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Detection of phosphorus species in water: technology and strategies

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Phosphorus species are the sum of naturally evolved phosphorus elements with diverse forms of exist-ence and unique properties. The detection and analysis of the optical properties of unknown phosphorus species *via* direct or indirect strategies offers unique advantages in understanding the growth processes and existence characteristics of various chemicals and microorganisms in water environments. This review highlights recent advances and future trends in methods of detection of total phosphorus in water, including photoelectric strategies, spectroscopy techniques, and modeling algorithms. These methods effectively explore the dynamic changes of total phosphorus content in complex water environments to reveal important signals in water, which is of great guiding significance for achieving accurate detection of water quality and promoting social development. We also discuss some extended strategies for its measurement and prediction *via* rational design and cross-combination, which may help inspire future design of more accurate and intelligent detection models or systems. The strategies based on these types of total phosphorus detection methods provide a versatile platform for novel sensors and thereby show great potential in the development of future water quality detection applications.

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Introduction

Water resources, which bear the origin of life, are nature's evol-ving 'masterpiece'. The ubiquity and significance of water resources can be affirmed in all domains of life.[1–6] However, the water pollution issue has been deteriorating year by year, seriously threatening the health of humans.[7–11] Therefore, it is of great importance to evaluate the water quality parameters for guaranteeing water safety. Water quality indexes are usually

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presented in terms of the type, composition and quantity of impurities in water and the detection of water quality can provide uniform and regular monitoring of chemicals, suspended solids, and aquatic ecosystems in water.[12–15] Notably, the current status and development trends of pollutants in water can also be reflected accurately and comprehensively through water quality detection. As the most effective analytical tool, water quality detection provides a scientific basis for water management, conservation and development planning.[16–20] Therefore, the study of water quality detection, especially exploring principles and methods in the manipulation, is important for understanding the complex mechanism in water and the exploration of uncertain water resources. It also opens many prospects for analyzing improper or undesired chemical material aggregation-related disorders[21–24] such as dental plaque, various inflammations, and cancer.

Phosphorus, as an important monitoring and analytical indicator in water quality detection, is an indispensable and limiting nutrient element for the growth of all life forms.[25–27] Excessive phosphorus (more than 0.02 mg L^{-1}) in a water medium stimulates overproduction of algae and phytoplankton, which leads to eutrophication of water bodies.[28] These plants consume more oxygen during the decomposition process, thus affecting the survival of aquatic organisms, reducing the transparency of water bodies and ultimately disrupting water balance. In more serious cases, harmful ecological phenomena such as 'cyanobacterial' bloom and 'harmful algal bloom' can be triggered.[29–31] This has attracted an increasing concern about the hazards of changes in the contents of phosphorus in water. From the perspective of analytical chemistry, phosphorus species, defined as the total amount of various forms of phosphorus in water, exist in the form of orthophosphates, pyrophosphates, metaphosphates, and organic bound phosphates.[28,32,33] Total phosphorus (TP) is one of the most complex indicators that is difficult to be monitored in a water quality detection process due to its complex composition and diverse forms. Before TP detection, pretreatment including digestion or oxidation of the water sample must be performed to convert all types of phosphorus to the readily analyzable form orthophosphate for better detection.[34–39] Subsequently, appropriate physical, chemical or even biological methods are employed to quantitatively analyze the concentration of the orthophosphate. With the advancement of analytical techniques, the pretreatment procedures for total phosphorus detection have experienced continuous revision and have improved a lot. In the following part of the review, total phosphorus is considered as a pretreated orthophosphate unless otherwise stated. In view of the important role of total phosphorus in water, the classification and summarization of methods for water quality detection based on total phosphorus are quite crucial.

Traditional methods for monitoring phosphorus content mainly include the gravimetric method, volumetric method, and potentiometric titration, all of which are based on the reaction with a quinoxalyl ketone reagent to form a precipitate. Such methods have been extremely popular for decades because of their economical utility, convenience, and large measurement range. Even so, traditional analytical methods still have some limitations, such as complex manual operation, poor stability, and low sensitivity.[40] The emergence of spectrophotometry has largely overcome these shortcomings, and at the same time has opened up new directions for the measurement of trace phosphorus.[41,42] In recent years a series of total phosphorus detection methods have been developed based on the optical properties of materials and the detection principle of spectrophotometry such as the use of chemosensor,[43,44] test strip,[45] photoelectric colorimetry,[46] automated and intelligent flow injection analysis,[47] microfluidics,[48] and some characteristic spectral techniques.[49] One of the representative examples is the utilization of test strips for the detection of environmental samples. The ammonium molybdate embedded in a test strip reacts with the orthophosphate under the action of ascorbic acid to form phosphorus molybdenum blue, which is quantitatively analyzed by comparing the depth

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of blue on the color card. The method is widely used in the detection of total phosphorus in water due to its fast speed and convenience that is suitable for on-site measurement. However, the shortcoming is that the precision is poor and the sample needs to be pretreated. Liu *et al.* present a novel sandwich structure test strip for organophosphorus (OP) assessment, which is applicable and portable for field application.[50] The OP assessment is based on the measurement of the concentration change of thiocholine when OP exists. The test strip also shows good sensitivity and high reliability in detecting river water samples, and holds great potential in environmental analysis. The photoelectric strategy utilizes the special optical properties of the substance and converts them into electrical characteristics, which not only improves the detection efficiency, but also makes the detection process intelligent, and the detection results can be visualized. Spectral technology, as one of the most authoritative means in the field of analysis, ensures the accuracy and precision during the detection process. The appearance of these emerging technologies has greatly promoted the development of total phosphorus detection, and also promises a bright future for their potential applications in many fields. The detection technology of total phosphorus is not limited to a single means but has been developed to a combination of multiple elements. This type of joint method is defined as a modeling algorithm. For small monitoring targets, the effects of impurities can be filtered out using different algorithms to obtain optimal results. At the same time, empirical relationships can be obtained through data acquisition and data processing to predict the content of large reservoirs. Therefore, the modeling algorithm is an effective aide in the water quality detection process.

The past few decades have witnessed the rapid advances in water quality detection and the evolution process to more efficient and accurate detection based on total phosphorus. Recent trends in this field show direction toward the construction of novel strategies with higher accuracy and lower limits of detection.[28,37,40,51–53] This review summarizes the recent progress made in the total phosphorus detection techniques and outlines the strategies including photoelectronic detection, spectral analysis techniques, and modeling algorithms to improve the detection efficiency, accuracy, and limits of detection. Finally, the potential applications, prospects and challenges of total phosphorus detection in analytical chemistry are also discussed.

Classification of total phosphorus detection methods based on photoelectric strategies

The so-called photoelectric detection system refers to a system monitored by means of photoelectric change and circuit processing for the optical quantity to be measured or those converted from the non-optical physical quantity.[54] With the

development of electronic and microelectronic technology, photoelectric detection platforms have achieved rapid progress with the emergence of various new types of photodetector devices and have also extended to almost all the industrial and scientific research fields. This also covers the determination of total phosphorus in water environments that we have studied. Traditional methods of chemical analysis mainly include gravimetric methods with various types of phosphorus precipitated as magnesium pyrophosphate and magnesium ammonium phosphate hexahydrate and volumetric methods by titration of ammonium phosphomolybdate with sodium hydroxide.[55–57] Although these methods seem simple and easy to understand, they all require pre-treatment of the sample, manual operation which is time-consuming and even produce toxic wastes. However, photoelectric detection, as an emerging method, can convert optical signals into electrical signals to facilitate the amplification, manipulation, measurement and control of the signals by mature electronic technologies. Photoelectric detection strategies based on spectrophotometry, flow control technology and other techniques have greatly improved the sensitivity and accuracy of the total phosphorus detection process, making the whole procedure more automated and the measurement results more intuitive.

