Transverse Zeeman background correction method for air mercury measurement*

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By utilizing a natural mercury lamp, the transverse Zeeman background correction method, which is used for trace mercury measurement in air, is studied. In this paper, a natural mercury lamp is used as a light source, and is placed in a 1.78-T magnetic field. The lamp emits two linearly polarized light beams $\sigma^{\pm}$ and π of 253.65-nm resonance line, which are used as bias light and absorbing light, respectively. A polarization modulation system is used to allow $\sigma^{\pm}$ and π light beams to pass through alternately with a certain frequency. A multipath optical cell with 12-m optical path is used to increase optical distance. Based on the system described above, the influence caused by UV absorbing gases, such as NO_2, SO_2, acetone, benzene, and O_3, is analyzed. The results show that it may reduce the detection limit when the concentrations of these gases exceed 83.4 ppm, 20.3 ppm, 142.3 ppm, 0.85 ppm, and 0.55 ppm, respectively. The detection limit of the system is calculated and can achieve up to 1.44 ng/m^3 in 10 minutes. Measurements on mercury sample gas and air are carried out, and the measured data are compared with the data of RA-915 mercury analyzer (Russia). The result shows that the correlation coefficient reaches up to 0.967. The experimental results indicate that the transverse Zeeman background correction method can be used to quantify trace mercury in air with high-precision.

Keywords: transverse Zeeman background correction, natural mercury lamp, magnetic field, multipath optical cell

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1. Introduction

Mercury pollution has spread over the whole world,[1] and it has done serious damage to human health and the environment.[2,3] At present, about 2100 tones mercury are released into atmosphere every year due to human action.[3] The study shows that about 500 t–700 t mercury has been delivered into air every year in China as a result of anthropogenic discharge.[4] Thermal power and smelting nonferrous metal contribute 80% of the result. The severe mercury pollution has received international critical attention, and a huge amount of mercury in the atmosphere has played a prominent role in evaluating environmental pollution. Mercury is released in the form of gas exchange and the ratio of gaseous mercury to total mercury in the atmosphere is 95%.[5] Gaseous mercury has a lifetime of 0.5 a–2 a in air and could be transferred to the whole world.[6,7] In short, accurately quantifying trace mercury in air and improving the mercury analytic technique are important tasks to be carried out.

For the moment, there are two common technologies for mercury detection, which are: gold amalgam technology and Zeeman background correction technology. According to measuring principles, the mercury analyzer used in gold amalgam technology has several types, such as MA2000 mercury analyzer (Japan) using atomic absorption method[8] and Tekran 2573A mercury analyzer (USA) using the atomic fluorescence method.[9] However, for gold amalgam technology, the maintenance cost is very high because of the necessity of washing the gold pipe, providing a carrier gas, and the complexity of the equipment. Hadeishi and Mclaughl,[10] and Hadeishi *et al.*[11] have proposed the longitudinal Zeeman background correction technology by utilizing an isotope Hg^{198} lamp with 0.7-T magnetic field, which uses σ^-- and σ^+-polarized light beams of 253.65 nm as absorbing light and bias light, respectively. Devices for trace mercury measurement, such as the RA-915 Zeeman mercury analyzer (Russia), have also been developed,[12] and they are currently used in atmospheric mercury measurement. However, in China the research of atmospheric mercury content and relevant measuring device is still insufficient.

In the longitudinal Zeeman technology, isotope Hg^{198} is used as a light source with 0.7-T magnetic field, but the isotope Hg^{198} is too difficult and costly to obtain. In order to overcome the difficulty in obtaining the isotope Hg^{198}, in this paper, trace mercury in air is quantified with transverse Zeeman background correction method, in which a natural mercury lamp is used as a light source with more than 1.5-T mag-

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netic field. A natural mercury source has been discussed by Hideaki and Kazuo.[13] In this paper, we analyze the interference caused by UV absorption pollution gases, compare measurement results of mercury sample gas and air with the data of RA-915 mercury analyzer. The feasibility of this method for air trace mercury detection is verified.

