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Further research on iodine speciation in seawater by capillary zone electrophoresis with isotachophoresis preconcentration

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Abstract

A novel, simple and highly sensitive CE method was developed to determine total iodine (TI) in seawater. The method is based on the on-capillary reduction of iodine species to iodide by a reductant, introduced into the capillary before sample injection, the preconcentration of iodide using isotachophoresis, followed by its UV detection. Under optimized conditions for reduction and CE separation, the limit of detection for TI (S/N = 3) reached 0.4 $\mu g\,L^{-1}$ (226 nm). The repeatability of migration time and peak area, expressed by relative standard deviation, was 0.46 and 1.45%, respectively (n = 19). The correlation factor was 0.9991 (n = 10) for the concentration range of 12–115 $\mu g\,I\,L^{-1}$. The CE results obtained for the real seawater analysis agreed with the data of ion chromatography. To determine the genuine TI by the proposed method, organic iodinated compounds in the sample were treated with H_2O_2 and irradiation with UV light before analysis.

Keywords: Iodine determination; Seawater; Capillary electrophoresis; Preconcentration; High-sensitive analysis; Transient isotachophoresis

1. Introduction

As essential micronutrients in seawater, chemical species of iodine play a special role in biological and a biological processes [1–3] and offer the important clues of marine environment, such as geochemically or biologically active process and hazardous contaminant, etc. [4]. To observe the information on the iodine speciation in seawater, many techniques and sophisticated instruments such as neutron activation analysis [5,6], inductively coupled plasma (ICP) atomic emission spectroscopy [7] or ion chromatography (IC)–ICP mass spectrometry [8] were applied. Recently, Huang et al. [4] and Yokota et al. [9] have developed on-capillary concentration techniques compatible with the following CE separation for the simultaneous determination of seawater IO_3^- and I^- without any sample pretreatment. Such simple operation and comparatively low investment and running costs of CE method make feasible a rapid and simple monitoring of iodine speciation.

Besides IO_3^- and I^-, dissolved organic iodine (DOI) represents important iodine components in seawater [3,10]. Importantly, DOI cannot be identified and measured by a direct and species-specific analytical method. For the determination of DOI, the accurate quantification of TI is necessary. Up to now, all approaches for determining DOI were based on the oxidation of iodine species to iodate or reducing them to iodide as the first pretreatment step. Afterwards, IC [10–14] and cathodic stripping square wave voltammetry [15,16] were used for iodide quantification or differential pulse polarography for the determination of IO_3^- [15–17]. DOI was calculated as a difference $[TI]-[IO_3^-]-[I^-]$, whose precision was as good as (but not better than) the precision of the applied methods for determining TI, IO_3^- and I^-. However, such methods with rather strict and onerous pretreatment usually caused uncertainty of the analytical results. Moreover, little is known about the composition and distribution of chemical forms of iodine in seawater apart from IO_3^- and I^-.

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If there exist other inorganic iodine species, they would be treated as DOI, so that the content of DOI will be overestimated. Such reported methods have provided a questionable evidence of the presence of DOI in seawater. Until now, there was no report on the analysis of seawater iodine species other than IO_3^-, I^- and CH_3I [18]. Only a few papers discussed the kinetic model of iodine speciation [19,20]. Our developed method, CE following transient isotachophoresis (tITP), has been successfully and simultaneously applied to determine IO_3^- and I^- in seawater with high sensitivity and accuracy [4]. Provided that all iodine species are reduced to I^-, the concentration of TI could be evaluated by CZE/tITP (as I^-).

