



Development of an anti-chloride interference and high sensitivity on-line analyzer for analysis of total phosphorus in industrial circulating cooling water

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ABSTRACT

An on-line total phosphorus (TP) analyzer was developed to meet the needs for determining the phosphonate concentration in industrial circulating cooling waters with low phosphorus and even phosphorus-free formulations and high Cl^- contents. A flow batch analysis technique was used to achieve high sensitivity over a wide range of total phosphorus concentration using a home-made low-power ring-shaped UV on-line digester operating at normal temperatures and pressures and a dual-spectrophotometer detector. The quantification range was 0.36–160 $\mu\text{mol L}^{-1}$, and the limit of quantification was low enough to detect low, and even no, phosphorus in the treatment reagents. Concentrations of chloride ions up to 700 mg L^{-1} in the cooling water would not interfere with the digestion. The analyzer was successfully deployed in an open circulating cooling water system. The results from the on-line system agreed well with those of discrete samples analyzed using a conventional analytical method in the factory laboratory.

1. Introduction

Although great progress has been made in corrosion science and techniques in recent years, corrosion problems in equipment and pipelines still exist in industrial circulating cooling water systems [1]. The use of anti-corrosion reagents is the most commonly used method to deter the fouling and corrosion in industrial water lines [2].

Organic phosphonates are effective chelating reagents, often used together with zinc ions (Zn^{2+}), as a corrosion inhibitor to prevent the formation of insoluble scales [3,4]. In circulating cooling water, phosphonates should be kept within a certain concentration range to be effective. Insufficient concentrations slow down the anti-corrosion effect, while excessive concentrations are not only wasted reagent, but also accelerate the equipment corrosion [2] and increase water pollution with phosphates. Therefore, rapid determination of the concentration of the organic phosphoric acid in the circulating cooling water is necessary for regulating the feed amount. The conventional measurement steps [5,6] are as follows: a water sample is collected off-line, then the total phosphorus (TP) in the water is digested and determined with conventional manual methods, and finally the concentration of phosphonates is calculated. However, conventional digestion methods of TP, such as the

dry ashing method, digesting with potassium persulfate at high temperatures/pressures, using nitric acid and perchloric acid, or performing a microwave-assisted method [7,8], all take a long time and introduce large errors in the analysis [8–10]. More importantly, the off-line analysis method can only provide TP concentration data on random samples, usually with a sampling frequency of only a few times per day at most, and the analysis results can take hours or even a day to obtain. During this time, the TP concentration in the circulating cooling water may have changed, directly affecting the reliability of the feed control.

On-line digestion using flow injection has proven to be an effective pre-treatment technique for the rapid determination of TP in various types of water [11–13]. Benson et al. compared microwave-induced on-line digestion [14] and UV/thermal on-line digestion [15] to determine the TP in water and waste water, and suggested that the UV/thermal method was more suitable for online monitoring. Gentle et al. [16] and Taylor et al. [17] successfully developed a portable flow analysis systems using UV/thermal or UV on-line digestion techniques for rapid determination of TP in estuarine and marine waters. However, the above methods and systems use stannous chloride as the reducing reagent in the phosphomolybdenum blue (PMB) reaction, a measurement method that is much more likely to be affected by the presence of chloride ions

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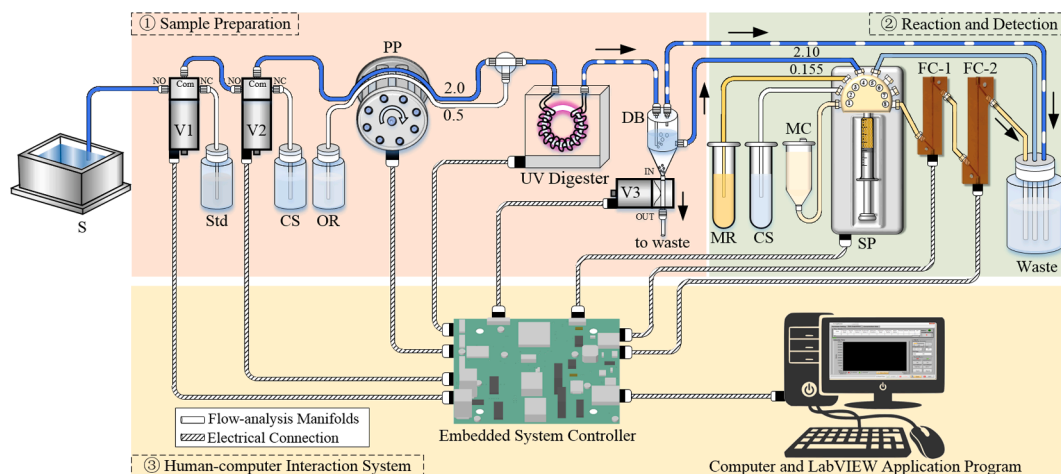


Fig. 1. Schematic diagram and flow manifold. S, sample; V1, V2, three-way normally open solenoid valve; Std, certified standard; CS, cleaning solution; OR, (neutral or alkaline) oxidation reagent; PP, peristaltic pump, numbers indicate flow rate, mL min⁻¹; DB, debubbler; V3, two-way normally closed solenoid valve; MR, mixed color developing reagent for orthophosphate determination; MC, mixing chamber; SP, syringe pump, numbers indicate volume taken, mL; FC-1, FC-2, Z-shaped flow cell 1, 2 of the spectrophotometric detector.

(Cl⁻) [18], and thus not suitable for application to circulating cooling water systems where high chloride ion concentrations are found. Based on an optical flow control technique, Li et al. [19] developed an integrated optofluidic platform that enabled on-chip thermal digestion and on-line spectrophotometric detection of TP. However, the digestion efficiency of the organophosphates was only ~50% and therefore was not suitable for on-line analysis of organic phosphonates.