2. Principle

The absorption spectrum describes mercury atomic absorption by the Lambert–Beer law. For the interference caused by other gases and particulate matter,[14] the Lambert–Beer law can be approximately expressed as follows:

$$I = I_0 \exp\{-l \cdot (n_h \cdot \varepsilon_h + n_m \cdot \varepsilon_m + n_p \cdot \varepsilon_p)\}, \quad (1)$$

where I and I_0 represents the final and initial intensities of the light beam; l is the absorbing optical length; n_h, n_m, and n_p denote the concentrations of mercury atomic, interfering gas, and particulate matter, respectively; and, ε_h, ε_m, and ε_p denote absorption coefficients of mercury atom, interfering gas, and particulate matter. In practice, equation (1) cannot be used for mercury measurements, or for the background interface caused by other gases, or for the particulate matter.

For the sake of accurate background correction, the transverse Zeeman background correction method by using a natural mercury lamp is investigated. In the direction perpendicular to the propagation of magnetic field, resonance line of 253.65 nm is split into two linearly polarized light beams, named $\sigma^{\pm}$ and π component. The polarization direction of π line is parallel to the magnetic field and the polarization direction of $\sigma^{\pm}$ line is perpendicular to the magnetic field. At magnetic of 1.78 T, the $\sigma^{\pm}$-polarized light beam is out of atomic absorption band, that is, it has zero absorption, whereas π light has a maximum absorption coefficient. So the method uses the $\sigma^{\pm}$ component as bias light and π component as light-absorbing, and equation (1) can be written as

$$I_{\sigma^{\pm}} = I_{\sigma_0^{\pm}} \exp\{-l \cdot (n_m \cdot \varepsilon^m_{\sigma^{\pm}} + n_p \cdot \varepsilon^p_{\sigma^{\pm}})\}, \quad (2)$$

$$I_{\pi} = I_{\pi_0} \exp\{-l \cdot (n_h \cdot \varepsilon^h_{\pi} + n_m \cdot \varepsilon^m_{\pi} + n_p \cdot \varepsilon^p_{\pi})\}, \quad (3)$$

where the initial intensity $I_{\sigma_0^{\pm}}$ is equal to I_{π_0}. For the broadband absorption and scattering of particles, ε^p_{π} is equal to $\varepsilon^p_{\sigma^{\pm}}$. Because of the small shift of $\sigma^{\pm}$ component (about 12 pm), there is a tiny difference between indices $\varepsilon^m_{\sigma^{\pm}}$ and ε^m_{π}, which is caused by interfering gases. If the concentrations of interfering gases are low, then the difference can be ignored and optical density (OD) can be defined as the logarithm of the ratio of I_{π} to $I_{\sigma^{\pm}}$; that is,

$$\mathrm{OD} = \ln(I_{\pi}/I_{\sigma^{\pm}}) = -l \cdot n_h \cdot \varepsilon^h_{\pi}. \quad (4)$$

According to Eq. (4), no interference is caused by particles. But if the concentration of interfering gases are high, then the difference between $\varepsilon^m_{\sigma^{\pm}}$ and ε^m_{π} causes a background correction inaccuracy. The minimum concentration of interfering gases must be determined by Eq. (4).

3. Experimental setup

The schematic diagram of the experimental system is shown in Fig. 1. The main units of system include an electrodeless discharge lamp (EDL), a 1.78-T permanent magnet, polarization modulation system, mercury calibration cell with saturated mercury vapor, 253.65-nm bandpass filter, and multipath optical cell with 12 m, and so on. The concentration of mercury calibration cell can be calculated by formula $C = m \cdot P_{\mathrm{hg}}/R \cdot T$, where C is actual mercury concentration, P_{hg} the saturated mercury vapor pressure at temperature T, m the atomic weight of mercury, R the universal gas constant.

