detecting the Hg concentration in fuel gases containing interference components, such as aromatic hydrocarbons, because of the detection cell contamination and the overlap of adsorption peaks. Although the Hg separation method by gold trap was developed to eliminate the interference, it was only a semi-continuous measurement technology. Therefore, this study proposed novel Hg CEM to continuously measure the Hg concentration in fuel gases. The novel Hg CEM mainly consisted of a chemical looping combustion (CLC) pretreatment unit and a CVAAS Hg detector. The pretreatment unit was an electric-heated quartz tube reactor filled with an oxygen carrier (NiO), which was dispersed into quartz sand. The proposed Hg CEM worked in the following way: First, the gas with a controlled flow rate was fed into the reactor at an elevated temperature. All of the flammable gases were converted into CO₂ and H₂O, and all Hg species were transformed into elemental vapor. Then, the product gases were introduced into the condenser to remove water. Finally, the concentration of elemental Hg in CO₂ was detected by CVAAS without any interference problem. With regard to the oxygen carrier, it was reduced to metal and then regenerated in air by oxidation. With two reactors, the real-time continuous Hg measurement via the proposed configuration can be realized by gas switch and oxygen carrier regeneration. Two types of gases containing Hg (toluene and coal pyrolysis gas) were continuously measured by the proposed Hg CEM. The results showed that satisfactory Hg recoveries were attained with CLC pretreatment, whereas the data without CLC pretreatment were totally distorted. Some technical challenges still remain unsolved, but it is believed that the proposed Hg CEM has a bright future for fuel gas.

1. INTRODUCTION

Hg, especially organic Hg, is neurotoxic to humans and animals.¹ Hence, anthropogenic Hg emission control has drawn worldwide attention. Hg emissions in the atmosphere have a long life cycle, which can be brought by an annual cycle of atmospheric circulation to anywhere on the planet and enter terrestrial and aquatic ecosystems by dry and wet deposition, and then it will be transformed into more toxic organic Hg (such as methylmercury), concentrated in organisms through the food chain, and finally harming creatures at the top of food chain. Control of emission sources of Hg can effectively reduce the ultimate harm to organisms. Coal-fired power plants are the largest stationary source of Hg emissions in the world, as well as for the U.S.A. and China.^{2–4} Legislations have been issued for the control of Hg emissions from coal-fired power plants in the U.S.A. and China. On July 29, 2011, the latest edition of “Emission Standard of Air Pollutants for Thermal Power Plants (GB13223-2011)” has been issued by the Ministry of Environmental Protection of the People's Republic of China and the General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China, to substitute the last standard numbered as GB13223-2003.⁵ In the new standard, besides particulate matters, SO_x, and NO_x, Hg and its compounds are also on the list of air pollutants, with the emission limit of 0.03 mg/m³. On December 16, 2011, the United States Environmental Protection Agency (U.S. EPA) has issued “Mercury and Air Toxic Standards (MATS)”, which

is the first national standard for protecting Americans from Hg and other air toxics emitted by power plants.⁶ These indicate that Hg pollution has raised more and more attention.

In addition to coal-fired power plants, cement plants, waste incinerators, iron and steel plants, etc. can produce flue gas containing Hg as well. Moreover, Hg also exists in flammable gases, e.g., coal bed methane, coal pyrolysis gas, syngas, and natural gas. Hg has not only physiological toxicity to humans and animals but also adverse impacts on the production process because of its unique physical and chemical properties. Hg can react with metal materials, forming amalgamate, resulting in equipment corrosion and metal embrittlement. For example, concentrated Hg will cause great damage to high-efficiency aluminum heat exchangers, which are widely used in natural gas production, and CO₂ liquefaction and separation in oxy-fuel combustion technology.^{7,8} In the catalytic reforming process of synthesis gas, Hg can cause catalyst poisoning, partially or even completely deactivating catalyst activity.^{9,10} To meet the needs of production and emission control, the Hg concentration should be detected. In comparison to complicated procedures

