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ORIGINAL PAPER

Automatic Determination of Water Hardness by Vector Colorimetry with Acid Chrome Blue K

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Abstract

Based on the Mg^{2+} complexation with acid chrome blue K (ACBK) at pH 10.2, an automatic system was designed to determine total hardness of water. The system consists of a vector colorimeter, a multi-channel sampling pump and both reagents A and B. Two kinds of reagent solutions were prepared and used in this system, i.e., ammoniacal buffer and ACBK—disodium magnesium EDTA solutions. The experimental results of the standard solutions containing 2 and 3 mg/L of total hardness showed that the relative standard deviations (RSDs) were 1.9% and 2.2%, respectively, and the limit of detection (LOD) was only 0.035 mg/L. The detection of four natural water samples showed that the recoveries were between 85.0% and 108.6%, consistent with those obtained by ICP-AES method.

Keywords Total hardness · Online automatic detection · Acid chrome blue K · Vector chromaticity measuring device

1 Introduction

Total hardness refers to the total amount of Ca^{2+} and Mg^{2+} in the water, which is one of the important water quality indicators. The water with high hardness will affect the dyeing of textile industrial fabrics [1], blocking boiler pipes [2] and even explosion. Drinking water with high hardness tastes bitter and astringent and may cause digestive disorders [3]. The common methods of water hardness detections include the ethylenediamine tetraacetic acid (EDTA) titration [4, 5], atomic absorption spectrometry (AAS) [6, 7], ICP [8, 9], ion selective electrode method [10] and so on. The EDTA titration is a commonly used traditional method, but it is time-consuming [11], laborious and easy to be interfered by other metal ions. The AAS and ICP methods must be operated by a professional person. Ion selective electrode method has a certain life and easy aging [12]. There are also some quick measurements, such as Serim research's water hardness detection strip and Cole Perlmer's EM Quant total hardness detection [13]. With the development of computer network technology, Europe, US, Japan and other countries have applied the water quality online automatic monitoring system to the actual water quality detection [14]. For example, Hach and YSI have been widely used for online analysis of water quality and pollution events [15]. However, Most of the total hardness online testing equipment is generally heavier, such as Hach EZ5000, which weighs 25 kg, and not easy to achieve portable measurement. Besides, a remote automatic monitoring device has not been developed, which is just necessary for remote areas to detect water quality anytime and anywhere.

Based on the principle that Ca^{2+} and Mg^{2+} can react with acid chrome blue K (ACBK) to form 1:1 red complex [16, 17], an automatic water hardness detection system mainly consisting of a vector colorimeter, multi-channel sampling pump and both reagents A and B was designed. The method has been successfully applied to the determination of total hardness of drinking water, tap water, ground water and surface water. The measurement cycle is only 5 min, and the standard recovery rates are between 84.1% and 109%. The device has the advantages of simple structure, easy operation, accurate measurement results and high efficiency and can meet the need of on-line detection of total hardness of natural water.

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2 Experimental

2.1 Apparatus and Materials

S-4100 UV–VIS spectrophotometer (Scinco, Korea); Agilent 720es ICP-AES (Agilent, USA), smart sy-01 injection pump (Nanjing Runze Fluid Control Equipment Corp., China); GE U1 vector colorimeter (Shanghai GreenEmpire Environmental S&T Corp., China), AL104 electronic analytical balance (Mettler Toledo, Switzerland), pHs-3c pH meter (Shanghai Leici Company, China).

The ammonia-ammonium chloride buffer solutions (Reagent A) were prepared by dissolving 5.4 g of ammonium chloride in 50 mL of deionized water, adjusting pH to 8.5, 9, 9.5, 10, 10.2, 10.4 and 11 respectively by adding ammonia. All the solutions were diluted to 100 mL with the deionized water. The ACBK-only solution was prepared by dissolving 0.0586 g of ACBK in 100 mL of deionized water. Meanwhile, Reagent B was prepared by dissolving 0.0586 g of ACBK and 0.25 g of disodium magnesium EDTA in 100 mL of deionized water. The calcium standard solution (1000 μg/mL Ca^{2+}) was provided by National Nonferrous Metals and Electronic Materials Analysis and Testing Center (China). Mg^{2+}, K^+, Na^+, Fe^{2+}, Al^{3+}, Cr^{3+}, Zn^{2+}, Ni^{2+} and Cu^{2+} standard solutions all in 1000 μg/mL were provided by Shanghai Aladdin Reagent Company. The fluoride standard solution (1000 μg/mL F^-) was provided by Beijing North Weiye Metrology Technology Research Institute.