Electrical energy is supplied to the lamp in the tank coil of the oscillator. The lamp gives rise to a stable and powerful emission in a 1.78-T magnetic field, which is produced by assembled magnet with dimensions of 70 mm × 70 mm × 90 mm. The polarization modulation system is composed of electro–optic crystal and polarizing prism, and it could make the polarization state of linearly polarized light rotate 90°. When no voltage is applied to the electro–optic crystal, the optical characteristic of crystal is not changed and neither is the polarization state of light modulated, so the $\sigma^{\pm}$ light can pass through the polarization modulation system but π cannot. When a voltage is applied to the crystal, optical characteristic of crystal will change, and polarization state of light passing through crystal will rotate 90°. Now, π-polarized light can pass through the polarization modulation system but $\sigma^{\pm}$ cannot. With this modulation system, the automatic modulation of polarized light is accomplished and the modulation frequency is about 50 Hz. After modulation, the light will reach a bandpass filter of 253.65 nm, which only allows the 253.65-nm wavelength to be passed through. Finally, the light will enter into multipath optical cell of 12-m optical length, which is constituted by three mirrors with a 253.65-nm high reflectance coating and the dimensions of 95 mm × 192 mm × 710 mm. In the experimental system a mercury calibration cell with saturated mercury vapor is used for calibration, and it is switched into the light path by a stepper motor with a cycle of two hours to revise the measurement result. Hamamatsu H11462 PMT is used as electrophotonic detector. A computer with data acquisition card is used to control the modulating frequency of the crystal and to gather data.

The flow path in system is shown in Fig. 1. The vacuum pump with 12 L/min velocity evacuates the air continuously. The mercury filer is used to absorb mercury in the flowing air to produce zero gas. Magnetic valves V1 and V2 are used to allow zero gas or airflow to pass through the multipath optical cell alternately. When the system is running, first, calibration

program is carried out every two hours, V1 is on and V2 is off, zero gas is detected for 3 min. Keeping the state of magnetic valve, mercury calibration cell is switched into light path by a stepper motor and the calibration coefficient is obtained. Then, the program of mercury detected in air is implemented. Zero gas is also detected for 3 min. By changing the states of V1 and V2, mercury in air is detected for 7 min. According to the calibration coefficient obtained above, the mercury concentration in air is gained. By the way, because of large volume of the multipath optical cell, it needs about 1 min for the multipath optical cell to change the air completely. We spent 3 min in achieving zero gas and 7 min in realizing a better accuracy of airflow.

