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Flow injection kinetic spectrophotometric determination of trace amounts of Se(IV) in seawater

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Abstract

A simple, accurate, sensitive and selective flow injection catalytic kinetic spectrophotometric method for rapid determination of trace amounts of selenium is proposed in this paper. The proposed method is based on the accelerating effect of Se(IV) on the reaction of ethexlenediamine tetrecetic acid disodium salt (EDTA) and sodium nitrate with ammonium iron(II) sulfate hexahydrate in acidic media. The absorbance intensity was registered in this reaction solution at 440 nm. The calibration graph is linear in the range of 5×10^{-9}–2×10^{-7} and 2×10^{-7}–2×10^{-6} g ml^{-1}. The detection limit is 2×10^{-9} g ml^{-1}. The relative standard deviation was 3.4% for 5×10^{-8} g ml^{-1} Se(IV) ($n = 11$), 2.7% for 5×10^{-7} g ml^{-1} Se(IV) ($n = 11$). This method is very simple, rapid and suitable for automatic and continuous analysis. The presented system has been applied successfully to determination of Se(IV) of seawater samples.

Keywords: Flow injection; Spectrophotometry; Catalytic–kinetic; Selenium; Seawater

1. Introduction

Selenium is an essential trace nutrient. Selenium deficiency is now recognized as the major aetiological factor in Keshan disease, an often fatal dilated cardiomyopathy, and Kaschin Beck disease or ‘enlarged joints’ [1]. On the other hand, in certain parts of the world where there are very high environmental levels of selenium. The ingestion of greater than trace levels of selenium shows clear signs of selenium toxicity, for example, loss of hair, roughening of nails, nausea and fatigue.

There has been an increasing demand for sensitive methods for the determination of trace amounts of selenium in different samples such as water, food, medicament and environmental, biochemical and biological materials. The method most commonly used for determination of trace of selenium is based on spectrophotometric measurement of the piazselenol formed by the reaction of selenium with 2,3-diaminonaphtalene [2,3]. These methods are time consuming and complicated procedures and the reagents used are toxic and relatively unstable. Hydride generation atomic absorption spectrometry or atomic fluorescence spectrometry [4–9] are also other sensitive methods that have been reported for determination of trace of selenium. But, in hydride generation method, coexisting ions cause interferences. Cathodic stripping voltammetry [10–13], neutron activation analysis [14–16], capillary electrophoresis [17] and gas chromatography and high performance liquid chromatography [18–21] with on line detection by inductively coupled mass spectrometry or flame atomic absorption spectrometry, have been developed for determination of selenium. Some of the methods have good sensitivity, but require very expensive reagents and instruments. Some methods require a preconcentration step.

Catalytic–kinetic spectrometry method [22,23] is an attractive alternative of the determination of trace amounts of selenium. These methods have the general advantage of combining high selectivity with relatively simple procedures and

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apparatus. However, these methods are time consuming and have a narrow linear concentration range and poor precision. Therefore, the requirement concerning improvement studies of linear concentration range, precision and automatic flow techniques of these methods is still necessary.

Automatic flow techniques have been applied to the determination of selenium. Few methods have been described, such as, flow injection analysis (FIA) combined with hydride generation atomic absorption spectrometry [24], with hydride generation atomic fluorescence spectrometry [25] and with spectrophotometric measurement [26]. Many hydride generation graphite furnace atomic absorption spectrophotometric [27,28], hydride generation electrothermal atomic absorption spectrometric [29,30], hydride generation atomic fluorescence spectrometric [31,32], coupled plasma mass spectrometric [33,34] and pulse cathodic stripping voltammetric [35] methods have been developed for determination of selenium in seawater samples. Some of these methods give good selectivity and sensitivity, but require very expensive or/and toxic reagents and expensive instruments. Their deadly disadvantage is impossibility of monitoring selenium at locale.

This paper describes a simple, sensitive and rapid method for the determination of trace amounts of Se(IV). A less expensive alternative that can provide a fast and simple quantitative measurement of selenium is the FIA kinetic spectrophotometric measurement. The proposed method is based on the accelerating effect of Se(IV) on the reaction of ethexlenediamine tetrecetic acid disodium salt (EDTA) and sodium nitrate with ammonium iron(II) sulfate hexahydrate in acidic media. The proposed method was applied satisfactorily to the determination of trace amounts of selenium in seawater and sea salt.

