ANALYTICAL SCIENCE & TECHNOLOGY
Vol.15, No.5, 445-450, 2002
Printed in the Republic of Korea

Determination of total iodide in seawater by gas chromatography-mass spectrometry

Ueon-Sang Shin
Korea Institute of Science and Technology, P.O. BOX 131, Cheongryang, Seoul 130-650, Korea
(Received Sep. 24, 2002)

Gas chromatography-mass spectrometry를 이용한 해수 중 총 요오드 정량분석

신원상
한국과학기술연구원
(2002. 9. 24 접수)

Abstract : A sensitive gas chromatographic method has been established for the determination of total iodide in seawater as their volatile organic derivative. The method is based on the formation of 4-iodo-2,6-dimethylphenol with 2,6-dimethylphenol in matrix and a single-step extraction of the derivative with ethyl ether, which are then measured by gas chromatography-mass spectrometry (selected ion monitoring). Iodate in sea water was completely reduced to iodide with ascorbic acid and acetic acid. The detection limit was 0.1 ng/mL in seawater and the calibration curve showed good linearity with r=0.9997. The method was sensitive, reproducible and simple enough to permit the reliable routine analysis of total iodide in seawater. Total iodide in sea water was found about 30 ng/ml.

요 약 : 해수에 함유되어 있는 요오드화합물의 총량을 휘발성 유기물로 유도체화 후 측정하는 방법을 확립하였다. 이 방법은 요오드 음이온은 요오드로 산화시킨 후 2,6-dimethylphenol과 반응하여 4-iodo-2,6-dimethylphenol로 전환시켜 ethylether로 1단계 추출 후 gas chromatography-mass spectrometry (selected ion monitoring)로 측정하는 것으로 구성되어 있다. Iodate는 ascorbic acid 와 acetic acid로 요오드 음이온으로 환원시킨 후 요오드 음이온 측정법과 동일하게 수행하였다. 이 방법은 검출한계가 해수에서 0.1 ng/ml이었으며 검량선은 0.9997의 좋은 상관계수값을 보였다. 이 방법은 또한 재현성이 우수하고 간단하여 해수에 인체의 필수원소인 요오드를 낮은 농도까지 분석하는데 유용하게 사용될 수 있다고 사료된다.

key words : Seawater, iodide, GC-MS, 4-iodo-2,6-dimethylphenol

1. Introduction

Iodine is an essential trace element that is necessary for normal thyroid function. It is used in the synthesis of thyroxine (T_4) and triiodothyronine (T_3) within the thyroid gland.[1,2] Daily adult requirements are about 100 to 300 μg. When iodine requirements are not adequately

★ Corresponding author
Phone : +82+(0)2-958-5173 Fax : +82+(0)2-958-5189
E-mail : us_shin12@kist.re.kr

met, a range of deficiency disorders can develop. Iodine intakes consistently lower than 50 ㎍/day usually result in thyroid hypertrophy (endemic goiter) and sever and prolonged iodine deficiency may result in hypothyroidism. Otherwise, an excess of iodine and iodides can produce goitre and hypothyroidism as well as hyperthyroidism.[1,2] Therefore, the ingestion of iodine in foods can have profound effects on the thyroid status of individuals. To ensure sufficient iodine uptake, many food products are enriched in iodine; iodinated table salt is the most prominent example.

The determination of iodine is always an analytical problem, especially at the relatively low natural concentration level, which is normally below 1 ㎍/g. In the literature, many methods including spectrophotometry,[3-7] neutron activation analysis,[8] inductively coupled plasma emission spectrometry (or mass spectrometry),[9-11] ion chromatography (IC),[12-23] gas chromatography (GC) after derivatization,[24-31] liquid chromatography,[32-34] stripping voltammetry,[35-36] size exclusion chromatography,[37] atomic absorption spectrometry[38] have been proposed for the determination of iodide. These methods based on different principles have been proposed for the determination of iodide in various matrices.

