Development of an unmanned device with picric acid strip for on-site rapid detections of sodium cyanide in marine water

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Abstract. In this study, a rapid detection method using picric acid test strip for detection of sodium cyanide in ocean water was established, and an automatic-integrated detection device was set up, which can be mounted on an unmanned surface vehicle. The optimal detection conditions were set as follows: for a 100-ml seawater sample, the weight of tartaric acid solid was 1.5 g, 1–2 drops of 150 g/L sodium carbonate were used to soak the picric acid test strip, the heating temperature was 80 °C, and the heating time was 5 min. Under the optimal conditions, the test result was satisfactory and the detection limit of the method achieved was 0.3 mg/L. This method realizes the remote and rapid detection of sodium cyanide in seawater, which greatly improves the detection efficiency and does not require any personnel to enter the contaminated site. It can be widely used for rapid detection scenarios such as leakage accidents from overseas transportation, lake pollution emergencies and on-site screening.

1. Introduction

Sodium cyanide has been widely used in electroplating, metallurgy and organic synthesis[1]. It exists in the form of cubic crystal or powder and dissolves in water easily[2]. Sodium cyanide is highly toxic to the living organisms as it inhibits respiration system in the cell mitochondria[3, 4]. Concerns on the consequences of sodium cyanide discharges into the environment have drawn global attentions especially after the explosive accident in Tianjin Harbour China, in September 2015[5].

Water contaminated with cyanide even at concentrations of lower than 0.05 mg/L is poisonous to aquatic organisms by inhibiting the respiratory enzymes and causing intracellular asphyxia[6]. Oral, dermal, and inhalation exposures to cyanide all lead to the death of aquatic organisms[7]. The acute toxicity of cyanide and the exposure symptoms identical to other medical conditions require a rapid, sensitive, and accurate online detection of cyanide[8]. The current measurement of sodium cyanide is mainly based on chromatography[9], spectroscopic[10], silver nitrate titration[11]and gas-thermo extraction[12]. The chromatographic and spectroscopic methods bring good separation and sensitivity but less mobility[13-15]. The automatic potentiometric titration offers high degree of automation as well as good precision of analytical results[16]. Recent advances in a gas-thermo extraction approach provide the possibility of on-site rapid analysis[12]. Very few studies reported in developing rapid analysis or portable technology of cyanide analysis.

In this study, we developed a rapid detection assay using picric acid test strip[17] for sodium cyanide in ocean and mounted the detection device on an unmanned surface vehicle[18] to achieve remote monitoring. Besides, a new tracking, monitoring and detection system for automated marine unmanned...
aerial vehicles was established to improve the rapid monitoring and assessment of emergency accidents at sea and the predictability of pollution incidents and environmental damages.

2. Materials and Methods
Sodium cyanide reacts with picric acid to form sodium isocyanurate, which is rose-red. And an integrated experimental device was designed for the detection of sodium cyanide in water.

2.1. Materials and reagents
1 g picric acid crystal was added to 20 ml of the 95% ethanol solution and stirred continuously until the picric acid was supersaturated. Filters cut into 70 mm×5 mm size were immersed in the supersaturated solution. After soaking completely, the sheets were removed from the solution at normal temperature and stored it in the dark. The artificial seawater \cite{19} was formulated following the national standard GB/T 10834-2008. Sodium cyanide of analytical grade was purchased from Sinopharm Group Co., Ltd.

2.2. Methodology
An integrated experimental device was designed for the detection of sodium cyanide in water, as shown in Figure 1. The prepared picric acid test strip was attached to the glass tube with a tweezers clip, and the fresh sodium carbonate solution was used to infiltrate the picric acid test strip through the glass tube (4). A small portion of the front end of the test strip was exposed to the outside of the glass tube. Then tartaric acid capsules (6) was added and the bottle stopper (5) was stuffed. A sodium cyanide stock solution with a concentration of 0.01g/100ml was prepared and diluted in series as testing samples. After the samples entered into the bottle through the sample tube (3), it was heated to 80°C on the heating device (7). After 10 min, the colour change of the test strip was observed and recorded. The detailed reaction mechanism had been reported elsewhere\cite{20, 21}.

