

Study and design of concentration measurement system of oil in seawater based on fluorescence technology

Ning Wu^{1,a}, Shuwei Zhang^{2,b} and Dongzhi Chu^{3,c}

¹Shandong Academy of Sciences Institute of Oceanographic Instrumentation, Qingdao 266001, People's Republic of China

^awn624097879@126.com

Keywords: Photomultiplier tubes, faint fluorescence signal, detection system, optical path, photoelectric detection circuit.

Abstract. A sensitive in-situ oil measurement scheme in seawater, consisting of the optical system, the photoelectric detection circuit system, the data acquisition and control system, is proposed to facilitate the measurement of the oil in seawater. It has long been supposed that there must be a linear relation between fluorescence intensity and concentration of oil. Now, it is difficult to detect the faint fluorescence signal which submerged into the strong noise by using traditional methods. To deal with this drawback, we devise a detection method of sampling integral to facilitate the extraction of the fluorescence signal from the background signal in the current work. The proposed scheme which comprise of the xenon flash lamp trigger to excite the fluorescent signal, the narrowband filter to filter out the additional environment light and the high sensitivity photomultiplier tubes (PMT) as detector to perceive of the faint fluorescent signal. In particular, the feeble fluorescence signal is well detected through the preamplifier circuit, filter circuit and an integrating circuit.

The obtained results indicate that the proposed detection system is much superior to the traditional system in the detection of oil in seawater with substantially reduced system and environment noise discrepancies. This permits the oil detection system to be capable of acquiring faint fluorescent signal which shielded by vast powerful noise.

Introduction

With the rapid development of our country industry, makes the rivers, lakes and seawaters of oil pollution is more and more serious, seriously damage to the ecological environment, and seriously affect the health of human beings. It is reasonable to employ more measurements for the oil concentration in seawater and provide scientific basis for seawater quality.

At present, the field sampling and laboratory analysis methods are also accepted for measuring the concentration of oil in seawater, which is cumbersome and time-consuming method that is difficult to determine the oil distribution, and these example studies exemplified the common drawbacks of the laboratory measurement and indicated the great incentives of devising effective strategies to tackle them.

In the present work, multi-point sampling points of ultraviolet fluorescence is proposed for measuring the concentration of oil in water, and the fluorescence signal submerged in the noise can be recovered by this method. In this system we improve the ratio between signal's power and noise's power together with the sensitivity of the system by the new demodulating method.

System design

The optical system and circuit system are included in this system which is sketched in Figure 1, consisting of the center wavelength of the 250nm xenon flash lamp module and the PMT of HS5783-01. They are respectively used as excitation light source to produce the fluorescence signal and detector to detection of the fluorescence signal. More specifically, Light from the flash lamp takes two paths, the reference beam and the detection beam. The reference beam takes a direct path to the reference photo diode without any lenses or filters. The detection beam from the flash lamp is optically filtered and focused out through the excitation port window to illuminate a volume of liquid specimen just above the detection port window, which is situated on the turret at 90 degrees to the excitation port. Light scattered or fluorescing from the specimen and passing through the detection (emission) port is directed via a prism, lens and optical filter onto the detection PMT. In addition, it is essentially to calculate the relative position of the lens and narrowband filters.

