

Comparisons of disposable and conventional silver working electrode for the determination of iodide using high-performance anion-exchange chromatography with pulsed amperometric detection

Lina Liang^a, Yaqi Cai^a, Shifen Mou^{a,*}, Jun Cheng^b

^a Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China

^b Dionex Corporation, Sunnyvale, CA 94088-3603, USA

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Abstract

The paper compared the performance of two kinds of silver working electrode in electrochemical detector—the disposable and conventional electrode for the determination of iodide using high-performance anion-exchange chromatography (HPAEC) hyphenated with pulsed amperometric detection (PAD). The comparisons were carried out on the time of equilibration, long and short-term reproducibility, limits of detection and linearity of calibration. Results showed that disposable working electrode manifested equal or better results than conventional working electrode and could be used for iodide analysis. Besides, the disposable electrode could work for consecutive 2660 min (about 44 h, 10 min needed for each run) with no degradation. Due to its “disposable” property, disposable working electrode could be discarded if the detection sensitivity decreased to 80% so the time for polishing and reconditioning was spared and good reproducible results could be obtained. At last, the disposable electrode was applied for the determination of iodide in soil and sea water samples with the spiked recovery ranging from 96–104% and the detection limit of 0.5 µg/L (10 µL injection, three times of the baseline noise).

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1. Introduction

As an essential trace element, iodine is abundant in sea-water and sea products with the main species as iodate and iodide [1–3]. Iodine plays an important role in influencing the proper function of thyroid gland. Too low or excess ingestion of iodine may lead to hypertrophy or hypothyroidism and hyperthyroidism [4,5]. Common sources of iodide intake are from table salt and seafood, but other food products also contain iodide. Iodide contents in food correlate closely with the soil the plants grow. So, the determination of iodide in soil helps to find out the approximate iodide contents in food and prevent the potential diseases caused by iodide deficiency or excess in the body.

Various analytical methods have been proposed to analyze iodide contents. The routine methods for iodide separation are IC and HPLC with the detection limit in the range of sub µg/L or µg/L [1,6–8]. The IC method can separate iodide directly by using anion-exchange column while HPLC method usually use reverse phase column modified by ion-pairing reagent in the mobile phase [6]. With the update of the stationary phase in anion-exchange columns, such as strong hydrophilic IonPac AS16 column from Dionex, the routine anions, such as chloride, bromide, nitrate, sulfate, etc., elute far before iodide and their electrochemical response is usually low compared with iodide. So, the iodide contents could be analyzed easily with no or simple sample preparations. As for the iodide detection, spectrophotometry detector is adopted widely but the sensitivity is usually low [7,9,10]. ICP-MS is a more sensitive method with low interferences to determine iodide contents in different matrix samples but confined to

* Corresponding author. Tel.: +86 10 6284 9182; fax: +86 10 6284 9239.
E-mail address: shifenn@mail.rcees.ac.cn (S. Mou).

the high cost of the instrument and maintenance. Pulsed amperometric detection (PAD) is one recently developed electrochemical detection method originally developed to solve the determination problems for carbohydrate analysis when UV detector was used [11] and now has been used widely for the determination of iodide [12–14]. The common working electrodes of PAD included gold, silver, platinum and glass carbon electrode. Disposable electrodes are the latest innovation in electrochemical detector, introducing a new level of reproducibility and ease of use to the customer [15]. The disposable gold working electrode has been commercialized for the determination of amino acids and carbohydrates. Based on this, the disposable silver electrode was further developed and the performance data was presented in this paper.

At last, the disposable electrode was applied for the determination of iodide in soil and sea water samples using the proposed method.

2. Experimental

2.1. Instrument

The ICS-2500 module ion chromatography system (Dionex, CA, USA) was used throughout the experiment. The system is composed of a GS50 gradient pump with on-line degassing, an ED50A electrochemical detector (Ag working electrode, Ag/AgCl reference electrode and titanium counter electrode), an AS50 autosampler and LC30 column thermostat. The injection volume is 10 μ L with 25 μ L injection loop installed and fulfilled by the autosampler. IonPac AS16 analytical column (250 mm \times 2 mm), IonPac AG16 guard column (50 mm \times 2 mm) and the ED50A detection cell were all put into LC30 column thermostat to keep the temperature constant at 30 $^{\circ}$ C.