2. Experimental

2.1. Reagents

All the chemicals used, including ammonium iron(II) sulfate hexahydrate, ethxlenediamine tetracetic acid disodium salt, sodium nitrate, metallic selenium, sodium chloride, sulfuric acid, etc. were of analytical-reagent grade and were used without further purification. All solutions were made with deionized water provided by the Water Purification Agency of Sichuan University.

Mixing solution of ethxlenediamine tetracetic acid disodium salt (EDTA) and sodium nitrate was prepared by dissolving 20 g of ethxlenediamine tetracetic acid disodium salt (Chengdu Fangzhou Chemical Reagent Plant, Chengdu, PR China) and 200 g sodium nitrate (Chengdu Fangzhou Chemical Reagent Plant, Chengdu, PR China) in 400 ml deionized water. The solution was filtered through a glass filter and it was a saturated solution of ethxlenediamine tetracetic acid disodium salt and sodium nitrate.

Ammonium iron(II) sulfate hexahydrate solution was prepared by dissolving 9.804 g of the solid product (Tianjin Nankai Chemical Reagent Plant, Tianjin, PR China) in 500 ml of 0.025 mol l^{-1} sulfuric acid.

An amount of 0.1 g metallic selenium (Shanghai Chemical Regent Plant, Shanghai, PR China) was dissolved by 10 ml nitric acid and 1 ml sulfuric acid in 25 ml beaker. The solution was dried up using electric cooker. The rudimental solid in beaker was dissolved by deionized water and taken in a 100 ml volumetric flask. That was selenium stock solution (1×10^{-3} g ml^{-1}). Working standard solutions were prepared by appropriate dilution of the stock standard solution.

2.2. Apparatus

A model ZJ-la automatic metallic elements analyzer made by our laboratory and equipped with an optical detector and optical flow cell has the dual functions of ion chromatography and flow injection analysis. The function of flow injection analysis was applied here to determine Se(IV). The flow scheme is shown in Fig. 1. The flow system employed two peristaltic pumps (Shanghai Huxi Analytical Instrument Plant, PR China), which used to deliver all flow streams. One delivered the stream (3% NaCl and sample) at a flow rate (per tube) of 0.3 ml min^{-1}. The other delivered regents (a mixture of $(NH_4)_2Fe(SO_4)_2$ in H_2SO_4 and EDTA-$NaNO_3$) at flow rate (per tube) of 0.1 ml min^{-1}. PTFE tubing (0.8 mm

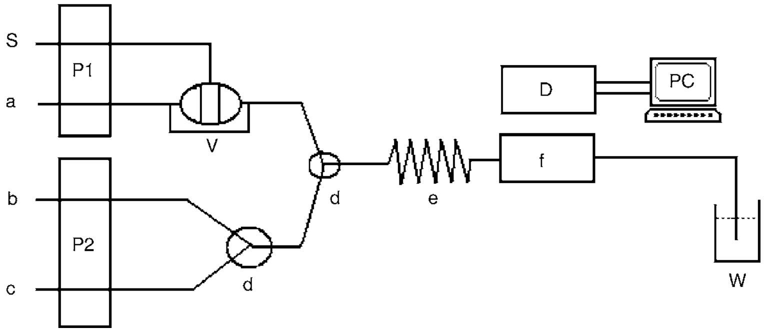

Fig. 1. Schematic diagram of the FIA system for the determination of Se(IV). (a) Carrier(3%NaCl); (b) $(NH_4)_2Fe(SO_4)_2$ (0.05 mol l^{-1}); (c) EDTA-$NaNO_3$ (saturated solution); (d) mixing coil; (e) reaction coil (12 m); (f) flow coil (1.5 cm); D, detector (440 nm); P1, peristaltic pump (0.3 ml min^{-1}); P2, peristaltic pump (0.1 ml min^{-1}); S, sample; V, sample valve (1.2ml); W, waste; PC, personal computer.

i.d.) was used as connect all components in the flow system. Sample solution (1.2 ml) was injected into the carrier stream by a six-way injection valve. The absorbance intensity was recorded at 440 nm using an IBM-compatible computer. Data acquisition and treatment were performed with N-2000 software running under Windows 98.