2.2 Analysis and Method

The vector chromaticity method is based on the vector chromaticity model [18] and uses the hue under the color reaction boundary condition to decompose the chromaticity vector. The color space is represented by lightness L, chromaticity C and hue H. The color sensor can measure the three primary colors of the color developing solution, and then calculate the vector chromaticity of the target color, which can get rid of the wavelength setting and filter components, and eliminate the background interference of the reactants.

The colorimeter is composed of LED light source, sample cell, color sensor, color separation processor, data acquisition and operation circuit, display terminal, etc. The principle is shown in Fig. 1.

2.3 Experimental Device and Components

As shown in Fig. 2, the automatic working system consists of the water and solution bottles (1, 2, 4 and 5), waste liquid tank (3), multi-channel pump (6), LED light source (7), measurement cell (8), color sensor (9), vector colorimeter (11), lithium battery (12) and operation software (10). According to Fig. 2, water sample, Reagents A, B and deionized water all were put into bottles of 100 mL (1, 2, 4 and 5), respectively. The solution bottles and waste liquid tank (3) were connected to the corresponding channels on the multichannel pump (6) with the PTFE pipes (inside diameter of $\phi = 1$ mm). The multi-channel pump (6) was controlled by the software program in the computer (10). The water and reagents (1, 2, 4 and 5) were aspirated into the syringe of 5 mL through the PTFE pipes and then the mixed solution was pushed into the measurement cell (8). The color information of solution was collected by the color sensor (9) and transmitted to the vector colorimeter (11) for calculating the vector colority. From the standard curve, the total hardness of water sample was calculated and displayed. After completion, the waste liquid entered the spent liquor through the PTFE pipe.

The vector colority was an updated concept [18], which was presented based on both the CIE Color Space Model and the spectral correction model. The vector colority indicates the colority fraction of one of two kinds of color substances mixing into a solution. Unlike spectrophotometer, the vector colorimeter (11) uploading the vector colority model uses the LED light source (7) and the color sensor (9) [19], which are not assembled with a monochromator. As a result, the

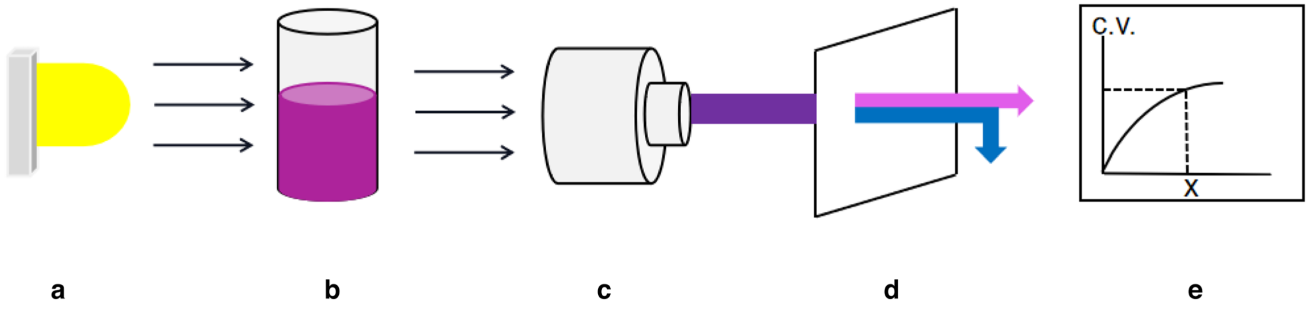


Fig. 1 Schematic diagram of the principle of vector colorimetry. **a** LED light source; **b** sample cell; **c** color sensor; **d** color separation processor; **e** display screen