The data were acquired and processed using Chromeleon 6.5 workstation. The detection waveform is listed in Table 1, which is brought forward and discussed in detail by one of the authors in another paper [16].

2.2. Reagents and standards

All chemicals were of reagent grade except where specified. Milli-Q water (18.3 M Ω cm) was used throughout the experiment after filtering through 0.22 μ m Nylon membrane.

Table 1
Waveform for iodide determination

Time (ms)	Potential (mV)	Integration
0.00	–50	
200	–50	Begin
900	–50	End
910	–600	
920	–600	
930	–400	
1000	–400	

The mobile phase consisted of 75% water and 25% 250 mM NaOH and was prepared according to literatures [17,18]. A 50% (w/w) NaOH solution was prepared and left to precipitate carbonate. Diluting 13.1 mL of 50% (w/w) NaOH solution to 1 L water yielded a 250 mM NaOH solution. Once the mobile phase was prepared well, it should be kept under nitrogen to prevent entry of atmosphere carbon dioxide.

Weigh in 1.3081 g KI (superior grade) and dissolve the whole amount with 1000 mL water to obtain 1000 mg/L iodide solution, then dilute to a lower concentration between 50 and 5000 μ g/L with water. Iodide (1000 μ g/L) was used to evaluate the lifetime and reproducibility of disposable electrode and reproducibility of the conventional electrode. All standards should be stored in a 4 $^{\circ}$ C refrigerator.

2.3. Description of conventional and disposable electrode

Conventional electrode is made from a 1-mm-diameter silver rod (0.785 mm²) force fit into a polypropylene block.

Disposable electrode is manufactured by depositing a thin layer of the working electrode material on a thin polyester film, which is similar to that used for the preparation of disposable gold electrodes [15,16]. The disposable electrode consists of three parts, a small circle—the working electrode, a large circle—the contact pad and one straight narrow lead to connect them. All three parts of disposable electrode consist of ca. 500 Å titanium with a top layer of ca. 6000 Å silver. The disposable electrode slice must be supported by one blank polypropylene holder block with structure similar to conventional electrode. The geometric area of the disposable electrode is 0.785 mm² also (circular electrode, 1 mm diameter) [16].

2.4. Sample preparation

The soil samples were air-dried and sifted out using 1-mm sieve. An aliquot of 25 mL 0.01 mol/L CaCl₂ was added to 2.5 g soil samples and shaken for 40 h at 25 $^{\circ}$ C. After centrifuging for 5 min at 10,000 rpm, 10 mL supernate was pipetted and 50 μ L 1% ascorbic acid was added to reduce iodate into iodide. This solution was filtered through 0.22 μ m Nylon membrane and diluted with equal aliquot of water before injected to the HPAEC-PAD system. The 300 μ g/L iodide standard was spiked into the dilution solutions.

Sea water samples were filtered through 0.22 μ m Nylon membrane then injected to the HPAEC-PAD system.

3. Results and discussion

3.1. Start-up time, background signal and baseline noise

In the first part of the study, the start-up time, background signal and baseline noise of the system was investigated. Start up the system with conventional or disposable elec-

trode installed in PAD and equilibrate under the standard initial conditions. Once the baseline has stabilized, the background signal was recorded (do not offset). Inject water blank and record the data for approximately 30 min. As for disposable electrode, different electrode was tested for 5 consecutive days. The start-up times of two kinds of electrodes were almost the same. Background signal and baseline noise of the conventional electrode were 110 nC and 0.12–0.25 nC, respectively. The background signal and baseline noise of the disposable electrode were lower than the corresponding values of the conventional one, with background signal and baseline noise of 15–32 nC and 0.01–0.03 nC, respectively. Usually, the background signal of new conventional silver working electrode was several nC when using HNO₃ as eluent [12–14]. While in our experiment, the conventional electrode had been used for many real samples analysis. Even after carefully mechanical polishing, the background signal and baseline noise of this conventional electrode are still higher than the disposable one.

3.2. Short and long-term reproducibility of electrode

The method reproducibility of silver working electrode, the conventional and disposable, was evaluated over short-term (within one day) and long-term (5 consecutive days) using 1000 µg/L iodide.

