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A new strategy for RRS determination of phosphate with bifunctional Fe_3O_4 magnetic nanoparticle surface molecularly imprinted polydopamine probe

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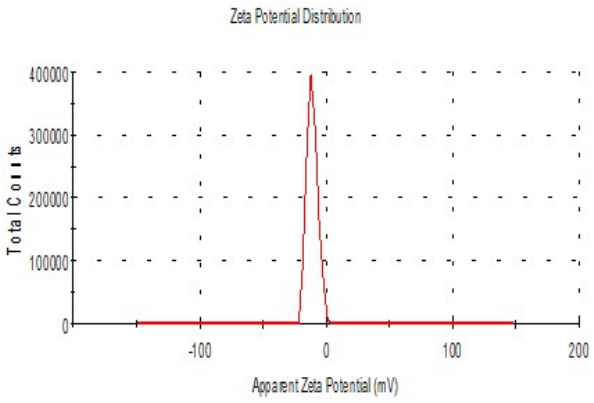
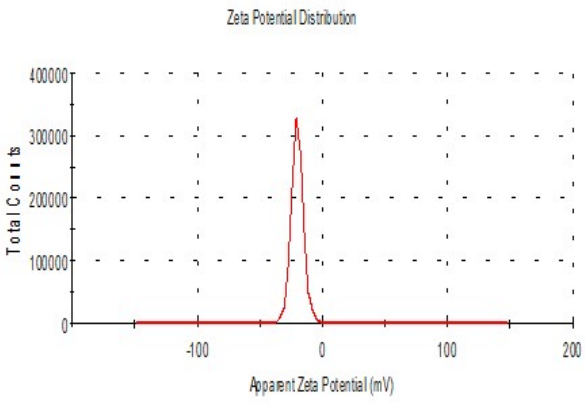