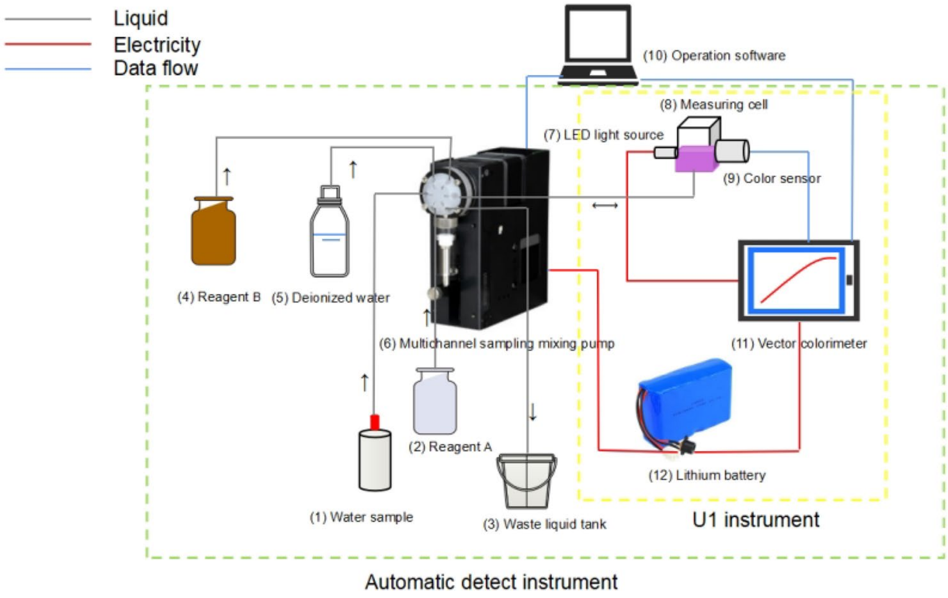
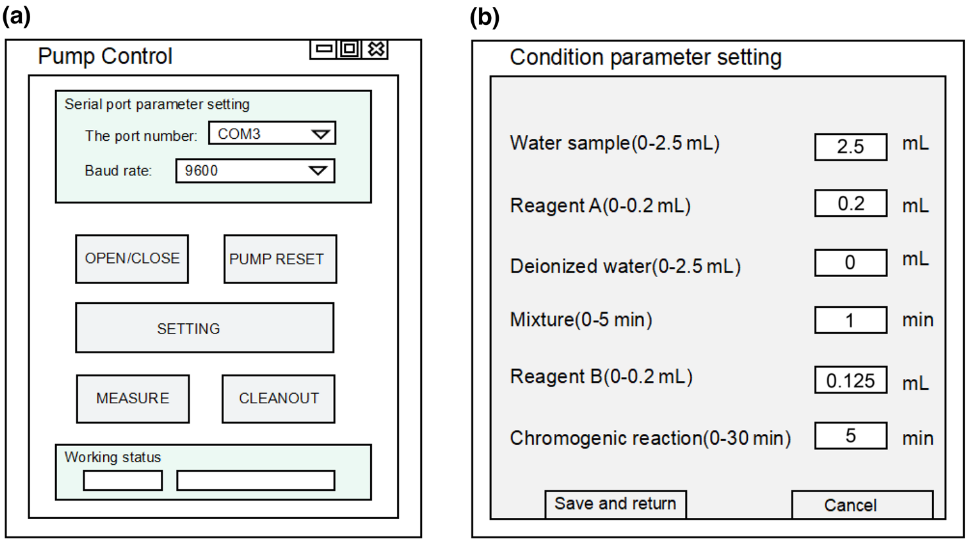


Fig. 2 Schematic diagram of the experimental setup. (1) water sample; (2) reagent A; (3) waste liquid tank; (4) reagent B; (5) Deionized water; (6) Multichannel pump assembling with a syringe of 5 mL; (7) LED light source; (8) Measuring cell; (9) Color sensor; (10) Operation software; (11) Vector colorimeter; (12) Li battery

measurement will be simpler, faster and more convenient than spectrophotometer.

2.4 Operation Procedures

The injection and reaction conditions were controlled by the operation program in the computer (10). According to Fig. 3, the conditions were set up as 9600 baud of baud rate, 0.1 mL of water sample, 0.2 mL of Reagent A, 0.125 mL of Reagent B and 5 min of the reaction time. As shown in Fig. 3, at the beginning, the multi-channel pump was controlled by the operation software to aspirate a certain amount of water sample into the syringe of 5 mL. If the upper limit was exceeded, the water sample would be diluted. After the pump aspirating Reagent A, the solution was pushed into the measurement cell and then aspirated into the syringe of 5 mL. Reagent B was aspirated, and the mixing step was repeated. After 5 min of color reaction, the solution was pushed into the measurement cell. After the measurement with the vector colorimeter completed, the extraction of waste solution was carried out twice. In the first extraction, the syringe and the measurement cell were washed simultaneously by aspirating 5 mL of deionized water. In the second step, the sample residual remaining in the sampling pipeline was washed away by aspirating 0.2 mL of water sample (the sampling pipe volume was between 0.1 and 0.2 mL) and 5 mL of deionized water. Thus, the cross-contamination may be avoided.