Many attentions have been paid to determine trace iodide in seawater[8,17,19,22,23,37] or table salt,[4] and IC has been mostly used for the objective.[17,19,22,23] Two factors in this case are necessary in order to achieve good sensitivity: (1) separation of iodide from an excess of chloride in seawater and (2) highly sensitive detection of iodide. Both of these difficulties are avoided in the following method by utilizing a suitable derivatizing reagent and proper reaction conditions, and this has enabled the develoment of a method for the determination of iodide at trace levels. We considered GC-MS determination after the derivatization of iodide in order to enhance the volatility of iodide. Derivatization of iodide to organo-iodine compound was performed in sea water.

2. Experimental

2.1 Materials

Potassium iodide were of analytical grade 99.9% from Sigma (ST. LOUIS, MD, USA). 2,4,6-Trichlorophenol (TCP), sodiumhypochlorite and 2,6-dimethylphenol (DMP) were of analytical grade 99.9% from Aldrich (Milwaukee, WI, USA). Ethylether, pentane, potassium hydroxide, sodium sulfate were used as reagents and solvents.

Seawater samples (salinity=3.41-3.48%, depth= 0-100 m) were collected with a Van Dorn sampler near Teahn, Korea (April. 1.- July. 31, 2002). Samples were stored in a refrigerater just after sampling and were analyzed within 1-2 weeks in the laboratory.

2.2 Sample treatment

A 10 mL volume of sea water was mixed with ascorbic acid and acetic acid (final concentration, 4×10^{-4} M and 0.06 M, respectively). After that, the treated samples were left standing for 1 h to complete of the reaction. Ascorbic acid (0.2 M) was made just before addition to the samples.

2.3 Derivatization and extraction

2 ml of phosphate buffer, a 20 ㎕ of 2,6-DMP solution (2500 ㎍/ml in MeOH) and 1 ml of 0.01 M sodium hypochlorite were added to the treated sample and shaken mechanically for 20 min at room temperature. 20 ㎕ of 2,4,6-TCP (8.25 ㎍/ml in MeOH) as an internal standard was added to the solution. The sample was extracted with 5 ml of ethyl ether by mechanical shaking for 15 min. The two phases were separated by centrifugation (5 min at 1500 g) and the organic phase was transferred into a 20 ml glass stoppered test tube and evaporated at reduced pressure, dissolved in 100 ㎕ of methanol, then a 2 ㎕ portion of the organic phase was injected directly into the GC.

2.4 Calibration and quantitation

Calibration curve for iodide was established by adding 0, 50, 250, 1000, 2,500, 5,000, 10,000 and 30,000 ng of standards and 165 ng of internal standard (2,4,6-TCP) in a 10 ml of sea water. The ratio of the peak area of standard to that of internal standard was used in the quantitation of the compounds.

2.5 Gas Chromatography-Mass Spectrometry

All mass spectra were obtained with a Agilent 6890/5973 N GC-MS. The ion source was operated in the electron ionization mode (EI; 70 eV, 230 ℃). Full-scan mass spectra (m/z 40-800) were recorded for the identification of analyte. The operating parameters of GC-MS were shown in *Table* 1.

Table 1. GC-MS conditions for the determination of iodide

Parameter	Conditions		
Column	HP-5MS(Cross-linked 5%phenylmethylsilicon, 30 m×0.25 mm I.D.×0.2 ㎛ film thickness)		
Carrier	He at 0.8 ml/min		
Oven Temp	15 ℃/min		
	100 ℃(2 min) → 220 ℃(2 min) → post run 280 ℃(3 min)		
Injector Temp	260 ℃		
Selected Ion	Group	Start time (min)	Selected Ions (m/z)
	1	2.20	198
	2	4.40	248

3. Results and discussion

3.1 Derivatization and extraction

The derivatization of iodine compounds was accomplished as follows. Iodate was completely reduced to iodide with ascorbic acid and acetic acid (reaction I). The quantitative oxidation of iodide to iodine respectively can be performed by hypochlorite (reaction II) without the interference of other reducing substances. Every mole of iodine formed from reaction (II) was converted into 1 mole of 4-iodo-2,6-DMP by substitution reaction (III). The iodide liberated in reaction (III) is again oxidized by hypochlorite until all iodide has been converted into 4-iodo-2,6-DMP.