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of all kinds of off-line technologies, a continuous emissions monitor (CEM) is favored by industry and laboratory for its advantages of real-time, online, and convenience. Aiming at measuring the Hg concentration in flue gas and ambient air, most Hg CEMs and semi-continuous emissions monitors (SCEMs) commercially provided by different manufacturers are based on cold vapor atomic absorption spectrometry (CVAAS).^{11–13} The main principle of CVAAS is that elemental mercury atoms can absorb ultraviolet (UV) wavelength 253.7 nm light. The test gas passes through a special optical cell, irradiated by a UV 253.7 nm light lamp, and an optical signal of 253.7 nm light is monitored by a UV detector. If test gas contains elemental mercury, the optical signal becomes lower; therefore, the mercury concentration can be measured. To obtain an accurate mercury concentration, the test gas cannot contain other compositions that can absorb UV 253.7 nm light, except mercury. The common gases (such as N₂, O₂, and CO₂) do not absorb UV 253.7 nm; therefore, the CVAAS Hg CEMs have been widely used in coal combustion flue gas and waste incineration flue gas. However, CVAAS Hg CEMs cannot be directly used in flammable gases, because aromatic hydrocarbons existing in flammable gases can absorb UV 253.7 nm. With more and more stringent mercury emission control requirements, the mercury measurement of flammable gases is very important. To obtain a precise mercury concentration of flammable gases, usually two methods can be used: one method is separating mercury from test gas, and the other method is removing aromatic hydrocarbons from test gas. During the past few decades, many researchers have been focusing on the mercury separation method. The Hg monitoring system for natural gas (MMS-NG) developed by Mercury Instrument Co.¹⁴ is such a product. The instrument uses gold trap to separate aromatic hydrocarbons and other interruptible gases with mercury, first, by absorbing mercury in natural gas by a gold trap in a short period of time, then switching the carrier gas to air, releasing Hg from the gold trap by heating, and finally detecting the Hg pulse in air by CVAAS. A few other Hg measurement techniques designed for flammable gas are similar to MMS-NG.¹⁵ However, the MMS-NG is incapable of real-time measurement. With the procedure of “adsorption and release”, the MMS-NG is not a real Hg CEM but a Hg SCEM. The mercury concentration measured by MMS-NG is an average value of a short period of time. If real-time measurement is required, the MMS-NG is not suitable. Moreover, if heavy tar is present in the gaseous analyte, the gold trap will be easily contaminated and incapable of realizing its separation function. Besides that, recently more and more research has been focused on the removal of mercury from coal pyrolysis gas and gasification gas. Many researchers have used various chemical absorption methods to separate mercury from coal pyrolysis gas and gasification gas;¹⁶ nevertheless, they are usually too complicated and non-real-time measurements. We know real-time measurement of mercury plays a significant role in doing research, but the mercury separation method obviously cannot realize real-time measurement. Therefore, a novel Hg CEM for flammable gases was proposed in this paper. The proposed Hg CEM is based on the combination of chemical looping combustion (CLC) and CVAAS. CLC is a combustion process, which burns and converts flammable gases. After CLC, aromatic hydrocarbons will become CO₂ and H₂O and mercury can be measured by Hg CEMs. It was expected that the pretreatment method by CLC could completely eliminate the

adverse effect of aromatic hydrocarbons and realize real-time continuous measurement of Hg in flammable gases.

2. PRINCIPLES OF THE NOVEL Hg CEM

The novel Hg CEM was based on CVAAS. Chemical looping pretreatment is added to solve the aromatic hydrocarbon interference of CVAAS Hg CEM. Figure 1 shows the schematic

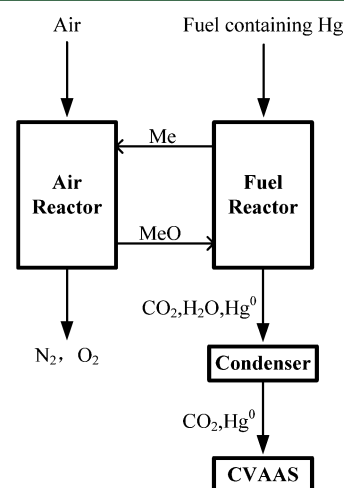
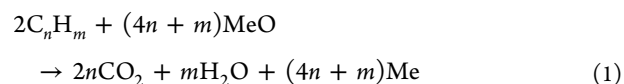


Figure 1. Schematic diagram of the novel Hg CEM.

diagram of the novel prototype Hg CEM, including the fuel reactor, air reactor, condenser, and Hg detector based on CVAAS. Therefore, with a few apparatuses added, it is easy to obtain the novel Hg CEM, if industries or laboratories already had CVAAS Hg CEMs. The novel Hg CEM has some potential advantages: (1) elimination of the adverse effect of aromatic hydrocarbons, (2) higher Hg concentration in exhaust gas compared to direct combustion in air (9 times for methane), and (3) no explosion risk because of no flame and no direct contact with gaseous oxygen. The function of the units will be described in detail as follows: (1) fuel combustion and Hg conversion, (2) moisture and acid gas separation by condensation, and (3) continuous measurement of Hg.

