Colorimetric detection of nitrogen, phosphorus, and potassium contents and integration into field irrigation decision technology

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Abstract. In order to precisely provide nitrogen, potassium, and phosphorus via irrigation, this study designed a method for their field detection based on photoelectric colorimetry. We determined the maximum UV-vis absorption wavelengths of nitrogen, phosphorus, and potassium solutions mixed with colorimetric reagents and experimentally determined their standard curves. The detection error was less than 5% by error analysis, and thus the method can be used to determine the concentrations of the target elements on site. We also combined the detection of potassium, nitrogen, and phosphorus with intelligent irrigation decision-making to achieve automatic irrigation. The accurate technology that we developed for controlling water-soluble fertilizers can detect the target elements on-site, which improves the controlled performance of accurate irrigation systems through fast and efficient on-site detection.

Keywords: nitrogen, phosphorus, potassium, photoelectric colorimetry, accurate irrigation, precision control of water-soluble fertilizers

1. Introduction
The appropriate utilization of water-soluble fertilizers is key to determining crop yields and water and fertilizer utilization rates. Water-soluble fertilizers integrated with irrigation can not only save irrigation water and improve the fertilizer absorption efficiency of the crop, but also reduce the fertilizer and pesticide pollution of groundwater, which reduces eutrophication. In recent years, water-soluble fertilizer integration has become a prevalent research topic in terms of water-saving technologies. Barradas and Matula [1] proposed the basic principles of a decision-making irrigation system and designed a fertilization simulator. Decision support systems optimize the design of irrigation fertilization systems and increase their environmental sustainability. The fertilization simulator consists of a database, model library, and user interface, which has a self-learning function that can select different irrigation methods according to the realistic environment to improve the efficiency and uniformity of water-soluble fertilizer irrigation. Hedleya and Yuleb [2] proposed a method for measuring soil moisture for different soil spatial structures using a wireless sensor network embedded into a computer to detect soil moisture information in real time. They developed effective water-holding and field water distribution maps based on a high-resolution soil surface conductivity regression model by uploading the obtained map to the irrigation variable system. Lin [3] developed
an irrigation system for greenhouses using fuzzy control theory. The system uses an ARM processor as the main control chip, combined with electrical conductivity (EC) and pH sensors to achieve the online detection of liquid nutrition. Hao [4] developed an ARM-based water-saving irrigation system that combines PID control with Smith’s estimator to precisely control the EC and pH of water-soluble fertilizer. However, there has been little research on the precise real-time detection of nitrogen, phosphorus, and potassium concentrations in fertilizers. In this study, a method for the field detection of nitrogen, phosphorus, and potassium contents and a decision-making irrigation system based on photoelectric colorimetry were developed.

Photoelectric colorimetry uses visible light as the light source to compare the color depth of a solution and thus measure the concentration [5]. A spectrophotometer measures the absorbance of a series of standard solutions; a standard curve is obtained and the concentration of the target substance is determined based on the absorbance of the tested solution [6]. Research has been carried out worldwide to determine the compositions of pesticides, pharmaceuticals, tobacco, biochemicals, and food ingredients based on photoelectric colorimetry [7-13]. However, no such studies have been performed toward determining fertilizer solution concentrations for on-site testing, and thus there is no precedent for the method proposed in this research.

As given by the Beer–Lambert law illustrated in Figure 1, the ratio of the intensity of transmitted light $I$ to the intensity of incident light $I_0$ is defined as the transmittance $T$. The absorbance $A$, defined as $\lg(1/T)$, indicates the absorption of incident light by the solution [14]. This can be applied to determine the concentrations of species in solutions because when a beam of parallel monochromatic light passes vertically through a uniform, non-scattering solution, the absorbance of the solution is proportional to the concentration of the absorbing substance $C$ and the distance that the light passes through in the fluid $b$. If $I_0$ and $b$ are fixed, then $I$ is dependent only on $C$. Thus, $C$ can be deduced [15] by measuring $A$.

$$A = \lg \frac{I_0}{I} = \lg \frac{1}{T} = \varepsilon bc$$  \hspace{1cm} (1)

![Figure 1. Beer–Lambert law](image)

$A$, solution absorbance; $T$, transmission; $\lg(1/T) = A$; $\varepsilon$, molar absorption coefficient; $b$, absorption layer thickness; $C$, substance concentration

2. Nitrogen, phosphorous, and potassium detection methods

2.1. Test device
A 722N visible photometer was used to qualitatively analyze samples in the near-UV and visible spectral regions. A tungsten halogen lamp (12 V, 30 W) with an adjustable wavelength range of 330–800 nm was used as the light source.