Currently there are a number of commercialized on-line analyzers for measurement of TP on the market, including HACH Phosphax Sigma [20] from USA, WTW TresCon P511 [21] from Germany, SHIMADZU TP-4210 [22] from Japan. These analyzers are mainly used for monitoring TP levels in natural water or wastewater with high accuracy, reliability and stability, but with low sample throughput, a high price and a large size. The above analyzers are designed to analyze environmental water samples with complicated matrices and wide TP concentration ranges, but at low sample throughput. The commercially available analyzers use high temperature and high pressure to digest the TP, and then measure the orthophosphate content with the PMB method. If such analyzers were deployed for high-throughput, long-term on-line monitoring, such as in a circulating cooling water system, the long term use at high temperatures and pressures could easily accelerate aging and lead to leakage at their tubing interfaces. Moreover, the reducing reagent, either ascorbic acid or stannous chloride, used in the PMB method would need to be frequently replaced and supplemented due to its poor stability [23] and large consumption in a high sample throughput and long-term continuous monitoring environment.

High-throughput and long-term on-line determination is essential for a factory to control the organic phosphonate concentration in their circulating cooling water. Conventional off-line sampling and analysis methods do not provide real-time measurement data, and existing on-line instruments are not designed and optimized for circulating cooling water. In our previous study [12], an analyzer based on an ultraviolet (UV)-thermal digester and vanadomolybdophosphoric acid (VMP) measurement method was developed, and the TP detection limit was 1.3 μmol L⁻¹, which met most of the monitoring requirements. However, water treatment reagents with low phosphorus contents are being required to protect the environment [4,24]; therefore, the application of current analyzers with higher TP detection limits are limited. On the other hand, as the shortage of water resource increases, raw water used in industrial cooling water systems may be taken from sources with a high salt content, and a large amount of boiler water or treated water from sewage treatment plants may also be added to the circulating cooling water. These raw water sources increase the Cl⁻ concentration

in the cooling water, sometimes upwards of hundreds of mg L⁻¹. High Cl⁻ concentrations greatly interfere with the digestion processes that use neutral potassium persulfate, such as those widely used in on-line analyzers.

In response to the challenges from both the environment protection and factory needs, this study aimed to improve the efficiency of an on-line digester that lowered the limit of detection and expanded the range of TP determination in circulating cooling water. This study also sought to find an effective phosphonate digestion method suitable for high Cl⁻ content water by means of improving the digestion formula. In this study, the typical reagent 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTCA), was selected as the representative phosphonate. Several advanced and well-suited methods and techniques to address these challenges were integrated and optimized to build a low-cost on-line automatic TP analyzer, including alkaline potassium persulfate digestion with a low-power ring-shaped UV on-line digester, flow batch analysis [25], VMP measurement mode, and dual spectrophotometers [26] in series. The developed analyzer was used in an open circulating cooling water system in a natural gas purification plant to perform continuous on-line monitoring of TP for 12 d with a measurement frequency of once per hour. At random times, water samples also were collected and analyzed by the factory laboratory using their conventional method.

2. Design of the analyzer

2.1. Overview of the analyzer components and analytical process

The TP analyzer included three modules: a sample pretreatment module, a reaction and determination module, and a human-computer interaction module, as shown in Fig. 1. The sample pretreatment module was tasked with injecting the sample and digestion reagent, and then performing the chemical digestion and de-bubbling the liquid. The reaction and determination module used batch flow analysis and a detector composed of dual spectrophotometers in series to analyze the orthophosphate in the digested sample. The human-computer interaction module realized the automatic control of the analyzer components and data acquisition, processing and display. With the exception of the personal microcomputer used for data processing and display, all other components of the analyzer were installed in a modified JXF base box (JXF-3040/20, Guokong Electric, China), with an external dimension of 40 × 30 × 20 cm. The total weight of the analyzer was approximately 5 kg.

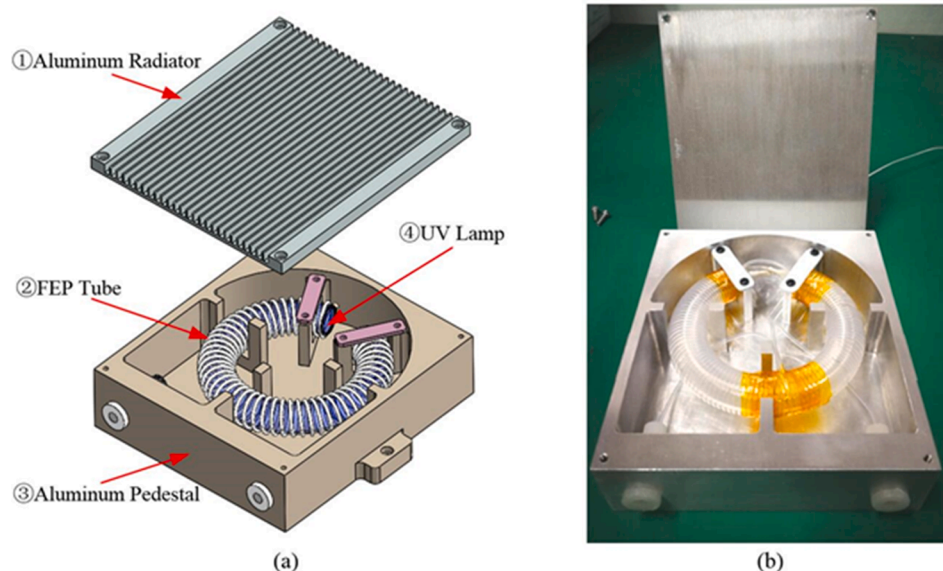


Fig. 2. Structure diagram (a) and photo (b) of the ring-shape UV on-line digester.