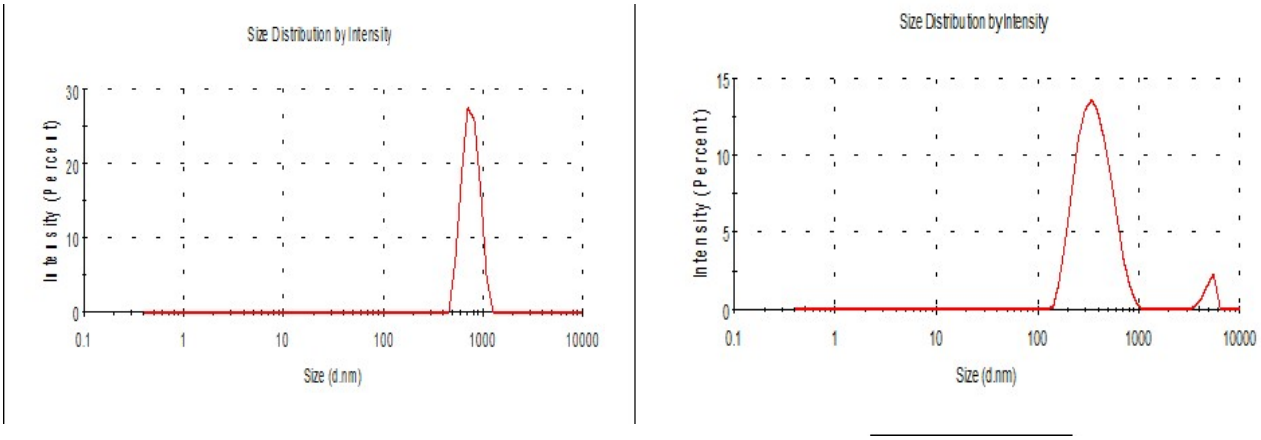


Fig.S1. Fe_3O_4,Fe_3O_4@MIP potential diagram and particle size diagram

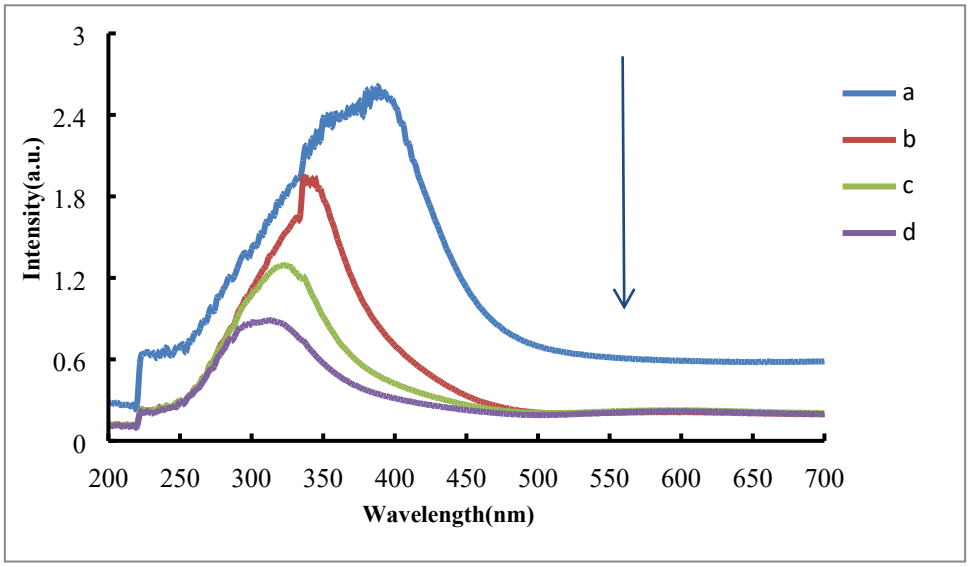


Fig.S2. Fe_3O_4@MIP UV spectrum of the elution templatea: First elution template; b: Second elution template; c: third elution template; d: fourth elution template3.3 RRS and Abs spectra of the Fe_3O_4@MIP- PO_4^{3-}MAS analysis system