Imaging colorimetry

Imaging colorimetry for total phosphorus determination is mostly based on ammonium molybdate spectrophotometric detection, using charge-coupled device (CCD) digital imaging technology to transform CCD electronic signals into digital signals. Yang *et al.* reported a combination technology of the CCD digital imaging theory with RGB theory for the detection of phosphates.[58] As shown in Fig. 1a, the digital image color of phosphomolybdenum blue solution is formed by the interaction of potassium dihydrogen phosphate with molybdate solution. Furthermore, the imaging color changes significantly as the concentration of the reactant phosphate increases. These phenomena are almost in accordance with the absorption spectra obtained by spectrophotometry (Fig. 1c). In addition, the RGB curve of the digital image (Fig. 1b) converted using Origin 7.0 and Scion Image software has a good linear relationship with the maximum absorption peak of phosphomolybdenum blue solution at 882 nm (Fig. 1c).
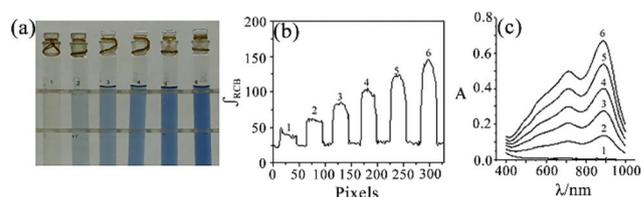

Fig. 1 Digital imaging colorimetry feature (a and b) and absorption spectra (c) of the interacting systems of potassium dihydrogen phosphate with molybdate solution and ascorbic acid molybdate solution, 1.0 ml; ascorbic acid, 3.57 g L^{-1}; total phosphorus (mg L^{-1}): 1, 0.00; 2, 1.78; 3, 3.57; 4, 5.36; 5, 7.14; and 6, 8.93. Reproduced from ref. 58 with permission from Elsevier B.V., copyright 2007.
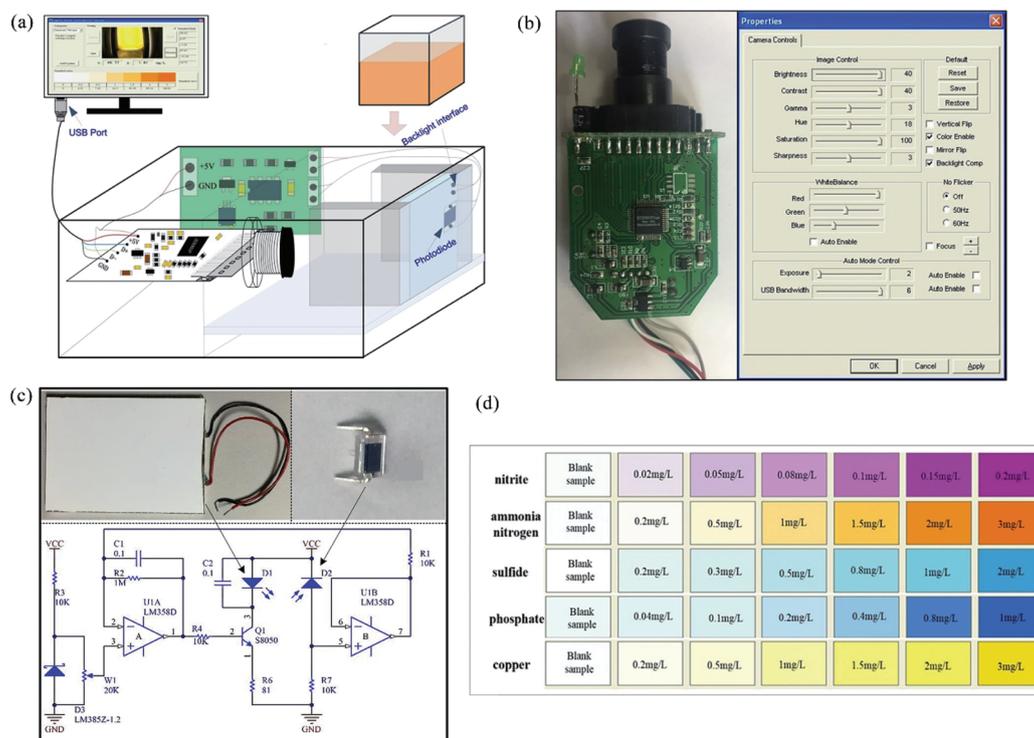
Fig. 2 (a) Schematic diagram of the instrument; (b) the disassembled camera and parameter settings; (c) constant light intensity circuit; and (d) color of the standard sequence and the corresponding concentration. Reproduced from ref. 64 with permission from the Royal Society of Chemistry, copyright 2018.

Slightly different from spectrophotometry, imaging colorimetry is more convenient for its ability to measure the total phosphorus content quickly and effectively. Therefore, this work holds great potential for practical applications in water quality detection.

Utilizing the same concept and measurement, beyond detection sensitivity, Barros *et al.* further explored the possibility of imaging colorimetry to achieve determination of total phosphorus in water.[59] A high pixel webcam was used to measure the wavelength of maximum absorption and concentrations of phosphate (PO_4^{3-}) in solutions. In this work, they utilized the least squares method to build a mathematical equation for calculating the wavelength of maximum absorption of the measuring substance by detecting its brightness, saturation, and hue and achieved the best fit. Furthermore, the sensitivity (slope) and coefficients for phosphate determination in water were improved by converting color values into absorbances. The reported procedure is simple, versatile, and also low cost, demonstrating that the high pixel webcam is a suitable detector for measuring phosphate (PO_4^{3-}) in water with adequate sensitivity and precision.

Promoted by the application of computer image processing technology and color analysis technology mentioned above, imaging colorimetry has become a novel and advanced methodology in water quality detection. Bao *et al.* obtained the color image of the mixture after the chromogenic agent reacted with the tested solution.[60] Meanwhile, the chromatic

aberration and fitting algorithm were also established. The structure of the instrument is shown in Fig. 2a. The system consists of a constant intensity circuit (Fig. 2c), a sample cell, an ordinary PC camera (Fig. 2b), and a microcomputer. When white light passed through the chromogenic solutions to the camera, the solutions reflected and transmitted the light of their own color and absorbed that of other colors, thus providing the transmission color information of the standard series of solutions in the RGB form, which was then converted to the corresponding LAB values. Fig. 2d shows the software interface of the designed upper computer to collect images. The software that they engineered can collect and process image data, form standard curves, and eventually achieve sample measurements mainly including phosphate, ammonia nitrogen, nitrite, sulfide, and copper in water. Compared with traditional methods, this method was especially suitable for on-site rapid water quality detection due to its high degree of automation, low cost and simple interface operation.[43] Nowadays, this principle is also being utilized to create various water quality detectors with high accuracy, including the detection of important elements such as total phosphorus and total nitrogen.

Flow injection analysis technology

Flow injection analysis is an automatic analytical strategy. It can be summarized as follows: a volume of sample solution injects into a flowing, non-air-spaced reagent solution (or

water), and mixes and reacts with the reagent of the carrier in the reaction tube. After that the reaction solution enters a flow detector which can continuously record its absorbance, electrode potential or other physical parameters. Finally, we can detect the concentration of the liquid according to the generated signal. Similar to the imaging colorimetric method, an automatic flow injection analysis (FIA) system and the automated intelligent detection method based on the principle of phosphorus molybdenum blue spectrophotometry have also attracted widespread attention.[61–64] As shown in Fig. 3a and b, Gentle and Hatta et al. have carried out the same work on a fully automated flow injection analysis (FIA) system for the determination of phosphate ions in solution after reaction.[52,65] High sampling frequency (120 samples per hour) and low reagent consumption (only 440 μL per analysis of total waste) are the most prominent contributions in determining the phosphate contents of the solutions. Subsequently, by applying the same strategy, Karadag et al. modeled with LabVIEW to control all the components (i.e. peristaltic pump, valves) in the

FIA system, generate absorbance versus time graphs for visualizing the experimental results, and at the same time calculate peak heights as analytical signals.[66] Experimental results have validated that the conditions of 0.50 mL L^{-1} flow rate, 60 cm path length and 100 μL sample volume can provide optimum dispersion and the highest analytical signal.