The on-line analysis consisted of two main steps: (1) TP digestion and (2) determination of the orthophosphates concentration. The sample was first mixed with the digesting reagent and sent into a home-made UV digester by a peristaltic pump (PP) for TP decomposition. The solid particles and bubbles were then removed from the digested sample by a debubbler (DB). The digested sample and the mixed color developing reagent (MR) were drawn into a syringe in turn using a multi-position selection valve and a syringe pump (SP). Sample mixing with the digesting reagent and the subsequent reaction were completed in the mixing chamber (MC). Finally, the sample solution was sent into the home-made dual-spectrophotometer detector for the determination of the absorbance. Detailed steps of the digestion and determination can be found in Table S1 in the [Supplementary Materials](#).

2.2. Sample pretreatment module

In our previous study [12], three digestion models, UV photooxidation, thermal digestion and UV-thermal digestion, were compared. Based on the previous results, UV digestion model was selected and a compact UV digester was designed in this study. As shown in Fig. 1, two three-way solenoid valves (103T3MP, Bio-Chem Valve, USA) (V1 and V2) were used to select one of the three solutions, sample (S), certified standard (Std), or cleaning solution (CS). Sample and digesting reagent were delivered by a two-channel peristaltic pump (Minipump, Baoding Shenchen, China) (PP), mixed through a Tee, and the digestion took place in a home-made ring-shape UV on-line digester (volume 3.93 mL). The debubbler (DB) was made of PTFE material, together with a two-way solenoid valve (100T2NC, Bio-Chem Valve, USA) (V3), and used for removing bubbles, splitting extra solution and discharging solid particles.

Components of the UV digester included a specialized ring-shape (90 mm o.d.) UV lamp with a wavelength of 254 nm (10 W, UVCN, China), a transparent vinyl fluoride (FEP) tube (1.0 mm i.d., 5.0 m long, JR-T-6806-M5, VICI, USA) wrapped around the lamp, a pedestal and a radiator made of aluminum. The configuration of the UV digester is shown in Fig. 2.

2.3. Reaction and determination module

Flow injection analysis was utilized in a previous study for its simple manifold and high analysis speed. In order to improve the digestion efficiency, enhance the detection sensitivity, and expand the

determination range, a flow batch technique was instead adopted in this study. After digestion, the sample was well mixed with the color developing reagents and the reaction was completed. The analysis speed was about 8 min per sample, which was slower than the 3 min reported for the previous method, but still fully meets the monitoring needs.

The core component of the reaction and determination module was a programmable bidirectional injection pump with an 8-position selection valve (Smart SY-01, Runze Fluid, China) and a home-made spectrophotometric detector. The operation of the injection pump is described in Table S1. The pump was equipped with a 2.5 mL airtight syringe (XP, ILS, Germany), and the flow rate precision was better than 0.3%. The common port of the selection valve was connected to the syringe, while the other ports were connected to the sample, reagent, cleaning solution, mixing chamber, detector and waste container, respectively. By switching the valve position and selecting the syringe flow direction, a designated volume of sample or reagent could be pumped into or out of the syringe. The mixing chamber was made of PTFE with effective volume of approximately 3 mL.

In order to expand the determination range of phosphonates, a dual-spectrophotometer detector was designed in this study. As shown in Fig. 1, the detector consisted of two spectrophotometers in series. The spectrophotometers had Z-type flow cells of 3 cm and 5 cm (1.5 mm i.d.), respectively. The two spectrophotometers, which were used for the quantification of orthophosphates in different concentration ranges, could simultaneously determine the absorbance of the VMP reaction product. The detection wavelengths of the two spectrophotometers were selected based on the previous study [12]. The spectrophotometer having 3 cm cell and 405 nm wavelength was for detection of orthophosphates at high concentration, while the other one having 5 cm cell and 375 nm wavelength was for low concentration. Monochrome LEDs were used as light sources, with peak wavelengths of 405 nm (UV5TZ-405-15, BIVAR, USA) and 375 nm (NS375L-5CLA, NITRIDE, Japan), respectively. High sensitive digital converters TSL2581 (TSL2581NF, TAOS, USA) were used as photoelectric sensors.

2.4. Human-computer interaction module

The human-computer interaction module was composed of a measurement application program written in the LabVIEW virtual instrument development platform (2017, NI, USA) and an embedded control system. The application program ran on a host processor (a personal computer or tablet) and could be connected to the embedded controller