2.1. Fuel Combustion and Hg Conversion. Traditional combustion directly burns fuel with air in a combustion chamber, while CLC decouples traditional single-stage combustion into two stages to isolate the fuel from air.¹⁷ Two reactions will perform the combustion: a chose oxygen carrier (normally a metal oxide) is reduced to metal by the fuel in the fuel reactor, and then the metal is oxidized in air, forming an oxide to complete the looping. According to our proposal, a known measured fuel flow (solid in mass flow and liquid and gas fuel in volume flow) is fed into the fuel reactor and reacts with the oxygen carrier at an elevated temperature generating CO₂ and H₂O and various forms of Hg in fuel are completely transformed into elemental Hg vapor by thermal decomposition and reduction.



The reduced metal is sent to the air reactor and reacts with oxygen in air, forming metal oxide, which is reintroduced into the fuel reactor, completing the looping.

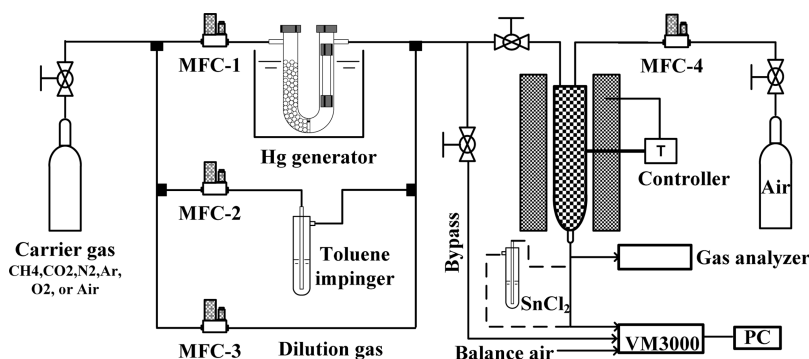


Figure 2. Experimental setup.



2.2. Moisture and Acid Gas Separation by Condensation. The main components of exhaust gas in the fuel reactor are CO_2 and H_2O , containing elemental Hg vapor and possible acid gases, such as HCl and SO_2 . Moisture can scatter the UV light, and the SO_2 absorption peak covers the Hg absorption wavelength of 253.7 nm, resulting in a higher output of CVAAS.¹⁸ In this stage, the exhausted gas passes through the condenser and the moisture is condensed into liquid water separated from the exhaust gas. Meanwhile, SO_2 , HCl , and other acid gases are removed because of their high water solubility. After this stage, CO_2 is the only major component in the exhaust gas, still containing all elemental Hg vapor because of its water insolubility. The stream is ready for measurement by CVAAS.

2.3. Continuous Measurement of Gaseous Elemental Hg. The stream after condensation is introduced into the detection cell of Hg CEM based on CVAAS, and the Hg concentration in CO_2 is analyzed online. However, the Hg concentration in CO_2 does not represent the Hg concentration in the fuel. The Hg concentration is then calculated using eq 4

$$C_{\text{fuel}} = \frac{C_{\text{CO}_2} V_{\text{CO}_2}}{V_{\text{fuel}}} \quad (4)$$

where C_{fuel} is the Hg concentration in analyte fuel ($\mu\text{g}/\text{m}^3$), V_{fuel} is the flow rate of analyte fuel (L/min), C_{CO_2} is the Hg concentration in CO_2 , shown in the Hg analyzer ($\mu\text{g}/\text{m}^3$), and V_{CO_2} is the flow rate of analyte CO_2 through the detection cell of the Hg detector (L/min).

The delay caused by fuel conversion, water separation, and gas transportation should be considered during the data processing.

3. EXPERIMENTAL SECTION

3.1. Instruments and Setup. To verify the novel Hg measurement method, main experiments were conducted in the customized experimental system shown in Figure 2, including gas cylinders, Hg vapor generator, toluene vapor generator, fixed-bed reactor, gas analyzer, and Hg CEM for flue gas.

3.1.1. Gas Analyzer. The gas analyzer (Gasboard 3100P, Wuhan Cubic Optoelectronics Co., Ltd., China) was used for continuous measurement of the gas composition at the outlet of the fixed-bed reactor. It was designed for simultaneously detecting six gases based on a non-dispersive infrared (CO_2 , CO , CH_4 , and C_nH_m), thermal conductivity detector (H_2), and electrochemical detector (O_2). The measurement range for each gas is as follows: CO_2 , 0–60%; CO , 0–40%; H_2 , 0–40%; CH_4 , 0–20%; C_nH_m , 0–20%; and O_2 , 0–30%. The precision is 2% full scale (FS) for $\text{CH}_4/\text{CO}/\text{CO}_2/\text{C}_n\text{H}_m$ and 3% FS for

H_2/O_2 . The resolution is 0.01% for each gas composition. The response time is less than 10 s.