2.3. Procedure

A series of working standard solutions with different concentrations between 5×10^{-9} and 2×10^{-6} g ml^{-1} were prepared by diluting a concentrated fresh standard solution of Se(IV). As shown in Fig. 1, flow lines were inserted into sample or standard solution, $(NH_4)_2Fe(SO_4)_2$, EDTA and $NaNO_3$ reagent solution, carrier solution (3% NaCl), respectively. With the injection valve in the load position, the pumps were started to wash the whole flow system until a stable baseline was recorded. When the switching valve is in the washing position, the pump propelled working solution of selenium or samples to waste. Then the switching valve was rotated automatically to the sampling position so that Se(IV) accelerated the reaction of EDTA-$NaNO_3$ with $(NH_4)_2Fe(SO_4)_2$ in acidic media. The absorbance signal was obtained by injecting 1.2 ml of the working standard solution or sample solution into the carrier (3% NaCl). The relative absorbance intensity versus Se(IV) concentration was used for the calibration.

3. Results and discussion

3.1. Absorbance studies

The reaction of $(NH_4)_2Fe(SO_4)_2$ solution and EDTA-$NaNO_3$ solution in acidic media proceeds slowly without a catalyst. However, trace amounts of Se(IV) catalyzes the reaction so that it proceeds much faster (see Fig. 2). The relative absorbance intensity (curve 3) was greater at the 20th minute. After 20th minute, the change of relative absorbance intensity was smaller. Therefore, this system is very propitious to automatic and continuous analysis at right flow rate and reaction coil length.

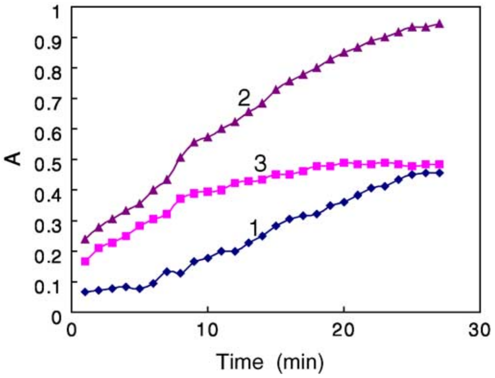

Fig. 2. Curve of A–t. (1) mixture solution of 0.4 ml $(NH_4)_2Fe(SO_4)_2$ (0.4 mol l^{-1}, H$^+$) and 2.4 ml EDTA-$NaNO_3$ (saturated solution), diluted with deionized water to 10 ml. (2) Mixture solution of 0.4 ml $(NH_4)_2Fe(SO_4)_2$ (0.4 mol l^{-1}, H$^+$), 2.4 ml EDTA-$NaNO_3$ (saturated solution) and 1 ml Se(IV) (2×10^{-6} g ml^{-1}), diluted with deionized water to 10 ml. (3) The relative absorbance intensity of two mixture solutions 1 and 2.

3.2. Choice wavelength

Fig. 3 shows the absorbance spectra of five different solutions. The greatest absorbance intensity of mixture of $(NH_4)_2Fe(SO_4)_2$ and saturated solution of EDTA-$NaNO_3$ at 390 nm, but the greatest relative absorbance intensity between mixture of $(NH_4)_2Fe(SO_4)_2$ and saturated solution of EDTA-$NaNO_3$ and mixture of $(NH_4)_2Fe(SO_4)_2$, saturated solution of EDTA-$NaNO_3$ and Se(IV) is at 440 nm. Therefore, 440 nm spectrophotometric detector was chosen for the further work.

3.3. Effect of flow injection variables

3.3.1. Effect of flow rate and reaction coil

In the application of any flow injection method, the change in absorbance intensity depends on the residence time of the sample zone in the system, i.e. on the flow rate and the reaction coil length. The effect of the flow rate on the peak height was studied between the ranges of 0.08–0.4 ml min^{-1} in each stream (Fig. 4). In Fig. 4, curve (a) was the effect of flow rate of the carrier pump on the peak height. Higher flow rates (higher than 0.3 ml min^{-1}) produced lower peak because of the lack of reaction time of working standard solutions or samples in reaction coil. Lower flow rates produced also lower peak. Lower flow rates had two drastic effects, decreasing sensitivity by decreasing peak height because of the dilution of reagent solution to working standard solutions or samples, and second, the driving force of each peristaltic pump roller was seen as noise (small peak) on the baseline. The latter effect decreases reproducibility and makes