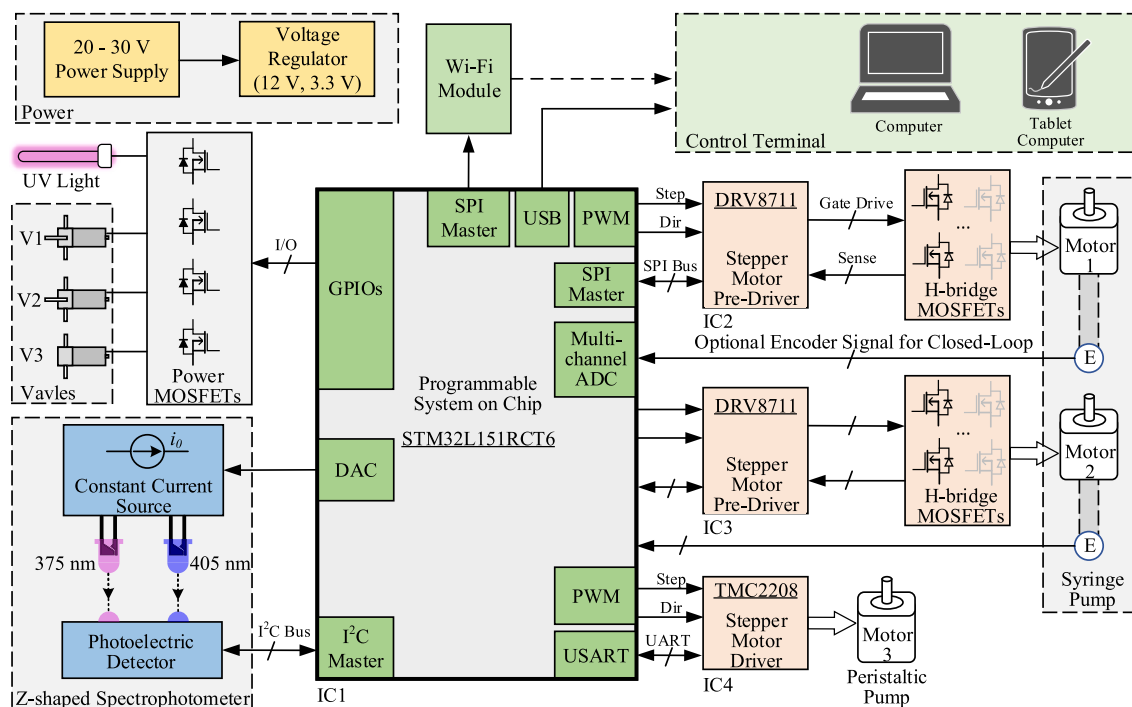


Fig. 3. Schematic diagram of the embedded control system.

via Wi-Fi or a USB port for sending instructions and receiving data. Combined with the embedded control unit, the host processor running the measurement application program could automatically control the processes of sampling, digestion, mixing, and detection and real-time analyze the resulting data.

A home-made embedded control system was adopted, which had functions to decode instructions, control equipment, acquire data and process signals. A photo of the hardware circuit of the home-made embedded control system is provided in Fig. S1. The hardware was based on an ultra-low power ARM microprocessor (STM32L151RCT6, ST, Switzerland). In addition to the ARM microprocessor, the system also consisted of a multiple output DC-DC isolated power supply, Wi-Fi communication circuitry, a solenoid valve powered amplifier circuit using MOSFETs, and a microstepping driver circuit for the stepper motors of the syringe pump and the peristaltic pump, as shown in Fig. 3. The detailed circuit diagram of each component is shown in the Supplementary Materials (Figs. S2-S6).

The firmware executed on the ARM microprocessor was written in C and provided functional control of each system component during the automatic operation. The firmware was based on a configured event-driven state machine. Firstly, the microprocessor obtained the control instructions from the host computer through a wireless or wired connection established via Wi-Fi or a USB, respectively. Secondly, according to the instructions, the microprocessor performed the tasks in a loop as follows: (1) controlling the status of UV lamp and solenoid valves (V1, V2 and V3) through the I/O port and power amplifier circuit; (2) rotating the stepper motor of the syringe pump and the peristaltic pump with microstepping driver circuit at a desired number of steps and speed; (3) adjusting the LED radiation intensity by changing the DAC output voltage and controlling the current of the constant current source; and (4) collecting the real-time signal of the light intensity using the I²C bus protocol from the photoelectric sensor TSL2581, and then sending it to an upper computer where the application program was performed.

3. Materials and methods

3.1. Reagents and materials

All the reagent solutions used in the study were prepared with analytical pure chemicals (Sinopharm Chemical Reagent Co., China) and ultra-pure water (resistivity $\geq 18.2 \text{ M}\Omega \text{ cm}$, Milli-Q Element system, USA), unless specially noted. Phosphate standard stock solution (10 mmol L^{-1}) was prepared by dissolving 1.3609 g potassium dihydrogen phosphate (KH_2PO_4 , dried at $110 \text{ }^\circ\text{C}$ dry for 2 h) in 1000 mL ultra-pure water, and stored in a $4 \text{ }^\circ\text{C}$ while not in use. Phosphate standard working solutions were obtained from the proper dilution of the stock solution. Standard stock solution ($2.44 \pm 0.02 \text{ mol L}^{-1}$) and certified standard ($100.0 \pm 0.5 \text{ }\mu\text{mol L}^{-1}$) of PBTCa were kindly provided by Shanghai Emperor of Cleaning Hi-tech. Neutral solution and alkaline solution of potassium persulfate, named as neutral oxidizing reagent (NOR) and alkaline oxidizing reagent (AOR), were prepared by dissolving 4.0 g and 30.0 g potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$, Alfa Aesar, UK) in 1000 mL ultra-pure water and 1000 mL 0.40 mol L^{-1} sodium hydroxide (NaOH) solution, respectively. The solutions should be stored in brown bottles and kept in dark. Mixing reagent (MR) for color developing was obtained as the following steps: 300 mL 33.3 mmol L^{-1} vanadomolybdophosphoric acid (VMP) solution was slowly mixed with 333 mL hydrochloric acid (HCl, 37 wt%) solution, cooling to room temperature, then added with 300 mL 66.7 mmol L^{-1} ammonium molybdate solution, and finally diluted to 1000 mL with ultra-pure water. The cleaning solution (CS) was 0.1 mol L^{-1} HCl solution. Solutions containing Mg^{2+} , Ca^{2+} , SO_4^{2-} , Cl^- for interference test were obtained from solid chemicals magnesium sulfate (MgSO_4), calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), sodium sulfate (Na_2SO_4) and sodium chloride (NaCl), respectively.

The manifold tubings were 0.75 mm Teflon (PTFE) tubings (JR-T-4036-M25, VICI, USA), and connected using standard $1/4$ -28 polypropylene (PP) fittings (CFL-1BK, VICI, USA).