There were five pieces of disposable electrodes involved in short-term reproducibility test. In order to evaluate the equilibration time of the electrode, the disposable electrode was installed after the oven temperature and column pressure reached to constant levels. And once the equilibration of the whole system achieved, the 50, 500, 1000 and 5000 µg/L iodide standard was injected. Each standard was injected for successive three times except that the 1000 µg/L iodide standard was injected for five times. Record the data and then obtain the average response value and standard deviation of 1000 µg/L iodide standard. As can be seen from Table 2, four disposable electrodes showed good relative standard deviation lower than 4%. And the third one had 6% RSD due to one lower value of 18.47 nC.

The long-term reproducibility was obtained by testing the response of one disposable electrode for 5 consecu-

Table 2
Short-term reproducibility of disposable silver electrode^a

Injection number	Peak height (nC)				
	E-1	E-2	E-3	E-4	E-5
1	20.43	19.55	20.04	17.87	17.97
2	20.06	18.62	18.47	17.06	17.65
3	19.67	19.82	19.27	17.46	18.44
4	20.27	19.30	21.16	18.32	19.14
5	18.93	19.24	21.86	18.69	19.44
Average	19.87	19.30	20.16	17.88	18.53
SD	0.60	0.44	1.37	0.65	0.76
RSD (%)	3.02	2.30	6.82	3.65	4.09

^a 1000 µg/L iodide, 10 µL injection.

Table 3
Long-term reproducibility of disposable silver electrode

Injection number	Peak height (nC)				
	1st day	2nd day	3rd day	4th day	5th day
1	20.43	22.01	19.78	18.37	18.45
2	20.06	21.78	19.33	18.80	19.19
3	19.67	21.53	19.61	18.12	18.56
4	20.27	20.88	19.58	18.45	18.68
5	18.93	20.63	19.55	18.90	19.44
Average	19.87	21.36	19.57	18.53	18.86
SD	0.60	0.59	0.16	0.32	0.43
RSD (%)	3.02	2.77	0.83	1.73	2.27

tive days. We selected the first disposable electrode to be used for the long-term reproducibility test. Once the experiment of the short-term reproducibility test had been finished, this electrode was installed and tested the response for 1000 µg/L iodide standard for five consecutive injections. The long-term reproducibility test results were shown in Table 3. The average peak height, the standard deviation and the RSD of 5 days were 19.64, 1.10 nC and 5.62%, separately.

The short-term and long-term reproducibility were also evaluated for conventional electrode using 1000 µg/L iodide. The operating procedures were the same as disposable electrode. The average peak height, the standard deviation and the RSD of short-term reproducibility were 14, 0.23 nC and 1.65%, separately. Though the peak height or sensitivity was lower than disposable electrode, the RSD was slightly better than disposable electrode. As for long-term reproducibility, the above values were 13.93, 1.07 nC and 7.32%, separately. The RSD was slightly worse than disposable electrode.

3.3. Electrode-to-electrode reproducibility

Electrode-to-electrode reproducibility mainly referred to disposable electrode and the conventional electrode was not discussed. From the above short-term results in Table 2 we could see that the electrode-to-electrode reproducibility was very well. The peak height for 1 mg/L iodide standard with 10 µL injection all lied from 17.88 to 20.16 nC with RSD less than 5%.

Once the detection sensitivity decreased to 80%, the disposable electrode could be discarded and new disposable electrode could be installed and behaved as well as the previous one. No polishing was needed to clean the electrode so the polishing and reconditioning time was saved.

3.4. Linearity and detection limit

Using two kinds of silver working electrode, we further compared the linearity and detection limit of them. As for the disposable electrode, we use one electrode throughout the performance experiment and it was still used after this experiment finished. The total run-time of this disposable

Table 4
Linearity of disposable and conventional silver working electrode

Electrode	Calibration curve	Linear range	R	Calculation style
Disposable	$Y = 0.0043x - 0.4114$	50 $\mu\text{g/L}$ –10 mg/L	0.9994	Peak area
	$Y = 0.0235x - 3.1138$	50 $\mu\text{g/L}$ –10 mg/L	0.9995	Peak height
	$Y = 0.0154x + 0.0793$	10–50 $\mu\text{g/L}$	0.998	Peak height
Conventional	$Y = 0.0042x + 0.8193$	50 $\mu\text{g/L}$ –8 mg/L	0.9977	Peak area
	$Y = 0.0130x + 1.0724$	50 $\mu\text{g/L}$ –8 mg/L	0.9992	Peak height