Artificial seawater solution of 0.1 g/L sodium cyanide was loaded onto the device to optimize experiment conditions. The concentration of sodium carbonate, the amount of tartaric acid, the heating temperature, and the heating time were determined to achieve the optimum output. In addition, 20L of seawater samples were collected at 7 sampling points along the East China Sea near Shanghai for validation on real environmental samples. The surface water was collected 0.5 m below the surface with a stainless-steel sampler and stored in a 10 L polyethylene bottle at 4 ℃.

3. Results & Discussion
Sodium carbonate concentration, dosage of picric acid, heating temperature and heating time are varied in the experiments, the optimization of experimental conditions were determined. And the detection limit of sodium cyanide was explored through the optimum conditions of the experiment.
3.1. Optimization of experimental conditions
At fixed dosage of sodium cyanide at 0.5 mg/L, the colour variations determined by different concentration combinations of sodium carbonate solution and tartaric acid were listed in Table 1. The optimal conditions to soak the test strip include 100 ml of sample solution, 1.5 g tartaric acid solid addition, and 150 g/L of sodium carbonate solution. Under such condition, the heating time was set from 5 to 20 min and the heating temperature from 50°C to 80°C. The colour change results were recorded at regular intervals. As shown in Table 2, colour rendering is significant at a temperature of 80°C and a heating time of 5 min.

### Table 1 Effects of different sodium carbonate concentrations and tartaric acid addition on cyanide determination

| Dosage and Reagent | Sodium carbonate   |
|--------------------|--------------------|
|                    | 5g/100mL | 10g/100mL | 15g/100mL |
| 1g tartaric acid   |  -       |  +        |  +        |
| 1.5g               |  -       |  ++       |  +++      |
| 2g                 |  -       |  +        |           |

**Note:** "-" indicates that the colour of the test strip did not change, "+" indicates that the colour of the test strip became red, and the more "+", the deeper the colour.

### Table 2 Effect of different reaction temperatures on the determination of sodium cyanide

| Heating temperature (°C) | Heating time (min) | Colour | Heating temperature (°C) | Heating time (min) | Colour |
|--------------------------|--------------------|--------|--------------------------|--------------------|--------|
| 50                       | 10                 | -      | 70                       | 10                 | ++     |
| 60                       | 10                 | +      | 80                       | 10                 | +++    |

**Note:** "-" indicates that the colour of the test strip did not change, "+" indicates that the colour of the test strip became red, and the more "+", the deeper the colour.

3.2. Determination of detection limits
According to the optimum conditions of the experiment, 1.5 g tartaric acid was placed in the capsule, the test strip was infiltrated with sodium carbonate solution of 150 g/L concentration, and the device was placed in the water bath. The temperature was set at 80°C, the time of heating was set to 10 min, and the seawater samples with different concentrations of sodium cyanide were tested (Table 3).

According to Table 3, the detection limit was about 0.5 mg/L. Thus, the gradient in the range of 0.01mg-0.05mg was set for further identification of detection limits. As shown in Table 4, a cyanide concentration of 0.3 mg/L can also clearly render the colour of the reaction. For the general picric acid strip, the detection limit of sodium cyanide is 0.2-0.4 mg/L. As shown in Table 4, the minimum detection limit reached 0.3 mg/L when using picric acid test strip to determine cyanide concentration in water.
### Table 3  Preliminary test results of sodium cyanide in seawater

| Concentration (mg/L) | 0  | 0.05 | 0.1 | 0.5 | 1   | 2   | 4   | 6   | 8   |
|---------------------|----|------|-----|-----|-----|-----|-----|-----|-----|
| Colour              | -  | -    | -   | +   | ++  | +++ | +++ | +++ | +++ |

*Note:* 
"-" indicates that the colour of the test strip did not change, "+" indicates that the colour of the test strip became red, and the more "+", the deeper the colour.

