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基于角反射镜的气体传感器

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摘　要:介绍了一种由两个角反射镜构成的气体传感器吸收池。利用角反射镜的反射特性和对光束的倾斜不敏感性,提高了吸收池的稳定性和灵敏度。用几何光学方法分析光束的传输特性。提出了探测光在单波长和双波长时的传输方程和系统的测量方程,构建了一种气体浓度检测系统。探测光在吸收池中来回传播的次数 N 由两个角反射镜的轴间距离决定,差分光吸收光谱(DOAS)的灵敏度与光在池内的传播次数 N 成正比。在 N 为 3 时,电池的检测阈值接近 50 ppm。

关键词:光谱分析;分光光度法;气体传感器;灵敏度;角反射镜

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Gas sensor based on corner cube prisms

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Abstract: A gas sensor absorption cell was introduced which was made of two corner cube prisms. The stability and sensitivity of the cell were improved using the reflectivity character and the senseless to tilting of light beam. The transmission characteristics of light beam were analyzed with geometric optics. Moreover, the transmission equation of probing light and the measurement equation of the system at both single-wavelength and dual-wavelength were put forward , and a gas concentration detection system was constructed. It is concluded that the times N of probing light traveling back and forth in the cell is determined by the distance between axes of the two corner cube prisms, the sensitivity for differential optical absorption spectroscopy (DOAS) is proportional to the times N. The sensor was used to detect concentration of methane. The results show that the inspection threshold of the cell approaches 50 ppm for methane at N is 3.

Key words: spectrum analysis; spectrophotometry; gas sensor; sensitivity; corner cube prisms

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Introduction

Absorption cell is an important component in a spectrum absorption gas sensor, its configuration affects sensitivity and stabilization of applica-

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tion system. Several smart configuration forms were introduced[1]. Their performances are stabilized, configurations are simple, and their factures are easy, but interaction length is small between probing light and gas to be measured, therefore, sensitivity is small. Generally, an optics cell is utilized in which probing light travels back and forth, in order to extend the interaction length. There are typical cells, such as White cell [2-3], Herriott[4] cell, and correlation changed cells[5]. White cell may achieve a few meters to thousands meters, but its configuration is complicated, and its adjustability is poor for online measurement. Herriott cell is simpler than White cell, due to a confocal configuration adopted, only fourfold length effective interaction length may come true, and in case the configuration is confirmed, its effective interaction length cannot change. White cell is influenced by the placement surroundings. A multi-path absorption cell was put forward by Chernin[5], the cell has long length configuration, but its combination precision is too high to suit real time measurement system.

In order to satisfy the changing of sensitivity in inspecting system[6], manifold high stability absorption cells were designed[7-8], their long-term stability was improved based on rectangular prisms. In the paper, a cell is introduced based on corner cube prisms[9]. The cell is provided with better characteristics.

1 Configuration and transmission equation of cell-based corner cube prisms

1.1 Configuration of cell-based coner cube prisms

It is known that corner cube prism is formed with three right-angle planes one to one, which is schematically depicted in Fig. 1. The underside is upright to the axis. Emergent light beam travels back in parallel with incident light beam through the underside.

Optical path of the cell constructed with two

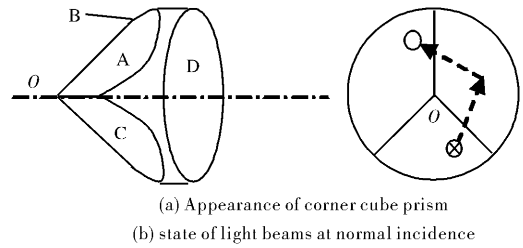

Fig. 1 Constructive characteristics of corner cube prism

corner cube prisms is shown in Fig. 2. Two undersides are parallel, and their axes are parallel with no superposition. Probing light is transforming into small parallel beam at side inlet of the cell, and is normally incident to underside of prism 1. Emergent light passing through prism 1 is normally incident to underside of prism 2. Emergent light from prism 2 is normally incident to underside of prism 1 too. Thus, to-and-fro running, the probing light is coupled into the cell. The probing light from prism 1 travels in reverse to original incidence light with a distance, such as shown as broken line in Fig. 2, this light is called as back emergent light. The probing light may run from prism 2, the light is called forward emergent light. The emergent light intensity is relation to the concentration of gas in the cell, the effective length of the cell and the times of probing light traveling in the cell, etc.