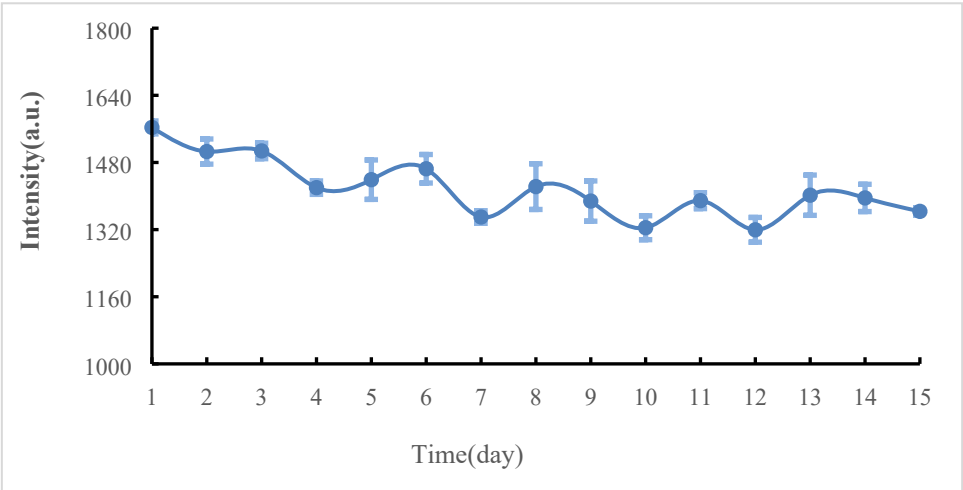


Fig.s3. The stability of Fe3O4@MIP

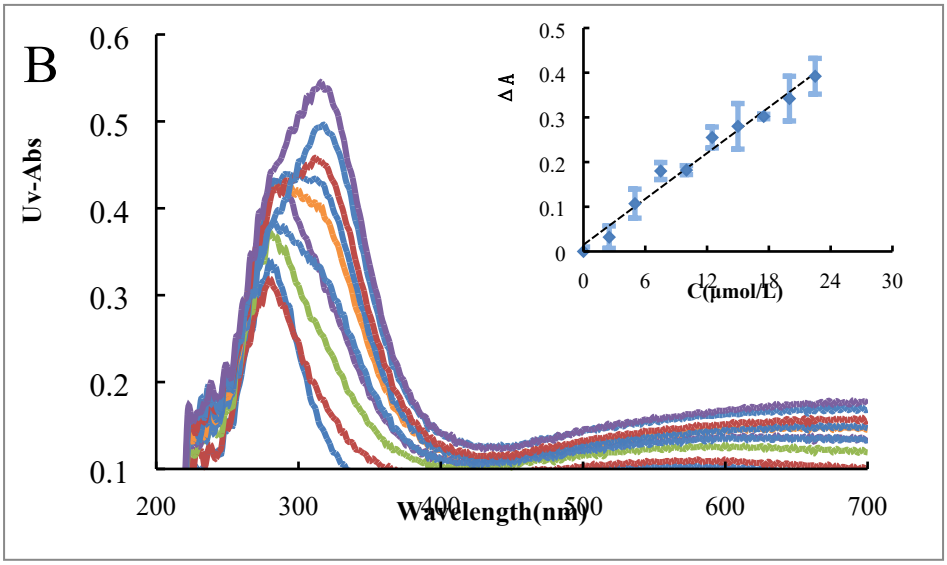
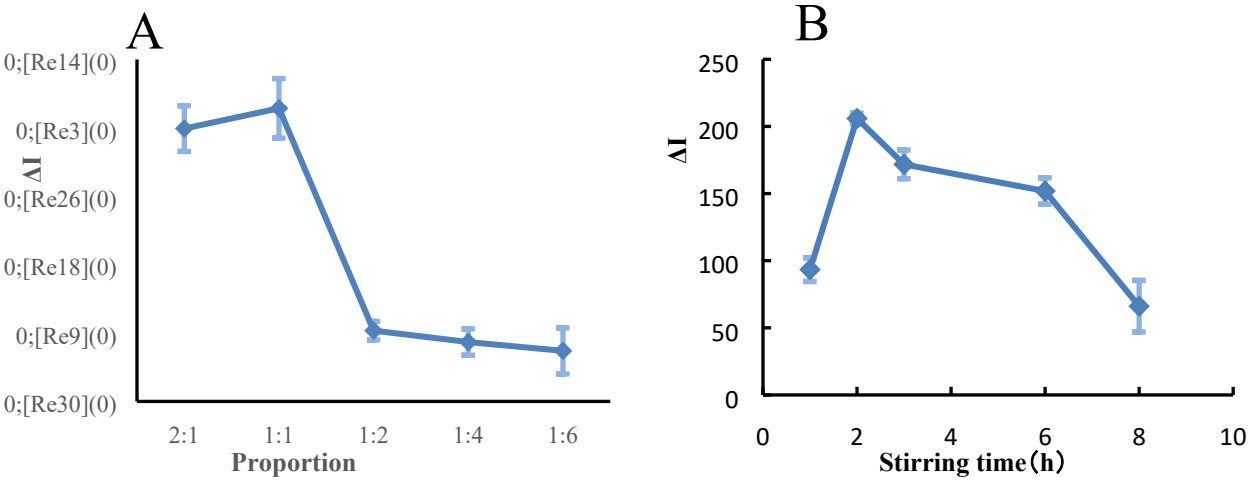


Fig.S4. Abs spectrum of Fe_3O_4@MIP- PO_4^{3-}-MSA (n=3)

0.0125g/L Fe_3O_4@MIP+ 3.5 mmol/L H_2SO_4 + 0.1 μmol/L MSA + 0.055 μmol/L Aa + (0, 2.5, 5, 7.5, 10, 12.5, 15, 17.5, 20, 22.5) μmol/L PO_4^{3-}-25℃−10min.