3.1.2. Hg Detector. The Hg CEM (VM3000, Mercury Instrument Co., Germany) was used for continuous measurement of the elemental Hg concentration in the gas stream. The measuring method of VM3000 is CVAAS based on the principle that elemental Hg vapor can effectively absorb the spectrum with the wavelength of 253.7 nm. The response time is 1 s. The detection limit is $1 \mu\text{g}/\text{m}^3$. It has three measurement ranges (1–100, 1–1000, and 1–2000 $\mu\text{g}/\text{m}^3$) for selection. The inlet flow was stabilized at $1.40 \pm 0.02 \text{ L}/\text{min}$ by a built-in membrane sampling pump, which was calibrated by the wet gas flow meter (W-NK-1B, Shinagawa, Japan). The instrument had a built-in condensing unit for drying analyte gas before being detected by CVAAS.

3.1.3. Fixed-Bed Reactor. The reactor consists of a quartz tube reactor (inner diameter of 22 mm) and a temperature-controlled electric furnace ($0\text{--}1100 \pm 1^\circ\text{C}$, Hefei Kejing Materials Technology Co., China). Considering the sintering performance, commercially available NiO was selected as the oxygen carrier. NiO that reacts with fuel will lose lattice oxygen, and contraction occurs. Hence, a mixture of NiO and quartz sand with the mixing ratio of 1:3 filled in the vertical reactor forms the fixed bed with the height of 150 mm. Quartz sand as the support frame of the bed material can avoid excessive fluctuation of the space velocity of the fixed bed for its small thermal expansion coefficient.

3.1.4. Hg Vapor Generation. As shown in Figure 2, the elemental Hg vapor generation system consisted of a carrier gas tank, mass flow meters, connection tubing, water bath, permeation tube, and glass U tube. Elemental Hg vapor was supplied by a Hg permeation tube ($171 \pm 17 \text{ ng}/\text{min}$ at 60°C , VICI Co., Houston, TX). The permeation tube was put in the glass U tube placed in the water bath, which was set at 50°C . The $122 \pm 4 \text{ ng}/\text{min}$ permeation rate of the permeation tube was calculated by the permeation formula, and calibration was made by the direct Hg analyzer (Hydra-C, Teledyne Technologies, Inc.). The flow of carrier gas from the cylinder was controlled by the mass flow meter MFC-1. The dilution ratio was attained by the dilution gas stream controlled by the mass flow meter MFC-3. The desired Hg concentration could be obtained by an appropriate dilution ratio.

3.1.5. Toluene Vapor Generation. As shown in Figure 2, the system for generating toluene vapor was similar to the Hg vapor generation system. An impinger filled with toluene was the toluene source. An exactly adjustable carrier gas stream was loaded with toluene vapor by passing through the impinger. The gas was oversaturated by cooling, and the excess toluene was removed by condensation to obtain exact saturation. The flow of carrier gas and dilution gas was controlled by the mass flow meters MFC-2 and MFC-3, respectively, obtaining the desired toluene concentration and gas flow.

3.2. Experimental Procedure. **3.2.1. Calibration in CO_2 .** The calibration was accomplished by introducing CO_2 stream containing Hg with different ever-known concentrations into CVAAS (VM3000). MFC-1 was kept constant at 1.4 L/min, while MFC-3 was set at six different flow rates (0, 0.6, 1.6, 2.6, 3.6, and 4.6 L/min). The input Hg concentration was calculated by (Hg permeation rate)/(total flow rate). The deviation and linearity can be obtained, and the calibration

curve was obtained by linear regression using the least-squares fitting method.

3.2.2. Signal Response Sensitivity. The same concentration of Hg in different carrier gases may produce different intensities of the absorption signal. Six carrier gases (Air, Ar, N₂, O₂, CH₄, and CO₂) were investigated. MFC-1 and MFC-3 were set at 0.2 and 1.2 L/min, respectively. Hg in each carrier gas was kept at the same concentration of $87 \pm 4 \mu\text{g}/\text{m}^3$ ($122 \pm 4 \text{ ng}/\text{min}$ divided by $1.40 \pm 0.02 \text{ L}/\text{min}$). The absorption signals of CVAAS (VM3000) in different atmospheres were measured in 10 min with a value per second, and the average value and standard deviation were calculated.