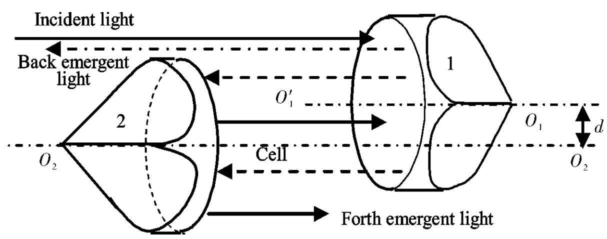

Fig. 2 Construction of cell composed of two corner cube prisms

1.2 Analysis of light traveling in cell

The tracks of light in cell may be figured with spots on the two underside of the prisms. According to the characteristics of corner cube prism, after perpendicularly coming into the cell, the tracks of probing light are parallel group beams, they are distributed with regard to the two prisms, as shown in Fig. 3. Let line x being coplanar with axes of the prisms, the line is vertical to the axes, taking the point O_2 as origin. Because of every incidence and emergent light spot on underside, D_1 and D_2 is symmetrical with regard to centre O_1 and O_2, separately. According to geometry and ray illustrating, the spots on undersides of the two prisms are uniformly distributed on sides of line X, the distances of spots to line x are uniform. Spots of light entering D_1 are arranged on line L_1, and spots coming out of D_2 are arranged on line L_2. On the other hand, spots of light entering into D_2 are arranged on line L_2, and spots departing from D_2 are arranged on line L_1. In terms of the median of a triangle, the distance between the two contiguous spots on L_1 and L_2 is $2d$, where d is the distance between axes of the two prisms. From Fig. 3, it is known that probing light travels back and forward in the cell, as well as the cell-based rectangular prism[7].

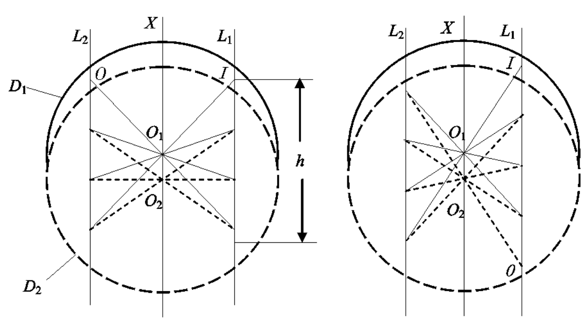

Fig. 3 Distribution of spots by light beams on D_1 or D_2

1.3 Light transmission equation in cell

Let the centre of incidence light spot place at point I on underside of prism D_1, and point I is on line L_1. The distance between point I and intersect point is expressed as h, the intersect point is formed by line L_1 passing through the edge of underside of prism 1. Times of probing light passing through the underside of prism 1 is

$$M=\mathrm{int}(\frac{h}{2d})+1 \tag{1}$$

If emergent light is back emergent light, the times of light travels in the cell is even, and if it is forward emergent light, the times is odd. Effective length of the cell is marked in l, the effective optical length of probing light for back emergent light is

$$L=2Ml \tag{2}$$

Total time of back emergent light passing through undersides D_1 and D_2 is $4M-2$. Interfacial reflection and loss of material made from prism for probing light are considered, the intensity of back emergent light is

$$I_{\mathrm{out}}=I_{\mathrm{in}}\tau^{M-2}\cdot e^{-k'M(l_1+l_2)}\cdot e^{-2kMl} \tag{3}$$

In Eq. (3), I_{in} is incidence light intensity, τ is transmission ratio of underside of the two prisms, it is about 96 %, l_1 and l_2 are the length of light travels through prism 1 and prism 2, separately, k is extinction coefficient of gas in the cell, k' is extinction coefficient of material from which prism is made. The absorption coefficient of quartz is vary small near infrared. Generally, the diameter of corner cube prism is less than 50mm. Both l_1 and l_2 are less than interval l between the prisms. If M is larger, the extinction coefficient k' may affect intensity of emergent light in evidence. Thus absorption of material may be ignored in the visible and near infrared range at small M.