2.2. Analyzed materials
(1) Urea: white, round, and grainy, with a nitrogen content of 46%. Urea is a component with one of the highest nitrogen contents in solid nitrogen fertilizers (neutral fertilizers).
(2) Potassium chloride: soluble in water-efficient potassium fertilizers and contains approximately 60% K₂O. It is a white, light yellow, or purple-red crystal.

(3) Potassium dihydrogen phosphate: a colorless quad crystal or white crystalline powder. The pure product consists of colorless quad crystals containing 34.61% K₂O and 52.16% P₂O₅.

Table 1. Nitrogen, phosphorous, and potassium fertilization ranges

|         | High level (mg/kg) | Medium level (mg/kg) | Low level (mg/kg) | Range     |
|---------|--------------------|----------------------|-------------------|-----------|
| N       | 200                | 100                  | 50                | 0~0.4‰    |
| P       | 150                | 100                  | 50                | 0~0.3‰    |
| K       | 300                | 200                  | 100               | 0~0.5‰    |

2.3. Experimental methods

(1) Preparation of standard solutions

a. Phosphorus standard solution and color reagents

Standard solution: analytically pure potassium dihydrogen phosphate was dried in an oven at 105 °C for 2 h and then placed in a drying dish to a constant weight. A mass of 1.4315 g of the dried potassium dihydrogen phosphate was accurately weighed and dissolved in 1000 mL of water in a volumetric flask. Five dilutions were performed to obtain a final phosphate concentration of 200 mg/L.

Color reagents:

Pre-made reagent A: 1.12 g of NH₄VO₃ was dissolved in 200~300 mL of water and mixed with 250 mL of nitric acid.

Pre-made reagent B: 27 g of (NH₄)₆Mo₇O₂₄·4H₂O was dissolved in a small amount of water.

Color reagent C: Color reagent B was slowly added to color reagent A under stirring. After thorough mixing, the solution was stored in a brown bottle. The formation of a precipitate during storage indicated that the solution could no longer be used.

b. Potassium standard solution and color reagent

Standard solution: superior-grade pure potassium chloride was dried in an oven at 105 °C for 2 h and then placed in a drying dish to a constant weight. An accurate mass of 1.05 g of the dried potassium chloride was dissolved in 1000 mL of water in a volumetric flask to a final potassium ion concentration of 500 mg/L.

Color reagent: 3.00 g of Na[B(C₆H₅)₄] was dissolved in 100 mL of water, and 10 drops of a 0.2 mol/L NaOH solution was added. The liquid was filtered with tight filter paper, and the filtrate was stored in a brown reagent bottle.

Masking reagent: 2.50 g of EDTA disodium salt was weighed and dissolved in 20 mL of a 0.05 mol/L sodium tetraborate solution (19.07 g constant volume sodium tetraborate in 1000 mL of water), after which 80 mL of a 3% formaldehyde solution (HCHO, analytically pure) was added. Mixing yielded a masking reagent at pH 9.2. Sodium tetrabenzene boron (3%) was used as a blank reference, and it was ensured that there was no turbidity.

c. Nitrogen standard solution and color reagent

Standard solution: 0.1 g of pure urea and 0.0212 g of urease were added to 1000 mL of water. Urease decomposes urea to produce amine and CO₂.

Color reagent (Nessler reagent): 15.0 g of sodium hydroxide was weighed and dissolved in 50 mL of water, then cooled to room temperature. Then, 5.0 g of potassium iodide was dissolved in 10 mL of water, to which 2.50 g of mercury dichloride powder was added under stirring until the solution was dark yellow or a light-red precipitate appeared and slowly dissolved. The solution was thoroughly mixed with the dropwise addition of a saturated mercury dichloride solution until a small amount of the vermilion precipitate did not dissolve.

Masking reagent (potassium sodium tartrate solution): 50.0 g of potassium sodium tartrate was weighed and dissolved in 100 mL of water. The solution was heated to boiling to drive off ammonia, and the remaining solution was diluted to 100 mL after fully cooling.
(2) Determination of maximum absorption wavelengths

We placed 5.00 mL of each standard solution in a 50-mL colorimetric tube with a stopper and added water to 35 mL, then added 10 mL of the respective color reagents and shook the tubes thoroughly. Zero absorbance was set with a blank after the color was developed for 10 min. Finally, we measured the absorbance of the solutions at wavelengths of 410–465 nm in 5-nm increments, then selected the maximum absorption wavelength $\lambda$ for each element.