$IO_3^- + 6H^+ +$ ascorbic acid $\rightarrow I^- + 3H_2O$ ------- (I)

$2OCl^- + 2I^- + 4H^+ \leftrightarrow I_2 + 2Cl^- + 4H_2O$ --------- (II)

$I_2 +$ 2,6-DMP $\rightarrow$ 4-iodo-2,6-DMP $+ I^-$ ---------- (III)

The reaction rate of iodide in sea water with derivatizing reagents was studied. This sample was analyzed at reaction times of 0, 10, 20, 30, 40, 50, 60, 90 and 120 min (*Fig*. 1). Complete reaction takes place in about 20 min at room temperature, provided that a sufficiently high concentration of 2,6-DMP is present in the reaction mixture. No significant variation in reaction yield was noted over this time period.

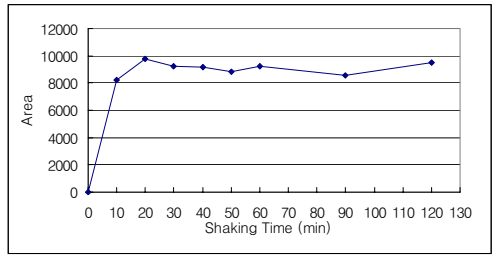

Fig. 1. The reaction rate of iodide with derivatizing reagents A.

Ethyl ether was found to be efficient for the extraction of 4-iodo-2,6-DMP from sea water. The extract is directly injected into the GC after concentration. Because of its simplicity, rapidity and specificity this procedure offers general advantages over existing methods

Freshly prepared standard solution of iodide was compared with standard solutions stored at 4 ℃ for 2 weeks. The compound was stable when stored at -10 ℃ and the derivative was stable during extraction and in chromatographic system, and for seven days at 4 ℃.

3.2 Analytical characteristics

For the GC separation of the derivative, the use of the non-polar stationary phase was found to be efficient. The column was stable over more than one thousand injections without notable change of the separation characteristics. Chromatograms are shown in *Fig*. 2. Separation of the derivative and internal standard from the background compounds of water was very good. There were no extraneous peaks observed in a chromatogram of blank water at the retention times of 3.75 and 4.82 min.

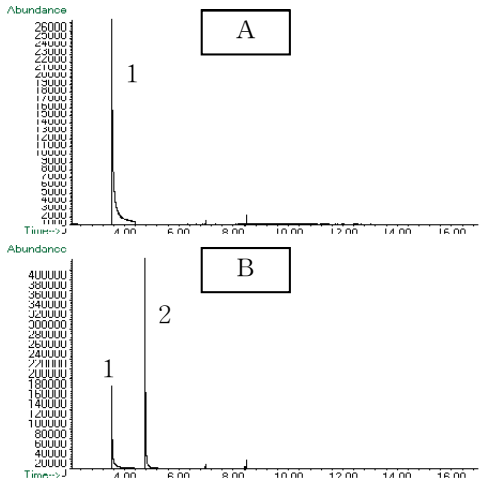

Fig. 2. Chromatogram of the extract of (A) reagent water and (B) water spiked with iodide (50 ng/ml) and internal standard (25 ng/ml). 1=2,4,6,-trichlorophenol (3.75 min); 2=4-iodo-2,6-dimethylphenol (4.82 min)

Examination of typical standard curves by computing a regression line of peak area ratios of 4-iodo-2,6-DMP to internal standard on concentration using a least-squares fit demonstrated a linear relationship with correlation coefficients being 0.9997. The line of best fit is y=0.0030x - 0.0853, where x is the analyte concentration (ng/ml) and y is the peak area ratio of the analyse to internal standard (*Fig.* 3).