Pump Control

Serial port parameter setting

The port number: COM3

Baud rate: 9600

Working status

Condition parameter setting

Water sample(0-2.5 mL) 2.5 mL

Reagent A(0-0.2 mL) 0.2 mL

Deionized water(0-2.5 mL) 0 mL

Mixture(0-5 min) 1 min

Reagent B(0-0.2 mL) 0.125 mL

Chromogenic reaction(0-30 min) 5 min

Fig. 3 Control interface and condition parameter setting window. **a** injection pump setting interface; **b** condition parameter setting interface

3 Results and Discussion

3.1 Absorption Spectra

It is well known that the water total hardness includes mainly Ca^{2+} and Mg^{2+}. They can react with ACBK to form the red complex at pH 10.2. As shown in Fig. 4, curve 1 was not coincided to curve 2 though their water hardness was the same at 5 mg/L $CaCO_3$. It indicated that the sensitivity of both the reactions was different. Mg^{2+} was more sensitive than Ca^{2+} to complex ACBK at pH 10.2. From curves 3 and 4, both of spectra changed near coincidentally when Reagent B was added. It indicated that Mg in disodium magnesium EDTA could be replaced by Ca^{2+} to release the same molar Mg^{2+} into the solution. Therefore, disodium magnesium EDTA must be mixed into the ACBK solution to accurately determine water hardness.

From curve 5, the maximal absorption wavelength of the reagent blank is at 570 nm. From curve 4, the peak and valley of the relative absorbance of the hardness—ACBK solution are at 510 and 590 nm. It indicates that the hardness—ACBK complex is red and the excessive ACBK complex is blue. The partial red chroma of the hardness—ACBK complex in the solution can be calculated by the color-vectorized model [18].

3.2 Effect of pH

The buffer solution (0.4 mL) at pH 8.5–11 and 0.25 mL of Reagent B were added in the solution containing 4 mg/L $CaCO_3$ hardness, then reacted for 5 min. The effect of pH on the absorbance of the solutions measured at 510 and 590 nm was shown in Fig. 5. The interval of the solution's absorbances approached to a constant maximum when pH was more than 10.

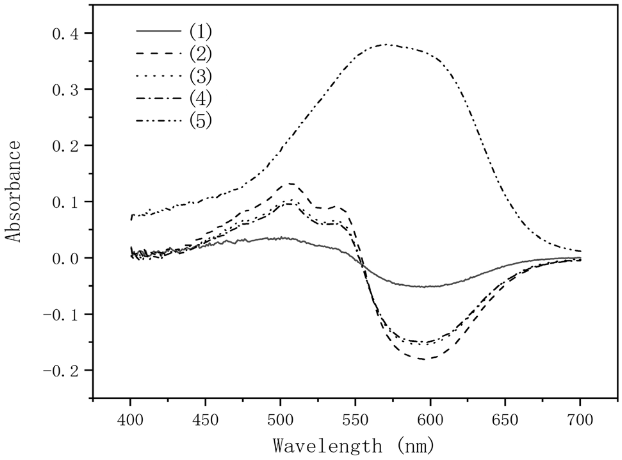


Fig. 4 Absorption spectra of the Ca^{2+} or Mg^{2+} ions—ACBK solution at pH 10.2. (1) the Ca^{2+}—ACBK mixed solution, (2) the Mg^{2+}—ACBK mixed solution, (3) the Ca^{2+}—Reagent B mixed solution and (4) the Mg^{2+}—Reagent B mixed solution. Both (1) and (3) contained 0.05 mmol/L Ca^{2+} and both (2) and (4) contained 0.05 mmol/L Mg^{2+}. (5) the reagent blank, i.e., ACBK-only solution. Solutions (1)–(4) were measured against the corresponding reagent blank and solution (5) against water reference with the UV–VIS spectrophotometer