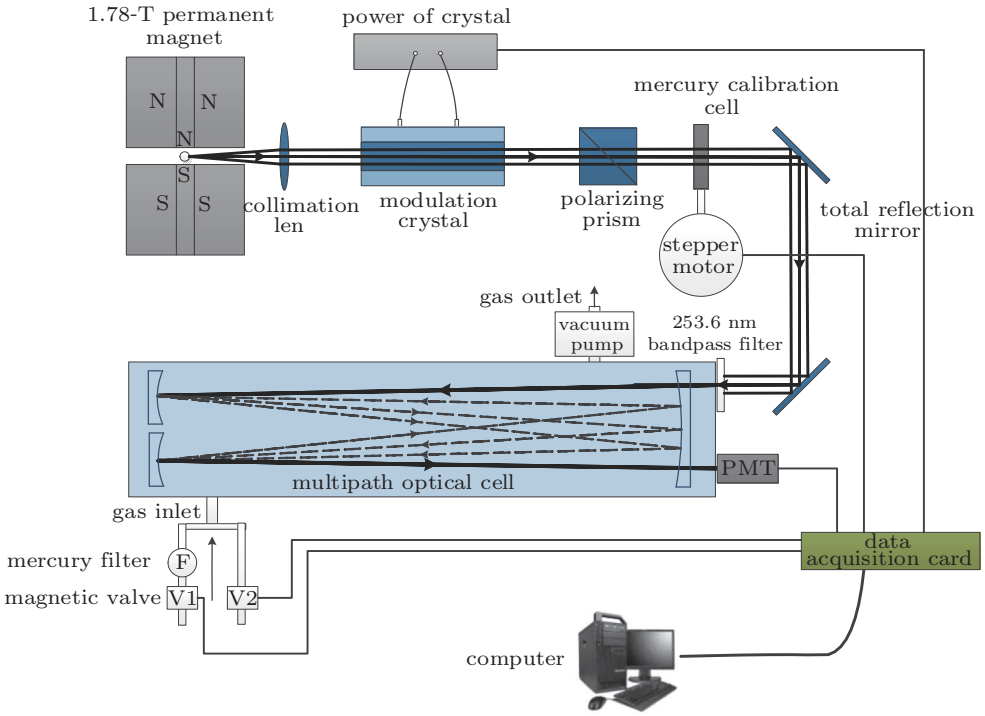


Fig. 1. (color online) Schematic diagram of the experimental system.

4. Experiments and result analysis

4.1. Analysis of interfering gases

There are several pollution gases in the atmosphere. Some of them have absorption in UV region around 253.6 5nm, including NO_2, SO_2, benzene series, and O_3. The absorption cross sections of gases[15–19] in a wavelength range of 253.50 nn–253.80 nm are shown in Fig. 2. There are some undulations in absorption cross sections of gases. The absorption cross section of NO_2 has strong fluctuations but its absorption intensity is low. Contrarily, SO_2 has trivial fluctuations but its absorption intensity is high. The cross section fluctuation and intensity of acetone are both small. However, for benzene and O_3, their cross sections have stronger fluctuations and their absorption intensities are also larger.

Because of fluctuation in absorption cross section, the background interferences caused by those gases with high concentrations are analyzed. Standard sample gases, including NO_2, SO_2, acetone, and benzene with concentrations of 526 ppm, 402 ppm, 10^4 pm, 10^3 ppm, respectively, and O_3, which is produced by OC500 ozonizer with a concentration of 10 ppm, have been inlet into multipath optical cell with N_2 as the background gas. According to Eq. (4), the background interference is analyzed and the result is shown in Fig. 3.

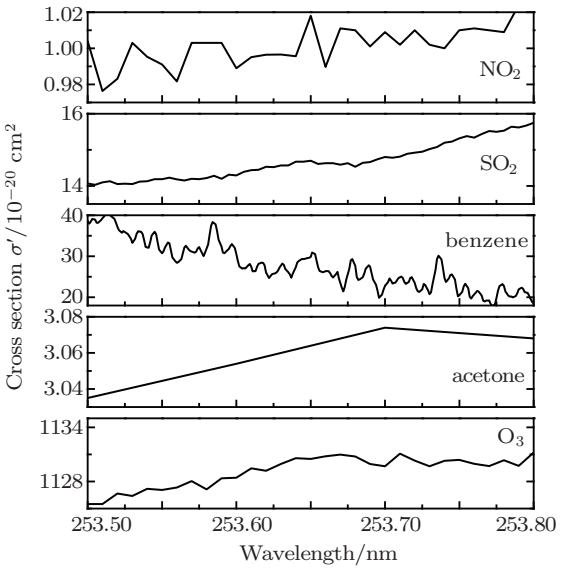


Fig. 2. Absorption cross section versus wavelength for different gases.

