Design and application of micro-automatic permanganate index online monitor

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Abstract. In view of the current large permanganate index detection equipment, such as large volume, low automation, high reagent dosage and long detection time, based on sequential injection technique and spectrophotometry, the method for determining the permanganate index was improved, and designed a miniature automatic permanganate index online monitoring system. The design enables fully automatic detection and reduction of reagent volume through rational design of the detection process and structural layout, while reducing the volume and improving the detection efficiency. The permanganate index is compared with the technical requirements of HJ/T 100-2003. The relative standard deviation of the repeatability error is ≤±2.198%, the zero drift ≤±1.07%, the range drift ≤±0.39%, the actual water sample contrast relative error ≤± 2.81%, total reagent volume 3 ml. The system is suitable for the determination of station, laboratory and floating permanganate indices.

1. Introduction
Deterioration of water quality and water shortages are among the most serious environmental problems in the world today and one of the most serious challenges facing humanity today. The permanganate index is one of the main indicators for the reaction of water bodies with organic matter and inorganic oxidizable substances, and can comprehensively reflect the degree of pollution of water bodies by reducing substances. At present [1], the acid KMnO₄ titration method is used as a national standard method for determining the permanganate index, which has many disadvantages such as large amount of samples and reagents, inconvenient operation, long analysis time, and large workload of analysts. The human error causes poor detection data repeatability. In recent years, with the improvement of permanganate index monitoring, there has been a significant improvement in digestion methods and detection methods. The use of ultraviolet-visible spectroscopy to determine the permanganate index has the advantages of high sensitivity and good precision [2-5]. However, the spectrophotometer used in this method is large in volume and high in cost, and it is difficult to meet the requirements of high-density gridded online monitoring. In addition, there are reports on the determination of permanganate index by sealed digestion [6-9], but the method only improves the digestion method, and still uses the titration method to detect, leading to the introduction of human error. At present, the permanganate index detection equipment is large in size, single in power supply, large in reagent usage, and high in maintenance cost. It is difficult to meet the current water environment detection requirements, and the above method detection process fails to achieve automatic analysis in the true sense.

In the study, a sequential automatic injection technique and spectrophotometry were combined to
design a micro-automatic permanganate index monitor based on acidic potassium permanganate oxidation [10-15]. Based on the principle of sequential injection platform, the monitor adopts the form of vertical syringe pump and multi-channel valve guide to form the liquid drive and multi-flow switching module in the detection process. The detection process of the microcontroller control system has the advantages of accurate liquid quantification, small repeatability error, and full automatic. By simplifying the light source, detecting the tube structure, and rationalizing the layout, the equipment cost is reduced and the equipment volume is reduced under the premise of ensuring detection sensitivity and precision [16-21]. In the detection process, the monitor has low reagent consumption and waste liquid discharge are low, the degree of automation is high, and the equipment volume is small, which is suitable for water quality monitoring platforms such as laboratories, monitoring stations, floats, etc.

2. Materials and methods

2.1. Instruments and reagents

Vertical injection pump: accurate liquid volume error ≤1%, liquid volume accuracy from 3‰ to 7‰, minimum liquid inlet accuracy of 0.0025 mm/1.0381 μL; multi-channel switching valve island, using special fluoroplastic, suitable for various corrosion Liquid, the valve core adopts multi-directional self-applying flat surface and has high reliability; outer diameter 3.2 mm Teflon tube; Japan high sand high pressure electromagnetic valve; 525 nm single wavelength luminous tube; detection tube; 0.1 μL—10 mL 10 different ranges Research plus single channel pipette; XP205 high precision electronic balance with resolution of 0.1 mg; dryer; solar controller; human-computer interaction screen for serial communication.

Prepare 0.01 ug·mL⁻¹ according to the technical requirements of GB11892-89 KMnO₄ and sulfuric acid (1+3). GBW (E) 080201 permanganate index standard material, GB/T6682-2008 ultrapure water, is purchased from the national standard material sharing platform. Required reagents before using configuration.