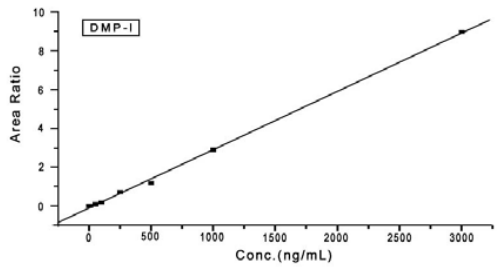

Fig. 3. Calibration curve of iodide in sea water.

Several 0.3% NaCl water samples of varing composition were prepared and the relative recoveries were calculated by percentage of derivatives recovered. The mean recoveries were about 95% at the concentration 25 ng/ml each of iodide, and it was found to be constant at several concentrations..

The reproducibility of the assay was very good, as shown in *Table* 2. For five independent determinations at about 10 and 100 ng/ml in 0.3% NaCl water, the coefficient of variation was less than 10%.

The combination of low background, high extraction yield, high derivatization yield, and the high aboundance of molecular ion of the derivative permit their determination in sea water and salt at concentrations well below those reported previously. Detection limits of iodide were 0.1 in sea water based upon an assayed sample volume of 10 ml. Limits were defined by a minimum signal-to-noise ratio of 3 and coefficients of variation for replicate determinations (n=5) of 15% or less.

Table 2. Within-run precision and accuracy of iodide in sea water and salt (n=5)

Sample	Spiked	Found (ng/L)	
	Conc. (ng/L)	Results	$\bar{X}$ ± SD (RSD)
Sea water	10	11.8, 12.7, 13.6, 12.8, 11.9	12.6 ± 0.7 (5.9%)
	100	104.0, 92.5, 87.2, 107.6	93.0, 96.9 ± 7.3 (8.3%)
Table salt	0	8.3, 9.1, 10.1, 8.7	10.6, 9.4 ± 1.0 (9.8%)
	100	96.9, 97.3, 90.9, 95.3	90.7, 94.2 ± 2.9 (3.1%)

$\bar{X}$ = mean value; SD = standard deviation ; RSD = relative standard deviation

3.3 Application to seawater and table salt

Partial application of the method to the analysis of iodide in 3 sea water was demonstrated. The results are given in *Table* 3. In sea water, we found about 30 ng/ml of total iodide. The concentration of total iodide in sea water varied slightly with depth. Iodide concentration decreased with an increase in depth.

Table 3. Analytical results of seawater and salt for total iodine

Depth	Analytical Results (ng/mL)
0.5 m	34.2 ± 2.5
20 m	30.3 ± 2.5
70 m	26.7 ± 1.8

4. Conclusion

This proposed method determines iodide selectively in large excess of chloride ion. The detection limit of iodide is 0.1 ng/mL for sea water. The method developed here is simple, sensitive and selective, and suitable for the determination of low concentration of iodide in sea water.