3.2. Digestion efficiency optimization

The sample digestion efficiency greatly affects the analytical

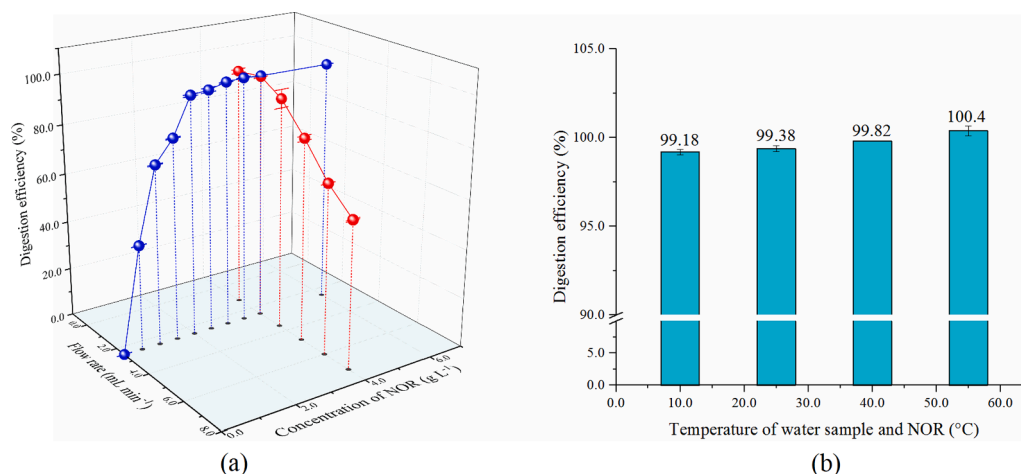


Fig. 4. Effects of NOR concentration and total flow rate (a) and temperature of water sample and NOR (b) on digestion efficiency of PBTCA ($100 \mu\text{mol L}^{-1}$, $n = 3$).

accuracy of the TP detection. A previous study [12] showed that the combined oxidation system of UV light and a persulfate can effectively convert PBTCA into orthophosphate, and the photoreaction time and reagent concentration are determining factors of the digestion efficiency. In addition, the reaction temperature has a positive effect on the digestion efficiency. Since the temperature of industrial cycle cooling water varies with time, the sample temperature is also a factor to consider when optimizing the digestion parameters.

The effects of the photoreaction time, concentration of potassium persulfate and sample temperature were examined in this study. The photoreaction time in the UV reactor could be adjusted three ways: (1) by changing the speed of the peristaltic pump to control the sample flow rate in the reaction tube; (2) by adjusting the length of the reaction tube on the ring-shape UV lamp; and (3) by controlling the stop-flow time of the sample in the UV reactor. In the present system, the UV reactor was a specialized device and it was not easy to change the length of reaction tube, and stopping the sample flow could lead to the accumulation of micro particles and block the sample tube. Therefore, the sample flow rate was selected as the control parameter to adjust the photoreaction time.

3.3. On-site application arrangement

To assess the performance and practicality of the TP analyzer, the analyzer was installed on a cycle cooling water system at a natural gas purification plant in Sichuan Province, China, to on-line monitor the TP concentration from November 24 to December 6, 2019. On-site photos are provided in Fig. S7. On-line analysis was performed once every hour during the continuous monitoring period of 12 d. A quality control sample was used to evaluate the accuracy of the on-line measurements. The plant analyst collected discrete water samples every morning and evening over the 12 d period and determined the TP concentration using the standard high temperature/pressure digestion method [5] and the conventional PMB method with a spectrophotometer (UV-1780, SHIMADZU, Japan) in the factory laboratory. The results of this manual analysis were compared with the results from the on-line analyzer.

4. Results and discussion

4.1. Optimization of digestion parameters

Some pre-experiments were carried out to study the effects of the NOR concentration, total flow rate of the sample and the NOR, and the temperature of the sample and digesting solutions on the digestion efficiency of $100 \mu\text{mol L}^{-1}$ PBTCA. Based on the preliminary results, those parameter effects on the digestion efficiency were further investigated,

and the results are given in Fig. 4.

As seen from Fig. 4a, there is a positive correlation between the NOR concentration and the PBTCA digestion efficiency. It is reported that persulfate can be converted to a sulfate radical ($\text{SO}_4^{\cdot-}$, $E^0 = 2.65\text{--}3.10 \text{ V}$ [27]) and a hydroxyl radical ($\text{OH}\cdot$, $E^0 = 2.70\text{--}2.80 \text{ V}$ [28]) under UV radiation [29]. Both radicals are strong oxidants for the decomposition of phosphonates such as PBTCA. However, this study found that when the NOR concentration was higher than 3.0 g L^{-1} , the digestion efficiency did not increase further. Huang et al. [30] also reported that using high concentrations of persulfate to digest samples did not improve the recovery rate of organophosphorus. In addition, persulfate can decompose and produce H^+ , which reduces the pH of the solution [31,32]. Therefore, to ensure that the phosphonates were effectively digested and that the pH of the digested solution was in the proper range for the subsequent color developing reaction, the NOR concentration was set to 4.0 g L^{-1} .

Fig. 4a also shows the effect of the total sample and NOR flow rate on the digestion efficiency. When the sample and digesting reagent were mixed and flowed into the UV digester, the slower the total flow rate, i.e. the longer the UV radiation time, the higher the efficiency of the PBTCA decomposition. At a low flow rate, the decomposition efficiency reached a plateau, which was consistent with previous findings of Xu et al. [33]. A total flow rate of 2.5 mL min^{-1} (sample flow rate of 2.0 mL min^{-1} and digestion reagent flow rate of 0.5 mL min^{-1}) was selected, thus the retaining time of the mixture in the UV digester was 94 s and the digestion efficiency of PBTCA was as high as 100%. The selected total flow rate ensured a smooth discharge of solid particles in the debubbler, while also providing a proper flow for subsequent spectrophotometric detection which required a flow rate of 1.8 mL min^{-1} . The experimental results showed that PBTCA could also be decomposed by UV radiation without added oxidants, but the efficiency was only 1.1% within 94 s, which was also consistent with results of Xu et al. [33].

The temperature of the sample and digesting reagent was controlled by a water bath or an ice bath, and the effect of the temperature on the digestion efficiency of PBTCA was studied. Fig. 4b shows the results. As sample and reagent temperatures increased, the digestion efficiency increased slightly; however, even if the temperature was as low as 10°C , the digestion efficiency was still close to 100%. Accordingly, a temperature controller was not necessary in the analyzer.