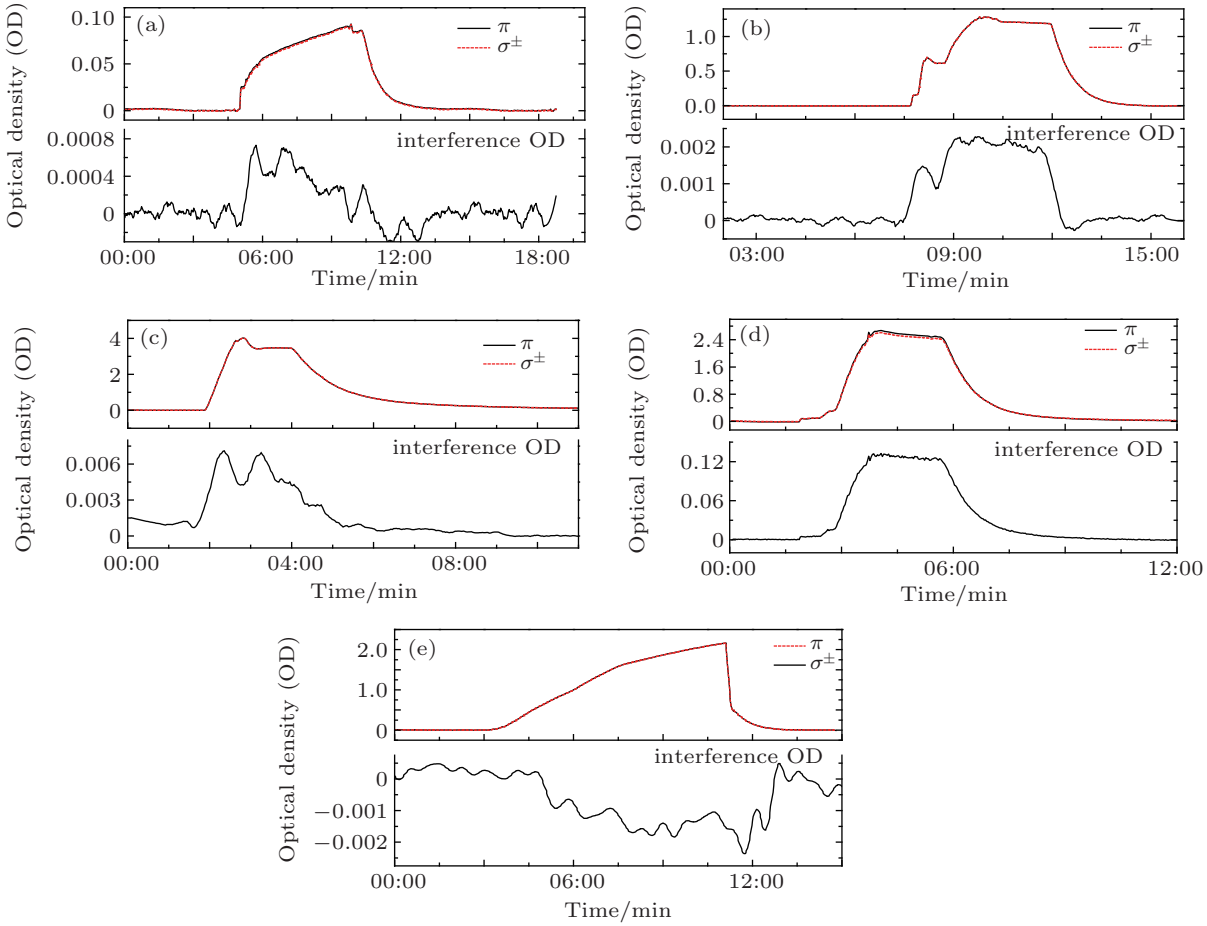


Fig. 3. (color online) Time evolutions of interference OD caused by pollution gases (the upper part of each of panels (a)–(e)) is for the ODs of $\sigma^{\pm}$ and π components, respectively, and the lower part is for the OD calculated from Eq. (4)). (a) Absorbance of NO_2, (b) absorbance of SO_2, (c) absorbance of acetone, (d) absorbance of benzene, (e) absorbance of O_3.