3.2.3. Toluene Effect. A 1.4 L/min CH₄ stream containing toluene of different concentrations was made by mixing five different flow rates (0, 0.25, 0.50, 0.75, and 1.00 L/min) of toluene-saturated CH₄ with balanced CH₄, which was introduced into CVAAS to investigate the effect of toluene on the intensity of atomic absorption.

3.2.4. Preliminary Test of CLC. Combustion of 0.1 L/min CH₄ was conducted by introducing CH₄ into the quartz reactor at 900 °C. The outlet gas of the reactor was diluted by 0.9 L/min N₂ to meet the measurement range. Then, regeneration was carried out by reacting with 1 L/min air at 900 °C. The gas compositions at the outlet of the reactor were analyzed by the Gasboard 3100P.

3.2.5. Hg Transformation in CLC. A stock of $7.4 \pm 0.3 \text{ mg}$ of Hg/L of HgNO₃ solution was prepared. A high-precision pipet of 0.1 mL of HgNO₃ solution ($0.74 \pm 0.03 \mu\text{g}$ of Hg) was added to a mass of quartz wool. The quartz wool with HgNO₃ was placed on the surface of the bed material (NiO and quartz sand) during the CLC of CH₄. SnCl₂ solution was used to convert the possible present oxidized Hg into the elemental form. For comparison, the experiments with/without SnCl₂ solution were both conducted.

3.2.6. Application for Simulated Gas. The 1.4 L/min CH₄ containing different concentrations toluene (same as section 3.2.3) was first introduced into the reactor to react with NiO. The absorption signals of CVAAS (VM3000) were recorded for 10 min with the sampling frequency of 1 Hz, and the average value and standard deviation were calculated. Then, 0.1 L/min CH₄ with $122 \pm 4 \text{ ng}/\text{min}$ Hg was introduced into the reactor to react with NiO. At 160 s, toluene-saturated CH₄ was switched on. The balance air was used to meet the gas flow requirements of the Hg detector.

3.2.7. Application for Coal Pyrolysis Gas. The coal pyrolysis gas was produced by pyrolyzing 4 g of bituminous coal in 0.5 L/min N₂ at 600 °C. With or without CLC pretreatment, the Hg concentration of pyrolysis gas was continuously measured by CVAAS. The Hg contents in coal and residue char were analyzed by the direct Hg analyzer (Hydra-C, Teledyne Technologies, Inc.). The balance air was used to meet the gas flow requirements of the Hg detector.

4. RESULTS AND DISCUSSION

4.1. Calibration in CO₂. Prior to Hg CEM, calibration should be made by elemental Hg vapor to test the Hg concentration. The measurement accuracy depends upon the linearity of the calibration curve. It is known that, in an atmosphere of N₂, O₂, and air, the Hg concentration and instrument response value have a good linear relationship. CO₂ stream containing Hg of different known concentrations passed through VM3000 to investigate the linearity of the Hg concentration and instrument response in a CO₂ atmosphere. The calibration results are shown in Figure 3. The linear regression was applied to the set of data, which led to $y = 1.06x - 0.17$, where x is known as the input Hg concentration in $\mu\text{g}/\text{m}^3$ and y is the signal output by VM3000 in $\mu\text{g}/\text{m}^3$. Although the instrument response value is a little higher than the real mercury concentration, the response values can exactly represent the real mercury concentration with a squared correlation coefficient of 0.999. It means that CVAAS can obtain satisfied accuracy using CO₂ as the carrier gas.

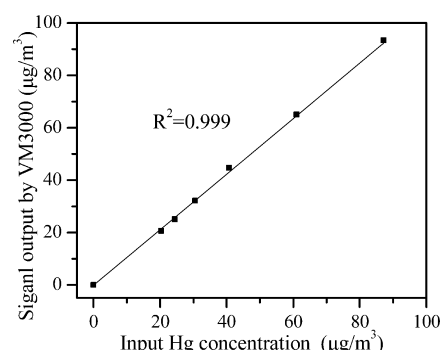


Figure 3. Calibration of CVAAS in the atmosphere of CO₂.

