Hydrogen sulfide gas drilling site online spectra monitor Feasibility Study

Guoliang Li
School of Southwest Petroleum University, Chengdu 610500, China

Mingzhu Chen
School of Southwest Petroleum University, Chengdu 610500, China

Mengjie Gao
Company of Zhongyuan Gas Technology Service Co.Ltd, Wuhan 430000, China

ABSTRACT: Through the hydrogen sulfide and other common small molecular gas near infrared absorption spectrum analysis, propose that analyzing spectral absorption peak at a wavelength of hydrogen sulfide 1.578um neighborhood undisturbed common gases and water vapor from small molecules, which can be used for quantitative analysis; By analyzing suitable NIR light sources and detectors, propose to use laser diodes, infrared photon detectors constituting the hydrogen sulfide-line near infrared detector. Transmission method is based on the difference in absorption peak of hydrogen sulfide and other common small molecular gas in the near infrared spectrum, use this method to achieve spectroscopic detection of hydrogen sulfide line can achieve multi-point line detection.
KEYWORD: Hydrogen sulfide, Near Infrared, Drilling, Spectroscopy.

1 INTRODUCTION

China has proven the country's total natural gas sour gas proven reserves of 1/4, where high H2S blocks are mainly distributed in Sichuan Basin, the basin 2/3 gas containing hydrogen sulfide. Hydrogen sulfide gas has a strong toxic and corrosive, domestic and foreign experts on hydrogen sulfide gas concentration detection using a variety of methods a lot of ongoing research, Hydrogen sulfide electrochemical sensor [Radu Ionescu, 2004, Feng zhong Dong etc, Gillian W, 2003] has the advantage of cheap and easy to use, but the traditional detection techniques are usually non-optical-based detection, such as electrochemical and semiconductor technology point sensors, although these sensors may be sufficient low detection limits, but these tests are susceptible to cross-sensitivity to other gas components and sensitive membrane surface pollution and other unfavorable factors, and its relatively slow response, reusable low, life is short, it is difficult to achieve real-time online continuous monitoring.

2 THE HAZARDS OF HYDROGEN SULFIDE

Hydrogen sulfide is a colorless, highly toxic, highly acidic gases. Hydrogen sulfide is soluble in water and alcohols, solvents and crude oil and other organic solvents. Since hydrogen sulfide is heavier than air, so often accumulate in poorly ventilated lower recesses. Hydrogen sulfide not only on human life caused by Viagra ribs, but also cause serious environmental pollution; the strongly acidic of hydrogen sulfide is likely to cause corrosion of drilling machinery and equipment, resulting in a downhole string broken off, which will lead to the ground manifold and instrument and wellhead equipment is damaged, or even lead to serious blow fire; and the strong acid of hydrogen sulfide will accelerate the aging of non-metallic materials, and equipment to make, wellhead equipment, downhole tools, non-metallic material seal failure hydrogen sulfide hazardous gas during drilling of the following four main square and [Yi kan Ke, 1998].

Table1 Its concentration of harmful levels of hydrogen sulphide

grade	concentration	harmful levels
Safety critical concentration	10ppm	Have obvious rotten eggs smell, allowing exposure to 8 hours
hazard concentration limit	100ppm	Permissible exposure for 10 minutes
High-risk critical concentration	300ppm	30 to 60 minutes limbs trembling, and even death
Death critical concentration	2000ppm	Exposure to death immediately

3 DRILLING FIELD OF HYDROGEN SULFIDE GAS MONITORING

3.1 *oilfield rapid chemical analysis commonly used*

(1) standard iodometric method: on-site detection of hydrogen sulfide in the drilling fluid volume fraction commonly used method is the standard iodometric method.

(2) Rapid assay tube method: Determination of the rate-determining field test tube method is atmospheric hydrogen sulfide content commonly used method.

(3) lead acetate paper test: lead acetate test paper reacts with hydrogen sulfide brown lead sulfide, and hydrogen sulfide obtained by comparing the standard shade guide volume fraction.