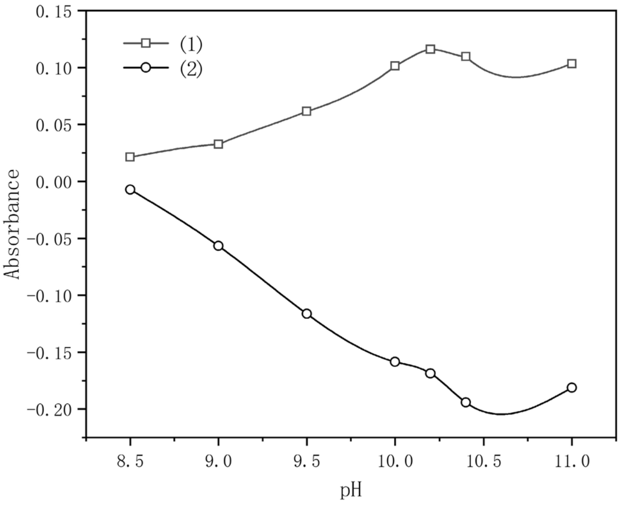


Fig. 5 Effects of pH. (1) 510 nm; (2) 590 nm

3.3 Effect of ACBK

The buffer solution (0.4 mL) at pH 10.2 and Reagent B (0.1–0.35 mL) were added in the solution containing 4 mg/L $CaCO_3$ hardness. The effect of ACBK on the absorbance of the solutions was shown in Fig. 6. The reagent blank (curve 1) increases with the increase of ACBK. From the interval between curve 2 and 3, the relative absorbance of the hardness solution approaches to a constant maximum when Reagent B is more than 0.25 mL. This indicates that all Ca^{2+} and Mg^{2+} react with ACBK. In this work, 0.25 mL of the ACBK solution was added.

3.4 Effect of Reaction Time

0.4 mL of buffer solution (pH 10.2) and 0.25 mL of Reagent B were added into $CaCO_3$ hardness solution of 4 mg/L. The absorbance of the solutions was measured at 510 and 590 nm against the reagent blank from 1 to 30 min of reaction time. The results indicated that the relative absorbance of the hardness solution remained constant after 3 min.

3.5 Analysis of Total Hardness of Standard Solution

The total hardness of standard solution series were 0, 1, 2, 2.5, 3, 4 mg/L. The automatic system and a spectrophotometer were used to measure the colority-vectorized (*c.v.*) and the absorbance of the solutions, respectively. The

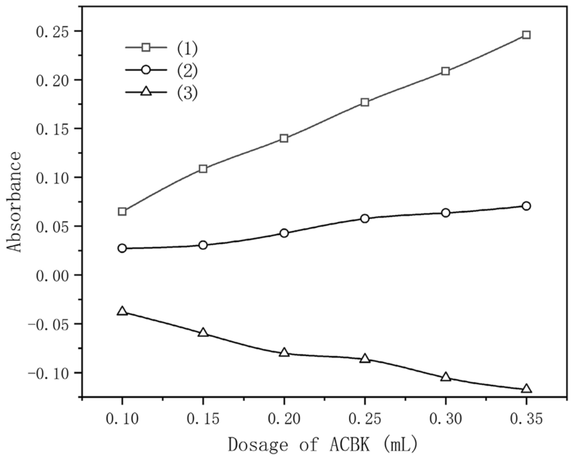


Fig. 6 Effects of ACBK on the Ca-ACBK complexation at pH 10.2. (1) the reagent blank against water measured at 510 nm, (2) 4 mg/L $CaCO_3$ hardness against reagent blank measured at 510 nm and (3) the same as (2) but measured at 590 nm

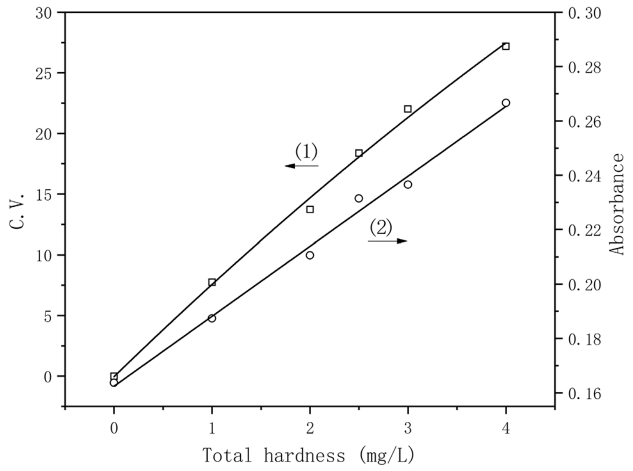


Fig. 7 Standard curves for determination of water total hardness. (1) Automatic measurement and (2) Spectrophotometry at 510 nm