Microfluidic technology

The microfluidic technique is used for precisely controlling and manipulating microscale fluids, especially submicron structures. In particular, micro means the following characteristics: tiny capacity (nanoliter or picoliter), tiny volume and low energy consumption.[67–69] A more complicated microfluidic system has further been developed as lab-on-a-chip by detecting, operating, and controlling fluids at microscopic dimensions.[70–72] McGraw et al. designed a new microfluidic chip which was fabricated with a 2 mm × 16 mm × 32 mm piece of clear polymethyl methacrylate (PMMA) through micro-milling techniques.[48] As shown in Fig. 4a and b, the samples
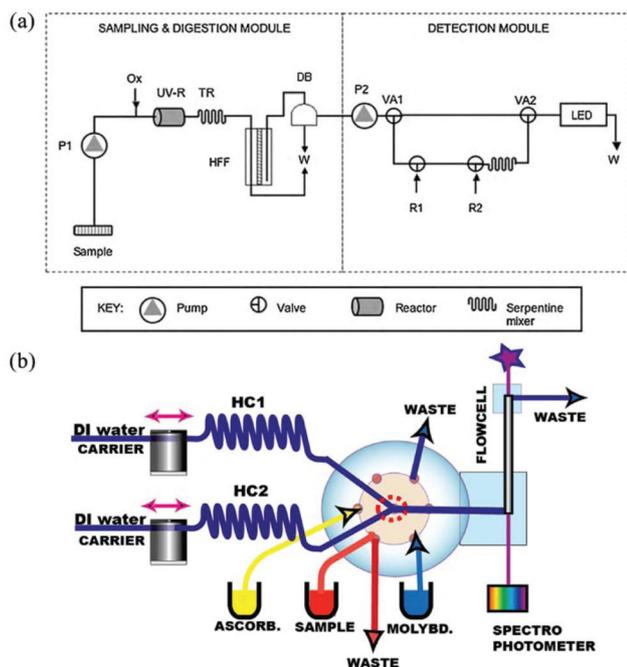
Fig. 3 (a) Diagrammatic description of the flow analysis system used for determination of total phosphorus. Sample or standard is pumped through a 100 m mesh, followed by the addition of an acidic peroxodisulfate oxidant (Ox). P1 and P2 are peristaltic pumps. The stream undergoes mineralisation in the UV reactor (UV-R) and a thermal reactor coil (TR), followed by filtration using a hollow fibre filter (HFF) and debubbling (DB), and overflow from the debubbler goes to waste (W). Filtered digested sample is pumped into a reagent injection flow analyser, where reagents (R1 – acidic molybdate solution and R2 – acidic tin(II) chloride reductant) are delivered into the stream. Absorbance is measured using a multi-reflective cell coupled with a low-power 660 nm light emitting diode source. Reproduced from ref. 69 with permission from Elsevier B. V., copyright 2010; (b) flow injection analyzer based on programmable flow, configured for automated analysis of phosphate. The confluence point is marked by the red circle. Reproduced from ref. 56 with permission from Elsevier B.V., copyright 2019.
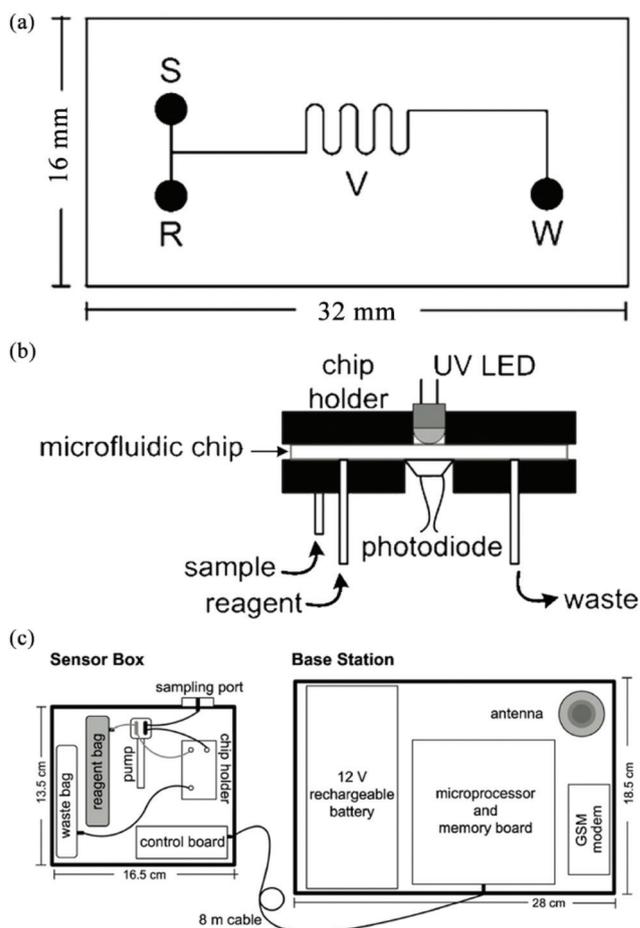
Fig. 4 (a) Microfluidic chip layout with sample (S) and reagent (R) inlets, a serpentine reaction channel and viewing area (V), and waste outlet (W); (b) cross-sectional view of the microfluidic chip holder and detection components; and (c) diagram of the phosphate sensor and base station. Reproduced from ref. 48 with permission from Elsevier B.V., copyright 2007.

and reagents were introduced into the chip through separate inlets R and S and mixed at a 1 : 1 ratio in a serpentine channel to avoid the interference of the bubble during the measurement. Upon illumination with an LED, the reacted solution experienced a spectral change and the subsequent electrical signal could be collected using a photodiode detector on the opposite side of the microcuvette, finally giving information on the phosphate content. Fig. 4c shows a system packaged and miniaturized into a compact and portable instrument. This completely autonomous device includes reagent handling, sampling, mixing of reaction products, waste containment, colorimetric detection, wireless communication, and a power supply. This strategy enables the autonomous microfluidic platforms to hold potential in long-term environmental monitoring.

Optofluidics, as a branch of microfluidic technology, integrates fluid and optical components onto one chip. It can be utilized for sensing applications owing to the high interaction efficiency between light and fluids.[73–75] With the same concept and measurement of microfluidics, Zhu *et al.* reported a combination technology of microscale resonators and optofluidics for the detection of phosphates.[76] As shown in Fig. 5a and b, the system consisted of two parts: a microreactor and an optical component. In the microreactor, the filtered samples and chromogenic reagent (ascorbic acid solution and a mixture of 8% antimony potassium tartrate solution, 12% ammonium molybdate solution, and 80% concentrated sulfuric acid) were injected into a curved channel. In optical devices, the Fabry–Pérot (F–P) cavity as the micro-optical part was made from two parallel reflectors by coating gold films on the surface of optical fibers. The probe light first entered into

the F–P cavity through one fiber and was then reflected multiple times in the reflectors to increase the optical feedback, finally collected by the detector. Compared with FIA and microfluidic technology, optofluidics inherits its advantages of shortening the detection time from 10 minutes to 6 seconds, and increasing the detection limit to 100 μmol L^{-1}. In addition, an autonomous field-deployable optofluidic device for detecting the phosphate in natural water is presented in Fig. 5c and d. In Conor Slater's work, a new system utilizing more power management methods and more power efficient components was designed to create a longer lifespan sensor.[77] The experimental results have demonstrated that its limit of detection (LOD) can be 0.2 mg L^{-1} and the dynamic linear range is 0–50 mg L^{-1}. Moreover, the optofluidic device could allow for at least 11 000 measurements with low reagent consumption (only 440 μL of total waste per analysis) and high sampling frequency (120 samples per hour). The system has made impressive improvement compared to the previous one and also demonstrated the long-term reliability of the device.

Most of the above photoelectric detection methods use spectrophotometry as the main mechanism, which could convert and amplify minor changes into electrical signals using the absorption characteristics of matter under light. The advantages of high integration, inspection automation and low limits of detection can meet the development requirements of intelligent water quality detection. However, it still has shortcomings. For example, imaging colorimetry has high requirements for the technology of image processing while the optical path design of flow injection analysis and microfluidics is very critical for high precision. Compared to most core devices, the cost of photoelectric conversion devices including photovoltaic cells, photoresistors and photomultipliers is very high. The accuracy of the system is entirely dependent on the rational design of the device and optical path. Therefore, the photoelectric detection strategies still have great potential in water quality detection.

Fig. 5 (a) A schematic of the chip. The microstructures are designed in the microchannel. The width of the channel in the microreactor is 250 μm and the width of the channel in the F–P cavity is 300 μm; and (b) the design of the microcavity, which is made from two parallel reflectors by coating gold films on the surface of optical fibers. Reproduced from ref. 76 with permission from the Royal Society of Chemistry, copyright 2017.