4.2. Signal Response Sensitivity. CVAAS is based on the natural phenomenon that elemental Hg vapor has a strong absorption of spectrum wavelength of 253.7 nm. The remaining main component is CO₂ after condensation of the exhaust gas of pretreated flammable gases by CLC. The application feasibility of CLC in Hg CEM is based on the assumption that CVAAS has enough sensibility for elemental Hg vapor in a CO₂ atmosphere. The signal response of VM3000 for a certain Hg concentration in CO₂ was investigated and compared to the results obtained in other atmospheres (air, Ar, N₂, O₂, and CH₄), as shown in Figure 4. The signal responses to the same

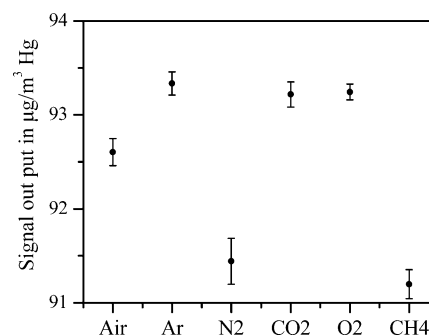


Figure 4. Sensitivities of CVAAS in different carrier gases on the response of VM3000 for Hg vapor with the same concentration.

Hg concentration show negligible difference. The order of the sensitivity is $\text{Ar} > \text{O}_2 > \text{CO}_2 > \text{air} > \text{N}_2 > \text{CH}_4$. The average value of signal response in CO₂ is just $0.1 \mu\text{g}/\text{m}^3$ less than the highest sensibility obtained in Ar. Even in the least sensibility atmosphere (CH₄), the signal response reached a high value of $91.2 \mu\text{g}/\text{m}^3$, and the biggest deviation of instrument response in different atmospheres is less 2.5%. In summary, the sensitivity of CVAAS in CO₂ can meet the requirement of Hg measurement.

4.3. Toluene Effect. Figure 4 shows that, in pure CH₄, CVAAS has good sensitivity. If the linearity of the calibration curve is favorable, CVAAS can also directly measure the elemental Hg concentration in CH₄. However, aromatic hydrocarbons are usually present in flammable gases, which also absorb a spectrum wavelength of 253.7 nm. As a representative aromatic hydrocarbon, toluene was selected for studying the effects of aromatic carbons on Hg analysis by CVAAS. The result in Figure 5 showed that CVAAS with a small amount of toluene could display a strong signal. The higher the concentration of toluene, the stronger the fake signal. As soon as the toluene presented in CH₄, CVAAS responded immediately and the signal strength continued to

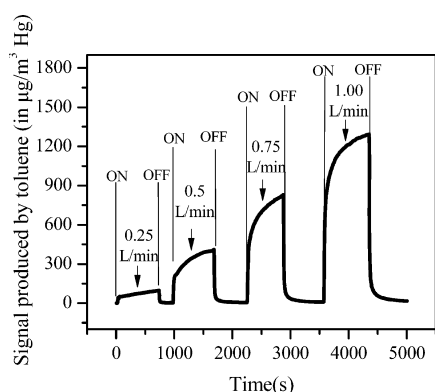


Figure 5. Effect of aromatic hydrocarbons (toluene) on the atomic absorption of CVAAS.

increase, which might be caused by two reasons: First, adsorption and desorption of toluene on the inner surface of tubing have not yet reached equilibrium, resulting in a continuous increase of the toluene concentration. Second, with the increase of the contamination of the detection cell by toluene, the absorption continues to increase. When toluene was switching off, the signal output of CVAAS did not disappear immediately. In fact, it took a long time to eliminate the impact caused by the two reasons mentioned above. The experimental results showed that toluene causes a high fake output of the Hg concentration and reduces the sensitivity of CVAAS. Therefore, it is necessary to remove the present toluene in carrier gas to avoid its adverse impact on CVAAS.

4.4. Preliminary Test of CLC. Extensive studies have been conducted on CLC, focusing on selection and development of oxygen carriers and other aspects. The purpose of this study was not to develop CLC technology; therefore, commercial NiO was purchased as the oxygen carrier. CH₄ was introduced into the quartz reactor loaded with a mixture of NiO and quartz sand. Figure 6a shows the components in exhaust gas during CLC of CH₄. At the initial stage of combustion, the concentration of CH₄ was very high for unknown reasons, which might have impacts on Hg analysis. During the stable reaction period, the conversion rate of methane was kept very high and the output product was CO₂. At 350 s, the methane conversion rate remained unchanged, CO₂ began to decrease, and CO began to be produced, suggesting that the oxygen carrier was not enough for providing oxygen. Figure 6b shows the gas components at the downstream of the reactor during regeneration of the oxygen carrier. At first, oxygen had been consumed completely and CO₂ and CO was produced, indicating that carbon deposition happened during CH₄ combustion. After reaction for 200–250 s, CO and CO₂ disappeared and oxygen began to totally react with metal Ni. With the consumption of metal Ni, the oxygen concentration continued increasing until it reached its origin concentration in ambient air, completing the regeneration progress. The regeneration process was longer than CH₄ combustion. The Hg continuous measurement can be realized by switching two reactors for pretreatment of CH₄ by CLC if the regeneration process was shorter than CH₄ combustion. The performance of the oxygen carrier needs to be further improved to meet the commercial needs of Hg CEM.