![Figure 2. Maximum absorption wavelength of phosphate standard solution](image1)

![Figure 3. Maximum absorption wavelength of potassium standard solution](image2)

![Figure 4. Maximum absorption wavelength of urea standard solution](image3)
(3) Formulation of standard curves

a. Phosphorus standard curve

As shown in Figure 5, we added 0.00, 1.00, 2.00, 5.00, 8.00, 10.00, 15.00, 20.00, and 25.00 mL of the potassium phosphate standard solution (1 mL containing 0.2 mg of phosphate) to took nine separate 50-mL colorimetric tubes. Water was added to 35 mL, 10 mL of the color reagent was added, and then water was added to the line. Using a 10-mm cuvette, the blank was used to set the absorbance to zero, and the absorbance of each solution was measured. The derived standard curve given as phosphate mass vs. absorbance is shown in Figure 6.

Figure 5. Change in color of phosphorus test solutions

![Figure 5](image)

| Equation | y = a + b|x
|----------|----------------|
| Intercept | 0.00461 ± 0.0149 |
| Slope | 0.06867 ± 0.8E-4 |
| Residual | 0.02858 ± 5 |
| R² | 0.99991 |

Figure 6. Standard phosphorus concentration curve

![Figure 6](image)

Standard curve: $y = 0.00461 + 0.16857x$

Linearity: $R² = 0.99$

The solutions showed obvious color gradation when the test time was approximately 2–3 min, and the standard curve was highly linear. The accuracy of the test is very high, and thus the method can meet the requirements of field situations if the change in concentration is linear. Thus, it can be used as a measurement method and standard for phosphorus elements in water-soluble fertilizer solutions.

(2) Potassium standard curve
As shown in Figure 7, we diluted the standard solution of potassium 5 times (100 mg/L), then added 0.00, 1.00, 2.00, 3.00, 4.00, and 5.00 mL to six separate 25-mL color tubes. The solutions were mixed with 1.00 mL of the masking reagent and 2.00 mL of the color reagent, pure water was added to the line, and the mixture was shaken well then added to a 10-mL cuvette. We also added 1 mL of the masking reagent and 2.00 mL of the color reagent to 15 mL of water to compare the absorbance at 430 nm. Color rendering was performed for 3–5 min. Figure 8 showed the standard curve given as potassium ion mass vs. absorbance. The standard curve had a high linearity and can thus be used as a standard for the measurement of potassium in water-soluble fertilizer solutions.

![Figure 7. Change in color of potassium solutions](image1)

![Figure 8. Standard potassium concentration curve](image2)

Standard curve: \( y = 0.05538 + 3.66057x \)

Linearity: \( R^2 = 0.92 \)

(3) Nitrogen standard curve

As shown in Figure 9, we added 0.00, 0.50, 1.00, 2.00, 4.00, 6.00, 9.00, and 10.00 mL of the urea standard solution to nine separate 25-mL color tubes. The corresponding urea contents were 0.00, 10.00, 20.00, 30.00, 40.00, 50.00, 80.00, and 100.00 μg, respectively. Then, 5 mL of the color reagent was added, followed by pure water to the line. The color rendering time was 10–15 min. We set the
blank tube as zero absorbance and used a 20-mm cuvette to determine the absorbance of the solutions at 420 nm. The standard curve plotted as urea mass vs. absorbance is shown in Figure 10. Since the nitrogen standard curve has a better linearity at concentrations of 0–0.1‰, fertilizer samples for field color testing should be diluted 5–10 times. The linearity of the standard curve is very high, and thus it can be used as a standard for the measurement of potassium in fertilizer solutions.

![Figure 9. Change in color of nitrogen solutions](image)

![Figure 10. Standard nitrogen concentration curve](image)

Standard curve: $y = 4.66063 \times 10^{-4} + 9.85671 \times 10^{-4}x$

Linearity: $R^2 = 0.99$

(4) Experimental error analysis

A sample of 0.2‰ potassium dihydrogen phosphate compound fertilizer was selected for the test. The absorbance of the solution at 450 nm was 0.287, corresponding to 1.44 mg of phosphate based on the standard curve. The actual quantity was 1.4315 mg, and thus the error was only 0.6%. The absorbance at 430 nm was 0.146, corresponding to 0.588 mg of potassium and thus an error of only 2% compared with the actual mass of 0.6 mg. The experimental results showed that this detection method can be used for measuring nitrogen, phosphorous, and potassium in compound fertilizers.