4.2. Effects of chloride and other common foreign ions in cooling water on the digestion efficiency

The effects of the four most common ions in circulating cooling water systems on the digestion efficiency were examined using the NOR digesting reagent. Since $100 \mu\text{mol L}^{-1}$ PBTCA was not well digested in

Table 1

Tolerated concentration of four common ions in determination of PBTCA (10 $\mu\text{mol L}^{-1}$) and their maximum regulated concentration.

Interference ion	Tolerated concentration (mg L^{-1})	Maximum regulated concentration (mg L^{-1}) [34]
Ca^{2+}	> 200	200
Mg^{2+}	> 600	600
SO_4^{2-}	> 1800	1800
Cl^-	< 200	700

the presence Cl^- , 10 $\mu\text{mol L}^{-1}$ PBTCA was used in these tests. The four ions tested and their concentration ranges were: Ca^{2+} , 0–200 mg L^{-1} ; Mg^{2+} , 0–600 mg L^{-1} ; SO_4^{2-} , 0–1800 mg L^{-1} ; Cl^- , 0–700 mg L^{-1} . The tolerated concentration of each ion and the maximum concentration regulated for industrial circulating cooling water are listed in Table 1.

The data in Table 1 indicate that the three common ions, Ca^{2+} , Mg^{2+} and SO_4^{2-} , at the maximum regulated concentrations did not significantly affect the PBTCA analysis. However, the presence of Cl^- ions had a significant effect. Zhang et al. [35] found that the UV-persulfate oxidation system was severely inhibited by Cl^- , which reduced the oxidation rate and efficiency of organic compounds.

4.3. The effect of high chloride ion concentrations and its elimination

Previous studies [36,37] have found that persulfates are converted to $\text{SO}_4\cdot^-$ in acidic and neutral solutions, while in alkaline solutions, the $\text{SO}_4\cdot^-$ reacts with OH^- to produce $\text{HO}\cdot$ radical. This study showed that even though both radicals are effective reagents for oxidation and digestion of PBTCA, their oxidation properties are very different in the presence of Cl^- . Under acidic condition and in the presence of Cl^- , $\text{SO}_4\cdot^-$ reacts with Cl^- which greatly hinders subsequent oxidation and degradation of organic materials. On the other hand, the consumption of $\text{HO}\cdot$ by Cl^- is too low in alkaline solutions to affect the oxidation [35,38]. That is, an AOR can maintain its strong oxidation performance in presence of large amounts of Cl^- . The results of Guo et al. [39] also showed that UV and alkaline conditions have a synergistic effect on the production of $\text{HO}\cdot$, and the combination of the two can effectively improve the digestion of organic compounds. In this study, the effect of Cl^- concentration on PBTCA digestion efficiency in NOR and AOR solutions was examined. Fig. 5 shows the effect of the Cl^- concentration on digestion efficiency of 10 $\mu\text{mol L}^{-1}$ PBTCA using NOR.

As shown in Fig. 5a, with 4.0 g L^{-1} NOR the digestion efficiency of PBTCA decreased with increasing Cl^- concentration. At a Cl^- concentration of 200 mg L^{-1} , the digestion efficiency was less than 95% and reached the maximum allowable deviation. If the concentration of Cl^-

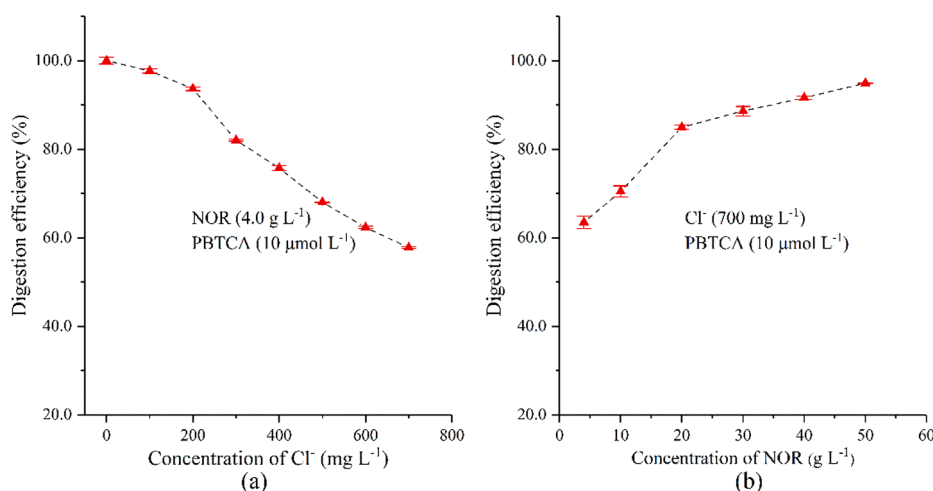


Fig. 5. Effects of Cl^- concentration (a) and NOR concentration (b) on digestion efficiency of PBTCA (10 $\mu\text{mol L}^{-1}$) in neutral solution ($n = 3$).

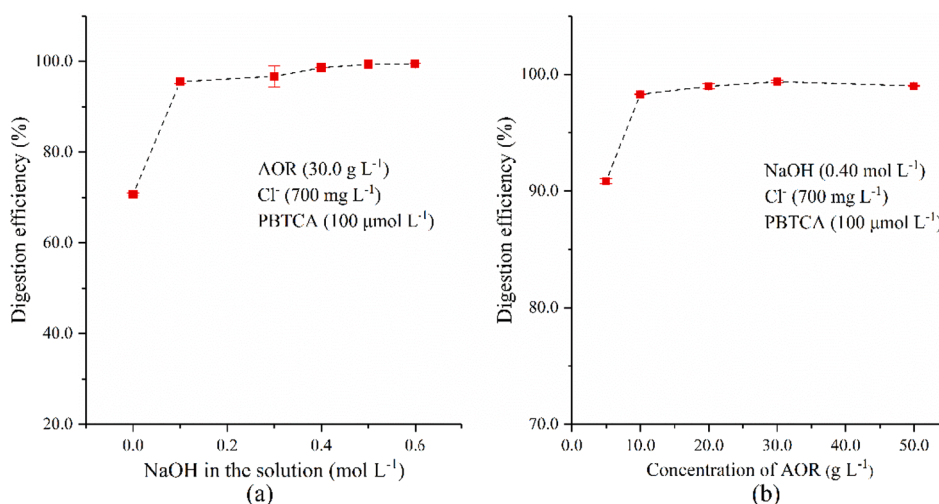


Fig. 6. Effects of NaOH (a) and AOR concentration (b) on digestion efficiency of PBTCA (100 $\mu\text{mol L}^{-1}$) at presence of high Cl^- concentration (700 mg L^{-1}) in sample ($n = 3$).