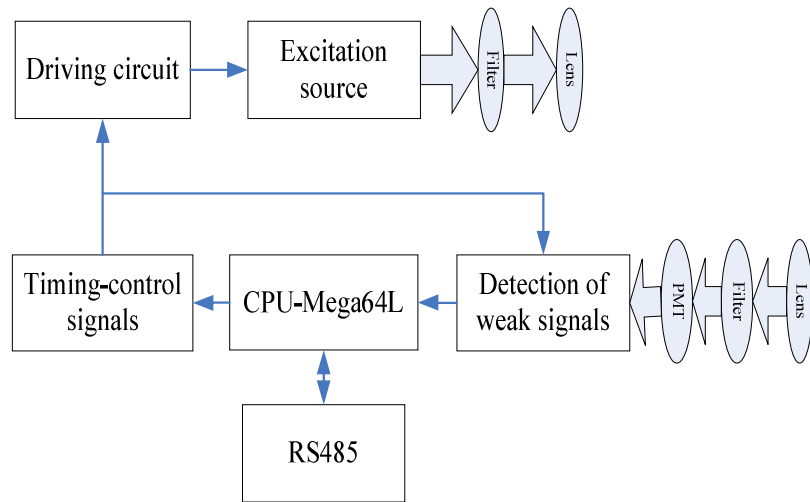


Fig. 1, The system scheme proposed for the detection of the oil in seawater

The design of the photoelectric detection circuit

Because of the excited fluorescence signal is weak signal relative to the ambient light noise signals. In the current work, an attempt is made to extract the faint fluorescence signal in the design and detect of the system with the circuit of current-to-voltage (I/V) convention, the circuit of low-pass filter, the circuit of secondary programmable simplifier and Boxcar integrator. Figure 2 depicts the signal detection process.

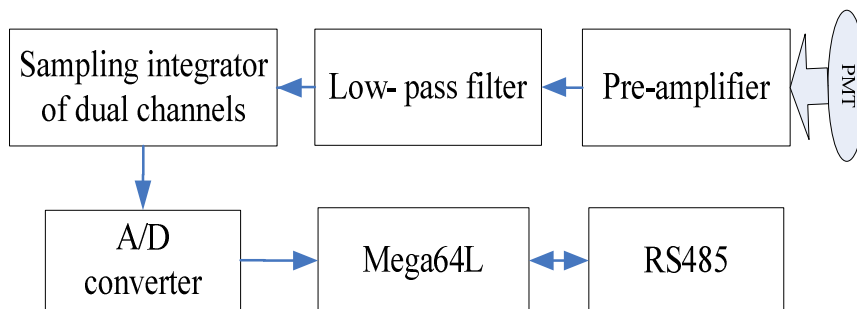


Fig. 2, The schematic of the photoelectric detection

The design of the I/V convention and amplifying circuit

The fluorescence signal is excited by the xenon flash lamp module from the oil in seawater and the current signal is output through the PMT. Since the output current was already found to be weak signal, it must turn the current into the voltage signal, and then amplify the voltage signal. So the

offset voltage, input voltage noise and input bias current of the amplifier will affect the signal, and then the LMP7721 amplifier was adopted with low input bias current of $3fA$, with a guaranteed limit of $20fA$ at $25^{\circ}C$ and $900fA$ at $85^{\circ}C$, low voltage noise ($6.5nV\sqrt{Hz}$), low DC offset voltage ($\pm 150mV$ maximum at $25^{\circ}C$) and low offset voltage temperature coefficient ($-1.5mV/^{\circ}C$).

I/V converter and amplifier circuits are shown in figure 3, which mainly convert the weak current to the voltage signal. The capacitor C1 mainly used to restrain the high frequency voltage noise. The U30B of voltage follower is used for absorption, seclusion and improving the load capacity. The

output voltage is calculated via the following equation, which is
$$A_{vi} = I_i \times (R_{88}/R_{86})$$

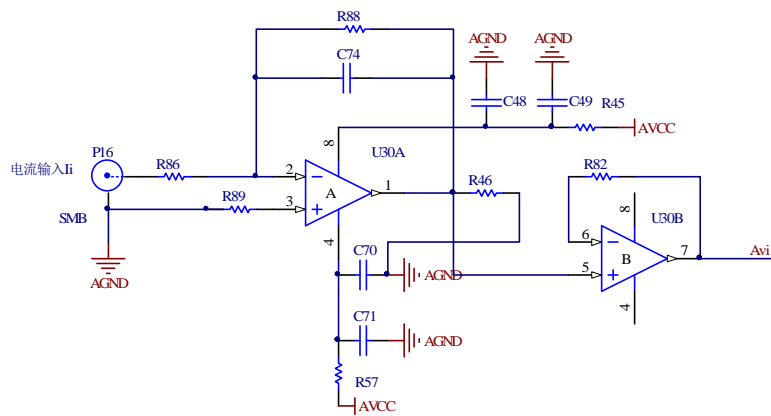


Fig. 3, The I/V convention and amplifying circuit

The design of the low-pass filter circuit

Because of the magnified signal contains a lot of noise signals of ambient light. A second-order low-pass filter circuit is shown in figure 4, which is proposed to pick up the weak signal from noisy background and can be filtered most of ambient light noise. In what follows, the cut-off frequency of the filter is basic equal to the frequency of the excitation light.

