Research on signal processing method for total organic carbon of water quality online monitor

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Abstract. At present, there is no rapid, stable and effective approach of total organic carbon (TOC) measurement in the Marine environmental online monitoring field. Therefore, this paper proposes an online TOC monitor of chemiluminescence signal processing method. The weak optical signal detected by photomultiplier tube can be enhanced and converted by a series of signal processing module: phase-locked amplifier module, fourth-order band pass filter module and AD conversion module. After a long time of comparison test & measurement, compared with the traditional method, on the premise of sufficient accuracy, this chemiluminescence signal processing method can offer greatly improved measuring speed and high practicability for online monitoring.

1. Introduction

With the development of modern industry, a large number of poisonous and harmful materials are directly discharged into rivers and sea, the water environment and ecological system caused great impact [1]. At present, water quality of more than half of the water function area is not up to standard in China. In the place of moderate and severe eutrophication, some river regions are called 'all rivers have been polluted' [2]. Therefore, water pollution and ecological security problems are increasingly outstanding, sudden environmental pollution accidents occur frequently [3].

Online monitoring of water quality is always lack of long-term effective environmental monitoring method in China [4]. The Solubility of the pollutants, particularly the persistent organic pollutants, is very low in water, but these pollutants are carcinogenic, that can cause deformity. After a series of low-dose & long-term intake, it will become a potential threat for human health. Therefore the pollution of water quality monitoring is imminent [5, 6].

Total organic carbon (TOC) is a kind of quickly comprehensive indicators for water quality, which could be defined as the containing carbon quantity of the total amount organic matter in the water [7]. TOC is able to fully reflect kinds of pollutants in water. The national standard method of TOC analysis is combustion oxidation - nondispersive infrared absorption method. The advantage is a single, simple process, good reproducibility, high sensitivity. But the disadvantage is that: the probe need frequent calibration, the instrument need large volume and long preheating time, the reaction process must use acid, catalyst and carrier gas. Other common methods include: UV oxidation method, the conductance measurement method, etc. At present, TOC analysis has been widely used in surface water monitoring, such as drinking water, industrial water, pharmaceutical water and so on, which has become the key...
means of the water quality control.

Nowadays the TOC online analyzers made by European or American manufacturers are already very advanced. The commercial TOC online analyzers including: a) Sievers-500 series, made by GE Analytical Instruments Co (United States), adopted the membrane conductivity measurement method, high accuracy, no reagent, but the measuring range is limited, which is mainly used in pharmacy, electric power and pure water quality occasions. b) Multi N/C ®UV HS, made by Analytik Jena AG(Germany), adopted the UV oxidation - non-dispersive infrared test, need regular replacement reagents, mainly used in biological, pharmaceutical, research and other industries. But there are still no rapid, stable and effective domestic methods of TOC online automatic measurement in the aspect of water pollution monitoring at present. So that is an urgent need to a series of independent research and development of TOC online monitoring instrument.

The emerging chemiluminescence fast measurement method can realize the TOC online, real-time and continuous measurement [8]. This chemiluminescence is produced by the oxidation reaction of ozone and organic matter in the sea water, and the luminous signal could be collected and recorded as digital signal by photoelectric conversion technology in the process of reaction. The advantage of this method: no reagent, no secondary pollution, fast response speed. So that, on the one hand, this method can avoid the big particles impact on the accuracy of the water, on the other hand, it can long-term work at the scene of the harsh environment. The method could be suitable for ship, monitoring stations and other occasions to use, which can realize real-time and continuous measurement on the scene [9]. But the disadvantage of this method is that it can't achieve the laboratory instrument measurement accuracy [10]. Therefore, the emphasis and difficulty in existing technology needs to solve is how to improve the measurement accuracy of the signal.

For this purpose, this paper proposes and implements a Photomultiplier tube (PMT) test at the scene of the chemiluminescence reaction of TOC analysis method of high speed, no pollution, and to ensure the enough accuracy of measurement. This paper mainly introduces the principle of PMT and its application in the analyzer, analyzes in detail the design of the signal processing circuit and the design of filter algorithm, finally provides the scene environment test result. Through a large amount of experimental data show that the proposed method compared with other traditional methods is convenient maintenance and high reliability, rapid measurement, no pollution and other characteristics, very suitable for online measurement [11].