As shown in Fig. 3, when there is N_2 background gas in the multipath optical cell with no interfering gases, the absorbance ODs of π and $\sigma^{\pm}$ components are zero and the background interference OD is also zero. When the interfering gases exist, as shown in the upper parts of panels, $\sigma^{\pm}$ and π-polarized light beams are strongly absorbed but the background interference ODs which are recalculated from Eq. (4) have small changes with concentration of gas, as shown in the bottom parts of panels. In Fig. 3(a), NO_2 with high concentration is inlet into the multipath optical cell, and the maximum interference OD is only about 7×10^{-4}. As figure 3(b) shows, when SO_2 exists, small interference OD is caused, and the value is about 2.2×10^{-3}. In Fig. 3(c), the interference OD of acetone absorbance is 7.8×10^{-3}. However, because of larger fluctuation and value, background interference OD of benzene increases up to 0.13. In Fig. 3(e), the interference OD of O_3 is only about -0.002. By the way, the OD of O_3 is negative because O_3 has stronger absorption with the $\sigma^{\pm}$-polarized light than with the π-polarized light.

Using N_2 gas as a zero gas, the OD standard deviation of the system is tested, and the deviations in 10 minutes is around 3.7×10^{-5}. The system detection limit is three times as great as the standard deviation. To avoid the interferences from NO_2, SO_2, acetone, benzene, and O_3, the interference OD should be smaller than the system detection limit. So according to the concentration and OD, the critical concentrations of these gases in air cannot exceed 83.4 ppm, 20.3 ppm, 142.3 ppm, 0.85 ppm, and 0.55 ppm, respectively. The concentrations of these pollution gases in the atmosphere are much less than the critical point. So, for practical measurements, the interferences caused by gases can be ignored and the method can realize accurate background correction.

4.2. Analysis of mercury experiment

The detection limit of system is calculated. The zero gas without mercury which is produced by mercury filter is inlet into the multipath optical cell. As figure shows, 41 sets of zero gas measured data are obtained, and the standard deviation is 0.48 ng/m^3. According to the equation $C_L = k \cdot S_b$ (C_L is the detection limit, k the confidence factor and its value usually is 3, S_b the standard deviation of zero gas measured data), the detection limit of the system is 1.44 ng/m^3. The zero drift of the system is tested 42 hours and the value is 1.09 ng/m^3.

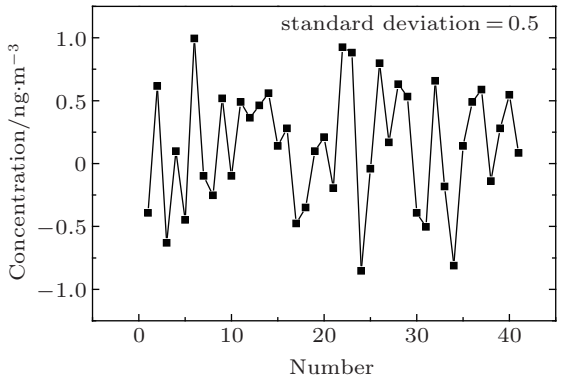


Fig. 4. Measured correction value of zero gas versus the number of measurements.

Then, the experimental system is used for mercury sample gas and air mercury experiments. In the experiment, a blob of mercury is placed in an open container. Because of the great density of mercury vapor, most of the mercury deposits at the bottom of the container and only a little mercury overflows. When the mercury vapor out of the container decreases, the container is shook to make more mercury vapor overflow. It takes three days to detect the mercury sample vapor. The time resolution of RA-915 is 5 min while it is 10 min for our experimental system. The data of RA-915 are averaged to match with the experimental system. The detection results are compared with those from RA-915 mercury analyzer (Fig. 5), showing that the trends of two results varying with time are well consistent.