In this study, a novel highly sensitive CE method based on the principle of tITP and on-capillary redox reaction was elaborated for iodine quantification in seawater. On the basis of our previous contribution [4], a proper reductant, namely hydroxylamine hydrochloride, was selected and its plug (or zone) was introduced into the capillary before (in front of) the sample zone. All analytical procedure steps, such as the reduction of iodine species, preconcentration, separation and detection, were successfully realized in one capillary without any extra treatment or use of complex instrumental design. The concentrations of all reduced iodine forms were determined as I^-. For unreducible iodine species, i.e. organic iodinated compounds (OIC), the usual oxidative method was used to break C–I and N–I bond first [16], so that they were re-mineralized to reducible iodine species. Then the genuine TI was determined by the proposed method. The analytical performance characteristics of the proposed method were discussed. The simple operation, intensive stacking enrichment, complete separation and low cost, make the method well suitable for the quantification of total inorganic I (TII) and TI, including DOI, in seawater.

2. Experimental

2.1. Determination of IO_3^- and I^-

The concentration of IO_3^- and I^- in seawater was determined simultaneously by our previous CZE/tITP method [4]. The IC procedure for the determination of inorganic iodine, involving sample preconcentration and iodine species reduction steps, was similar with those published earlier by one of the coauthors [11,12].

2.2. Determination of total inorganic iodine (TII)

The instrument was a CAPI-3100 CE system (Otsuka Electronics, Osaka, Japan) equipped with a photodiode array detector. Fused-silica capillaries of 100 cm (87.7 cm effective length) and 75 μm I.D., obtained from Otsuka Electronics, were utilized throughout. Capillary initial and between-run conditioning cycles were basically the same as used previously [21]. The temperature of capillary chamber was set at 25 °C for capillary chamber. The separation electrolyte (SE), reductant electrolyte (RE), sample and terminating electrolyte (TE) were introduced sequentially into the capillary by negative pressure (0.5 kg cm^{-2}). A negative voltage, generating a constant current of −195 μA, was applied. Electropherograms recorded the UV absorbance data at 226 nm to calculate the peak area of iodide.

Components used for the analysis of iodine species by IC were sample and mobile-phase delivery pumps (CCPD, Tosoh, Tokyo, Japan and Shimadzu LC-10AD, Kyoto, Japan, respectively), a Rheodyne 7125 injector equipped with a sample loop of 2 mL (Cotaci, CA, USA), a Hitachi L-4200 UV–vis detector (Tokyo, Japan) and a chromato-processor (Shimadzu C-R8A). The wavelength was set at 226 nm. The separation column used was a semi-micro column (35 mm × 1.0 mm I.D.) preceded by a microconcentrator (10 mm × 1.0 mm I.D.); both packed with a high-capacity anion exchanger TSKgel SAX, 5 μm particle size (Toso, Tokyo, Japan). The eluent was pumped at a flow rate of 0.3 mL min^{-1}. For the determination of TII (iodate + iodide), iodate both from artificial and real seawater was reduced to iodide with 1 mM ascorbic acid in 100 mM acetic acid (final concentration). Sample injection volumes were 2 and 0.5 mL for iodide and TII respectively.

2.3. Determination of TI

Two microliter of 15% (v/v) H_2O_2 was added to 1.0 mL sample and then irradiated with UV light from a 300 W Hg vapor lamp for 2 h in order to convert all iodine species including OIC into IO_3^-, so that the concentration of TI could be finally determined by the proposed reduction method as I^-.

2.4. Working and standard solutions

The NaCl (99.999% grade) was purchased from Rare Metallic Co. LTD. (Tokyo, Japan). All other chemicals used for CE and IC measurements were of analytical-grade (or equivalent) quality. All solutions were prepared in a Milli-Q water obtained by a Millipore Labo-system (Tokyo, Japan). The $NaIO_3$, NaI, 31% hydrogen peroxide and hydroxylamine hydrochloride were purchased from Katayama Kagaku (Osaka, Japan). The hexadecyltrimethylammonium chloride (CTAC), CH_3I and *p*-iodoaminline were purchased from Tokyo Kasei (Tokyo, Japan). The 3-iodo-L-tyrosine and L-thyroxine were purchased from Sigma–Aldrich (St. Louis, MO, USA). 2-Morpholinoethanesulfonic acid monohydrate (MES) was purchased from Fluka (Buchs, Switzerland). The SE composition comprised 0.5 M NaCl and 12.5 mM CTAC with the pH adjusted to 2.4 with HCl. The TE was 0.5 M MES at pH 6.5. A mixture of 20 mM $NaClO_4$ and 0.5 M NaCl with a 5 mM sodium phosphate buffer (pH 6.5) was used as the IC eluent system. Standard solutions were made up by serial dilutions of 10 mM iodate stock solutions in artificial seawater with 35‰ salinity, which was prepared as described previously [22].