For forward emergent light, the effective optical length of probing light may be expressed in the form:

$$L=(2M+1)l \tag{4}$$

The total time of forward emergent light passing through undersides D_1 and D_2 is $4M$; the intensity of forward emergent light can be written as

$$I_{out}\approx I_{in}\tau^{4M}\cdot e^{-k(2M+1)l} \tag{5}$$

From Eq. (1)~Eg. (3), it is known that the effective length of probing light can be changed with changing of distance between centre axes of both prisms, sequentially the sensitivity of cell can be changed. When d is smaller, effective length L is larger, and L is changed with d obviously. It is shown that if d is smaller, the adjusting efficiency of the cell light length is higher. It is indicated that the cell based on corner cube prism is propitious to miniaturization of gas sensor configuration.

In Eq. (3) and (5), the back reflection of undersides of prisms is not considered. If there is lean between undersides of prisms, back reflected light is not repeated, and therefore the back reflection of interface may be ignored. Here incidence light beam is taken as benchmark being referenced by d, d is distance between parallel lines passing through both prisms separately.

2 Analysis on sensitivity of cell

For the sensor, input physical magnitude is intensity of gas measured, and output magnitude is light intensity or absorbance[10]. The sensitivity of cell is defined as the output magnitude produced by unit input magnitude.

2.1 Sensitivity for single wavelength measurement

Emergent light intensity is given by Eq. (5), if there is no gas to be measured, emergent light intensity can be written as

$$I_{\mathrm{out}}(\lambda) \approx I_{\mathrm{in}}(\lambda) \tau^{4M} \tag{6}$$

where $I_{\mathrm{out}}(\lambda)$ is equivalent to incidence light intensity of the cell, Eq. (5) can be rewritten in the form:

$$I'_{\mathrm{out}}(\lambda) \approx I_{\mathrm{in}}(\lambda) \tau^{4M} \cdot e^{-k(\lambda)(2M+1)l} \tag{7}$$

where $k(\lambda)$ is extinction coefficient of the gas measured at wavelength λ. Therefore absorbency for single wavelength measurement is expressed as

$$A = -\ln \frac{I'_{out}(\lambda)}{I_{out}(')} = Nk(\lambda)cl \tag{8}$$

In Eq. (8), N is times of probing light travels back and forward in the cell, and $N=2M+1$. The sensitivity of cell is defined as change in absorbency or light intensity produced by unit gas concentration. Thus sensitivity of cell for single wavelength measurement is put forward as

$$S(\lambda) = \frac{\Delta A}{\Delta c} = Nk(\lambda)l \tag{9}$$

From Eq. (9), it is known that sensitivity of cell is proportional to N, and sensor sensitivity may be changed with adjusting distance d.

2.2 Sensitivity for differential optical absorption spectroscopy

There is weak absorption of else gases, or the absorption coefficient changes slowly with wavelength in arrange of absorption of the gas measured. The single wavelength light is selected as probing light; measured gas absorption coefficient is larger than the ones of else gases at the wavelength. Another wavelength light is utilized as referenced light, at which absorption is weaker for measured gas and else gases. The wavelength of probing light is marked as λ, and that of referenced light is marked as λ_r. Molar absorption coefficients of gas measured for probing light and referenced light are marked as $\alpha(\lambda)$ and $\alpha(\lambda_r)$, separately. $\beta(\lambda)$ and $\beta(\lambda_r)$ are taken separately to describe loss of light intensity produced by probing light and referenced light running in the cell except absorption. Probing light intensity exported from the cell is

$$I'_{\mathrm{out}} = I_{\mathrm{out}}(\lambda) e^{-N\alpha(\lambda)l-\beta(\lambda)} \tag{10}$$

Referenced light intensity exported from the cell is given by

$$I'_{\mathrm{out}}(\lambda_r) = I_{\mathrm{out}}(\lambda_r) e^{-N\alpha(\lambda_r)l-\beta(\lambda_r)} \tag{11}$$

From Eq. (10) and (11), we can get

$$\ln \frac{I_{\mathrm{out}}(\lambda) I'_{\mathrm{out}}(\lambda_r)}{I_{\mathrm{out}}(\lambda_r) I'_{\mathrm{out}}(\lambda)} = Ncl[\alpha(\lambda) - \alpha(\lambda_r)] + [\beta(\lambda) - \beta(\lambda_r)] \tag{12}$$

Let probing light and referenced light travel along same optical path, and wavelength of probing be close to that of referenced light. Therefore there is relation of $\beta(\lambda) \approx \beta(\lambda_r)$. Measured gas concentration may be expressed by

$$c = \frac{1}{Nl[\alpha(\lambda) - \alpha(\lambda_r)]} \ln \frac{I_{\mathrm{out}}(\lambda) I'_{\mathrm{out}}(\lambda_r)}{I_{\mathrm{out}}(\lambda_r) I'_{\mathrm{out}}(\lambda)} \tag{13}$$