2. The research methods
The key point of the signal processing method research of the proposed TOC online monitoring technology is the weak chemiluminescence detection method, which could avoid the complex process of laboratory analysis, and can truly reflect the complex and changeable situation at the scene [12]. In order to achieve the purpose of the TOC measurement technology research, based on the maturely existing technology: technology of ozone oxidation kinetics of chemiluminescence curve, we adopt a novel and mature thread of technology for environmental pollution monitoring technology development. The research emphasis is as follows:

2.1. In order to ensure the validity of the data, the scheme adopt multistage amplifier technology & bandpass filtering technology
Because the signal of chemiluminescence reaction is very weak, the PMT voltage signal is very weak (only 1-3 mV). It needs to be amplified and converted to digital signal output through phase-locked amplifier, programmable gain amplifier, bandpass filter and AD converter. Through chemiluminescence signal superposition response of the different organic matter in water samples, we can get the total luminous intensity curve of the dynamics with the change of time. This method uses the chemiluminescence time-resolved technology to capture the signal during the reaction process, and achieve high efficiency light intensity time series integral. At last we can get total chemiluminescence intensity.
2.2. In order to ensure the reliability of data, the scheme improved the compound digital filter algorithm

A kind of disturbance signal of large particle of microorganisms in the water often influences the reliability of the measurement. Therefore, technical scheme improves the compound digital filter algorithm and data correction techniques, after the original analog signal be amplified & filtered. And a series of piecewise analysis and calculation for this detection curve is designed, which can effectively remove such disturbance signal.

3. The technical scheme of chemiluminescence for TOC online measurement

This paper puts forward a kind of special used for online monitoring of TOC content, it can solve the existing methods technology of complex operation, not on-line monitoring, and poor reliability problems. In order to solve these problems, we present designs of the technical scheme as follows:

- Stage of sampling control: Firstly, the process will set the three-way valve in fully open station and open peristaltic pump A (water pump), so that the water samples can flow into the circulation pool through a filter membrane of 50 μm diameter( filter out most of the grains of sand and other inorganic pollutants in water samples).
- Stage of reaction: Secondly, the process will open the peristaltic pump B (Solution pump) to inject ozone solution into the circulation pool by certain velocity and blend with the water samples, so that an oxidizing luminous reaction can be happened with the TOC & the ozone solution. Weak chemiluminescence intensity signal produced by this oxidizing luminous reaction could be transmitted to the photoelectric detection module through an optical fiber.
- Stage of analysis: At the same time, the three -way valve should be closed, ensuring that the new water samples will not enter the circulation pool, so that ozone solution will deplete TOC of the water samples in the circulation pool. The light intensity of curvilinear integral calculation, through the correlation algorithm can be concluded that the content of TOC in sea water samples;
- Stage of back flush: At last, the solenoid valve B should be closed, and the three-way valve should be switched to the normally open state. The ozone solution can back flush the filtration system on time, so that the flow system could keep free from contamination & attachment.

The technical scheme of TOC online measurement is shown in figure 1:

![Figure 1. The technical scheme of TOC online measurement.](image)

4. Design of signal processing method for TOC online measurement

4.1. Rectifier filter circuit design scheme

Because the signal of chemiluminescence reaction is very weak, so the voltage output from photomultiplier tube is very low [13]. Therefore, the voltage is needed to become a digital signal output through phase-locked amplifier, bandpass filter and analog-digital conversion, and many details
needed to pay attention to in the design. The circuit diagram of the signal acquisition processing part is shown in figure 2:

![Circuit Diagram](image)

**Figure 2.** The circuit diagram of the signal acquisition processing part.

The signal processing circuit of the core research includes the following three modules:

4.1.1. *The precision rectifier module.* This design chooses AD630 phase-locked amplifier output signal of photomultiplier tubes for the first level of front phase-locked amplifier. The AD630 is a high precision balanced modulator/demodulator that combines a flexible commutating architecture with the accuracy and temperature stability afforded by laser wafer trimmed thin film resistors. A network of on-board applications resistors provides precision closed-loop gains of ±1 and ±2 with 0.05% accuracy. These resistors may also be used to accurately configure multiplexer gains of 1, 2, 3, or 4. External feedback enables high gain or complex switched feedback topologies. AD630 within the two op-amp constitutes the direction and reverse amplifier gain of 2, and using the analog switch to switch. When the input signal is on time, analog switched to synthetic amplifier side, but when the input signal is negative, the analog signal is switched to reverse amplifier side. So that the output impedance of signal source has certain requirements, if the input signal of the output impedance is higher, need to increase the level of the buffer level [14].

