A portable NDIR sensor for rapid detection of hydrogen cyanide in environment

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Abstract. Cyanide pollution refers to the environmental pollution caused by cyanide and its compounds. As a derivative of cyanide, the leakage and excessive discharge of hydrogen cyanide will cause great harm to the surrounding animal and plant environment. Rapid detection of hydrogen cyanide can avoid some unnecessary environmental pollution. Based on the principle of non dispersive infrared(NDIR) detection, the infrared absorption of hydrogen cyanide at 3.0 μm and 14.3 μm was selected as the qualitative and quantitative basis. Two NDIR sensors were designed to detect 3.0 μm and 14.3 μm infrared absorption respectively after assembly. The standard curve between the concentration of hydrogen cyanide and the voltage response value was determined, and the performance of the two sensors was tested. Their detection ranges is 10ppm-3000ppm and 22ppm-3000ppm respectively. The maximum response time is less than 11s and RSD < 2%. After comparing the performance of the two sensors, the display values of the different sensors were processed. Finally, the two sensors were assembled into one sensor, the hydrogen cyanide concentration was displayed with one indication and different gases were mixed with hydrogen cyanide to pass into the gas chamber, which improved the anti-interference ability.

1. Introduction
Cyanide is the general term of a class of cyanide containing compounds, which are widely used in electroplating, rubber and metallurgy. It has caused great harm to the environment in recent years. As a derivative of cyanide, hydrogen cyanide usually exists in the form of gas[1]. Because cyanogen in cyanide has a strong coordination ability, it can combine with trivalent iron ions in cells, affect the normal respiration of cells. Once the cyanide enters the water body and pollutes the water source, it will not only cause fish death, but also cause human poisoning. In addition, some cyanide seeps into the surface to pollute the soil, which will also lead to a large number of withered vegetation. For the detection of hydrogen cyanide, there are gas chromatography, ion chromatography, spectrophotometry, volhard method, chemical chromogenic method, catalytic combustion method and electrochemical method. However, most of these methods have the disadvantages of cumbersome operation, expensive instruments, long reaction time and easy "poisoning" of devices[2-4].
The non-dispersive infrared (NDIR) method uses the absorption of specific infrared spectra by gas as a qualitative basis, and Lambert Beer’s law as a quantitative basis. It can not only detect gas qualitatively and quantitatively in time, but also has a wide detection range. The NDIR sensor based on this principle means that after infrared light irradiates the gas chamber to be measured, a filter is used to let the infrared light of a specific wavelength pass through. Usually, the characteristic infrared absorption of the gas to be measured is selected as the detection wavelength, and the optical signal is converted into electrical signal by the infrared detector to obtain unknown concentration[5-7]. Therefore, it has a good prospect to detect hydrogen cyanide by NDIR sensor.

2. Materials and Methods

2.1. Materials
Hydrogen cyanide(HCN, 3000ppm), N₂(99.99%), CO₂, CO, NO, NO₂, SO₂, H₂, O₂, He, CH₄, C₂H₄, and C₂H₅OH.

FTIR Spectrometer(Bruker company), Programmable Temperature Chamber, Gas Sample Compounder.

2.2. Infrared spectrum of HCN
Turn on the FTIR Spectrometer for preheating. After the instrument is stable, start the computer and run the IR software, nitrogen is introduced into the gas pool as background, the parameter background of FT-IR spectrometer is set as scanning times 32, scanning times of gas to be measured is 64, resolution is 4, and scanning wavelength range is 400cm⁻¹-4000cm⁻¹. Then the gas pool is filled with hydrogen cyanide gas, after scanning, the infrared spectrum of hydrocyanic acid appears.

2.3. Measurement of NDIR sensors
As shown in figure 1, according to the selected wavelength, the light source, gas chamber, filter and detector of the sensor are selected and assembled. The light source emits periodic infrared light. Different concentrations of hydrogen cyanide gas were introduced into the gas chamber by Gas Sample Compounder. When hydrogen cyanide gas passes through the gas chamber, the infrared light is absorbed by hydrogen cyanide gas. The appropriate filter is selected to let the selected wavelength range pass through. The infrared detector converts the optical signal into electrical signal output and collects the signal by computer. The response time, repeatability and temperature were tested by the relationship between response value and concentration.