2.5. Samples

Seawater samples were collected at different sites in Pacific Ocean. After filtration through a 0.45 μm membrane filter, samples were stored at 4 °C in refrigerator and subjected to CE or IC analysis.

3. Results and discussion

3.1. Choice of reductive electrolyte

One of DOI species, CH_3I, was determined by GC with electron capture detector (ECD) [18]. However, using almost all methods DOI was calculated as the difference between TI and the sum of IO_3^- and I^-. In our previous studies [4,21,22], I^- and IO_3^- in seawater were determined by CZE/tITP method. In order to determine DOI, it was therefore intended to introduce a proper reductant into the CE system for the detection of all reducible iodine except for DOI. Hydroxylamine hydrochloride was considered as an appropriate selection due to its strong reducing ability in acidic medium and cationic nature. With the designed sequence of solutions injection as shown in Fig. 1, the complete redox reaction between the sample and reductant takes place, followed by the migration of the excess of hydroxylamine hydrochloride in the opposite direction to that of anions, i.e. without any impact on the detection of I^-. Such a practical scheme poses little (if any) influence on the sensitivity and other analytical characteristics of the determination of I^- [4,20].

3.2. Optimum reduction conditions for iodine species

The concentration and amount of loaded reductant should be optimized to ensure that all reducible iodine species are converted into I^- for subsequent detection, so that the formed I^- represents the true concentration of I in the sample. But an excessive RE may affect the peak of I^-. Shown in Fig. 2 is the effect of introduced RE volume on the peak area and height of I^- evaluated for real seawater with the concentration of TI of ca. 0.48 μM. The concentration of hydroxylamine hydrochloride in RE ranged from 100 to 500 mM and the concentration of Cl^- was kept constant at 500 mM. As can be seen, hydroxylamine hydrochloride presenting at more than 200 mM retarded the peak of I^- that caused peak broadening and height diminishment. Therefore, the optimal concentration of hydroxylamine hydrochloride in RE was 200 mM in 300 mM NaCl.

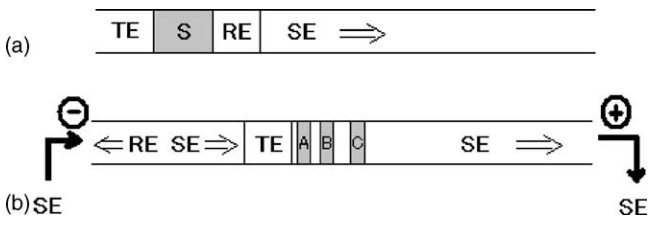

Fig. 1. Schematics for reductant migration, tITP preconcentration and CE separation. (a) The capillary is filled with separation electrolyte (SE), reductant electrolyte (RE), sample (S) and terminating electrolyte (TE). (b) Constant current was applied so that reduction, tITP preconcentration and CE separation could occur.