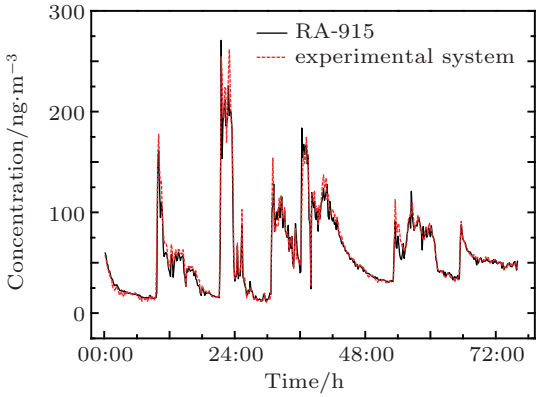


Fig. 5. (color online) Comparison between the results of mercury vapor in three-day measurement and those obtained from RA-915.

This experimental system is also used to measure mercury in air in the laboratory, which takes about two days. The results are shown in Fig. 6. Although there are some differences between the experimental results and the results obtained from RA-915, the main trends of the results varying with time are highly consistent.

As figure 7 shows, the correlation of two systems is analyzed. The correlation coefficient reaches up to 0.967 and the slope is 1.038. It represents that two systems are greatly accordant.

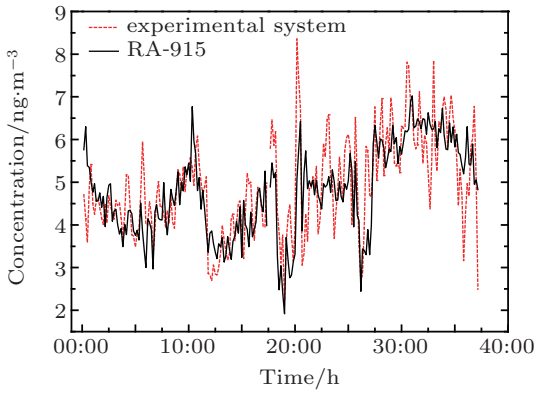


Fig. 6. (color online) Comparison between the measured results of air mercury in laboratory and the results obtained from RA-915.

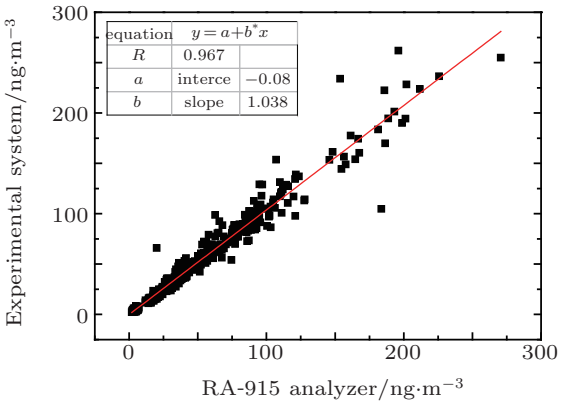


Fig. 7. (color online) Comparison between the results detected by experimental system and those obtained from RA-915.

Considering the optimization space of this experimental system, the detection limit can be improved. The background concentration of trace mercury in the atmosphere is about 1.5 ng/m–2.0 ng/m.[20] So the transverse Zeeman background correction method is feasible to measure trace mercury in air.

5. Conclusions

In this paper, we described the method of making transverse Zeeman background correction and the experimental setup, and analyzed the interfering gases and mercury. The analysis of interfering gases shows that the accuracy of background correction method reduces when the concentrations of interference gases, such as NO_2, SO_2, acetone, benzene, and O_3, exceed 83.4 ppm, 20.3 ppm, 142.3 ppm, 0.85 ppm, and 0.55 ppm, respectively. However, these pollution gases in atmosphere are much less than the critical point. The results of mercury measurement show that the experimental setup has a good performance and its detection limit of average 10 minutes can reach up to 1.44 ng/m^3. In brief, the method is feasible and suitable for monitoring mercury in ambient air. Furthermore, it has several advantages, such as a simple light source with natural mercury, no gold amalgam beneficiation, and a simple system.

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