Classification of total phosphorus detection methods based on spectroscopy strategies

Spectroscopy, as a method of identifying the chemical composition and relative content of a substance, possesses the ability to measure the wavelength and intensity of the emission, absorption or scattering of the material due to energy level transitions upon light illumination. With the continuous development of spectroscopy, various new spectral techniques and corresponding spectral analysis instruments have been discovered. Meanwhile, spectral analysis has become one of the most comprehensive, widely used and most powerful analytical methods in modern analytical chemistry. It is prevalently used in many fields, such as the medicine, food, chemical and environmental fields, owing to its high sensitivity, low limit of detection, easy operation, fast speed analysis and
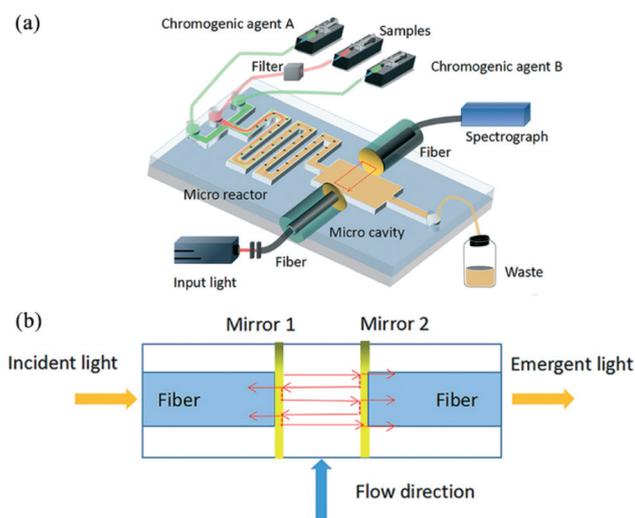
excellent selectivity.[78,79] A common classification method is based on the nature of the particles or substances that produce the spectrum and how the electromagnetic radiation works. According to the wavelength region, the spectrum can be divided into an infrared spectrum, visible spectrum, ultraviolet spectrum, X-ray spectrum and so on; according to the different particles in the generated spectrum, the spectrum can be divided into an atomic spectrum and molecular spectrum; according to the different spectral forms, the spectrum can be divided into a line spectrum, band spectrum and continuous spectrum; according to the mode of action of the substance and electromagnetic radiation, the spectrum can be divided into an emission spectrum, absorption spectrum and scattering spectrum. Recently, spectroscopy has gained more and more attention in the detection of total phosphorus or in other water quality detection areas due to the unique structures and good optical properties of the substances in water.[80–82] In this section, we will summarize recent examples of how spectroscopy techniques could be used to guide the determination of total phosphorus for better detection outcomes.

Ultraviolet–visible absorption spectroscopy

The molecular absorption spectrum is generated by the energy level transitions of valence electrons and electrons in the molecular orbital. When these electrons absorb the energy of the external radiation, they experience a transition from a low energy level to a high energy level. Therefore, each transition corresponds to absorbing a certain amount of energy radiation. Ultraviolet–visible absorption spectroscopy is a method for qualitatively and quantitatively analyzing a substance by measuring the absorbance or luminescence intensity of light at a specific wavelength or a certain wavelength range (usually from 200 to 1000 nm). So far, ultraviolet-visible absorption spectroscopy has become the most common analytical technique used for total phosphorus determination in water samples. In the presence of ascorbic acid, the phosphorus molybdenum heteropoly acid can be reduced to a blue complex called phosphomolybdenum blue. Due to its special molecular structure, the degree of light absorption is proportional to the concentration of phosphorus molybdenum blue at a wavelength of 700 nm or 880 nm. At the same time, the phosphate ions in the sample can first react with the molybdate and then with malachite green to form a green ion pair in acidic medium. The absorbance of the mixed solution can be measured at 625 nm. These methods have been recognized internationally and included in the national standards of China because of their relatively low cost, simple operation and stable results. In addition, the principle of the phosphorus vanadium molybdenum yellow method is similar to that of the phosphorus molybdenum blue method. The orthophosphate solution produced by the digestion of the sample can react with ammonium molybdate and ammonium metamonate in nitric acid to form a stable phosphorus–vanadium–molybdenum complex, which can be detected in the range of 400 to 460 nm for the samples of 0–50 mg L^{-1}. In the determination of low phosphorus contents, the international standards of ISO, EU, France and US AOAC have all adopted this method.

Even though these methods have been internationally accepted due to their sensitivity and simplicity, they are greatly affected by their external environment and have poor anti-interference ability, which may limit their development to some extent. For example, the interference of various metal ions and related compounds in water samples could change the position and intensity of the absorption peaks. Scientists have made great efforts to further improve the accuracy of detection and overcome the shortcomings of different methods. Bendicho et al. developed a miniaturization method for the determination of phosphate in water by combining direct suspension droplet microextraction (DSDME) with microvolume spectrophotometry.[83] This method is based on extracting an ion pair formed between 12-molybdate phosphate and malachite green onto a droplet of methyl isobutyl ketone. As shown in Fig. 6a, the intensity of the absorption peak at 627 nm increased with the increase in the concentration of the trace phosphate, which could be a key indicator in the detection process.
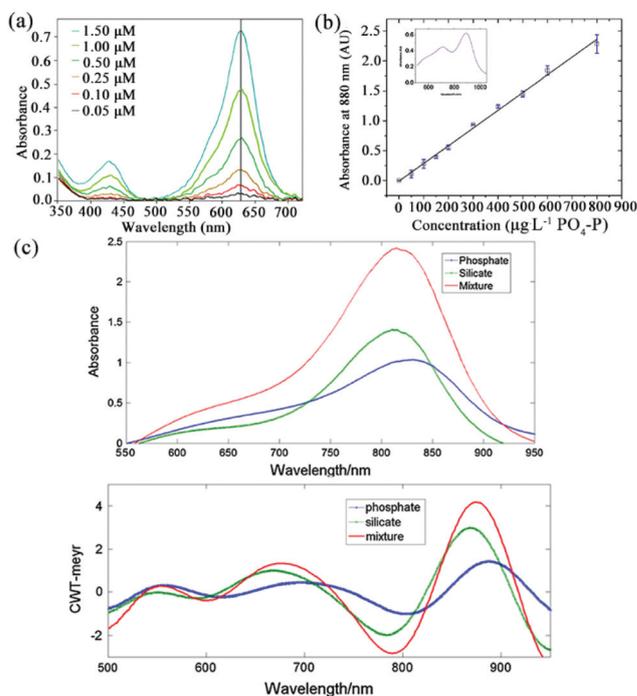

Fig. 6 (a) Absorption spectra of phosphate (0.05–1.5 µM) obtained by DSDME microvolume spectrophotometry. Reproduced from ref. 83 with permission from Elsevier B.V., copyright 2011; (b) calibration curve obtained on the PhosphaSense system using prepared phosphate standards, where error bars show one standard deviation, with a slope of 0.003 AUL µg^{-1} and an R2 of 0.9958. The absorbance spectrum of the molybdenum blue product is shown in the top left inset. Reproduced from ref. 28 with permission from Elsevier B.V., copyright 2017; (c) absorption spectra for 2.0 mg L^{-1} phosphate and its mixture and CWT spectra of species, in the presence of 0.02 mol L^{-1} ammonium molybdate and 3.0×10^{-2} mol L^{-1} ascorbic acid. Reproduced from ref. 85 with permission from Springer Nature, copyright 2016.

The high sensitivity of phosphate determination and low consumption of the organic solvent and sample have made the proposed method more attractive in the field of water quality detection. In a subsequent study, Miller *et al.* verified the correctness of ultraviolet-visible absorption spectroscopy by detecting the phosphate content in soil moisture.[84] This principle can also be used in water quality detection. Moreover, the utilization of a specific wavelength in UV-Vis absorption spectroscopy plays a pivotal role in the detection of orthophosphates with different concentrations in the background medium. The effects of impurities such as inorganic and organic substances on the accuracy of phosphorus UV-Vis absorption spectroscopy analysis should be further investigated to refine the optimum absorbance in various water samples. In the same year, Tarighat's group applied continuous wavelet transform and zero-crossing techniques to overlapping visible spectra for simultaneous determination of phosphates and silicates without any pretreatment.[85] By analyzing the composition of the different binary mixtures, the constructed calibration function was tested and a calibration map of the composite estimate was obtained as shown in Fig. 6c. Miller's correct and feasible point of view has also been confirmed by the experimental data. The CWT algorithm for UV-Vis absorption spectroscopy provided higher peak amplitudes, sharper peaks, and less noise. In the new research, Duffy *et al.* developed a centrifugal microfluidic optical sensor by integrating microfluidics, imaging colorimetry and other techniques.[28] However, the core part is still used to calculate the phosphate content by combining the UV-Vis absorption spectroscopy with the functional relationship to obtain the corresponding change in the trend (Fig. 6b). We can conclude from the above paradigms that UV-Vis absorption spectroscopy is one of the most critical and effective methods in water quality detection.