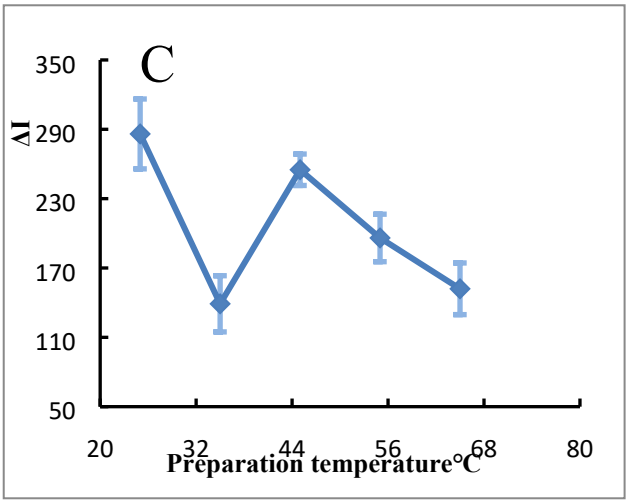
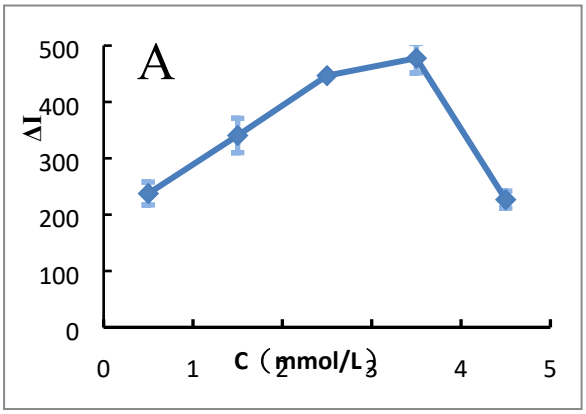
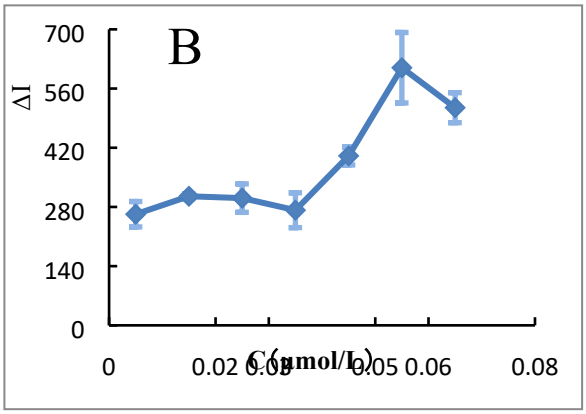
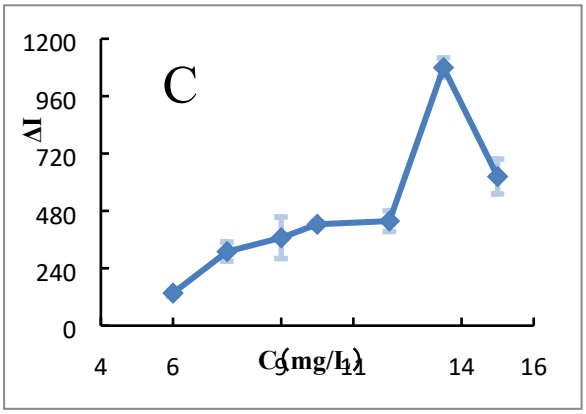


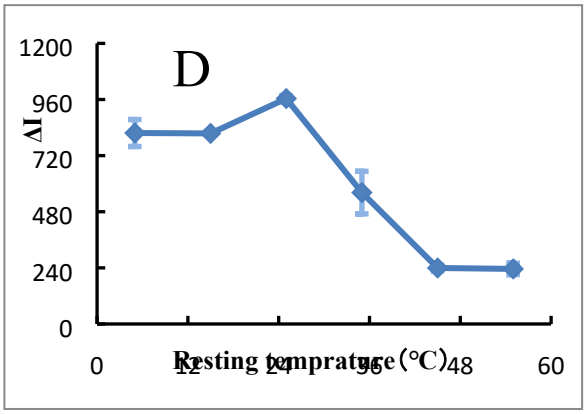
Fig.S5. Optimization of material preparation conditions(n=3)

A: Effect of functional monomer dosage: 0.5mmolPMo-（0.25, 0.6, 1, 2, 3mmol）PD-70mgFe$_3$O$_4$NP-25℃-4h；B: Effect of preparation time：0.5mmol PMo-0.6mmol PD-70mg Fe$_3$O$_4$NP-25℃-（2, 3, 4, 7, 9）h；C: Effect of preparation temperature：0.5mmolPMo-（0.25, 0.6, 1, 2, 3）mmol PD-70mg Fe$_3$O$_4$NP-（25, 35, 45, 55, 65 ℃-4 h.