Figure 1  Sensor structure and signal acquisition
3. Results and discussion

3.1. Molecular structure and infrared spectrum

Infrared is a kind of electromagnetic wave. The condition for producing infrared absorption is that after molecular absorption selectively absorbs certain radiation, the dipole moment changes. For HCN, it is composed of 3 atoms. The CN group has a strong electron withdrawing effect. The positive and negative charge centers do not overlap, and the dipole moment changes. The dipole moment function $\vec{\mu}$ is as follows [8]:

$$\vec{\mu} = \sum r_i \vec{q}_i$$

Here, $q$ is the charge, which is generally considered to be a constant, $r_i$ is the position vector. After the change of $r$, the dipole moment changes, which is reflected in the molecular vibration and rotation. As shown in the figure 2 is the spatial structure diagram of hydrocyanic acid, which is linear. The vibration of HCN molecule can be decomposed into several normal vibrations, that is, the mass center of HCN remains unchanged, the whole molecule does not rotate. The C, N, and H atoms make simple harmonic motion near the equilibrium position, and the vibration frequency is consistent with the phase. The infrared spectrum of hydrocyanic acid gas is obtained by Fourier infrared spectrometer, as shown in the figure 3, the absorption peaks of hydrocyanic acid are 3300 cm$^{-1}$ and 700 cm$^{-1}$. For the infrared spectrum of 3300 cm$^{-1}$, it is the stretching vibration peak of C-H and has obvious absorption; 700 cm$^{-1}$ is the bending vibration of H-C≡, there is no obvious interference of ambient gas at this absorption position, and the absorption intensity is the highest; theoretically, there should be an absorption peak of C≡N, but due to the small intensity, it can not be reflected in the figure 3. Therefore, the beams at 3300 cm$^{-1}$ and 700 cm$^{-1}$ are selected as the detection wavelength of hydrogen cyanide. Two sensors for detecting hydrogen cyanide are designed to detect 3300 cm$^{-1}$ (3 $\mu$m) and 700 cm$^{-1}$ (14.3 $\mu$m) respectively.

![Molecular structure of hydrogen cyanide](image1)

![Infrared spectrum of hydrogen cyanide](image2)

3.2. Fabrication of NDIR sensors

Refer to the selected detection wavelength, the light source is IR-200, the inner wall of the gas chamber is plated with gold to reduce corrosion, the filter is a band-pass filter, each sensor has two filters, one is for reference and the other is for testing, testing filters can pass through the wavelength of 3 $\mu$m and 14.3 $\mu$m, and the detector type is pyroelectric. The center of the light source, the central axis of the gas chamber and the center of the detector should be in a straight line during assembly, so that the infrared light can enter the detector through the gas chamber in parallel, and nitrogen is used as the reference gas to eliminate the background interference.

3.3. Standard curve

When the gas absorbs the infrared light of a certain wavelength, the light intensity of the infrared light of the specified wavelength will be weakened. According to Lambert Beer’s law, the relationship between the intensity of infrared light at a specific wavelength and the gas concentration satisfies the following formula [9]:
\[ I = I_0 e^{-kcl} \]  

\( I_0 \) is the infrared light intensity at the incident wavelength of a specific wavelength, \( I \) is the infrared light intensity after absorption at a specific wavelength, \( c \) is the gas concentration, \( l \) is the length of the gas chamber, and \( k \) is the absorption coefficient of the gas. The sensor has a reference light path and a measurement optical path, which can eliminate the errors caused by the radiation weakening of the light source and the aging of the gas chamber. The detector in the sensor converts the same optical signal into optical signal, so the following formula is obtained:

\[ U_{\text{ref}} \propto I_{\text{ref}} \]  
\[ U_{\text{act}} \propto I_{\text{act}} \]

\( I_{\text{act}}, I_{\text{ref}} \) represents the light intensity of the hydrogen cyanide channel and the reference gas channel respectively after irradiation. \( U_{\text{act}}, U_{\text{ref}} \) represents the voltage signal of the hydrogen cyanide channel and the reference gas channel respectively after irradiation. In Lambert Beer law:

\[ I_{\text{act}} \propto \frac{1}{c} \]

The result is as follows:

\[ U_{\text{ref}} - U_{\text{act}} \propto c \]

There is a proportional relationship between the reference voltage minus the detection voltage and the concentration of hydrogen cyanide. When \( kcl \ll 1 \), the relationship between different concentration and voltage was measured to make a linear fitting. The different concentrations of hydrogen cyanide was intruduced into gas chamber by Gas Sample Compounder. Figure 4 and figure 5 shows the standard curve of the sensor 1 and senor 2. For the sensor 1, the hydrogen cyanide standard curve equation in the linear range of 120ppm-3000ppm; and for the sensor 2, the hydrogen cyanide standard curve equation in the linear range of 75-3000ppm. Therefore, the sensors have fine result in the detection of hydrogen cyanide. After obtaining the standard curve of hydrogen cyanide. The detection limit of sensor 1 is 10ppm (S/N=3), and the detection limit of sensor 2 is 22ppm (S/N=3).