Difference of absorbency is introduced

$$\delta A = A - A_r = \ln \frac{I_{\mathrm{out}}(\lambda)}{I'_{\mathrm{out}}(\lambda)} - \ln \frac{I_{\mathrm{out}}(\lambda_r)}{I'_{\mathrm{out}}(\lambda_r)} \tag{14}$$

or is rewritten in the form:

$$\delta A = Nlc[\alpha(\lambda) - \alpha(\lambda_r)] \tag{15}$$

here, A and A_r are separately absorbency of probing light and referenced light. For differential optical absorption spectroscopy (DOSA)[11], sensitivity of the cell is

$$S_d = \frac{\Delta(\delta A)}{\Delta c} = Nl[\alpha(\lambda) - \alpha(\lambda_r)] \tag{16}$$

Generally, ratio of intensity at two near wavelengths from same source may be regard as constant. From Eq. (13), influence from changing in the light source may be ignored. Eq. (16) indicates that sensitivity of DOAS is proportional to N. On the other hand, in order to improve inspecting sensitivity, probing and referenced wavelength light should be chosen, in which difference between $\alpha(\lambda)$ and $\alpha(\lambda_r)$ is larger.

3 Experiment results and analysis

3.1 Observation of cell stability

The same two corner cube prisms were used to form an absorption cell. The diameter of the prism is 38 mm. The position of the incident spot is adjusted at the lower side of the prism 1 so that the distance h is 30 mm. From Eq. (1), it is known that M varies with distance d, and the variation curve is shown in Fig. 4. If the distance d is less than 2 mm, M may change from one number to another as d changes in 0. 1 mm. When d is small, the probing beam is destroyed, especially when the beam cross section is larger, it is easier to destroy. Therefore, the cross section of the probe beam should be limited. When the distance d is large, M keeps stable, distance d varies greatly, d varies within 0. 2mm and M keeps at 9. When m is less than 8, d can be changed in a larger displacement. Generally, the absorption cell is stable when d changes in a small displacement range due to environmental factors at a certain value.

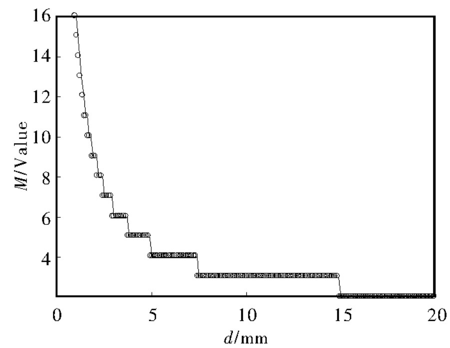

Fig. 4　M changing with distance *d*

3.2 Cell used into inspecting of methane

There are absorption peaks of methane near wavelength 1. 33 μm and 1. 65 μm. Halogen tungsten lamp was used as light source. Light of wavelength 1. 33 μm from the source is obtained by spectrometer. It is considered that there are gases of CO, CO_2, NH_3 and H_2S, etc. in the air, there being absorption near wavelength 1. 65 μm with them, and they may disturb measurement for CH_4. Therefore referenced wavelength was taken as 1. 27 μm, and InGaAs-PIN detector was used. Effective length of cell was taken as 50 cm, diameter in section of cell is 6 cm. Two planes made of fused quartz were used window at two ends of cell, and they are placed in parallel. Set-up of measuring concentration of CH_4 is shown in Fig. 5, being measured sample is natural gas.