References

1. J. E. F. Reynolds, Martindale, The extra pharmacopoeia, thirtieth Edition, London, The Pharmaceutical Press, 970 (1993).
2. A. G. Gilman, L. S. Goodman, T. W. Rad, F. Murad, The Pharmacological Basis of Therapeutics, Seventh Edition, New York, Macmillan Publishing Company, 964 (1985).
3. S. Kartikeyan, T. Prasada Rao, C. S. P. Iyer, A. D. Damodaran, Talanta, **40**(6), 771 (1993).
4. J. Sun, X. Chen and Z. Hu, Fresenius Journal of Analytical Chemistry, **357**(7), 1002 (1997).
5. N. Nashine, R. K. Mishra, Analytica Chimica Acta, **285**(3), 365 (1994).
6. B, Rezaei, Analytical Letters, **33**(12), 2553 (2000).
7. E. A. Guenther, K. S. Jhonson, K. H. Coale, Anal. Chem., **73**(14), 3481 (2001).
8. X. L. Hou, H. Dahlgaard, B, Rietz, U. Jacobsen, S. P. Nielsen, A. Aarkrog, Anal. Chem., **71**, 2745 (1999).
9. S. P., Dolan, S. A. Sinex, S. G. Capar; A. Montaser, R. H. Clifford, Anal. Chem., **63**, 2539 (1991).
10. M. Haldimann, B. Zimmerli, C. Als, H. Gerber, Clin. Chem., **44**, 817 (1998).
11. G. Raedlinger, K. G. Heumann, Anal. Chem., **70**, 2221 (1998).
12. Y. Miura, T. Koh, Bunseki Kagaku, **41(7)**, 331 (1992).
13. M. Nishimura, M. Hayashi, Bunseki Kagaku, **41(4)**, 185 (1992).
14. L. G. Daignault, D. P. Rillema, J. High Resolut. Chromatogr., **15(5)**, 293 (1992).
15. W. Buchberger, H. Malissa, E. Mulleder, J. Chromatogr., **602**, 51 (1992).
16. A. A. Almeida, L. F. C. Jun, Mikrochimica Acta, **127** (1), 55 (1997).
17. S. Chandramouleeswaran, B. Vijayalakshmi, S. Kartihkeyan, T. P. Rao, C. S. P. Lyer, Mikrochimica Acta, **128** (1), 75 (1998).
18. H. L. Tucker, R. W. Flack, J. Chromatogr. A., **804**, 131 (1998).
19. A. C. M. Brandao, W. W. Buchberger, E. C. V. Butler, P. A. Fagan, P. R. Haddad, J. Chromatogr., **706**, 271 (1995).
20. A. Y. Yashin, T. T. Belyamova, J. Anal. Chem., **53**, 334 (1998).
21. Y. Bichsel, U. Von Gunten, Anal. Chem., 71, 34 (1999).
22. W. Hu, P.-J. Yang, K. Hasebe, P. R. Haddad, K. Tanaka, J. Chromatogr. A, **956**(1), 103 (2002).
23. K. Ito, Anal. Chem., **69**, 3628 (1997).
24. P. E. Moss, W. I. Stephen, Anal. Proc., **22**, 5 (1985).
25. K. K. Verma, S. K. Sanghi, A. Jain, D. Gupta, J. Chromatogr. , **457**, 345 (1998).
26. S. Grys, J. Chromatogr., **100**, 43 (1974).
27. L. Maros, M. Kaldy, S. Igaz, Anal. Chem., **61**, 733 (1989).
28. S. Chen, H. Wu, M. Tanaka, T, Shono, K. Funazo, J. Chromatogr. , **396**, 129 (1987).
29. H. S. Shin, Y. S. O-Shin, J. H. Kim, J. K. Ryu, J. Chromatogr., **732(2)**, 327 (1996).
30. S. -H. Chen, S. -M. Wu, H. -S. Kou, H. -L. Wu, J. Anal. Toxicol., **18(2)**, 81 (1994).
31. S. Mishra, V. Singh, A. Jain, K. K. verma, The Analyst, **125**, 459 (2000)
32. J. Rendl, M. Luster, C. Reiners, J. Liquid Chromatogr., **20(9)**, 1445 (1997).
33. F. Moussa, M.-C. Raux-Demay, F. Veinberg, F. Depasse, J. Chromatogr. B, **667(1)**, 69 (1995).
34. P. Mura, Y. Papet, A. Sanchez, A. Piriou, J. Chromatogr. B, **664(2)**, 440 (1995).
35. M. L. A. M. Campos, Mar. Chem., **57**, 107 (1997).
36. V. Stipanicev, M. Branica, Sci. Total Environ., **182**, 1 (1996)

37. H. B. Li, F. Chen, X. R. Xu, J. Chromatogr. A, **918** (2), 335 (2001).
38. O. Haase, J. A. C. Broekaert, Spectrochimica Acta, **57(1)**, 157 (2002)