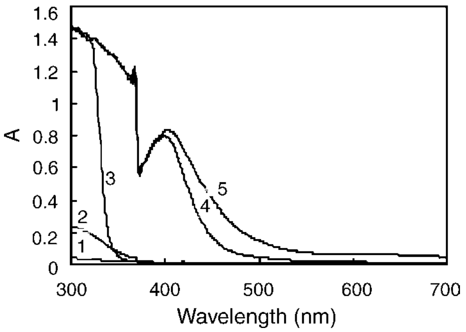

Fig. 3. Absorbance spectra. (1) Mixture solution of 10 ml Se(IV) (5×10^{-8} g ml^{-1}) and 10 ml deionized water. (2) Mixture solution of 5 ml saturated solution of EDTA-$NaNO_3$ and 15 ml deionized water. (3) Mixture solution of 5 ml $(NH_4)_2Fe(SO_4)_2$ (0.05 mol l^{-1}) and 15 ml deionized water. (4) Mixture solution of 5 ml $(NH_4)_2Fe(SO_4)_2$ (0.05 mol l^{-1}), 5 ml saturated solution of EDTA-$NaNO_3$ and 10 ml deionized water. (5) Mixture solution of 5 ml $(NH_4)_2Fe(SO_4)_2$ (0.05 mol l^{-1}), 5 ml saturated solution of EDTA and $NaNO_3$ and 10 ml Se(IV) (5×10^{-8} g ml^{-1}). The absorbance spectra were obtained after standing for 10 min in the bark.

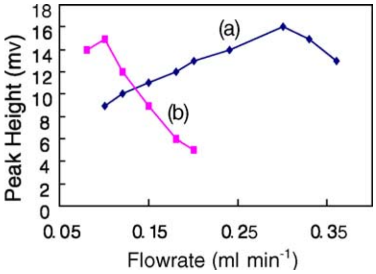

Fig. 4. The effect of flow rate on the peak height. (a) Carrier pump; (b) reagent pump. Conditions: Se(IV) 5×10^{-8} g ml^{-1}; $(NH_4)_2Fe(SO_4)_2$ 0.05 mol l^{-1} (0.025 mol l^{-1} H_2SO_4); EDTA-$NaNO_3$ saturated solution; reaction coil 12 m; sample loop 1.2 ml.

the detection limit of the system worse, hence a flow rate of 0.3 ml min^{-1} was selected. Curve (b) was the effect of flow rate of the reagent pump on the peak height. The flow rate was changed between 0.08 and 0.2 ml min^{-1}. The maximum absorbance intensity was obtained with 0.1 ml min^{-1} flow rate of the reagent pump, so 0.1 ml min^{-1} flow rate of the reagent pump was chosen for further work.

Reaction coil lengths of 3–18 m were tested (Fig. 5). The peaks became higher as the length of coil increased from 3 to 12 m, but a further increase did not increase peak height and caused peak broadening. The reaction coil length of 12 m was chosen for further work.

3.3.2. Effect of sample loop

To obtain the best overall response, the effect of sample loop was also investigated in the range of 0.6–2.4 ml (Fig. 6). The maximum absorbance intensity was obtained with 1.2 ml sample loop. Sample loop was greater than 1.2 ml, the peak height lower. The cause of this is peak shape broadening and unquiet baseline. Simultaneity, the time of sampling and analysis became longer for greater sample loop that affected rapid analysis of this system.

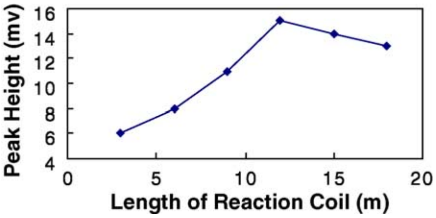

Fig. 5. The effect of length of reaction coil on the peak height. Conditions: Se(IV) 5×10^{-8} g ml^{-1}; $(NH_4)_2Fe(SO_4)_2$ 0.05 mol l^{-1}(0.025 mol l^{-1} H_2SO_4); EDTA-$NaNO_3$ saturated solution; sample loop 1.2 ml; flow rate 0.1 ml min^{-1} (reagent pump) and 0.3 ml min^{-1} (carrier pump).