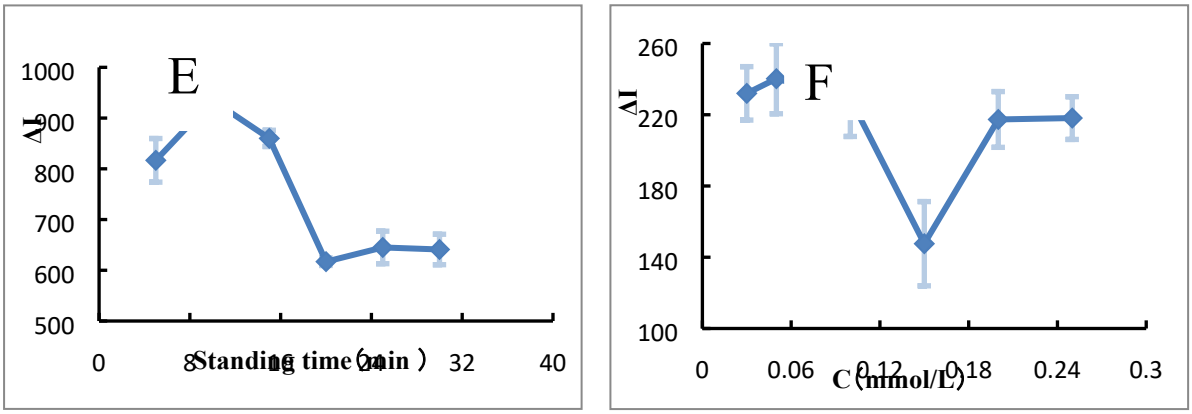
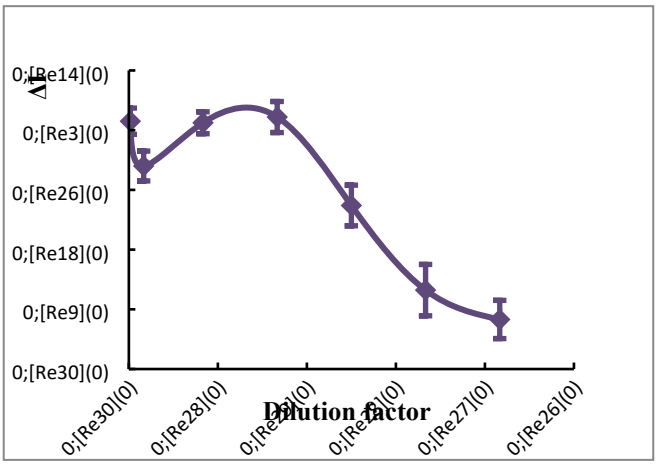
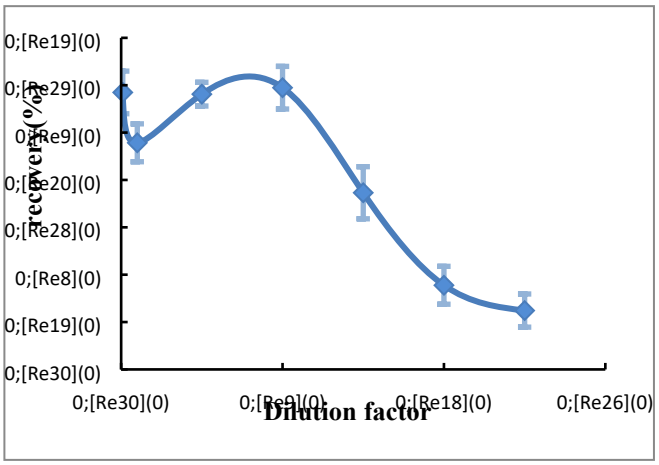