3.2 *Comprehensive Judgement*

Comprehensive evaluation method is mainly for logging work with high volume fraction of hydrogen sulfide formation occurs when one turtle jump drilling, drilling speed or venting, pump pressure drop, drilling fluid tank rises, accompanied by intermittent wells Chung and hydrogen sulfide odor; second, the drilling fluid density and pH valuedecrease ,the viscosity rises, the color changes to gray; the third is well temperature of logging and borehole fluid resistivity values drop by resistance, when the drilling fluid in the wellbore still some time , due to the diffusion of hydrogen sulfide gas expansion heat, so cooling gas cut-segment display as increasing resistance, which can be used the well temperature and fluid resistivity anomaly, the card takes the hydrogen sulfide-containing layer.

Since the conventional method susceptible to cross-contamination of other gases, thus lagging response, repeatability and low range of issues, it is difficult to achieve large-scale continuous monitoring. Near-infrared spectral properties of the gas detected gas concentration method can solve these problems, near-infrared spectroscopy combined withfiber-optic communications, which can meet a wide range of hydrogen sulfide gas, long distance and continuous monitoring.

4 HYDROGEN SULFIDE ONLINE NEAR INFRARED DETECTION PRINCIPLE

Spectral detection of hydrogen sulfide is based on light absorption Lambert - Beer law, the mathematical expression is as follows,

$$A = \log(Io / I) = kbc$$

A - - - Absorbance
Io- - - incident light intensity
I - - - transmitted light intensity
k - - - absorptivity
b - - - absorbing optical path
c - - - light-absorbing substance concentration

From Lambert - Beer law shows that the ratio of intensity of incident light and the transmitted light intensity is only related to the concentration of light-absorbing substance, measure the change in intensity of incident light and the transmitted light intensity through the spectrometer detector, you can get light-absorbing substance concentration changes.

4.1 *Analysis of infrared absorption characteristics of Hydrogen sulfide*

In the infrared absorption spectrum, the light-absorbing substance molecule or group absorbs infrared light certain frequency later, when their energy level transitions from the ground state to the first excited state; and the absorption peak of the fundamental frequency peak; from the ground state to the second excited state absorption peak produced an octave peak; peak transition to the third generation of the excited state as a secondary harmonic peaks. Wherein the strongest peak of the fundamental frequency[Yi kan Ke, 1998].Hydrogen sulfide (H2S) molecular structure: molecule is V-shaped molecular structure, bond angle is 92 °, hydrogen sulfide molecule is a polar molecule. According H2S molecular structure has been that they have three different basic vibration frequency [L. R. Brown, 2004]: v1 = 2564.34927cm-1, v2 = 1159.44766cm-1 and v3 = 2565.37647cm-1.Each natural vibration corresponding to a spectral absorption region, the corresponding wavelengths, respectively 3.89962 μm , 8.62480 μm , 3.89806 μm . Its frequency in the near infrared combined in Table 2,

Table2 The molecular of hydrogen sulfide's vibrational absorption line in the near infrared

Co-frequency	E $\nu\left(cm^{-1}\right)$	$\lambda\left(\mu m\right)$	$S\left(cm^{-1}/\left(molecule\cdot cm^{-2}\right)^{-1}\right)$
$3\nu_2+\nu_3$	6.077.5947	1.6454	8.32×10-23
$\nu_1+3\nu_2$	6074.5808	1.6462	9.03×10-23
$5\nu_2$	5797.2380	1.7250	6.93×10-24
$\nu_1+\nu_2+\nu_3$	6289.1734	1.5900	7.96×10-21
$\nu_2+2\nu_3$	6385.2990	1.5661	4..99×10-23
$2\nu_1+\nu_2$	6288.1462	1.5903	2.23×10-21

Table $E_\nu = (1/\lambda)\times 10^{-4}$.From the table we can see that hydrogen sulfide gas in the vicinity that is $\nu_1+\nu_2+\nu_3$ has strong absorption. Absorption line position and strong line spectra in different literature gives different, the literature [H. Riris, 1994] line spectrum position $\nu_1+\nu_2+\nu_3$ gives vibration line of 1.578 μm , strong line spectrum S is $1.3\times 10^{-22} cm^{-1}/(molecule\cdot cm^{-2})^{-1}$, you can choose 1578 μm wavelength as the absorption center. Near infrared absorption spectroscopy using a gas absorption techniques, we can achieve common small molecule gas rapid detection sensitivity [Long jiang Zheng, 2007, Wang Shutao, 2005]