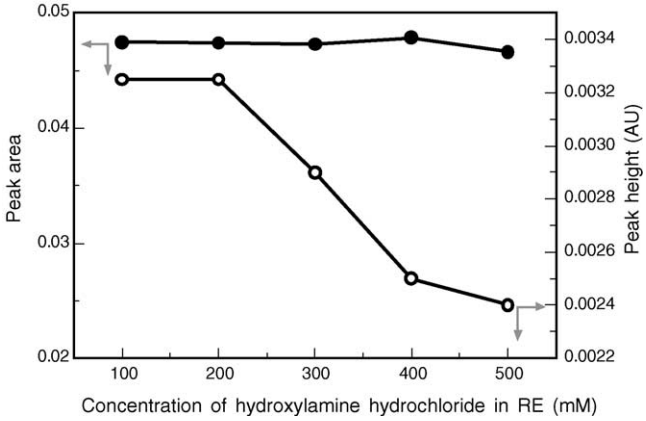

Fig. 2. Changes in signal responses (solid circles—peak area; open circles—peak height) with increasing loaded RE concentration. CE conditions: SE: 12.5 mM CTAC and 0.5 M NaCl (pH 2.4); TE: 500 mM MES (pH 6.5); RE introduction time: 7 s; sample introduction time: 4 s; TE introduction time: 10 s; capillary, fused-silica, 100 cm total and 87.7 cm to detector (75 μm I.D.); CE current: −195 μA; detection wavelength: 226 nm. Sample: real seawater collected from Kochi coastal.

To attain the largest reductive capability, the amount of RE injected into the capillary was considered as another key factor the effect of which should be optimized with due account for sufficient reducibility without any impact on the detection of I^-. The injection time of RE, containing 200 mM hydroxylamine hydrochloride, was varied from 1 to 11 s. As shown in Fig. 3, the peak area and height of I^- in a sample, containing ca. 1.00 μM I in artificial seawater with 35‰ salinity, were a little lower at injection time of 2 s due to insufficient reduction stage. Especially notable, at the injection time over 7 s the peak of I^- was retarded due to the

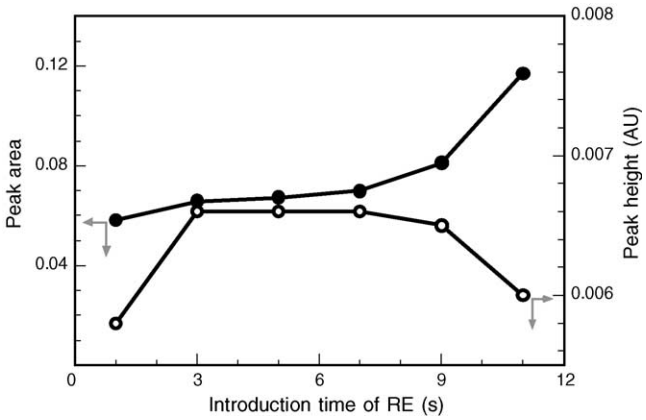

Fig. 3. Plot of the peak area (solid circles) and height (open circles) of iodide against the loading amount of RE. CE conditions: RE: 200 mM hydroxylamine hydrochloride and 300 mM NaCl; other conditions were as described in Fig. 2.

excess of RE introduced and the peak was broadened significantly. From 3 to 7 s, the signal intensity for I^- had no observable change that indicates that the reductive capability was sufficient for the complete conversion of iodine species in the sample. To our knowledge based on the published literatures, the concentration of TII more than 1.00 μM has not been found in seawater. Therefore, injection time of 7 s was chosen as the optimum value for practical applications.

3.3. Optimum conditions of sample loading

To our experience, although more sample load is beneficial to decrease limit of detection (LOD), but if the loaded sample amount is too much or the concentration of iodide in the sample is too high, the iodide peak recorded at the detection wavelength of 226 nm might be distorted [23]. Consequently, an appropriate amount of sample for seawater analysis was so important that peak distortion or sample dilution may then be avoided.

To find the optimal sample load, the artificial seawater fortified with 1 μM IO_3^- was used to simulate the real seawater, in which the concentration of TI should not be found over 1 μM. The sample load was varied from 2 to 6 s, as shown in Fig. 4. Obviously, the iodide peak was broadened and distorted and the analyte could not be stacked completely when the sample load was over 4 s. Thus, 4 s appeared the optimal sample injection time to avoid the distorted peak shape at 226 nm.