Fig.S6. Analysis condition optimization(n=3)

A: Effect of H_2SO_4 concentration : 0.0125 g/L Fe_3O_4@MIP + (0.5, 1.5, 2.5, 3.5,4.5) mmol/L H_2SO_4 + 50 μmol/L MSA + 0.055 μmol/L ascorbic acid + 10μmol/L $PO4^{3-}$—25°C-10 min B: Effect of Aa concentration：0.0125 g/L Fe_3O_4@MIP+ 3.5 mmol/L H_2SO_4 + 50 μmol/L MSA + (0.005,0.015,0.025,0.035,0.045,0.055,0.065) μmol/L Aa+ 10 μmol/L $PO4^{3-}$-25°C -10 min；C: Effect of Fe_3O_4@MIP concentration：（0.006，0.0075，0.009，0.01，0.12，0.125，0.135）g/L Fe_3O_4@MIP + 3.5mmol/L H_2SO_4 +50 μmol/L MSA + 0.055 μmol/L Aa+ 10μmol/L PO_4^{3-}—25 ℃-10min；D: Effect of resting temperature：0.0125 g/L Fe_3O_4@MIP+ 3.5mmol/LH_2SO_4 + 50 μmol/L MSA + 0.055 μmol/L Aa + 10 μmol/L PO_4^{3-}(5，15，25，35，45，55，65)℃-10min；E: Effect of standing time：0.0125 g/L Fe_3O_4@MIP+ 3.5mmol/L H_2SO_4 + 50 μmol/L MSA + 0.055 μmol/L Aa+ 10μmol/L PO_4^{3-}—25℃-（5，10，15，20，25，30）min。F: Effect of MSA concentration： 0.0125 g/L Fe_3O_4@MIP +3.5 mmol/L H_2SO_4 + (30,50,100,150,200,250)μmol/L MSA + 0.055μmol/L ascorbic acid + 10μmol/L $PO4^{3-}$-25 °C-10min





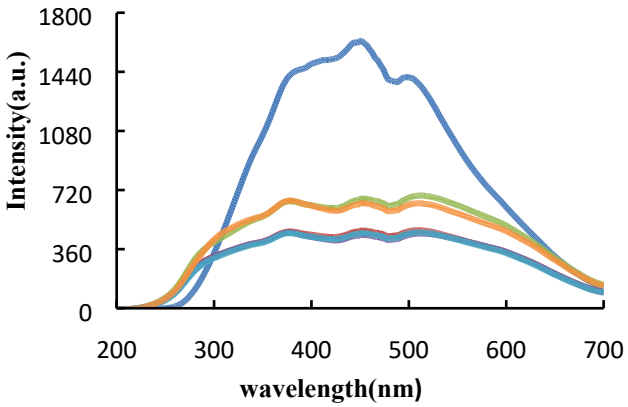


Fig.S7. Fe_3O_4@MIP magnetic separation enrichment δI-dilution ratio (n) diagram (A); Fe_3O_4@MIP magnetic separation and enrichment recovery-dilution ratio (n) diagram (B); RRS spectra with enrichment recoveries of 95.69%-116.90% (n=1,10,50,100,150) (C)