3. Nitrogen, phosphorous, and potassium colorimetric detection results
The results showed that the maximum absorption wavelengths of the phosphate, potassium, and urea solutions were 450, 430, and 420 nm (Figures 2–4), respectively. Any changes in absorbance intensity
were the most apparent at these wavelengths. The phosphorous standard curve had a good linearity in the concentration range of 0–0.3‰, and the color rendering time was 1–2 min, making it applicable for on-site rapid detection. The potassium curve had a good linearity in the concentration range of 0–0.1‰, and the color rendering time was 3–5 min. After the fertilizer solution is diluted 5 times, it can be used for on-site rapid detection. The nitrogen curve had a good linearity in the concentration range of 0–0.1‰, and the color rendering time was 10–15 min. After the fertilizer solution is diluted 5–10 times, it can be used for rapid on-site detection.

4. Discussion
Precision fertilization control can be achieved by applying the discussed method. The detected concentration can be fed back to the control unit to adjust the amount and concentration of the fertilizer solution for accurate control [16]. At the same time, soil can be collected on-site, subjected to a simple filtering treatment, and analyzed using the photoelectric colorimetric method to adjust the potassium, nitrogen, and phosphorous contents in real time according to the actual needs of the crop. The difference between the input and set potassium concentrations can be used by the inverter to adjust the amount of fertilizer via the speed of the fertilization motor until the measured concentration is consistent with the set value [17].

Through the above method, the appropriate amount of fertilizer can be accurately determined, and intelligent irrigation equipment can achieve the automatic quantitative output of nitrogen, phosphorus, and potassium. A small diaphragm pump draws in the fertilizer to the main pipeline, where the amount of fertilizer drawn in is adjusted by the speed of the pump. The pump speed is adjusted using PID control mode, and fuzzy control is introduced to improve the system performance by optimizing unreasonable parameters and reducing system vibration. In fuzzy control systems, the error (e), error change (ec), and error change rate (ecc) of the controlled object are often used as input variables. According to the number of system input variables, fuzzy systems can be divided into one-dimensional controllers (e as the input object), two-dimensional controllers (e and ec as the input objects), and three-dimensional controllers (e, ec, and ecc as the input objects). The control accuracy of the system increases with increasing input variables, but the complexity also increases. Based on these factors, the present system employed a two-dimensional fuzzy controller as it is the most common. To build the fuzzy PID controller, we used e and ec as the inputs and employed fuzzy control rules and synthetic reasoning [18] to obtain the PID correction parameters ΔKp, ΔKi, and ΔKd and online real-time correct parameters ΔKp, ΔKi, and ΔKd. The system structure is shown in Figure 11.

MATLAB was used to validate the simulation experiments. We established the corresponding PID and fuzzy PID models in the Simulink simulation tool environment and used MATLAB’s Fuzzy Logic Toolbox to design the corresponding fuzzy controller, as shown in Figure 12. The SIMULINK module library establishes the corresponding fuzzy and conventional PID control structures and uses a step input signal to carry out the corresponding control simulation experiments on the water-soluble
fertilizer irrigation flow control system. Figures 13 and 14 show the MATLAB simulation structure and results, respectively. The results showed that the overshoot was smaller using the fuzzy PID controller than with the conventional controller, and the value rapidly peaked and was stable in approximately 7 s in fuzzy PID controller. Compared with the non-fuzzy PID control, each performance index was greatly improved, resulting in appropriate control of the irrigation of water-soluble fertilizer and reduced fluctuations.

**Figure 12.** Fuzzy controller construction

**Figure 13.** MATLAB simulation structure
5. Conclusion
In this research, the maximum absorption wavelengths of phosphorus, potassium, and nitrogen solutions combined with their respective color reagents were determined as 450, 430, and 420 nm, respectively. We used standard solutions of the target elements to plot standard absorption curves with errors of less than 5% as determined by analyses of a compound fertilizer. The photoelectric colorimetry method can be used for the on-site determination of nitrogen, phosphorus, and potassium concentrations.

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