3.4. Oxidation of OIC for estimation of TI and DOI

Since the bonding energy of C–I and N–I in DOI [16,24] was high (209 and 159 kJ/mol, respectively) and the chemical valence of iodine in OIC could be looked as −1, C–I and N–I bond could hardly be broken by hydroxylamine hydrochloride. This could be confirmed by a poor recovery of OIC when the present reduction method was applied. For this reason, the common oxidative method was used to break C–I and N–I bond in order that all re-mineralized DOI species could be detected as I^-.

To optimize the oxidation conditions, the concentration of H_2O_2 and irradiation time of UV light were varied from 0.01 to 0.06% and from 1 to 3 h, respectively (Fig. 5). From the results obtained for an OIC sample of 0.10 μM L-thyroxine, it can be concluded that 0.03% H_2O_2 in the sample and 2 h of irradiation time with a 300 W Hg vapor lamp was enough to complete the re-mineralization of DOI.

3.5. Recovery testing for iodine species

The efficiency of the reductive conversion of inorganic iodine species to I^- under the optimized conditions was tested by evaluating the recovery of IO_3^- and I^-. The recovery data of TI (IO_3^- and I^- spiked in artificial seawater) are compared in Table 1 with the result obtained from the non-reductive CZE/tITP method [4] in good agreement. Furthermore the samples spiked, respectively, with known concentrations of four OICs, methyl iodide (CH_3I), *p*-iodoaniline, 3-iodo-L-tyrosine and L-thyroxine in 35‰ artificial seawater and subjected UV-irradiation, were also tested by the proposed method. The 35‰ artificial seawater with higher known concentration of TI (including IO_3^-, I^- and OIC) than the real seawater was determined by the proposed method after oxidation. Table 1 shows about 100% recoveries for all the analytes except CH_3I whose recovery is a little lower presumably due to strong volatility. Consequently, the reductive capability of the proposed method was recognized sufficient for the conversion of seawater iodine species including re-mineralized DOI. Likewise, the complete oxidation of DOI could ensure

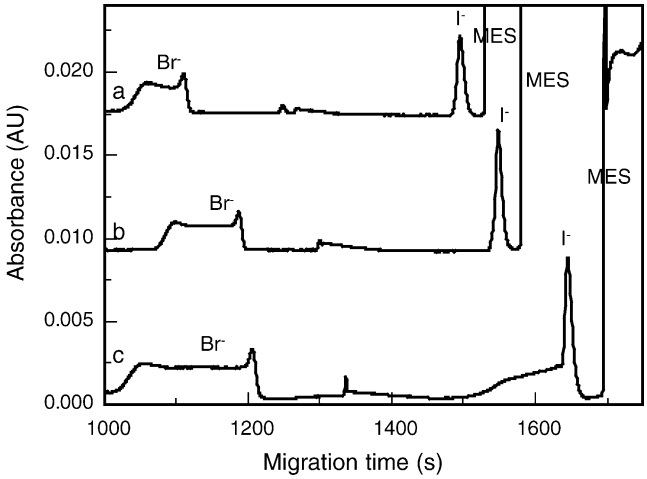

Fig. 4. Electropherograms for 1.0 μM IO_3^- in 35‰ artificial seawater at different injection time: (a) 2 s, (b) 4 s and (c) 6 s. CE conditions: RE: 200 mM hydroxylamine hydrochloride and 300 mM NaCl; other conditions were as described in Fig. 2 without including sample injection time.