2.2. Principle of determination of permanganate index

KMnO₄ has the maximum absorption wavelength at 525 nm, so the standard operating point of potassium permanganate solution is measured at 525 nm, sulfuric acid is added to the standard potassium permanganate solution, and kept at 100°C for 30 minutes to be digested. Determination of absorbance with ultrapure water as absorbance zero reference point, and the absorbance formula is as shown in formula (1) and formula (2). Taking the absorbance as the abscissa and the permanganate index as the ordinate, the standard working curve was drawn and the preliminary algorithm was obtained.

\[
A = \log_{10}\left(\frac{1}{T}\right) = KBC = -\log_{10}\left(\frac{\text{Sample} - \text{Dark}}{\text{Reference} - \text{Dark}}\right) \times 100\%
\]  

In the formula, A, T, K, B, C, Reference, Dark, Sample, are the absorbance of the water sample, the transmittance of the medium, the molar absorption coefficient, the optical path, the concentration, the water reference photoelectric signal recorded when the light source is turned on, the photoelectric signal of water reference dark background when the light source is off and the reagent digests the photoelectric signal after the color development is completed.

\[
A = A_2 - A_1
\]

In the formula, A, A₂, and A₁ are actual absorbance, sample absorbance, and blank experimental absorbance.

Take any permanganate index calibration working point solution as the water sample to be tested, add a known amount and excess potassium permanganate solution to the sample, add sulfuric acid, hold it at 100°C for 30 min, dilute to volume The reactive ion equation is as shown in the formula (3),
and the absorbance is measured at 525 nm using ultrapure water as the absorbance zero reference point, whereby the absorbance is obtained by a preliminary algorithm to obtain the remaining potassium permanganate content in the water sample. Thus, the consumption is calculated by the difference between the initial amount of potassium permanganate and the remaining amount, and the permanganate index of the water sample is obtained from the formula (4). Absorbance analysis was performed using ultrapure water instead of potassium permanganate standard solution as a blank experiment.

\[
2\text{MnO}_4^{2-} + 5\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ \rightarrow 8\text{H}_2\text{O} + 2\text{Mn}^{2+} + 10\text{CO}_2
\]  

(3)

\[
I_{\text{Mn}} = \frac{0.01 \times (C_1 - C_0)}{V_1 \times 4} \times 1000 \times 32
\]  

(4)

Wherein \(I_{\text{Mn}}\), \(C_1\), \(C_0\), \(V_1\) are permanganate index (\(\mu g/mL\)), water curve permanganate content (mmol), working curve. The resulting blank test showed permanganate content (mmol), sample volume.

2.3. System design

2.3.1. Digestion pool structure design. The self-designed digestion cell structure includes a quartz digestion tube, a PTC heating sheet, a heat dissipation fan, a light source, and a detection tube. The quartz digestion tube adopts a central rectangular structure design, which facilitates the installation and heating of the PTC heating sheet and reduces the amount of reagent and waste liquid. The PTC heating sheet holder is fixed on the front and back surfaces of the quartz digestion tube through the insulating thermal conductive glue, and PTC heater chip is mounted on the holder by insulating thermal paste. The glue is mounted on the fixing frame, and the quartz digestion tube is fixed on the digestion tank frame through the sealing joint, and the heat dissipation fan is fixed on the front and rear surfaces of the digestion tank by screws. The PTC heating plate is easy to maintain the optimum digestion temperature by constant temperature heating, so that the monitor can provide better temperature conditions in the low temperature environment, and the cooling fan can quickly cool the digestion tank until the optimal detection temperature. The 525 nm single-wavelength light source is fixed on the digestion tank through the light source fixing frame, and the photodiode with the collimating lens is fixed on the digestion tank through the fixing frame. The structure of the digestion pool is shown in figure 1.

![Figure 1](image)

Figure 1. Schematic diagram of the digestion pool structure.

2.3.2. Principle design of detection system platform. Aiming at the design requirements of the current permanganate index online monitoring system, a permanganate index online monitoring platform based on sequential injection technology was designed, as shown in figure 2, by the control display
module, sequential injection module, high temperature and high pressure sealed digestion module. The water sample pretreatment module and the signal acquisition module are composed. Through the reasonable layout between the modules and the precise control of the system action, the occupied space is reduced and the stability and reliability of the system platform are improved. The water sample pretreatment module is composed of activated carbon and fiber filter paper as the main material, and the suspended matter and impurities in the water sample are filtered out; the sequential injection module is mainly composed of a valve island, a syringe pump, a liquid storage ring and each kit, and the reagents are completed. And the sequential injection of the water sample; the signal acquisition module is mainly composed of a 525 nm single-wavelength light source and a photodiode with a collimating lens to complete the collection of the photoelectric signal.