4.1.2. *The signal filtering module.* After two-stage amplification of signal, only amplify the signal and noise at the same time, did not improve the signal-to-noise ratio of the input signal. Therefore a bandpass filter is required before the signal getting into A/D. If we set a suitable center frequency of bandpass filter to the signal frequency, a large amount of high frequency and low frequency noise and interference would be filtered. Therefore, AD795 operational amplifier is selected as a bandpass filter in this design. The AD795 is a low noise, precision, FET input operational amplifier. It offers both the low voltage noise and low offset drift of a bipolar input op amp and the very low bias current of a FET input device. The 1014 Ω common-mode impedance insures that input bias current is essentially independent of common mode voltage and supply voltage variations. It has both excellent dc performance and a guaranteed and tested maximum input voltage noise. It features 2 pA maximum input bias current and 500 μV maximum offset voltage, along with low supply current of 1.5 mA maximum. Furthermore, the AD795 features a guaranteed low input noise of 3.3 μV p-p (0.1 Hz to 10 Hz) and a 11 nV/√Hz maximum noise level at 10 kHz. AD795 application can be used in many high input impedance and low noise.

4.1.3. *The signal conversion module.* In order to improve the resolution of the measurement, we need a 14-bit high precision analog-digital conversion (ADC) chip. The AD7940 is a 14-bit, fast, low power, successive approximation ADC. This chip operates from a single 2.5 V to 5.5 V power supply and features throughput rates up to 100 kSPS. It contains a low noise, wide bandwidth track-and-hold amplifier that can handle input frequencies in excess of 7 MHz, and it uses advanced design
techniques to achieve very low power dissipation at fast throughput rates. The reference for the part is taken internally from VDD, which allows the widest dynamic input range to the ADC. Thus, the analog input range for this part is 0 V to VDD. The conversion rate is determined by the serial clock (SCLK) frequency. The conversion rate is determined by the SCLK frequency. The conversion process and data acquisition process are both controlled by chip select (CS) signal and SCLK signal, interfaced with microprocessors.

Through the above, a series of signal processing, the output of the photomultiplier weak voltage signal into digital signal input MCU, the signal needs in a program for later analysis.

4.2. Research of digital filtering processing algorithms

As is known to all, all of the filtering algorithm can't both sensitivity and perfectly smooth degree. Therefore, we have to find a balance between an acceptable sensitivity and possible smooth degree. When the data changed fast, filtering results can follow up sensitivity in time(prefer sensitivity), but when the data tends to be stable, oscillated at a fixed point up and down, the filtering results can be smoothly (prefer smooth degree).

A first-order filter algorithm formula is shown as follow:

\[ Y(n) = \frac{A \times X(n)}{256} + \frac{(256 - A) \times Y(n-1)}{256} \]

Description: \( A \) - filter coefficients (integer data); \( X(n) \) - the sampling value; \( Y(n-1) \) - the last filter output value; \( Y(n) \) - the filter output values.

This algorithm could get an effective filter value through weighting the sampling value and the last filtering output value, and then the output signal could supply a feedback to the input signal. The formula needs to use loop addition & subtraction to implement multiplication & division for the microprogrammed control unit (MCU) without multiplication & division instructions. But it will increase the computational complexity of system and affect the calculation efficiency by too many times of multiplication & division.

In order to reduce the computational complexity of MCU, the formula must be simplified. Based on this principle, a kind of automatic identification algorithm is put forward, the calculation efficiency could be doubled. The improved algorithm is as follows:

If \( X(n) < Y(n-1) \),
\[ Y(n) = Y(n-1) - \frac{(Y(n-1) - X(n)) \times A}{256} ; \]

Else if \( X(n) > Y(n-1) \),
\[ Y(n) = Y(n-1) + \frac{(X(n) - Y(n-1)) \times A}{256} ; \]

Description: \( A \) - filter coefficient (value range: 0 ~ 255). The value of the coefficient is the determinant of the weights about \( X(n) \) in the filtering results, and could realize automatic calculation in the process by the following dynamic adjustment algorithm shown in figure 3.