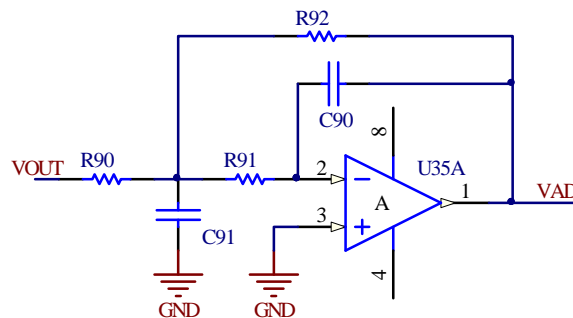


Fig. 4, The circuit of the low-pass filter

The design of the sapling integral circuit

In order to improve the ability of detecting fluorescent signal and completely avoid to the ambient light, a method of sampling integral of dual-channel is presented in this paper. In this method, the proposed scheme consists of two sampling channels, with one is fluorescence signal sampling channel aimed to detect the fluorescence signal and the rest is excitation signal sampling

channel aimed to detect the excitation signal. The obtained result is the value of the fluorescence signal divided by the excitation signal. The principle of this method are sampled at a time interval of the periodic pulse signal which is submerged in the noise, and the output signal tends to the average value of the measured signal sampling points.

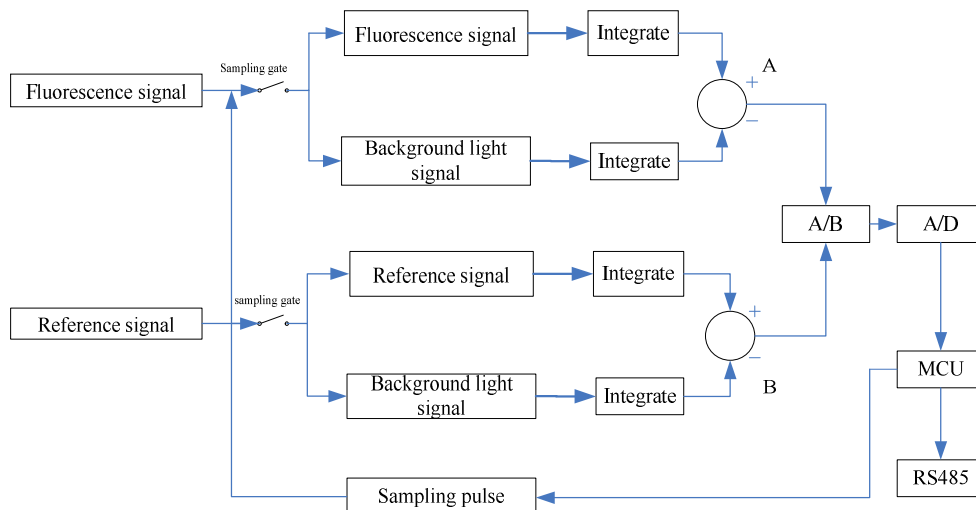


Fig. 5, The schematic of sapling integral

As shown in figure 5, fluorescence signal and the reference signal detection channels are included. They are in charge of the detect fluorescence light signal, reference light signal and background light signal, respectively. More specifically, two new difference values between the fluorescence signal and the reference signal, excitation signal and background light signal can restrain the influence of the variational intensity of the light and the fluctuation of the excitation signal. The 24-bits ADC switches the analog signal into a digital signal, and output to the upper computer by RS485 serial.

The experimental results and analysis

The 0 # diesel oil is added to an ethanol solvent to form standard solution of 25mg/L. Then the 0 # diesel oil is added to the test vessel with gradient of 5ug/L. When the concentration increased to 100ug/l, the 0 # diesel oil will be added to 500ug/L with gradient of 50ug/L. During this time, stir the solution rapidly and continuously to prevent stratification of the 0# diesel. The obtained results is shown in the figure 6, and indicated that the relationship between the fluorescence intensity and the concentration of oil will coincidence with linear relation. In addition, one kind of contrast test has been done and performance curves are depicted in table 1, which shows that the performance of the instrument is comparable with imported foreign instrument.