4.5. Hg Transformation during CLC. Because CVAAS can only detect Hg in the form of the gaseous element, the transformation of Hg during CLC needs consideration. Figure

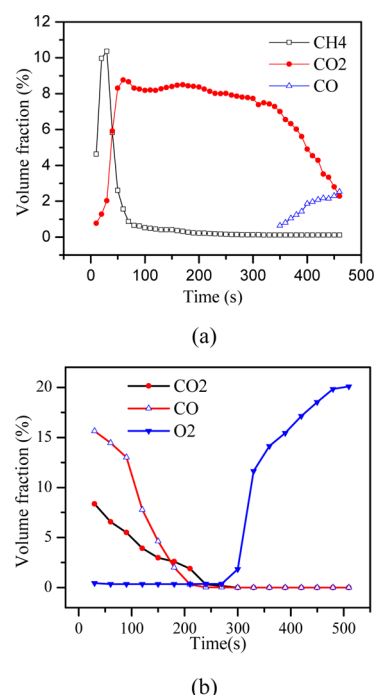


Figure 6. Gas composition of (a) CLC of CH₄ and (b) regeneration of the oxygen carrier.

7 gives the continuous signal of VM3000 for pretreatment of CH₄ containing oxidized Hg by CLC. The thin black line

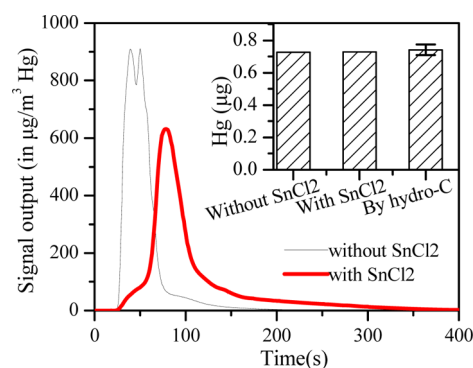


Figure 7. Hg transformation during CLC of CH₄.

represented the data without a SnCl₂ impinger. The red thick line represented the data with a SnCl₂ impinger. The result showed that SnCl₂ scrubbing shortened the peak and overlapped two peaks. The inset graph in Figure 7 shows the mass of fed HgNO₃ detected by Hydra-C and the integration of the signal output in VM3000. The integration of each curve was nearly equal and very close to the results of Hydra-C, indicating that the fed HgNO₃ was completely converted to elemental Hg vapor during CLC.

4.6. Application in Simulated Gas. Figure 8 shows the signal response of different toluene concentrations treated by CLC. It is noted that, after treating by CLC, the toluene has little influence on signal adsorption of CVAAS (VM3000). In comparison to Figure 5, the signal adsorption is about 1 µg/m³, which means toluene was combusted by CLC.

Figure 9 shows the Hg CEM resulting from CH₄ stream containing elemental Hg vapor with or without toluene using CLC as the pretreatment method. A sharp decrease in toluene

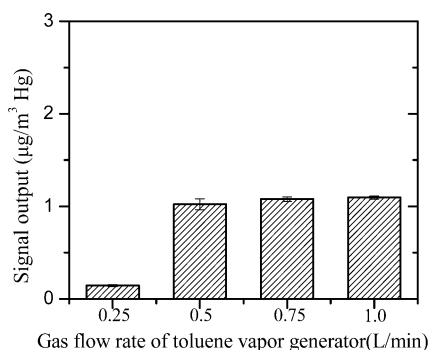


Figure 8. Signal response of different toluene concentrations treated by CLC.