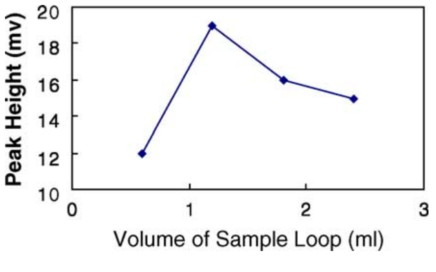

Fig. 6. The effect of volume of sample loop on the peak height. Conditions: Se(IV) 5×10^{-8} g ml^{-1}; $(NH_4)_2Fe(SO_4)_2$ 0.05 mol l^{-1} (0.025 mol l^{-1} H_2SO_4); EDTA-$NaNO_3$ saturated solution; reaction coil 12 m; flow rate 0.1 ml min^{-1} (reagent pump) and 0.3 ml min^{-1} (carrier pump).

3.4. Effect of chemical reaction variables

3.4.1. Effect of concentration of $(NH_4)_2Fe(SO_4)_2$

Effect of $(NH_4)_2Fe(SO_4)_2$ on absorbance intensity was studied at different concentrations from 0.001 to 0.2 mol l^{-1}. Curve (a) in Fig. 7 shows $(NH_4)_2Fe(SO_4)_2$ concentration on the absorbance intensity of selenium. The maximum absorbance intensity was obtained with 0.05 mol l^{-1} $(NH_4)_2Fe(SO_4)_2$ for selenium. So 0.05 mol l^{-1} $(NH_4)_2Fe(SO_4)_2$ was chosen for the further work.

3.4.2. Effect of concentration of sulfuric acid

The sulfuric acid concentration was varied in the range 0.001–0.1 mol l^{-1} in order to maximize the absorbance signal. Curve (b) in Fig. 7 shows the effect of sulfuric acid concentration on the absorbance intensity of selenium. The maximum absorbance intensity was obtained with 0.025 mol l^{-1} sulfuric acid. Therefore, the 0.025 mol l^{-1} sulfuric acid was chosen for further work.

3.5. Calibration curve, reproducibility and detection limit

Under the selected conditions given above, the calibration graph of absorbance intensity (*A*, mV) versus Se(IV) concentration was linear in the range of 5×10^{-9}–2×10^{-7} and 2×10^{-7}–2×10^{-6} g ml^{-1}. The regression equation was $A = 0.3266C + 0.3073$ ($n = 7$, correlation coefficient $R^2 = 0.9996$), $A = 0.1147C + 121.65$ ($n = 6$, correlation coefficient $R^2 = 0.9963$) (C being the Se(IV) concentration, μg l^{-1}), respectively. Using a signal of three times the noise ratio, as the limiting requirement, the experimental detection limit was found to be 2×10^{-9} g ml^{-1}. The relative stan-

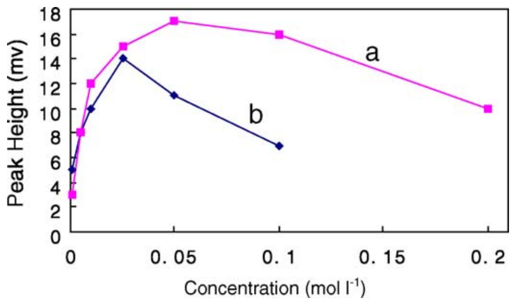

Fig. 7. The effect of reagent concentration on the peak height. (a) Ammonium iron(II) sulfate hexahydrate; (b) sulfuric acid. Conditions: Se(IV) 5×10^{-8} g ml^{-1}; EDTA-$NaNO_3$ saturated solution; reaction coil 12 m; sample loop 1.2 ml; flow rate 0.1 ml min^{-1} (reagent pump) and 0.3 ml min^{-1} (carrier pump).

dard deviation was 3.4% for 5×10^{-8} g ml^{-1} Se(IV) ($n = 11$), 2.7% for 5×10^{-7} g ml^{-1} Se(IV) ($n = 11$).