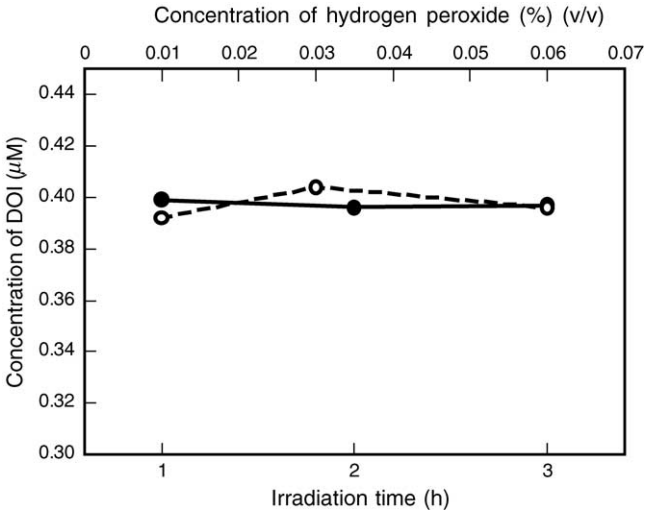

Fig. 5. Changes in peak area of iodine converted from DOI at different concentration of H_2O_2 (dashed line with open circles) and various times of UV irradiation (solid line with solid circles). Sample: 0.1 μM L-thyroxine in 35‰ artificial seawater.

Table 1
Recovery of iodine species upon CE methods

Compounds	Added I (μM)	Concentrated found (μM)			Recovery of TI (%)
		IO_3^-	I^-	TI	
IO_3^- and I^- [a]	0.35 and 0.025	0.352	0.027	0.379	101.1
IO_3^- and I^- [b]	0.35 and 0.025			0.372	99.1
IO_3^- and I^- [a]	0.50 and 0.150	0.502	0.149	0.651	100.1
IO_3^- and I^- [b]	0.50 and 0.150			0.648	99.6
CH_3I [c]	0.50			0.417	83.4
p-Iodoaniline [c]	0.40			0.400	100.0
3-Iodo-L-tyrosine [c]	0.40			0.396	99.0
L-Thyroxine [c]	0.40			0.396	99.0
IO_3^-, I^- and *p*-Iodoaniline [c]	0.40, 0.10 and 0.20			0.689	98.4

[a] Analyzed by CZE/tITP method for simultaneous determination of IO_3^- and I^- [4].
[b] Analyzed by CZE/tITP method for determination of TII with on-capillary reduction.
[c] Analyzed by the proposed CZE/tITP method for determination of TI after irradiation.

the determination of genuine TI independently from the concentration and the chemical nature of inorganic I and DOI present in seawater. The concentrations of I^- measured by the proposed method with and without UV-irradiation could quantitatively indicate the concentration of TI and TII, respectively.

3.6. Analytical performance for determination of TI

As generally accepted, the concentration of TI in seawater is about 60 μg L^{-1} (0.5 μM) [3]. In some areas, it is slightly higher, up to 80 μg L^{-1} (0.65 μM) [10]. But the concentration of TI more than 100 μg L^{-1} can hardly be observed in the ocean. To ensure the precision of DOI, which is calculated from the difference between TI and TII, high sensitivity, excellent reproducibility and large linearity of the method for determination of TI and TII were required.

The limit of detection of the proposed method (at S/N = 3) was 0.003 μM (0.4 μg L^{-1}). The reproducibility of migration time and peak area was evaluated for the real seawater sample containing ca. 0.48 μM I. Relative standard deviations for 19 runs performed within 3 days were 0.46 and 1.45% for migration time and peak area, respectively. Quantifications of both TI and TII as I^- were carried out using external calibration method in the range 0.1–0.9 μM I (12–115 μg I L^{-1}) (n = 10), and both of the correlation factor were 0.9991. Such analytical characteristics could ensure not only the adequate precision for TII and TI but also for DOI.

3.7. Seawater analysis

Based on high sensitivity and precision of our CE methods for the determination of TI and TII, organic I, calculated as their difference, may then be quantitatively obtained with confidence.

To demonstrate practicability of the proposed method, the concentrations of TI and TII in five samples collected from two marine sub-environments from different depths were systematically analyzed. The corresponding electropherograms are shown in Fig. 6. The average concentration of TII with three times repeated measurements and the corresponding standard deviation (S.D.) are listed in Table 2. The range of TII concentration in these samples varied from 0.394 to 0.467 μM with S.D. less than 0.003 μM. The concentrations of IO_3^- and I^- in these samples were obtained by the previous CZE/tITP method [4]. After treatment with H_2O_2 and UV irradiation, TI was determined by the proposed method as I^- so that the total re-mineralized DOI was distinguishable from ([TI]-[inorganic I]). The results for DOI also shown in Table 2 demonstrate that the different concentration of DOI presents at depths in the ocean.