The principle of this dynamic adjustment algorithm is as follows:

- When the data is changing toward inconsistent direction, it means that the data is not stable, it is necessary to reset the filter coefficient and ignore the new sampling value;
- When the data is changing toward one direction, it is necessary to gradually improve the filter coefficient and improve the weight coefficient of the new samples values;
- When the data is changing rapidly, it is necessary to accelerate improve the filter coefficients.
Figure 3. The algorithm of the filter coefficients dynamic adjustment process.

Figure 4. The signal filter processing result contrast.
4.3. Simulation of the filter signal
Most of the signal noise could be removed by the noise reduction filter processing. To test and verify the feasibility of algorithm, the same sample water was chosen for testing experiment, the measured signal curve as shown in figure 4.

Curve A is original measurement signal without filtering algorithm, curve B is measurement signal with filtering algorithm. Obviously, compared with the curve A, the smoothness of curve B has been greatly promoted, and could provide the reliable data for the next step oxidation aeration by integral calculation of photoelectric signal.

5. Sea trials experimental data analysis and about the effects of salinity

5.1. Sea trials experimental data analysis
In order to test and verify the data parallelism and the feasibility of the proposed signal processing method, we installed the instrument on the experimental vessel and joined multiple voyages. Comprehensive comparison of measurement experiments have been carried out in the appointed position coordinate. The comparison measuring method is as follows: In each voyage and gathering the same samples of laboratory methods of TOC data measured at the same time.

The real-time data of TOC online analysis is collected and recorded in each coordinate of the voyage. At the same time, seawater sample should be collected and sealed up at the position. It would be measured by laboratory equipment in accordance with the standard of GB 2007-17378.4 (The specification for marine monitoring-Part 4: Seawater analysis). At last, the data achieved from the lab would be compared with the data of TOC online analysis instrument at the same time and the same position.

![Contrast Measurement Data](image)

**Figure 5.** TOC comparison measurement data.

After the comparison measurement, the trend chart is as shown in figure 5: the diagram ordinate unit is ‘μg/L’, abscissa unit is ‘Times’, the I-TOC line is the instrument method real-time data, L-TOC line is laboratory method measuring data. A conclusion can be clearly drawn by observing the graph: the two kinds of data have a great match with each other, and have a same trend. Data parallelism is higher than 85% through a discrete degree calculation, which can meet the requirement of online analysis instrument index in China.

5.2. Monitoring results analysis of the effects of salinity
To test the effect of salinity of different sea area on the TOC concentration, we went ahead with two
voyages: the Jiaozhou Bay voyage in February 2017, and the Luzon Strait voyage in August 2016. At last, we completed a gradient analysis of seawater samples with different salinity. Several measurement results are as follows: In February 2017, the measured value is $(2.4 \pm 0.22)$ mg/L in the sea area of 15.3 salinity, and the measured value is $(1.8 \pm 0.12)$ mg/L in the sea area of 22.2 salinity. In August 2016, the measured value is $(0.72 \pm 0.15)$ mg/L in the sea area of 33.9 salinity. The experimental data of suffer diagram is as shown in figure 6. The experiment results show that: the measurement method of the proposed TOC online analyzer can be applied whether in high salinity areas or low salinity area.

![Jiaozhou Bay voyage in February 2017](image)

![Luzon Strait voyage in August 2016](image)

**Figure 6.** The influence of salinity on the gradient of TOC measuring data.

6. **Conclusions**

This paper proposes a kind of photoelectric signal processing method for total organic carbon (TOC) online analysis: using chemiluminescence fast measurement method combined with dynamic curve model, through the photomultiplier tubes testing weak light signal, and a series of hardware, software, signal processing, finally realizes the TOC concentration measurement. Through long-term test, the method of compare the measurement data and laboratory data, the data parallel performance enough to achieve the online analytical instrument standard. Compared with the existing various TOC analysis method, this method is more suitable for ship, buoys, ocean stations, used in situations such as offshore oil platform, greatly improve the field monitoring ability of Marine ecological environment, has good popularization and application value, in the ocean of eutrophic ecological disaster monitoring has very important significance, and also provide technical support to protect the health of the Marine ecological environment.

**Acknowledgments**

The authors acknowledge funding from National Key R & D Plan (No. 2016YFC1400801, 2016YFC1400802, 2016YFC1400803, 2016YFC1400804), Natural Science Foundation of Shandong Province (No. ZR2016DM17, ZR2014YL006), and Special Funds for Scientific Research of Marine
Public Welfare Industry (No. 201505007-2).

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