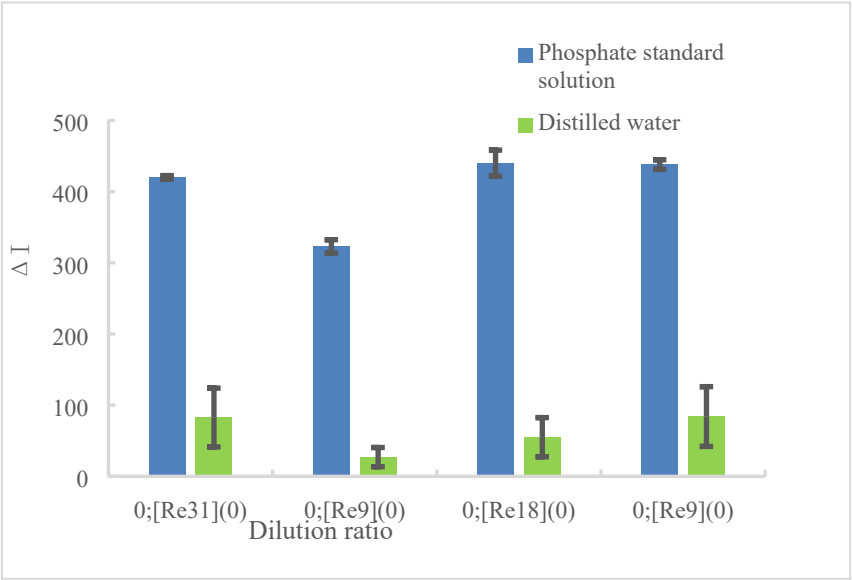


Fig.S8. Comparison between enriched experimental phosphate solution group and blank group

Table S1 Working curves

Probe	method	Regression equation	Linear range（μmol/L）	Regression equation	Limit of detection（μmol/L）
Fe_3O_4@MIP	RRS	ΔI=35.2C+2.6	1-22.5	0.98	0.49
	Abs	ΔA=0.0171C+0.015	2.5-22.5	0.98	1.06
MIP	RRS	ΔI=17.5x + 4.6	2.5-20	0.99	0.99
Fe3O4@MIPm	RRS	Δ I=17.24x – 2.36	2.5-17.5	0.99	1.00
Fe3O4@NIP	RRS	Δ I=25.69x + 52.96	2.5-17.5	0.95	0.67

Table S2 Interference assays

Interfering ion	Relative multiple	Relative error（%）	Interfering ion	Relative multiple	Relative error（%）
Ni^{2+}	500	-3.5	SO_4^{2-}	100	-0.4
Mn^{2+}	500	2.9	K^{+}	100	1.6
SiO_3^{2-}	500	4.7	Al^{3+}	100	3.2
NO_3^{3-}	300	-5.0	Ca^{2+}	100	-5.1
Zn^{2+}	300	-8.7	Co^{2+}	100	3.9
Mg^{2+}	300	-5.7	$NO2^{-}$	50	6.8
Fe^{2+}	100	2.0	$NH4^{+}$	50	5.0

Table S3 Determination **results of** PO_4^{3-} in water samples(n=5)

Sample	Mean value（μmol/L）	Added（μmol/L）	Measured value（μmol/L）	Recovery（%）	RSD（%）	Dilution ratio	Content（μmol/L）	Photometry (μmol/L)
Lake1	10.44	5	15.00	91.29	1.85	10	104.38	104.21
Lake2	6.78	5	12.01	104.62	8.90	10	67.82	70.18
Lake3	10.38	5	15.33	98.99	1.57	25	259.5	274.75
Lake4	11.41	5	16.66	104.95	0.74	25	285.25	289.25
Lake5	10.61	5	15.33	94.17	2.67	25	265.25	274.75
Lake6	7.31	5	12.09	95.59	3.30	20	146.2	142.6
River1	7.24	5	11.78	90.95	9.22	10	72.36	75.26
River2	15.13	5	19.64	90.20	10.34	20	302.6	298.2
River3	15.94	5	21.02	101.83	0.62	20	318	288.8
River4	3.68	5	8.66	99.56	9.62	10	36.8	31.5
River5	11.54	5	16.78	104.98	1.09	20	230.8	214
River6	7.12	5	12.19	101.20	5.57	20	142.4	152
Tap water1	13.73	5	18.37	92.67	2.90	10	137.32	130.87
Tap water2	1.63	5	6.98	107.22	8.54	10	16.3	18.4
Tap water3	1.77	5	7.16	107.79	9.62	10	17.7	19
Tap water4	6.03	5	11.54	110.19	7.24	20	120.6	131
Tap water5	6.21	5	11.55	106.25	0.91	20	124.2	123.6
Tap water6	2.05	5	7.39	106.77	8.6	20	41	47.6

Note: Mean value refers to the average value of 5 measurements before adding standard to the water sample. Measured value refers to the measured value of the

sample after spiking. Recovery=100×(Measured value-Mean value)/Added concentration.