Fluorescence spectroscopy

Fluorescence, referring to a photoluminescence phenomenon, is the light emitted by a substance after absorbing light or other electromagnetic radiation. The fluorescence spectrum can reflect the relationship of the intensity and the corresponding wavelength and can be divided into the excitation spectrum and emission spectrum. The former reflects the relationship between the luminous efficiency of the luminescent material and the wavelength of the excitation light under different excitations and the latter refers to the change of the luminescence intensity under different wavelengths. A relatively large number of physical parameters can be provided by fluorescence spectroscopy such as the fluorescence intensity, quantum yield, fluorescence lifetime, fluorescence polarization and others. These parameters can also reflect various properties of the analytes and give more detailed information.[86–89]

Because of the low fluorescence quantum yield and relatively low energy of characteristic radiation, the determination of the phosphorus element content is largely hindered. In view of this, some attempts have been made to improve sensitivity and limits of detection by indirect methods applied for the determination of Cl^-, SO_4^{2-}, Be^{2+} and Li^+. By precipitation of Ag_2TlPO_4 and then measuring the fluorescence of silver, Stork and Jung have successfully determined orthophosphate contents. Smith utilized the precipitation of $Bi_3(PO_4)_2$ and obtained the concentration of bismuth. Under the same principle, Pytlakowska *et al.* proposed an indirect method for the determination of phosphates by energy dispersive X-ray fluorescence spectrometry (EDXRF).[90] This method based on the determination of phosphates through molybdenum in a phosphomolybdenum blue complex can overcome the shortcomings of low fluorescence quantum yield and low energy of phosphorus radiation. Fig. 7a shows the EDXRF spectrum of the sample containing 20 mg phosphorus. As the Kα line of phosphorus was not sensitive enough to determine the content of phosphorus, the high fluorescence quantum yield of molybdenum (0.77 for molybdenum and only 0.07 for phosphorus) ensured the accurate detection of phosphorus. Under the optimized conditions, determining a low concentration of phosphorus can be accomplished *via* a significant ratio of phosphorus to molybdenum (1 to 37) and a sensitive Ka line of molybdenum was obtained as shown in Fig. 7b. It shows a good linear relationship ($r \leq 0.9995$) and the limit of detection can reach 2.8 ng mL^{-1}. Utilizing the same concept, the same group combined a miniaturized ion-associated complex-based preconcentration method with energy dispersive X-ray fluorescence spectrometry (EDXRF).[91] In the proposed work, phosphorus was determined *via* EDXRF measurement at an appropriate molar ratio of phosphorus to molybdenum (1:12). Compared to previous experimental data, a good linearity (Fig. 7c, up to 2 μg mL^{-1} of phosphorus, $r = 0.9991$) and a
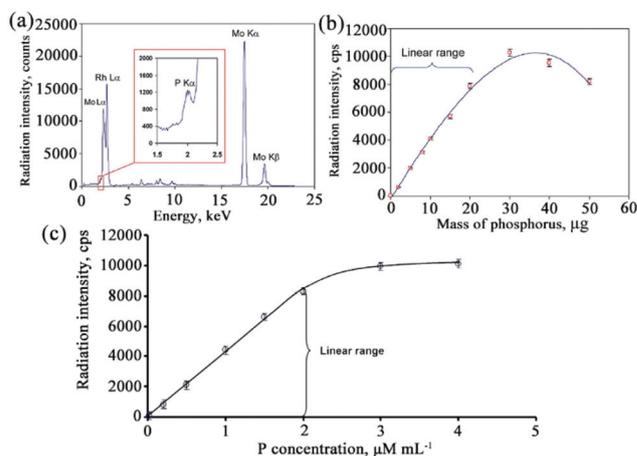

Fig. 7 (a) The EDXRF spectrum of the sample containing 20 mg of phosphorus. Measurement was carried out under a helium atmosphere; and (b) relationship between the molybdenum radiation intensity and mass of extracted phosphorus. Error bars represent the standard deviation for N = 6. Reproduced from ref. 90 with permission from the Royal Society of Chemistry, copyright 2012; and (c) relationship between the molybdenum radiation intensity and concentration of preconcentrated phosphorus. Error bars represent the standard deviation for N = 3. Reproduced from ref. 91 with permission from John Wiley and Sons, copyright 2015.

detection limit of 1.3 ng mL^{-1} enabled this strategy to achieve a wider range of detection.

Apart from the detection method of replacing phosphate ions with other ions with high fluorescence yield, some fluorescence strategies as natural driving forces can also be introduced to phosphorus detection systems. One method is to quench the fluorescence of rhodamine 6G with the reactant phosphomolybdate.[92] Fig. 8a shows that the fluorescence intensity signal of the reacted complex gradually decreased as the concentration of the phosphate increased. The other one is a photoinduced electron transfer (PET) based fluorescent on/off sensor.[93,94] Borse *et al.* reported the synthesis and characterization of thioglycolic acid (TGA) capped cadmium telluride (CdTe) QDs[95] and their utilization in fluorescence sensing assay for phosphate ion detection.[96] From Fig. 8b and c we can first find that the fluorescence of the QDs was quenched/turned off with the increase in Eu(NO$_3$)$_3$ due to their conjugation. Then with the addition of phosphate ions, the fluorescence in the QD–Eu complex gradually was recovered as the phosphate ion content increased, and the peak position slightly shifted. The fluorescence signal recovery was found to be as high as 98% for the highest chosen concentration 2.4 mM of phosphate ions. The probable mechanism could be ascribed to the complex formation between phosphate ions and Eu^{3+}, which causes the removal of Eu^{3+} from the surface

of TGA capped CdTe QDs for fluorescence recovery. In addition, the authors have also verified by experiments that the presence of ions other than phosphate cannot cause any interference with fluorescence recovery, highlighting the specific effect of phosphate. Thus, it can be concluded that the concentration of phosphate can be quantitatively analyzed in terms of the fluorescence recovery intensity. Under optimized conditions, the relationship between the fluorescence intensity and phosphate concentration is fitted to a sigmoid shape (Fig. 8d). This 'turn on' sensing assay method can also be applied to determine trace phosphates in water due to its high sensitivity, repeatability and specificity.

Other spectroscopy

Apart from the previous common spectroscopy techniques, some other spectroscopy strategies are also widely used in practical fields. Inductively coupled plasma atomic emission spectrometry (ICP-AES), as one of the most widely used techniques, is an indispensable spectral analytical tool utilizing an inductively coupled plasma torch as the excitation source for applications in metallurgy, machinery, and geology. The sample of ICP undergoes processes including atomization, ionization, and excitation, and finally emits energy in the form of light. When atoms of different elements return to the ground state after excitation or ionization, they emit characteristic spectra of different wavelengths, thus enabling qualitative and quantitative analyses according to the characteristic peaks and corresponding intensities of different elements. For example, Okamoto and colleagues reported the determination of phosphorus and sulfur in environmental samples by electrothermal vaporization inductively coupled plasma atomic emission spectrometry.[97] Subsequently, Viso *et al.* also applied this method to detect phosphorus and boron in fertilizers.[98] This spectroscopy technology which eliminates the need for sample pretreatment allows simultaneous measurement of multiple elemental contents. Besides this, near-infrared spectroscopy (NIRS) can also be applied to various elements in agricultural environments. Zhang *et al.* obtained the near-infrared reflectance spectra of soil samples with different soil moisture levels and particle sizes and determined the absorbance values.[99] Then they described the procedures to remove the effect of soil moisture and particle size on total phosphorus prediction. In recent years, many scientists have devoted more effort to the research of the application of near-infrared spectroscopy in water quality detection.

As a promising analytical and research technique, Raman spectroscopy has attracted more and more attention in recent years. Essentially, it can be thought of in its simplest form as a process where a photon of light interacts with a sample to produce scattered radiation of different wavelengths. Raman scattering, found by the Indian scientist C. V. Raman, is an inelastic scattering effect of molecules on photons. By far, the stronger process in Raman is Stokes scattering, whereby the photon is scattered at lower energy. A small number of molecules will be in a higher vibrational level, and hence the scattered photon can actually be scattered at a higher energy,
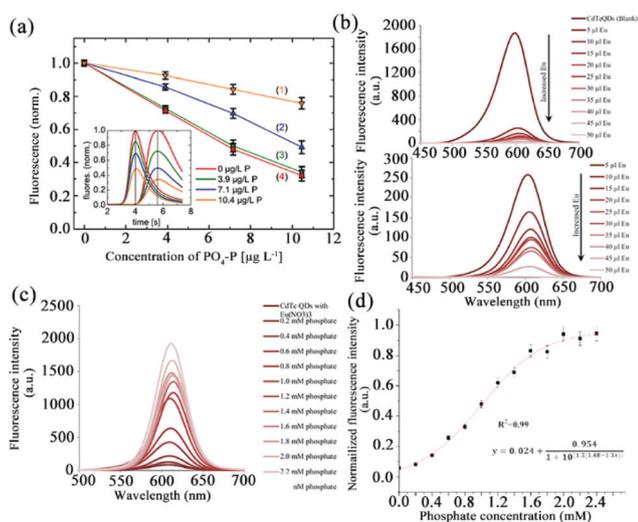