![Figure 2. Schematic diagram of the sequential injection platform.](image)

2.3.3. **Signal processing flow design.** The control display module communicates with the valve island and the injection pump through the 485 signal, and the control of the solenoid valve, the fan, the PTC heating device, the light source and other electrical components through the main board control relay board to improve signal stability, accuracy and anti-interference. The signal processing flow is designed for the purpose of the purpose, and the flow chart is shown in figure 3.

![Figure 3. Signal processing flow chart.](image)

2.3.4. **Spatial layout design.** After the principle design of the sequential injection platform is
completed, the spatial layout design of each module is monitored by multi-parameter online monitoring from the perspectives of space utilization, water and electricity separation, compression volume, cost saving and convenient maintenance. The power module is composed of solar panels, solar controllers and batteries to supply power to the system. The layout design is shown in figure 4.

Figure 4. Layout design diagram.

2.3.5. Design of detection process for permanganate index online monitoring system. The design of the digestion detection control process as the core of the entire analysis system has a significant impact on the measurement accuracy, system stability, and detection efficiency. Therefore, the design of the digestion detection control process strictly follows the determination of GB11892-89 water quality permanganate index. In the technical requirements, and on the basis of improving sampling accuracy, detection accuracy, detection efficiency and reducing reagent consumption, power consumption, waste liquid displacement for the purpose of improving the detection process, the detection process is shown in figure 5.

Figure 5. Detection flow chart.

3. Results and analysis

3.1. Interference factor exclusion
- Eliminate ambient light interference by installing a light-shielding cover on the digestion cell and performing a blank test.
- Light source—The detection tube unit is preheated for about 20 minutes before detection to reach a steady state.
- Each reagent injection is isolated with a small section of air. The system cleaning fluid, the waste liquid and the ultrapure water in the liquid storage ring are separated by a small amount of air, and each reagent is isolated from the valve island by a small section of air.
3.2. Establishment of standard working curve
The absorbance of ultrapure water is used as the zero reference point of the experimental absorbance, and the absorbance of the blank test and the standard test is determined. The blank experiment is divided into ultrapure water instead of the standard sample, and the reagents and analysis steps are exactly the same as the standard sample. The permanganate index standard substance is diluted 20 times, and the 19.75 μg·mL⁻¹ permanganate index standard solution is obtained, and 0.00, 0.5, 1, 3, 5, 7, 10, 11, 13, 15, 17 are respectively taken. 20 mL of 19.75 μg·mL⁻¹ permanganate index standard solution was added to water to 20 ml, the permanganate index of the solution was 0.00, 0.4937, 0.9875, 2.9625, 4.9375, 6.9125, 9.875, 12.8375, 14.8125, 16.7875, 19.75 μg·mL⁻¹, the 11 standards were placed in the water sample bottle and the detection process was performed. The scatter plot was drawn to establish a mathematical model and the absorbance-concentration working curve was fitted as shown in figure 6.

![Figure 6. Absorbance - concentration working curve.](image)

| Measuring parameter | Surface I ~ V water Permanganate index standard limit / (μg·mL⁻¹) | Range / (μg·mL⁻¹) | Minimum detection limit / (μg·mL⁻¹) | Fitting function | Correction decision coefficient |
|---------------------|---------------------------------------------------------------|-------------------|------------------------------------|------------------|-------------------------------|
| Permanganate index  | 2~15                                                          | 0~20              | 0.1                                | y=-81.1329x+35.9676 | 0.99899                      |

3.3. Repeatability and performance comparison data analysis
The instrument has a range value of 20 μg·mL⁻¹. According to "HJ/T100-2003 Permanganate Water Quality Automatic Analyzer Technical Requirements", use GBW (E) 080201 permanganate index standard material and GB/T6682-2008 ultra-pure water configuration range value 80% permanganate refers to the range calibration solution, taking six parallel samples, the permanganate index is measured by the permanganate index on-line monitor for the range calibration solution, and the repeatability error is analyzed by calculating the relative standard deviation (RSD), the permanganate index repeatability error is shown in table 2.