Table 5
Total iodine contents in soils (calculated as iodide) and iodide contents in sea water samples

Samples	Iodide contents	Spiked	Recovery (%)
Soil-1	553 \pm 18 ng/g	300 ng/g	99 \pm 3
Soil-2	758 \pm 22 ng/g	300 ng/g	104 \pm 4
Sea water-1	29 \pm 1 $\mu\text{g/L}$	23.5 $\mu\text{g/L}$	99 \pm 2
Sea water-2	21.2 \pm 0.4 $\mu\text{g/L}$	23.5 $\mu\text{g/L}$	96 \pm 2

electrode was 2660 min, which meant we could inject 266 times of standards or samples (10 min for each run). Further studies of other disposable electrode showed that it could be used for up to 10 working days.

The linearity was performed using 10 $\mu\text{g/L}$ –10 mg/L iodide standard solutions prepared in water. All the results are listed in Table 4. For conventional electrode, good linearity was found between 50 $\mu\text{g/L}$ and 8 mg/L, with the correlation efficient of 0.9977 and 0.9992 if calculated as peak area and peak height, respectively. For disposable electrode, good linearity was found between 50 $\mu\text{g/L}$ and 10 mg/L, with the correlation efficient of 0.9994 and 0.9995 if calculated as peak area and peak height, respectively. The disposable electrode was further used to determine 10–50 $\mu\text{g/L}$ iodide standard solutions. The linearity was much better if calculated as peak height than as peak area because of the peak tailing of the ultra low concentrations of iodide.

The detection limit of disposable and conventional electrode was 0.5 and 2 $\mu\text{g/L}$ (three times of the baseline noise), respectively. If increasing the injection volume from 10 to 500 μL , the detection limit could be greatly further decreased.

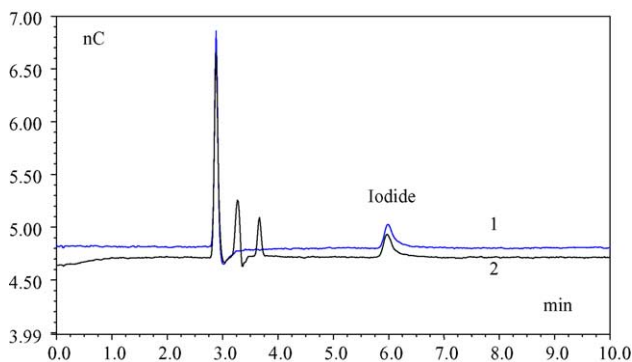


Fig. 1. Chromatograms of iodide in standard solution (1, 25 $\mu\text{g/L}$) and sea water-2 sample (2) (10 μL injected).

3.5. Application

Two kinds of samples, soils and sea waters, were analyzed using the disposable working electrode and the spiked recovery are shown in Table 5. The resulted were all calculated as peak height. As could be seen, the iodide concentrations in sea waters were about 20–30 $\mu\text{g/L}$ and the recovery ranged from 96 to 99%. The total iodine concentrations in soils were about 500–800 ng/g (calculated as iodide) and the recovery ranged from 99 to 104%. The chromatogram of 25 $\mu\text{g/L}$ iodide standard and sea water-2 sample is shown in Fig. 1.

4. Conclusion

The paper carried out preliminary study on the performance of disposable silver working electrode and made comparisons between disposable and conventional silver electrode for the determination of iodide using high-performance anion-exchange chromatography (HPAEC) hyphenated with pulsed amperometric detection (PAD). The comparisons results showed that disposable working electrode manifested equal or better results than the conventional one in the limit of detection, linearity of calibration, and reproducibility. So the disposable electrode could be used for iodide analysis to obtain reproducible results. Besides, disposable working electrode could be discarded if the detection sensitivity decreased to 80% so the time for polishing and reconditioning was spared. At last, the disposable electrode was applied for the determination of iodide in soil and sea water samples. The detection limit was 0.5 $\mu\text{g/L}$ based on 10 μL injection, which could be further decreased by increasing the injection volume to 500 μL and further studies have confirmed this.

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