Fig. 8 (a) Fluorescence signals *versus* phosphate concentrations for different flow velocities (7.1 (1), 6.1 (2), 4.3 (3) and 3.5 (4) mL min^{-1}) at constant injected volumes of 15 μL. Inset: original measurement data of the flow rate experiments for 4.3 and 6.1 mL min^{-1} are shown. Error bars ±3 standard deviation, n = 15. Reproduced from ref. 92 with permission from Elsevier B.V., copyright 2014; (b) quenching of the fluorescence intensity of TGA capped CdTe QDs (400 μL, 2 mg ml^{-1}) when titrated with 0.39 mM Eu(NO$_3$)$_3$. Spectra with control and spectra without control (elaborated to view the readings); (c) restoration of the fluorescence intensity of the QD–Eu complex on addition of increasing concentrations of phosphate; and (d) change in the peak fluorescence intensity of the QD–Eu complex, with various concentrations of phosphate. Reproduced from ref. 96 with permission from Elsevier B.V., copyright 2016.

which is the much weaker anti-Stokes Raman scattering. Moreover, the Raman shift depends on changes in the molecular vibrational level and molecular vibrations characteristic of different chemical bonds or groups, and thus the corresponding Raman shift is also characteristic. In view of this, Raman spectroscopy can offer a scattering spectrum with different incident light frequencies for analysis to obtain information on molecular vibration and rotation.[100,101]

With the continuous advancement of technology, various Raman spectroscopy techniques have been widely applied to determine different contaminants in water environments, including organics, inorganics, and biological components.[49,80,102] For example, Gajaraj et al. made use of Surface Enhanced Raman Spectroscopy (SERS) to simultaneously determine nitrate and nitrite levels in water (Fig. 9a).[103] Moreover, Du et al. reported the SERS-based detection of 10 ppb to 1000 ppb standards in solutions (Fig. 9b).[104] There are countless examples of such specific examples. However, due to the particularity of phosphorus, there have been few reports on total phosphorus detection by Raman spectroscopy. It is worth mentioning that Ozaki and his group have successfully designed a simple semiconductor-based SERS sensor to achieve detection of phosphate anions in aqueous solution.[105] Since the Raman intensity of the phos-phate ion is quite weak, quantitative analysis is usually realized by indirectly measuring the change of the Raman intensity. Under acidic conditions, the chelation between pyrocatechol and colloidal TiO_2 NPs was inhibited by the pre-adsorbed phosphate anions on the colloidal TiO_2 NP surface, resulting in a gradual decrease in the SERS intensity of the pyrocatechol molecule. As shown in Fig. 9c, as the concentration of phosphate ions increased, the Raman intensity of catechol gradually declined. Measurement of such "turn-off" SERS exhibits excellent selectivity for phosphate anions in water samples. In summary, ICP-AES, near-infrared spectroscopy, and Raman spectroscopy are ultrasensitive techniques that allow the determination of analytes in a wide variety of matrices, and at the same time do not require complex pretreatment procedures. Although there are limited studies for their applications in total phosphorus detection, they still provide new ideas for the development and technological innovation of water quality detection.

Compared with photodetection strategies, spectral technology places more emphasis on the microscopic properties of substances. Most substances in water can absorb light to excite electrons from the ground state to the excited state, followed by the release of energy in the form of heat through nonradiative decay. This principle is used by ultraviolet absorption spectroscopy for phosphorus elements, measuring and analyzing them quantitatively. The emission characteristic is utilized by fluorescence spectroscopy to measure the luminescence intensity of substances at different wavelengths of excitation light. The principle of ICP-AES is that the excited atoms will emit the characteristic spectrum of different wavelengths when returning to the ground state. Raman spectroscopy makes use of the molecular scattering principle to determine the molecular vibration level and molecular vibration characteristics of different chemical bonds and groups. In summary, these ultrasensitive technologies are the most effective methods among water quality detection technologies, but there are still some shortcomings. On the one hand, spectrometers have extremely high requirements for optics and optical path design. Simultaneously, they also have the disadvantages of complicated structures, high cost and being unsuitable for on-site measurement. On the other hand, the spectral technology needs to be combined with related circuits such as the photoelectric conversion circuit, amplification circuit, and filter circuit, which also includes a variety of optimization algorithms. It is foreseeable that spectroscopy technology will be further developed towards intelligent and high integrated performance.
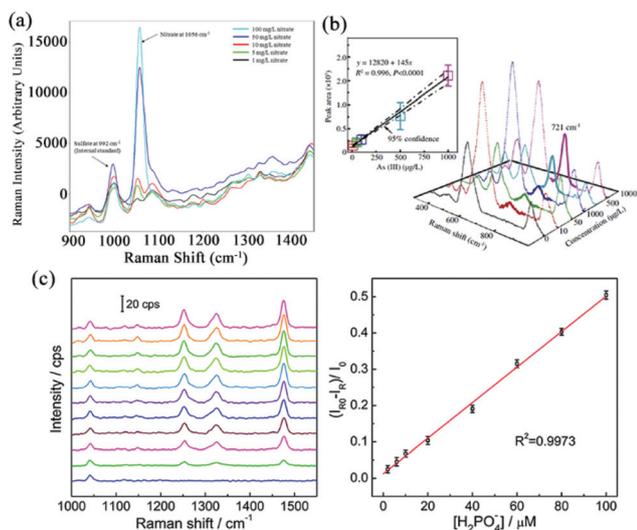

Fig. 9 (a) Concentration-dependent Raman intensities of nitrate (1056 cm^{-1}) and nitrite (1326 cm^{-1}) in DI water determined by SERS coupled with gold nanosubstrates. The nitrate and nitrite concentrations (ranging from 1 to 1000 mg L^{-1}) in each sample were the same. Reproduced from ref. 103 with permission from Springer Nature, copyright 2013; (b) SERS spectra of As(III) at different concentrations of 0, 10, 50, 100, 500, and 1000 ppb, and calibration curves for As. Reproduced from ref. 104 with permission from the Royal Society of Chemistry, copyright 2014; (c) SERS spectra of pyrocatechol on colloidal TiO_2 NPs in the presence of phosphate anions with different concentrations. The concentrations from top to bottom are 0, 2, 6, 10, 20, 40, 60, 80, 100, 150, and 300 μM. The relative Raman intensity [(IR0 − IR)/IR0] at 1481 cm^{-1} versus the phosphate anion concentration. Reproduced from ref. 105 with permission from the Royal Society of Chemistry, copyright 2015.

Classification of total phosphorus detection methods based on modeling and algorithm strategies

With the development of mathematics and computer techniques, mathematical models and algorithms have gained more and more attention, and at the same time have promoted water quality evaluation.[106] However, the diversity, complexity

and irregularity of water environments have caused a lot of uncertainty and ambiguity in water quality assessment. Until now no method has been widely accepted, and the development and improvement of a comprehensive evaluation model for water quality are under way. In this section, we will summarize recent examples of how mathematical models and algorithms could be combined with total phosphorus detection techniques for rapid and accurate measurement, including the genetic algorithm, artificial neural network, and fuzzy inference system.[107]

Modeling and estimation

For large reservoirs and lakes, the construction of a total phosphorus measurement model is a typically complex process due to its severe random disturbance, strong nonlinearity and time-variation. It can combine the mature total phosphorus detection technology with the emerging algorithms and build models to improve measurement data processing and analysis. At the same time, the modeling algorithm is also a supervised learning method. By analyzing the training set of known categories, we can find classification rules and accumulate experience to predict new data of relevant rivers and reservoirs, further establishing relevant water quality warning systems.[108] Hudson and his colleagues developed a model to estimate the total phosphorus concentration by a modified Rigler bioassay.[109] There are two main assumptions of this model under P-limited aquatic environments. One is that planktonic phosphate regeneration is approximately identical to planktonic phosphate uptake (Fig. 10a). The other is that the majority of regenerated P is phosphate or can quickly become phosphate. As shown in Fig. 10a and b, the formula calculation can be described as:

$$\text{ssPO}_4^{-3}{}_{\text{predicted}}\ (\text{pM}) = R_{\text{predicted}}\ (\text{pM min}^{-1})\ \div\ k\ (\text{min}^{-1})$$

$$R(\text{pM min}^{-1}) = \left(^{33}\text{P released}(\text{cpm L}^{-1}) \times \text{Total P}(\text{pM})\right)$$
$$\div\ \left(\text{Total }^{33}\text{P added to incubation}(\text{cpm L}^{-1})\right)$$

They applied the measured data of 20 lakes to a new set of 33 lakes, and then compared and screened these estimates to obtain a new empirical relationship. The published empirical relationship between phosphorus regeneration (R) and total phosphorus (TP) based on data from 53 lakes ($n = 53$, $r^2 = 0.97$, $\log_{10} R$ (pM min^{-1}) = 1.084($\log_{10}$ TP (pM)) − 4.535) was exploited by this strategy to predict the total phosphorus concentration and phosphate regeneration rate in more lakes. The rapid estimation of TP proposed here, though still having a relative error, does not require sample pretreatment for oxidation of the phosphate, and can be easily and conveniently used to observe and predict the change of the total phosphorus content in large reservoirs and lakes.