Table 2
Performance of the analyzer.

Item	Result		
Linearity (at 375 nm, range 0–40 $\mu\text{mol L}^{-1}$)	$A_1 = 0.0197C_1 + 0.2260$ ($R^2 = 0.9999$, $n = 9$)		
Linearity (at 405 nm, range 10–100 $\mu\text{mol L}^{-1}$)	$A_2 = 0.0066C_2 + 0.0474$ ($R^2 = 0.9994$, $n = 6$)		
Linearity (at 405 nm, range 10–160 $\mu\text{mol L}^{-1}$)	$A_3 = 0.0061C_3 + 0.0676$ ($R^2 = 0.9969$, $n = 8$)		
LOD (at 375 nm, $3\sigma/s$, $n = 11$)	0.11 $\mu\text{mol L}^{-1}$		
LOQ (at 375 nm, $10\sigma/s$, $n = 11$)	0.36 $\mu\text{mol L}^{-1}$		
Relative standard deviation ($n = 11$)	3.20% (4.0 $\mu\text{mol L}^{-1}$); 0.83% (60 $\mu\text{mol L}^{-1}$)		
Accuracy	Certified value of a standard	Measured value	t-test ($n = 5$)
	100.00 \pm 0.50 $\mu\text{mol L}^{-1}$	99.89 \pm 0.07 $\mu\text{mol L}^{-1}$, $n = 5$	t-value = 0.18, t-threshold value = 2.78
Tolerated Cl^- concentration	neutral oxidizing reagent	200 mg L^{-1}	
	alkaline oxidizing reagent	700 mg L^{-1}	
Sampling frequency	8 samples h^{-1}		
Volume of reagent consumed per sample	3.25 mL NOR/AOR; 155 μL MR		
Cost	Less than 2200 US\$		
Size and weight	40 \times 30 \times 20 cm; 5 kg		

was 700 mg L^{-1} , the efficiency was further reduced to 60%. Figs. 5b and 4a indicate that increasing the NOR concentration would improve the digestion efficiency of PBTCA. However, when the Cl^- concentration was 700 mg L^{-1} (Fig. 5b), even if the NOR concentration was as high as 50 g L^{-1} , the digestion efficiency of the PBTCA was only 94.9%.

On the other hand, AOR might solve the problems caused by Cl^- and improve the oxidation of the phosphonates. The effects of NaOH addition and AOR concentration on the digestion efficiency of 100 $\mu\text{mol L}^{-1}$ PBTCA at a high concentration of Cl^- (700 mg L^{-1}) were studied, and the results are presented in Fig. 6. In Fig. 6a, the concentration of NaOH in the AOR was 0.00, 0.10, 0.30, 0.40, 0.50 and 0.60 mol L^{-1} , and the corresponding pH was 7.0, 13.0, 13.5, 13.6, 13.7 and 13.8, respectively. The results in Fig. 6a indicate that even though the Cl^- concentration was as high as 700 mg L^{-1} , a near 100% digestion efficiency of 100 $\mu\text{mol L}^{-1}$ PBTCA could be reached if 30 g L^{-1} AOR mixture (0.40 mol L^{-1} NaOH) was used as the digesting reagent. Fig. 6b shows the effects of AOR concentration on the digestion efficiency of PBTCA. It was

found that with 700 mg L^{-1} Cl^- , a higher concentration of AOR was needed to maintain a 100% digestion efficiency. Finally, 30 g L^{-1} AOR was selected as optimal concentration.

Therefore, when the concentration of Cl^- in circulating cooling water is relatively low (0–200 mg L^{-1}), a NOR reagent with potassium persulfate concentration of 4.0 g L^{-1} can be used for the digestion reaction. When the concentration of Cl^- in the water is high (200–700 mg L^{-1}), a 30 g L^{-1} AOR with 0.40 mol L^{-1} NaOH is suggested. In practice, it is recommended to select the digesting reagent according to the concentration of Cl^- in the water system, to save the reagent and reduce wastewater pollution.

4.4. Performance of the analyzer

Using the optimized parameters, determination of the linearity, limit of detection (LOD), limit of quantitation (LOQ), precision, accuracy and sample throughput of the analyzer were evaluated, and the results are listed in Table 2. The LOD and LOQ were calculated as $3\sigma/s$ and $10\sigma/s$ [40], respectively, where σ is the standard deviation of 11 measured absorbance values of a blank sample of ultra-pure water, and s is the slope of the calibration curve.

From Table 2 it can be found that although the calibration curve obtained at 375 nm has a higher intercept that indicates a higher reagent blank than the calibration curve at 405 nm, it also has a higher slope that shows a higher detection sensitivity. Therefore, the calibration curve at 375 nm is more suitable for accurately quantifying low concentration of phosphonates (0–40 $\mu\text{mol L}^{-1}$), while the curve at 405 is more suitable for high concentration of phosphonates (10–100 $\mu\text{mol L}^{-1}$). Even if the phosphonate concentration is as high as 160 $\mu\text{mol L}^{-1}$, the analyzer can still provide a satisfactory result. When measuring the absorbance, the analyzer microcontroller first collects the signal intensity at 405 nm, calculates the TP concentration based on the calibration curve $A_3 = 0.0061C_3 + 0.0676$, and then determines the appropriate concentration range. Afterwards, according to the selected range the microcontroller automatically acquires the absorbance measured at the corresponding wavelength and calculates the concentration with the corresponding calibration curve for a more accurate quantification.