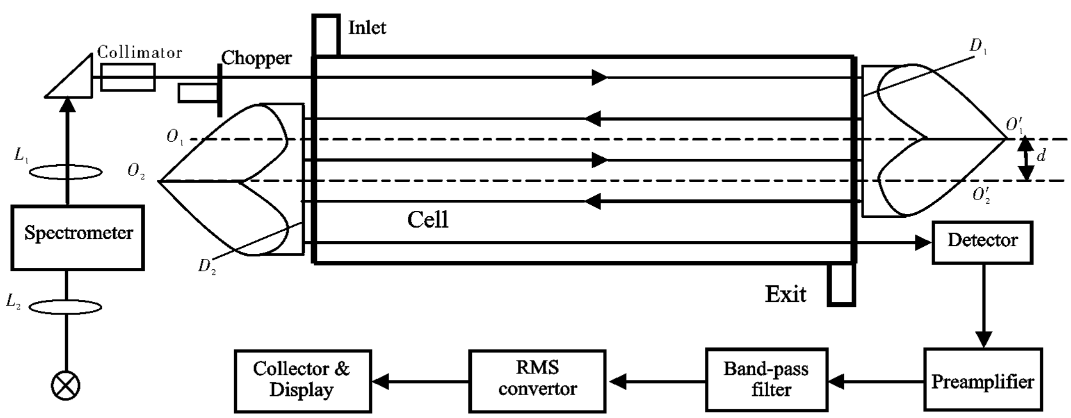

Fig. 5　Diagram of measuring concentration of CH_4

3.3 Data processing and analysis on results

From Eq. (13), concentration of measured methane may be expressed as

$$c=\frac{1}{Nl[\alpha(\lambda)-\alpha(\lambda_r)]}\ln\frac{U_0(\lambda)U_{\text{out}}(\lambda_r)}{U_0(\lambda_r)U_{\text{out}}(\lambda)} \tag{17}$$

Here, $U_0(\lambda)$ is output voltage from data collector being relational to equivalent incidence probing light, and $U_{out}(\lambda)$ is belong to emergent probing light. $U_0(\lambda_r)$ is relational to equivalent incidence referenced light, and $U_{out}(\lambda_r)$ comes from emergent referenced light.

Under no changing in the gas concentration, distance d was changed, i. e. time of probing light traveling changed from N to $N'=N+\Delta N$, output voltage related to probing light and referenced light were changed as $U'_0(\lambda_r)$ and $U'_{out}(\lambda_r)$. Eq. (17) was rewritten as

$$c=\frac{1}{N'l[\alpha(\lambda)-\alpha(\lambda_r)]}\ln\frac{U_0(\lambda)U'_{out}(\lambda_r)}{U_0(\lambda_r)U'_{out}(\lambda)} \quad (18)$$

By Eq. (17) and (18), we can get

$$c=\frac{1}{\Delta Nl[\alpha(\lambda)-\alpha(\lambda_r)]}\ln\frac{U_{out}(\lambda)U'_{out}(\lambda_r)}{U_{out}(\lambda_r)U'_{out}(\lambda)} \quad (19)$$

It is shown in Eq. (19) that concentration of gas may be acquired with probing and referenced light intensity output at different N in the cell.

In the application, $\alpha(1.33\ \mu\text{m})-\alpha(1.27\ \mu\text{m})\approx 1.6\text{m}^{-1}$, $l=0.5\text{m}$, $N=3$, $N'=5$, $\Delta N=2$. Output voltages from data collector are separately

$U_{out}(1.33\ \mu\text{m})=1.396$ V

$U_{out}(1.27\ \mu\text{m})=1.233$ V

$U'_{out}(1.33\ \mu\text{m})=1.342$ V

$U'_{out}(1.27\ \mu\text{m})=1.190$ V

From Eq. (19), concentration of methane for the sample is about 2470ppm, the result approaches that of gas chromatography method. Precision of A/D in the collector is 15 bits, drift instability of output voltage is less than 1 mV, and precision of output voltage is about 0.02%. If N is 3, it is tested that detection threshold of the cell for methane is about 120 ppm. Times of probing light traveling in the cell was increased to 7, detection threshold of the cell approached 50 ppm. The threshold is about quarter of the data by Ref. [12].

Sensitivity of the cell dependence on times of probing light traveling for single wavelength is shown in Eq. (16). Action produced by portion reflection of the undersides on sensitivity of the cell was observed. When times of probing light traveling back and forward is smaller, sensitivity of the cell is proportional to N. If the times is larger, relation of sensitivity of the cell dependence on the times is not proportional. But sensitivity of DOAS is proportional to N, whether N is large or small.

4 Conclusion

Light transfers equations of the cell based on corner cube prism may be used as measurement equations for gas concentration. Back emergent light and probing light are placed two sides of plane formed by axes of the two prism separately, they are apart a large distance. Both incidence and emergent light may be placed same terminal, and configuration of measurement system can be compact. Sensitivity of the cell is proportional to times of probing light traveling back and forward in single wavelength under certain condition, but sensitivity of DOAS is always proportional to N. The detection threshold of the absorption cell is inversely proportional to the number of light returns in the cell.

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