Access to high-quality empirical data is quite essential for the modeling analysis process. In another research, Anders Grimvall *et al.* used process-based models to observe natural changes of nitrogen and total phosphorus in river water.[110] As
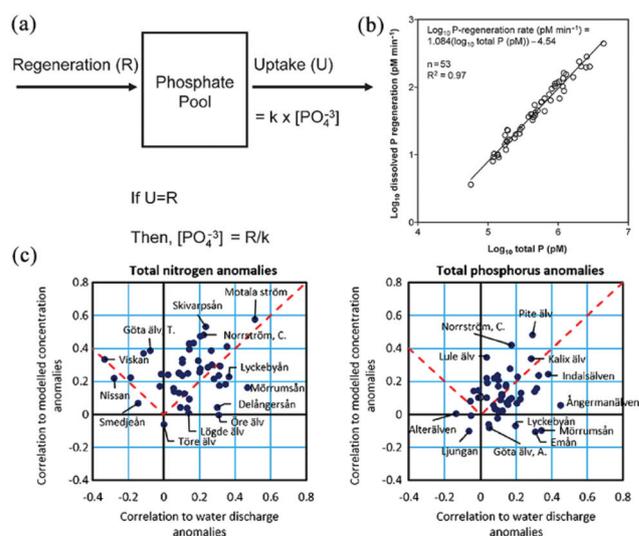

Fig. 10 (a) Conceptual model for estimating steady state phosphate concentrations in P-limited aquatic environments; (b) total planktonic regeneration of dissolved phosphorus as a function of total P for all lakes. Reproduced from ref. 109 with permission from Springer Nature, copyright 2005; and (c) scatter plots summarizing how annual anomalies in measured total nitrogen and phosphorus concentrations were correlated with anomalies in modelled concentrations and water discharge for each of the investigated sites. Reproduced from ref. 110 with permission from Springer Nature, copyright 2014.

a HYPE setup covering the whole of Sweden, they utilized the output results of S-HYPE to simulate and predict changes of nitrogen and total phosphorus in soil, stream and lake precipitation.[111,112] The output of the process model S-HYPE included data average sampling points for nutrients (nitrogen and phosphorus) near 45 river basin outlets from 1992 to 2010 in Sweden. The trend of total nitrogen and total phosphorus concentrations was further obtained by calculating and analyzing the anomalous data series and performing Mann-Kendall (MK) tests on monotonic trends. Then, the introduction of animated graphics has promoted visual checking for abrupt shifts in the smoothing trend and regression residuals. Finally, a mixed linear model was applied to estimate both this trend and level changes. In addition to predicting the concentration of nutrients, this modeling method can also be used for meteorological standardization observations and monitoring watershed emissions. However, due to the presence of a large amount of particulate phosphorus, the output of the total phosphorus monitoring process model had a large systematic error. Their evaluation of model performance indicated that the annual anomaly of the measured total phosphorus concentration was usually poorly correlated with the S-HYPE output due to the presence of large amounts of particulate phosphorus (Fig. 10c). Even so, the method is not unacceptable because such errors can be effectively eliminated by means of laboratory digestion and there is no doubt that it represents the direction in which the modeling algorithm moves forward.

Apart from this, Pöthig *et al.* applied a versatile estimation algorithm to evaluate the phosphorus loss potential from soil

to aquatic ecosystems.[113] Combining near-infrared spectroscopy as a measurement tool, Zhang *et al.* developed a soil total phosphorus prediction model based on LS-SVM.[99] Similarly, Ba *et al.* developed a combination of affine projection algorithms and autoregressive (AR) models to predict the water quality time series (chlorine, conductivity, total organic carbon, and turbidity).[114] Then, the online change-point detection method was applied to the estimated residual to determine the presence or absence of a pollution event. Currently these algorithms are being widely used in soil detection while there are few reports on directly monitoring the TP concentration in water. With the continuous innovation and development of water quality detection technology, the algorithms have become an indispensable strategy in improving the accuracy of water quality detection. In summary, compared to purely statistical correlation analyses, advances in modeling algorithms have created new possibilities to interpret time-varying water quality data, which is more conducive to promote two-way communication between environmental monitoring and modeling.

Remote sensing algorithm strategy

Remote sensing technology is an effective tool for detecting and recognizing electromagnetic waves, visible light, and infrared rays reflected or radiated from distant targets. It collects electromagnetic radiation information from targets of satellites, aircraft or other aircraft to identify changes in the Earth's environment and resources. With the recent boom in computer applications and space science, remote sensing technology makes it possible to identify spatial and temporal variations in water quality variables among large-scale regions.[115] According to the available literature, a relevant conclusion is that water quality parameters can be measured using various space-borne and airborne sensors with reliable precision. For example, the newly developed coastal ocean hyperspectral imager can record up to 200 spectral channels to measure and monitor various water quality parameters because of simultaneously collecting narrower and continuous bands.[116] Although the ability of remote sensing to evaluate water quality is conspicuous, the technology alone is not perfect enough and must be combined with on-site measurements and computer water quality modeling to gain more accurate insight.[117]

In general, total phosphorus does not directly reflect optical signals in water, but is closely related to other water quality parameters such as phytoplankton,[118] total suspended matter (TSM), turbidity and Secchi disk depth (SDD).[119] Many studies have shown that the concentration of TP in water is positively correlated with the concentration of chl-a,[120] while the depth of the Secchi disc decreases with an increase in the TP concentration. These studies suggested that both the chl-a concentration and Secchi disc depth can be considered as representative parameters for indirect prediction of the TP concentration in water. Therefore, an empirical model combining remote sensing and algorithms is usually considered as the most appropriate method for remote estimation of TP in water.[116,117,121]

Wu *et al.* developed an estimation model in which the TP concentration was indirectly related to the reflectance values of Chl-a and SDD observed with satellite sensors.[122] They chose a spectral band centered on the blue (450–520 nm), green (520–600 nm) and red (630–690 nm) spectral regions that were highly sensitive to water quality. There was a correlation between remote sensing observation and the TP concentration in water, namely reflectance = f[Chl-a(TP), SDD(TP)]. Then a combination of TM3/TM2, TM1/TM3 and TM1 data was obtained to evaluate Chl-a and SDD, where the TM3/TM2 ratio was the best predictor of the Chl-a concentration[123] and a combination of TM1/TM3 and TM1 was the best for SDD.[124] The chl-a concentration and SDD measurements were correlated with the TP concentration to obtain a regression model:

$$\ln(\text{TP}) = -21.45\left(\frac{\text{TM3}}{\text{TM2}}\right) - 14.42\left(\frac{\text{TM1}}{\text{TM3}}\right) + 42.99(\text{TM1}) + 27.1.$$