3.6. *Effects of foreign ions*

The effect of foreign substances was tested by analyzing a standard solution of selenium (5×10^{-8} g ml^{-1}). The tolerable concentration ratios with respect to 5×10^{-8} g ml^{-1} selenium for interference at 5% level were over 10,000 for Cl^-, Na^+, and K^+, over 1000 for Ca^{2+}, Mn^{2+}, $SO_4{}^{2-}$, and $NO_3{}^-$, 800 for Ba^{2+} and $PO_4{}^{3-}$, 500 for Zn^{2+}, Al^{3+} and Co^{2+}, 100 for Cr^{6+}, Cr^{3+}, Pb^{2+}, Sn^{4+}, Cd^{2+} and SCN^-, 5 for Cu^{2+} and 1 for Fe^{3+} and Fe^{2+}, respectively. The results showed that the proposed method has good selectivity. Only Cu^{2+}, Fe^{3+} and Fe^{2+} cause interference. But, iron is present in very low iron concentrations in the oceans (0.05–2 nM) [36,37], and concentration of copper is very low in seawater [38,39]. Therefore, the proposed method was applied successfully to the determination selenium in seawater without any pretreatment.

3.7. *Application*

The proposed method was further applied to the determination of Se(IV) in several samples of seawater (samples came from Fujian and Qingdao, PR China) and sea salt at a sampling frequency of 7 h^{-1}. Concentration of sea salt solution was 3%. Samples were diluted 1:1 (v/v) with 3% NaCl. Recovery tests were carried out on samples to which known amounts of Se(IV) were added. The recoveries for the different concentration levels varied from 95 to 104%, as shown in Table 1.

Recovery test results of different salinity seawater are given in Table 2, 3.5% salinity seawater sample was obtained though concentrating 3% salinity seawater with electric cooker and 1–2.5% salinity seawater samples were obtained though diluting 3% salinity seawater with deionized water. Samples of 1.5–3.5% salinity were diluted 1:1 (v/v) with 3% NaCl and 1% salinity seawater were diluted 1:1 (v/v) with 5% NaCl.

Table 1
Determination of Se(IV) in seawaters

Sample	Se(IV) (μg l^{-1})			
	Sample	Added	Proposed method[d]	Official method [40][d]
1#[a]	0.00	20.00	19.23 (±2.3%)	20.19 (±1.4%)
1#	0.00	50.00	50.89 (±2.5%)	50.12 (±2.9%)
2#[b]	0.00	20.00	19.77 (±1.3%)	20.09 (±1.2%)
2#	0.00	50.00	48.98 (±1.6%)	49.86 (±1.7%)
3#[c]	0.00	20.00	18.03 (±3.1%)	19.59 (±0.8%)
3#	0.00	50.00	50.38 (±2.7%)	49.27 (±1.3%)

[a] Seawater sample of Fujian, taken 15 November 2004.
[b] Seawater sample of Qingdao taken 17 November 2004.
[c] Sea salt sample.
[d] The data represent the average from three determinations (±R.S.D.).

Table 2
Determination of selenium in seawaters

Sample taken (ml)	Se(IV) (μg l^{-1})			Recovery (%)
	Sample	Added	Found[a]	
3.5% Salinity (12.5)	0.00	80.00	76.59 (±2.9%)	95.7
3% Salinity (12.5)	0.00	80.00	80.27 (±0.8%)	100.3
2.5% Salinity (12.5)	0.00	80.00	82.86 (±3.7%)	104.4
2% Salinity (12.5)	0.00	80.00	77.87 (±2.6%)	97.3
1.5% Salinity (12.5)	0.00	80.00	82.52 (±1.4%)	103.2
1% Salinity (12.5)	0.00	80.00	78.54 (±1.1%)	98.1

[a] The data represent the average from five determinations (±R.S.D.).

4. Conclusion

The proposed method adopted was significant with respect to the development of a simple, precise and rapid flow injection method for the analysis of the trace amounts of selenium in seawater and sea salt samples. High sensitivity, selectivity and broad dynamic range of selenium determination are just some of the advantages of this method. As we know, this proposed method is only flow injection catalytic kinetic spectrophotometric method for rapid determination selenium in seawater. A model ZJ-la automatic metallic elements analyzer made by our laboratory is cheap, small shape and fit to move, so there is very importance meaning to monitor selenium in sea and oceans with the proposed method in this paper.

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