3.4. Measurement

3.4.1. Response time.

The response time of the instrument refers to the time required for a certain concentration of gas to reach 90% of the stable value from zero. The response value to reach 90% of the stable value is recorded. figure 6 and figure 7 shows the maximum response time of sensor 1 is less than 10s, and the maximum response time of sensor 2 is less than 11s. Both sensors can quickly respond to hydrogen cyanide and can monitor the concentration change of hydrogen cyanide rapidly.
3.4.2. Precision and stability.
To explore the precision of the instrument, 20 parallel experiments were carried out with different concentrations of hydrogen cyanide. The results show that the RSD<2%. The sensors are feasible for the detection of hydrogen cyanide. For the study of the stability of the instrument, the readings of the two sensors were recorded within half a month, 20 times a day at different times, a total of 15 days, the test concentration was 3000ppm, the results is shown in figure 8. The absolute error of sensor 1 is less than 20ppm, the absolute error of sensor 2 is less than 15ppm, and the stability of sensor 1 is better than sensor 2.

3.4.3. Detection value selection.
Two sensors are designed to detect different wavelengths of hydrogen cyanide simultaneously, and finally the two sensors are assembled together. When the actual concentration is displayed to the user, it is enough to display only one indication. Therefore, it is necessary to compare the performance of the two sensors. The F-Test method was used to test whether there was significant difference in the precision of the two sensors. The two sensors measured 300 ppm hydrogen cyanide respectively, and each sensor was tested 10 times, n=10, \( S_1^2 = 13.1, S_2^2 = 12.1 \), F is calculated as follows (confidence level is 95%) [10]:

![Sensor response time](image1)

**Figure 6** Sensor response time, a b c d e f is 3000ppm, 2400ppm, 1800ppm, 900ppm, 600ppm, 300ppm. Sensor1 for detecting 3.0μm.

![Sensor response time](image2)

**Figure 7** Sensor response time, a b c d e f is 3000ppm, 2400ppm, 1800ppm, 900ppm, 600ppm, 300ppm. Sensor2 for detecting 14.3μm.

![Stability of both sensors](image3)

**Figure 8** Stability of both sensors within 15 days. (a)Sensor1 for detecting 3.0μm. (b)Sensor2 for detecting 14.3 μm.
The results show that there is no significant difference between the two sensors in the detection of hydrogen cyanide. The repeatability, stability and response time are basically the same, the detection limit of sensor 1 is slightly lower than that of sensor 2, but the overall performance of the two sensors is similar.

Choosing two wavelengths to make two sensors is for the purpose of qualitative detection simultaneously and improving the accuracy. Only one sensor responds to the input gas, which is not hydrogen cyanide. Therefore, three display schemes are designed for digital display. (1) When both readings are not zero and the difference is less than 30ppm, the average value is displayed; (2) When both readings are not zero and the difference is greater than 30ppm, the minimum value is displayed; (3) When there is only one zero value, the zero value is still displayed.

3.4.4. Anti-interference.
According to this method, the experiment of mixing gas was carried out, the interference gas (CO₂, CO, NO, NO₂, SO₂, H₂, O₂, He, CH₄, C₂H₄, and C₂H₅OH gas) and hydrogen cyanide were mixed into the sensor respectively, the time of each gas injection is 30s. As shown in the figure 9, the hydrogen cyanide indication remained stable basically. The design of this scheme can avoid gas interference and improve the accuracy and stability of the instrument effectively.

4. Conclusion
The experimental results show that it is feasible to detect hydrogen cyanide in the environment based on NDIR principle. In this paper, two detection wavelengths of hydrogen cyanide are selected and detected at the same time, both sensors have excellent performance. Different from the general gas NDIR sensor, the value of the two sensors is converted into an indication, which shows that the sensor has good selectivity and stability, and can monitor hydrogen cyanide rapidly. Therefore, the detection of hydrogen cyanide by NDIR principle can reduce the occurrence of cyanide pollution accidents.

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