In another subsequent study, Song *et al.* used the airborne imaging data (AISA) in the red (around 690 nm) and NIR (around 710 nm) spectral regions to estimate the total phosphorus concentration of three water supply reservoirs in Indiana based on the principle of close association of TP with TSM, SDD, and Chl-a.[125] As depicted in Fig. 11a, the designed hybrid model (GA-PLS) well combined genetic algorithms with partial least squares algorithms. The AISA image spectrum of the TP concentration map in GA-PLS was relatively stable, indicating that the simple model can estimate the TP concentration with high accuracy from hyperspectral imaging data and proving that these techniques can be applied to sensors and sensor platforms as shown in Fig. 11b. Utilizing the same concept and measure, Sun *et al.* classified the water bodies studied into three types with the developed NTD675 threshold method.[126] Then, they specifically reflected the spectral region sensitive to each water type in several band ratios, and established an indirect relationship model between the surface reflectance and TP concentration as shown in Fig. 11c. Based on previous water classification and support vector regression (SVR) machines, a new TP remote sensing algorithm was developed with relatively high prediction accuracy (Fig. 11d). Similar to Sun's research work, Lim *et al.* evaluated the potential application of the Landsat 8 Operational Land Imager (OLI) in estimating the water quality of the Nakdong River in South Korea.[127] Based on the correlation analysis of the 'Landsat 8-band combination and ratio' and *in situ* measurement, multiple regression equations were constructed and related water quality models were established to estimate the TP content. Fig. 11e demonstrates the potential of combining remote sensing measurements and algorithms to effectively detect spatial pattern changes in water quality parameters. In the latest research, Abdelmalik *et al.* summarized previous research findings and demonstrated a significant empirical relationship between the ASTER data and observed water quality parameters.[128] The measured parameters obtained from the ASTER reflection band can be accurately predicted using mathematical equations derived from statistical and
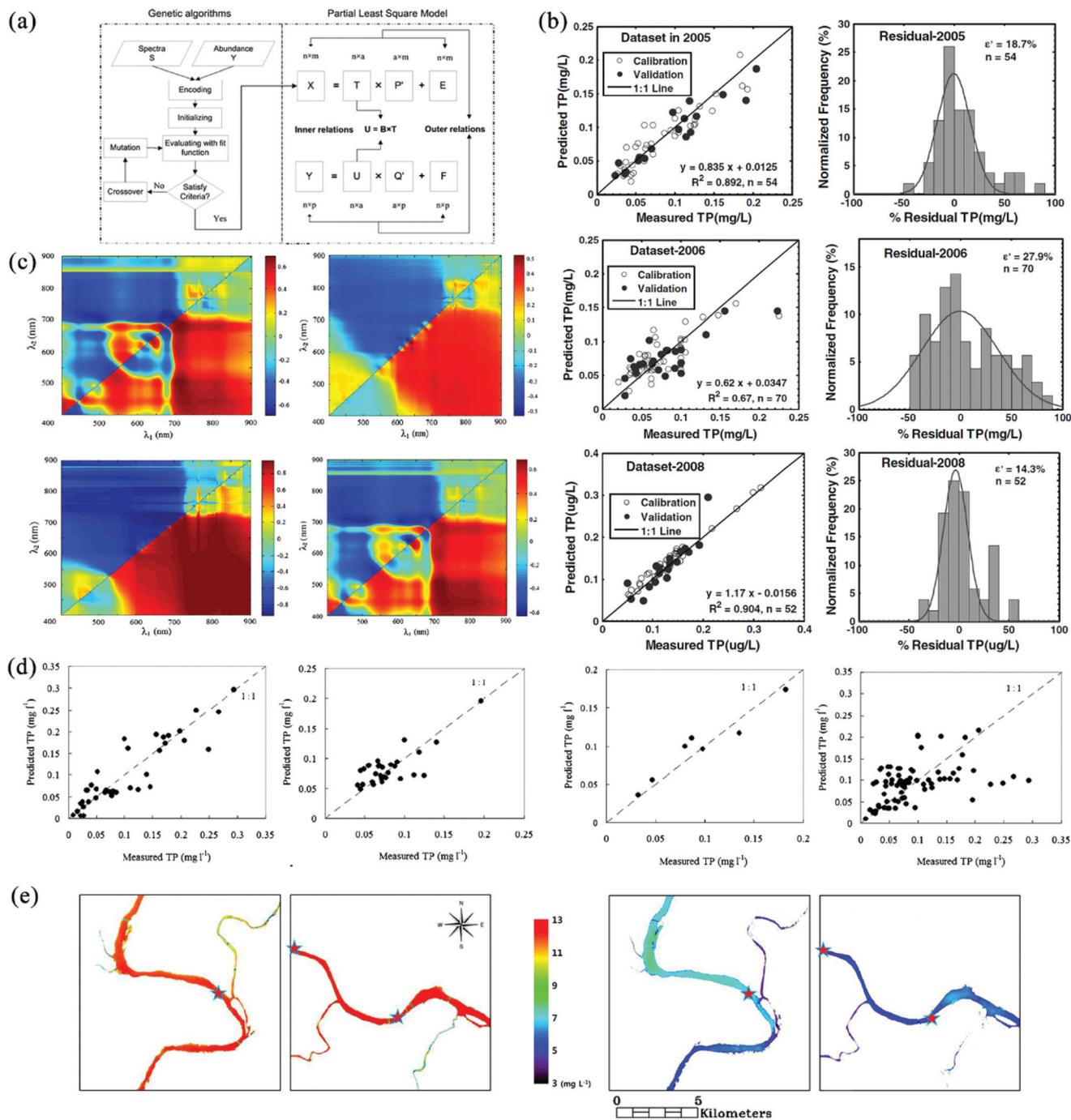
Fig. 11 (a) Flow chart for the GAPLS model; the left diagram shows how GA processes spectral variables according to water quality parameters and the diagram on the right shows how PLS performs the regression according to both spectral variables determined *via* GA and water quality parameters. (b) Scatter plot of measured *vs.* predicted TP for GA-PLS and error residual histogram for various datasets. Reproduced from ref. 125 with permission from Springer Nature, copyright 2012; (c) variations of the correlation coefficient between TP and band ratios Rrs (λ_1)/Rrs (λ_2) in the spectral range of 400−900 nm, obtained by using the total samples of three water types and the aggregated data; and (d) scatter plots between measured and predicted TP concentrations by using the developed SVR models. Reproduced from ref. 126 with permission from Springer Nature, copyright 2014. (e) Spatial pattern of the total phosphorus concentration. Reproduced from ref. 127 with permission from Springer Nature, copyright 2015.

regression analysis. The current research has shown that the spatial distribution of important environmental parameters in water bodies through the combination of remote sensing and algorithms discussed in this section should be the fastest and

cheapest way to obtain effective data for environmental science. It can be effectively exploited for routine monitoring of lakes and reservoirs that cover large geographic areas. In summary, the development and progress of remote sensing

algorithms represent the direction and unremitting motivation for the successful detection of the TP concentration in water.

The modeling algorithm strategy is the fruit of the continuous development of mathematics and computer technology. As an effective auxiliary tool, the development of the modeling algorithm strategy could not move forward without the continuous improvement of detection technology. Large reservoirs or lakes can be regarded as typical complex models, whose characterization data including directly or indirectly generated associated data could be collected. Then in these sample data, we could take advantage of regression and classification rules and accumulate experience to simulate and predict new data to further refine the relevant water quality detection models. In addition to improving the accuracy of the test, the strategy has the advantage of monitoring multiple substances and finding connections between various substances in order to make the total phosphorus detection more specific and enhance the anti-interference ability. The introduction of intelligent algorithms makes the model have early warning and alarm functions, and the total phosphorus detection technology is proceeding towards automation and intelligence. However, the modeling algorithm is just in the initial state in phosphorus detection techniques. Taking comprehensive requirements of samples into account, the modeling algorithm requires more complete reports and more effective applications, which encourages us to continue the research and improve the strategy to apply more compelling modeling algorithms to water quality detection.

Conclusion and perspective

The construction of methodology with high selectivity, sensitivity, and low limit of detection has recently emerged as a promising field for water quality detection based on total phosphorus. In this review, three major types of strategies for accurate detection of total phosphorus in water, including photoelectronic detection, spectral analysis techniques, and modeling algorithms, have been described in detail. Some selective examples were considered aimed at illustrating the importance of rational utilization of natural optical and chemical properties of phosphorus species as driving forces to achieve highly credible analysis and detection, which may provide guidance for the design and proposal of new strategies.

In comparison with other strategies, the photoelectric detection strategy can convert the optical characteristics into electrical signals, thus intuitively reflecting the measurement results by digital electronic technology. Obviously, the development of automation and intelligent analysis should be an inevitable trend in the field of current water quality detection. Furthermore, spectral technology is one of the most effective analytical tools developed on the basis of the photoelectric technique for water quality detection. It not only improves the detection accuracy and lowers the limit of detection, but also represents the direction in which the total phosphorus detec-

tion moves forward. For example, the rapidly developing Raman spectroscopy and atomic emission spectroscopy technologies hold more potential to analyze the contents of various forms of phosphates, organophosphorus and elemental phosphorus in phosphorus species. As an auxiliary tool, the modeling algorithm strategy can be effectively combined with other strategies to establish water quality models, which can not only analyze and predict the total phosphorus content in water, but also improve our understanding of the spatiotemporal dynamics of total phosphorus in water.

Although these achievements and progress are encouraging, there are still many challenges waiting to be overcome. Firstly, the methods for detecting and analyzing total phosphorus are not abundant enough and are still evolving. Due to the lack of cross-applications between various disciplines, the combined available driving forces are just beginning to be explored. Secondly, unknown water environments may contain more complex chemicals and microorganisms. Their existence characteristics and growing mechanisms remain unclear, which may limit the precise control and analysis of total phosphorus. Lastly, the characteristics, properties, and intrinsic relevance of phosphorus species with diverse forms in water environments should be considered to develop more advanced photosensors, chemical sensors, and biosensors for directed measurement, effectively avoiding complex sample pretreatment processes. Future studies will be focused not only on measuring and analyzing the total phosphorus content and complicated morphologies in water through a combination of effective strategies, but also on the accumulation of phosphorus in soil, the human body and other conditions that may trigger related diseases to broaden their applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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