A group of parameters of the sensor are worked out. The average background value of this sensor is 4977mV the mean squared error is 0.687 and the determination limit is 0.1ug/L.

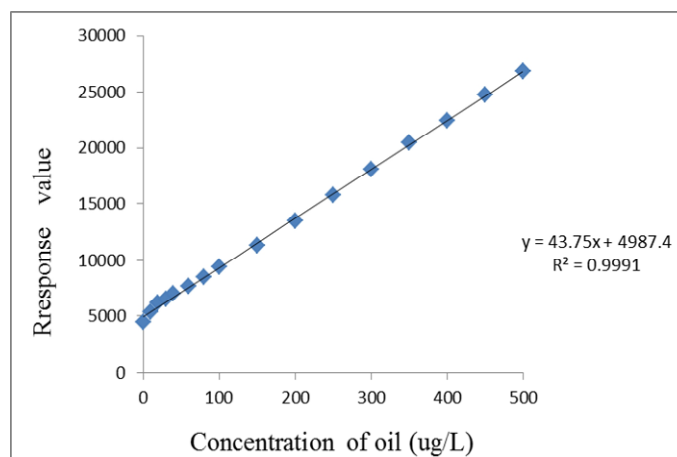


Fig. 6, The response curve of this sensor

Table 1, Proficiency testing

Concentration of oil (ug/L)	0.1	0.2	0.5	1	2	10
UV Aquatracka of Ctg (ug/L)	0.09	0.21	0.47	1.05	2.05	9.96
Sensor of design (ug/L)	0.12	0.20	0.47	1.01	2.08	10.02

Conclusion

In this work, a new in situ oil detection scheme has been proposed. The experimental has been demonstrated that the new detection scheme behaves much better than the traditional detection methods. The measurement results were compared with the UV AqualTrack of CTG, which showed high consistency, high sensitivity and low noise. The measure accuracy, battery life and power consumption has reached the highest level of the contemporaneous commercial products. It has a good application prospect. Therefor one of our future research tasks will be centered on the studies of the mathematical model about measuring factor of temperature, turbidity, salinity, PH value and ambient light.

The great advantages of this detection technique justify the employment of the feeble fluorescence measurements from measured signal with noise as compared with the currently available signal detection technique. The measurement accuracy, battery life and stability had reached the highest level of the detection system.

Acknowledgements

This work was financially supported by the Qingdao Strategic Emerging Industry Development Scheme (14-9-1-2-hy), The National Natural Science Fund (41206076), The Natural Science Foundation of Shandong Province (ZR2014YL006), Science and Technology Development Project of Shandong Province (2015GSF115001) and The National Marine Scientific Resrarch Project (201505007).

References

- [1] P.E.Kepkay, J.B.C.Bugden, K.Lee et al. Application of Ultraviolet Fluorescence Spectroscopy to Monitor Oil-Mineral Aggregate Formation. *Spill Science&Technology Bulletin*, 2002, 8(1): 101-108
- [2] JerryAL, Jea-Philippe C. Pee Reviewed: Characterizing Aquatic Dissolved Organic Matter [J]. *Environ. Sci. Technol.* 2003, 37(1): 18-24.
- [3] Mathieu Thoury, Mady Elias, Jean Maric et al. Nondestructive Varnish Identification by Ultraviolet Fluorescence Spectroscopy. *Applied Spectroscopy*, 2007, 61(12): 1275-1282.
- [4] P.Lambert. A literature review of portable fluorescence-based oil-in-water monitors. *Journal of Hazardous Materials*, 2003,102: 39-55.
- [5] Wang Lirong, Yang Jinghai. Measurement of Micro oil in Water by Using Ultraviolet Fluorescence Spectrum Technology. In: *The Eighth International Conference on Electronic Measurement and Instruments*. 2007. 556~559.
- [6] A.A.Olajire, R.A.Oderinde. Study of aromatic hydrocarbons in heavy residual oils by a combination of spectroscopic analytical techniques. *Journal of African Earth Sciences*, 1998, 27(1): 165~174