Using the ultra-pure water of GB/T6682-2008 as the zero point calibration solution, the zero-point calibration solution is continuously measured by the instrument for 24 hours. Using the initial zero value in the time period, the maximum amplitude is calculated relative to the range value percentage, and the zero point drift is obtained.
Table 2. Repeatability analysis table.

| Experiment Numbering | Permanganate index /μg mL⁻¹ | Mean value /μg mL⁻¹ | RSD /% |
|----------------------|-------------------------------|---------------------|--------|
| 1                    | 16                            | 15.76               | 2.198  |
| 2                    | 16.12                         |                     |        |
| 3                    | 16.31                         |                     |        |
| 4                    | 15.63                         |                     |        |
| 5                    | 16.56                         |                     |        |
| 6                    | 15.88                         |                     |        |

The range calibration solution was tested three times before and after the zero-drift test, and the average value was calculated. The amplitude of the change after subtracting the zero-drift component was calculated, and the range drift was calculated relative to the range value.

Compare the measured values of the actual water samples of Guizhou Qizhong Hub, Yushe, Xingxi Lake, Baihua Lake, Puding, Songbai Mountain and Lihe Reservoir with the third-party experimental data of Beijing Daheng Technology Co., Ltd., and analyze the relative error is shown in table 3.

Table 3. Error analysis of actual water samples of the seven great reservoirs.

| Reservoir name       | Third-party data /μg mL⁻¹ | Permanganate index /μg mL⁻¹ | Relative error /% |
|----------------------|---------------------------|-----------------------------|-------------------|
| Central hub          | 1.97                      | 1.94                        | -1.52             |
| Yushe                | 0.97                      | 1.02                        | -2.06             |
| Xingxi Lake          | 0.96                      | 0.95                        | -1.04             |
| Baihua Lake          | 2.01                      | 2.03                        | 1.99              |
| Puding               | 1.17                      | 1.12                        | -2.56             |
| Songbai Mountain     | 0.71                      | 0.75                        | 2.81              |
| Lihe                 | 1.12                      | 1.14                        | 1.78              |

In order to further clarify the research significance, the permanganate index detection equipment of five brands on the market was investigated, and the performance comparison is shown in table 4.

Table 4. Performance comparison table.

| Determination parameter | Manufacturer model | Range /μg mL⁻¹ | Minimum detection limit /μg mL⁻¹ | Repeatability /% | Measurement time /min | Size / mm |
|-------------------------|--------------------|----------------|---------------------------------|------------------|-----------------------|-----------|
| Permanganate index      | Beijing Zhongxi Yuanda Technology RenQ-IV-P24 | 0~15 | 0.20 | ≤±5% | 45 | 600*450*900 |
|                         | Hangzhou Mudi Technology CODMn-8000 | 0~10 | 0.20 | ≤±5% | 30 | 500*320*780 |
|                         | bbe Moldaenke CODMn-PWRII | 0~20 | 0.40 | ≤±5% | 60 | 580*380*1600 |
|                         | HACH COD-203A | 0~20 | 0.50 | ≤±5% | 60 | 520*400*1500 |
|                         | Shanghai Wowei Instrument WM-8716 | 0~100 | 0.50 | ≤±10% | 30 | 550*450*1500 |
|                         | The instrument | 0~20 | 0.10 | ≤±2.198% | 30 | π*80*80*520 |
4. Discussion and conclusion

- The design uses the sequential injection technology and the application of acid potassium permanganate oxidation method to develop a permanganate index online monitor. Under the condition of optimizing the interference factors, the experimental results show that the standard operating point absorbance of the instrument has a good linear relationship with the permanganate index, the correlation coefficient is 0.99899, the linear range is 0~20 μg·mL⁻¹, and the minimum detection limit is 0.1 μg·mL⁻¹. The permanganate standard sample was prepared by GBW(E)080201 permanganate index standard material, and the system performed six parallel determinations on the permanganate standard sample after water sample pretreatment, and the relative standard deviation of the repeatability error is 2.198%, and the test results show that the range drift ≤±1.07%, zero drift ≤±0.39%, the actual water sample and the third-party test data contrast relative error ≤ ±2.81%, indicating that the system repeatability is good, stability, accuracy, reliability is higher.

- The micro-automatic permanganate index online monitor has high automation degree, compact structure and obvious advantages compared with the current permanganate index detection equipment on the market. It is easy to integrate into water quality monitoring equipment, providing hydrological services and environmental protection. Technical support has a high application prospect.

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