4.2 *Hydrogen sulfide NIR technology and equipment Characteristics*

A differential absorption spectrum narrowband light source detection techniques HZS gas detection. To achieve hydrogen sulfide gas drilling site near infrared spectrum online monitoring, supporting the need for an appropriate signal source, near-infrared detector detector and near-infrared spectroscopy qualitative discriminant analysis algorithm. For a single substance NIR inspection can be used to provide direct light of a specific wavelength narrowband signal, more mature narrowband light source super luminescent diode, tunable distributed feedback laser diodes and semiconductor diodes Figure 1.

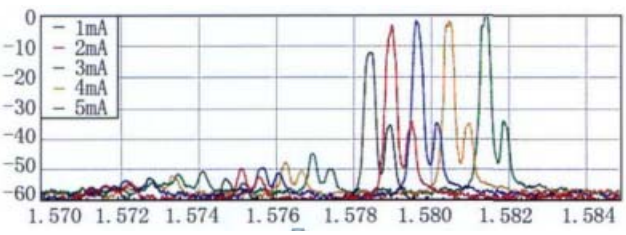

Figure 1 V L- 1580 Tunable diode laser spectroscopy radiation pattern (20 ℃)

Near infrared semiconductor detector has an infrared photon detector (InGaAs,PbS, InAs,etc.), inductively coupled detector (e.g. CCD) and the like. Core semiconductor infrared photon detector is a photodiode, which converts light energy may be irradiated thereon to electric current, the current size of the energy associated with light, so by measuring the current intensity of the light can be reflected, and to determine the concentration of the sample. Figure 2 is one kind of Thorlabs InGaAs PIN photodiode spectral response curve of the detector is a wavelength of 1. 0 - 1. 7 μm light have good response, especially in the wavelength range of 1.30 to 1.67μm response of best.

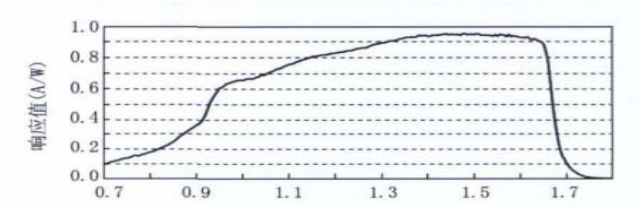

Figure 2 InGaAs PIN Photodiode spectral response curve

5 HYDROGEN SULFIDE LINE NEAR INFRARED SPECTROSCOPY DETECTION

Given the near-infrared spectroscopy only near infrared light signal to a predetermined bandwidth through the test material, detecting light absorption band and the absorbance was measured to determine the concentration of the test substance，which has a non-contact and non-destructive characteristics, which provides the possibility for the realization of hydrogen sulfide line Near Infrared Spectroscopy Detection. When the condition of the other on-line detection, you can select an octave S-H bonds as hydrogen sulfide gas absorption line spectrum detection.

5.1 *Spectral transmission method*

Spectral transmission method using near-infrared spectroscopy of hydrogen sulfide directly into the outlet drilling, drilling fluid extraction outlet on the back drilling fluid passage through real-time and near-infrared spectrometer by hydrogen sulfide detection channel Figure 4. After the measurement is based on the basis of a predetermined bandwidth of the optical signal through the fluid to be measured, the intensity of light emitted to determine the extent of decrease of the target substance and whether there exist strength. Considering the test substance has a low concentration, the absorption length and enough to meet the accuracy of detection, the light source and the detector window for an appropriate distance.