The concentrations of TII in these samples were also determined by IC method, in which inorganic iodine species were converted into I^- before analysis. The comparative data (in Table 2) shows the results of CZE/tITP agreed with IC. It is noted that the total concentrations of iodide and iodate are lower than the concentrations of total inorganic iodine in

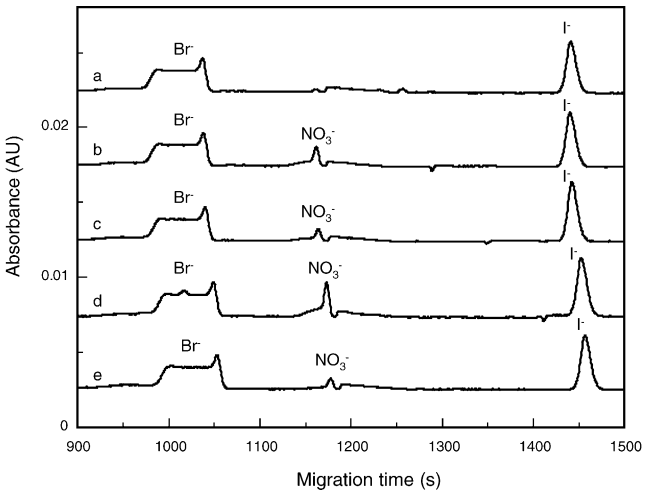

Fig. 6. Determination of TII of surface seawater (a) and deep seawater (b) at Kochi, surface seawater (c) and deep seawater (d: 100 m; e: 710 m) at 41°N, 155°E in Pacific Ocean. CE conditions: RE: 200 mM hydroxylamine hydrochloride and 300 mM NaCl; other conditions were as described in Fig. 2.

Table 2
Measured concentration (μM) of TI in seawater compared with IC results

Sample	TI	TII		$[IO_3^-] + [I^-]$	DOI
	CE[c] ($n = 3$)	CE[b] ($n = 3$)	IC ($n = 2$)	CE[a]	$[TI]-[TII]_{CE}$[b]
Kochi pref. Japan					
Surface water	0.420 ± 0.003	0.394 ± 0.002	0.444 ± 0.001	0.363	0.026
Deep water (320 m)	0.437 ± 0.002	0.426 ± 0.002	0.424 ± 0.001	0.341	0.011
Pacific: 41°N, 155°E					
Surface water	0.481 ± 0.002	0.467 ± 0.002	0.497 ± 0.008	0.444	0.014
Deep water (100 m)	0.435 ± 0.002	0.426 ± 0.003	0.405 ± 0.008	0.422	0.009
Deep water (710 m)	0.472 ± 0.002	0.461 ± 0.002	0.449 ± 0.005	0.429	0.011

[a] Analyzed by CZE/tITP method for simultaneous determination of IO_3^- and I^- [4].
[b] Analyzed by CZE/tITP method for determination of TII with on-capillary reduction.
[c] Analyzed by the proposed CZE/tITP method for determination of TI after irradiation.

all seawater samples treated here. However we do not have sufficient evidences to explain the cause of the difference between them. It still needs more information to discuss such a controversial issue.

4. Conclusions

The analytical scheme was proposed for the determination of TII by CE, which was for first time advanced for TI and DOI. In combination with tITP preconcentration of IO_3^- and I^-, the proposed method provides a highly sensitive, simple (no sample preparation), and low cost assay to discriminate essential iodine forms in seawater. As a result of such assays, DOI was found to contribute significantly in TI content in seawater, the finding which should not be neglected for iodine relative biology and geochemistry in marine environment. The method developed can be adopted for the routine analysis of the samples with high salt content such as urine and serum. Our further research on assessing the distribution of iodine forms in deep ocean is in progress.

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