4.5. Application of the analyzer

The long-term data recorded by the plant suggested that the Cl^- concentration in the circulating cooling water was about $100 \pm 20 \text{ mg L}^{-1}$. Therefore, the NOR at a concentration of 4.0 g L^{-1} was used as the digesting reagent. During the field application, the TP analyzer ran continuously for almost 12 d without any outside monitoring or

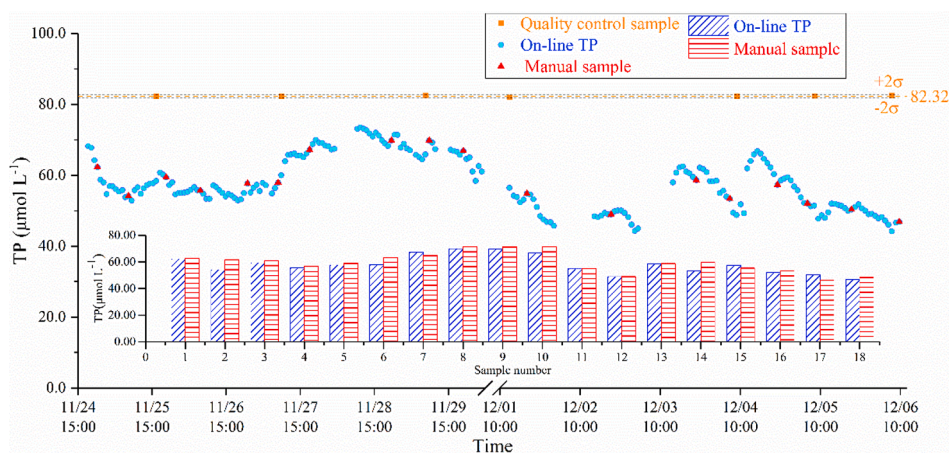


Fig. 7. Field measurement data of the on-line TP analyzer. The blue circles represent the data measured by the analyzer; the orange squares are data of the quality control sample (TP concentration 82.25 $\mu\text{mol L}^{-1}$) measured by the analyzer, of which the mean is 82.32 $\mu\text{mol L}^{-1}$ and σ is the standard deviation; the red triangles are data of the manually collected sample measured in the laboratory; and the inserted figure is the comparison of the two analytical methods for 18 samples.

maintenance.

During the 12 d monitoring period, 279 valid TP measurements were completed, and the results are shown in Fig. 7. There were four breaks (3:00 to 9:00, 2019-11-28; 2:00, 2019-11-30 to 12:00, 2019-12-1; 3:00 to 13:00, 2019-12-2; and 4:00 to 13:00, 2019-12-3) when the on-line analyzer did not collect a water sample due to a connection problem between the water outlet of the cooling water system and the sample inlet of the analyzer. The TP data during these four breaks are omitted and not shown in Fig. 7.

As can be seen from Fig. 7, the results of the randomly collected quality control samples met the quality control requirements with a standard deviation of less than 3σ , showing good accuracy. As illustrated in Fig. 7, the on-line measurement results of the analyzer were consistent with those of the discrete samples collected at the corresponding time and analyzed by the factory laboratory using a standard digestion method and conventional PMB detection method. The *t*-test of the two method results showed no statistically significant difference ($p = 0.05$, $n = 18$). In addition, among the 279 valid data ($44.21\text{--}73.49 \mu\text{mol L}^{-1}$, mean $\pm 1 \text{ SD} = 57.95 \pm 7.32 \mu\text{mol L}^{-1}$) obtained by the analyzer, 122 data (43.7%) exceeded the regulated TP concentration ($5\text{--}9 \text{ mg PO}_4^{3-} \text{ L}^{-1}$, i.e., $52.71\text{--}94.88 \mu\text{mol L}^{-1}$) while only 4 data (22.2%) among the discrete samples did not meet the requirement. It can be clearly seen that the developed on-line analyzer not only fully automates the analysis, but also has a much higher time resolution than the conventional discrete sample analysis method and can quickly detect any change in the TP concentration in the cooling water.

5. Conclusion

Due to the needs for environmental protection of water, corrosion inhibitors used in industrial circulating cooling water will be formulated with low phosphorus contents. Also, making full use of water resources sometimes means that the circulating cooling water is mixed with raw and secondary waters containing a high Cl^- content. In order to increase the detection sensitivity and expand the detection range, this study combined on-line UV digestion and flow batch analysis equipped with a dual-spectrophotometer detector. Meanwhile, the digesting reagent was studied and optimized to eliminate the negative effects of Cl^- ions on the digestion efficiency. Based on the above study results, an on-line TP analyzer was successfully developed to meet the needs for determining the phosphonate concentration in industrial circulating cooling waters with low phosphorus and even phosphorus-free formulations and with different Cl^- contents. Successful field application has shown that the analyzer was capable of measuring the TP content in harsh industrial environments with high sample throughput, high accuracy and automation. Compared with other commercial TP analyzers, the developed analyzer has the advantages of low cost, small size, anti-bubble interference, and high reagent stability. The analyzer can then be coupled with a phosphonate supplement device to establish a more intelligent dose adjustment and TP control system by means of a fuzzy PID [41], rule-based expert system [42], machine learning [43] and other advanced control techniques, to enhance water usage efficiency and reduce wastewater pollution.

CRedit authorship contribution statement

Jin Xu: Writing - original draft, Methodology, Investigation. **Heng Li:** Validation. **Xiaochang Zhang:** Software. **Ting Wang:** Visualization. **Yongming Huang:** Resources. **Dongxing Yuan:** Writing - review & editing, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.measurement.2021.109351>.

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