### Table 4  Detection limit of sodium cyanide in seawater

| Concentration (mg/L) | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 |
|---------------------|-----|-----|-----|-----|-----|
| Colour              | -   | -   | +   | +   | +   |

*Note:* 
"-" indicates that the colour of the test strip did not change, "+" indicates that the colour of the test strip became red, and the more "+", the deeper the colour.

3.3. Analysis of the remote applicability of the method

The device can be used to conduct on-site detection of sodium cyanide in the waterbody on an unmanned surface vehicle (Fig. 2). When testing, the unmanned surface vehicle could be located in an ocean or lake. The control room is located on the mother ship or the land. The field detection equipment on the unmanned craft includes the mechanical arm, the detection integration device, the drip tube and a container. The data transmission equipment included the communication equipment, such as the camera, shooting platform, processor and signal transmitter.

If there are cyanide chemical leaks or accidents in an ocean or lake, an unmanned surface vehicle can enter the scene of the accident. After sampling, loading and heating by the automation arm and heating plate on the unmanned surface vehicle, the test strip will show the result of red or uncoloured (still yellow). The test strip is photographed with the camera, and then the test strips are transmitted to the control room with latitude and longitude marked. According to the colour displayed on the strips, professionals can judge whether cyanide is present in the sampled area.

![Fig.2 Schematic diagram of on-site detection of cyanide chemical](image)

3.4. Validation with seawater sample

As mentioned above, 3L of seawater sample was taken in Polyethylene sampling bottle from the south-eastern coastal area of Shanghai. The treated water samples were spiked with the cyanide standard. And the samples were analysed according to the above optimized experimental conditions. The validation results are presented in Table 5.

It can be seen from Table 5 that the seawater detection limit of the device is basically the same as that measured by the lab experiment, which is about 0.3 mg/L. In order to improve the sensitivity of the
bitter acid test strip, the subsequent study was tried to combine the device with a photoelectric sensor. Based on the photoelectric data, the detection limit of sodium cyanide is about 0.2 mg/L, which is a little bit higher than that obtained by ordinary naked eyes. In this case, photoelectric sensor[22] might not be applicable for the system, because the sensitivity improvement is very slight and the data interaction is full of challenges for the unmanned surface vehicle.

Table 5  Test result of seawater sample spiked with cyanide standard

| Concentration (g/L) | 0 | 0.05 | 0.1 | 0.5 | 1 | 2 | 4 | 6 | 8 |
|--------------------|---|------|-----|-----|---|---|---|---|---|
| Colour             | - | -    | -   | +   | + | ++| +++| +++| +++|

Note: "-" indicates that the colour of the test strip did not change, "+" indicates that the colour of the test strip became red, and the more "+", the deeper the colour.

4. Conclusions
In this study, a method for the rapid detection of sodium cyanide in the marine water was developed. The optimal detection conditions were set up as follows: the addition of tartaric acid was 15 g, the concentration of sodium carbonate in the saturated test was 150 g/L, the optimal heating temperature was 80°C, and the optimal heating time was 5 min. The detection limit of this method was 0.3mg/L.

This approach is a novel method for emergency monitoring and management of hazardous chemicals in oceans and other large waterbodies. The developed sodium cyanide detection device can be carried on an unmanned surface vehicle. And a set of detection system can carry out automatic sampling, and then transmit the results to the console through test photographs and GPS coordinates to locate and quantify the cyanide pollution. This method greatly improves the detection efficiency of cyanide pollutants in the sea. It does not require any personnel to enter the pollution site. It has high security and little dependence on a laboratory and staff. Moreover, it can identify the presence of sodium cyanide in the field, and can be widely used in marine pollution leakage area, lake pollution, site screening and other occasions where are inconvenient to approach.

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