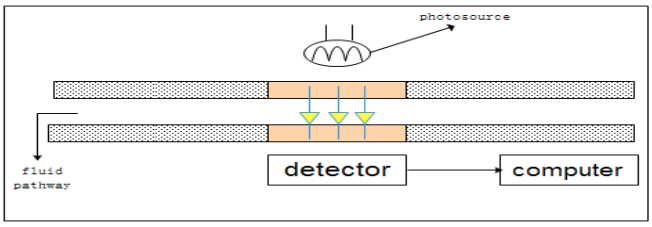

Figure 4 Transmission Method

5.2 *ATR attenuated total reflection*

ATR attenuated total reflection method using near infrared spectroscopy instruments hydrogen sulfide directly into the outlet drilling, using real-time drilling fluid passage outlet on the back extraction of the drilling fluid, and hydrogen sulfide by near-infrared

spectrometer detection channel Figure 5. Measurement is based on a predetermined bandwidth based on the attenuation of the optical signal to multiple reflections within the waveguide chip after determining the presence or absence of the target substance and existing strength.

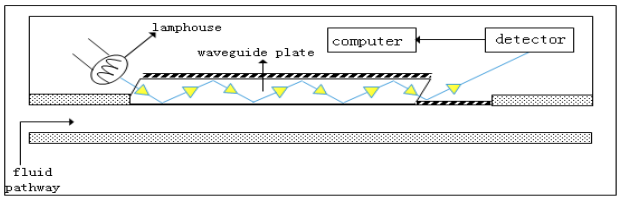

Figure 5 ATR attenuated total reflection

5.3 *Transmission Method and ATR attenuated total reflection Comparative Analysis*

Transmission measurement is based on changes in light intensity transmitted through the drilling fluid, the signal is relatively stable, given the low concentration of the test substance of the case, enough to meet the absorption length and precision, the light source and detector spacing for an appropriate window. TR attenuated total reflection measurement is based on the change in the intensity of the reflected light, although affected by the drilling fluid solid particles scatter large, but the optical path of the measurement process is not affected and there is no drilling fluid passage jam phenomenon. Two detection methods should be selected according to the type of drilling site geological structures and drilling fluid.

6 CONCLUSION

Hydrogen sulfide in the near-infrared absorption peak absorption of other ingredients are far apart, hydrogen sulfide can be measured directly. Near infrared light can be transmitted through the fiber, this article only hydrogen sulfide in drilling site of online real-time measurements were performed to explore the feasibility of, if it is applied in the field still need further experimental test site. 2001 Hoed Chung Using near-infrared wavelength spectrum of discrete binding point how far the linear regression (MLR) of gasoline octane were detected [Hoed Chung, 2001], and also on-line measurement of hydrogen sulfide is not just a theoretical method for detecting the It can be used in actual production.

REFERENCES

Feng zhong Dong etc Tunable diode laser absorption spectroscopy technology and its applications in air quality monitoring ［J］ Chinese Journal of Quantum Electronics

Gillian W, George S, Kathryn A, et al. Optical fibre instrumentation for environmental monitoring applications. [J]. Journal of Optics A: Pure and Appl. Opt., 2003, 5:140-145.

Hoed Chung, Hyeseon Lee, and Chi-Hyuck Jun. Bull. Korean Chem. Soc. Determination of Research Octane Number using NIR Spectral Data and Ridge Regression [J].2001,22(1):37-42.

H. Riris, C. Carlisle, L. Carr, et al Design of an open path near-infrared diode laser sensor: application to oxygen, water, and carbon dioxide vapor detection [J].Appl. Opt. 1994,33, 7059-7066 (1994).

L. R. Brown, O. V Naumenko, E. R. Polovtseva, and Leonid N. Sinitsa. Hydrogen sulfide absorption spectrum in the 5700-6600cm-1 spectral region. Proc. SPIE 5311, 59 (2004).

Long jiang Zheng, Xinyan Huang, and Gen feng Bi. Study of optical fiber carbon monoxide gassensor with DFB LD [J]. Proc. SPIE, 2007, 6625(1Y): 1-7

Radu Ionescu, Anders Hoel, et al. Highly sensitive and selective W03 nanoparticle gas sensor operating in thermally modulated dynamic mode [J]. Proc. SPIE, 2004, 5472: 347-358.

Wang Shutao, Che Rensheng. Novel spectrum absorption fiber methane sensor with DFB LD [J] Proc. SPIE, 2005, 5634:619-626.

Yi kan Ke, Hui Ru Dong, Spectral Analysis [M] Handbook of Analytical Chemistry (Second Edition Volume III) Beijing: Chemical Industry Press, 1998: 868-879.