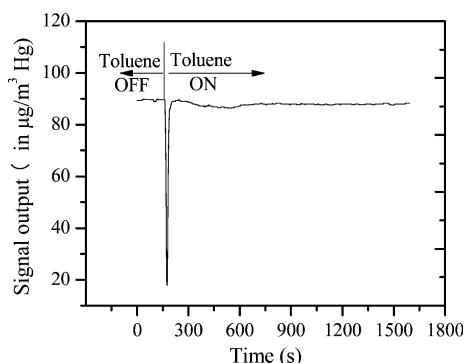


Figure 9. Continuous measurement of Hg in CH₄ with or without toluene by the novel Hg CEM.

switch was caused by dilution and delay of the toluene impinger. The signal output very slightly changed when toluene was present in the carrier gas, which meant CLC had converted all toluene into other molecules without interference. It is noted that, after adding the toluene vapor generator in the system, the signal output was not as stable as before and had a slight decrease, which might be caused by fluctuation of the pressure and flow produced by the bubbling action of the impinger. To stabilize the signal, it is necessary to improve the stability of the system pressure and flow.

4.7. Application in Coal Pyrolysis Gas. Although a good result of Hg continuous measurement in simulated gas was achieved, the gas composition was too simple to fully reflect the performance of the novel Hg analyzer. To further evaluate the performance of Hg CEM of the combination of CLC and CVAAS, a continuous measurement of the Hg concentration in pyrolysis gas of 4 g of coal at 600 °C was carried out. Most Hg in coal can be released at 600 °C.¹⁶ Figure 10 shows the results of VM3000 with/without CLC. The signal output of VM3000 without CLC was much higher than that with CLC, which had an obvious tail and could not go back to the baseline. The gaseous products of coal pyrolysis are very complicated, containing H₂S, SO₂, HCl, alkanes, aromatics, etc. Some substances, e.g., H₂S, SO₂, and aromatic hydrocarbons, can scatter or absorb the spectrum of 253.7 nm.¹⁸ Heavy tar can even contaminate the detection cell and make it disable. As shown in the red thick line in Figure 10, the signal curve of VM3000 had no tail and finally went back to the baseline, indicating that CLC can effectively remove bad substances for Hg analysis by CVAAS. The inset graph shows the total mass of Hg in coal, char, and gas (by integrating). A Hg recovery of 87% was attained by (Hg in gas + Hg in char)/(Hg in coal). To

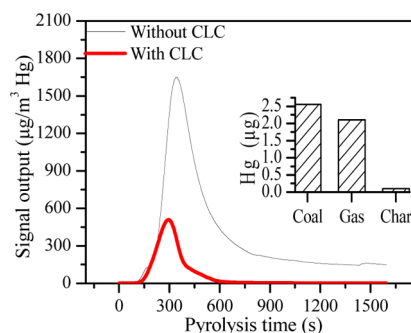


Figure 10. Continuous measurement of Hg in coal pyrolysis gas with or without pretreatment by CLC.

check out the repeatability of the measurement, a continuous measurement of the Hg concentration in pyrolysis gas of another two coals was carried out. The heating ramp was 10 °C/min from room temperature to 1000 °C. The Hg recoveries for each coal were 91 and 93%. The results indicated that the repeatability of the measurement was good.

5. CONCLUSION

A novel technology to Hg CEM of flammable materials was proposed in this paper, which was based on a combination of CLC and CVAAS. The analysis process is stated as follows: In the fuel reactor, the flammable gases react with the oxygen carrier (NiO) at an elevated temperature and produce CO₂ and H₂O. Meanwhile, all Hg in various forms are completely transformed into elemental Hg vapor. Through condensation, acid gases are removed with liquid water because of high water solubility. The remaining CO₂ as carrier gas for Hg passes through CVAAS for continuously measuring the Hg concentration. The metal produced from the oxygen carrier by reduction in the fuel reactor is regenerated by reacting with oxygen in the air reactor, which regenerates the oxygen carrier. A series of tests showed that CVAAS has high sensibility for Hg in CO₂, and the linearity of the calibration curve is quite good ($R^2 = 0.999$). Hg in the exhaust gas of CLC of CH₄ existed in the elemental form. CLC can effectively remove adverse effects of toluene on Hg CEM based on CVAAS. For direct continuous measurement of Hg in coal pyrolysis gas without CLC, the analysis data were totally distorted. With CLC, CVAAS succeeded in continuously monitoring Hg in the coal pyrolysis gas. In short, the proposed novel Hg CEM using CVAAS combined with CLC provides a promising solution for the problem of continuous measurement of the Hg concentration of flammable gases containing interference components.

AUTHOR INFORMATION

Corresponding Authors

*Telephone/Fax: 86-27-87545526. E-mail: guangqian.luo@mail.hust.edu.cn.

*Telephone/Fax: 86-27-87545526. E-mail: hyao@hust.edu.cn.

Notes

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