measurement values (y) were given in Fig. 7 and then fitted with the water total hardness (x). The automatic detection method was fitted by a quadratic term with the equation $y = -0.236x^2 + 7.815x - 0.005$ ($R^2 = 0.9983$) and the spectrophotometric method was fitted by linearity with the equation $y = 0.0195x + 0.1478$ ($R^2 = 0.9788$).

The total hardness of 2 and 3 mg/L were prepared and measured in parallel for six times according to the recommended procedures. The relative standard deviations (RSDs) were calculated to be 1.9% and 2.2%, respectively. The limit of detection (LOD), defined as 3 times S_b (standard deviation of 21 blanks) divided by m (slope of standard curve), was calculated to be 0.035 mg/L of total hardness.

3.6 Effect of Interfere Ions

The standard solutions containing 3 mg/L total hardness were prepared with 1000 mg/L of K^+ and Na^+, 0.5 mg/L of Fe^{2+}, Al^{3+}, Cr^{3+}, 0.2 mg/L of Zn^{2+}, Ni^{2+}, 0.1 mg/L of Cu^{2+}, 1 mg/L of F^-, 10 mg/L of NO_3^- and 50 mg/L of SO_4^{2-} were added, respectively. The results showed that the relative error of the total hardness was within ± 10%. Although common metals ions such as Fe^{2+}, Cr^{3+}, Cu^{2+} and Zn^{2+} would react with ACBK, their contents co-existing in natural water were much lower than Ca^{2+} and Mg^{2+}.

3.7 Analysis of Water Samples

Four types of water samples were analyzed according to the recommended method, including mineral water (1#—NONGFU spring water commercially bottled, containing 52 mg/L of total dissolved solid and 11 mg/L of dissolved oxygen, pH 7.52), drinking water (2#—water commercially barreled containing 16 mg/L of total dissolved solid and 13 mg/L of dissolved oxygen, pH 6.97), river water (3#—Huangpu River) and tap water (4#—laboratory). The turbid water samples were pre-filtered with the hole size of ϕ 0.45 μm membrane. The determination results were listed in Table 1. From the total hardness of four water samples determined by the automatic method, the RSDs were 0.8% (1#), 1.4% (2#), 0.8% (3#) and 3.8% (4#), respectively. By comparing this method to the ICP-AES, the relative errors of total hardness were − 4.3% (1#), − 4.7% (2#), − 7.8% (3#) and − 4.5% (4#), respectively. Thus, the measurement deviation of the same samples was less than 5% and the error between two detection methods less than 10%. In addition, the recovery rates of the standard hardness added were between 85.0 and 108.6%. Therefore, the automatic method recommended was accurate and feasible for determination of total hardness in natural water.

4 Conclusion

By designing an on-line automatic monitoring method combining sampling, mixing and measurement, a rapid automatic detection method for total hardness was studied. The quantity and composition of the detection agent were determined through conditional experiments, and the accuracy and precision of the automatic detection method were analyzed. This method has advantages of portability, simple operation, high sensitivity, simplicity and speed, etc., which lays the method foundation for further research and development of a portable automatic online water quality detector.

Table 1 Determination of total hardness in water samples ($n = 3$)

Sample No.	Added (mg/L)	Found (mg/L $CaCO_3$)		RSD(%)	Recovery (%)
		This method	ICP-AES		
1#	0	37.7 ± 0.3	39.4 ± 0.2	0.8	–
	30.0	66.7 ± 0.9	–	–	96.7
2#	0	5.87 ± 0.08	6.16 ± 0.02	1.4	–
	5.00	11.3 ± 0.1	–	–	108.6
3#	0	130 ± 1	141 ± 2	0.8	–
	100	215 ± 4	–	–	85.0
4#	0	105 ± 4	110 ± 1	3.8	–
	100	190 ± 1	–	–	85.0

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Declarations

Conflict of Interest The authors declare that they have no conflicts of interest.

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