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Analysis of alkyl organoiodide mixtures by high-performance liquid chromatography using electrochemical detection with a post-column photochemical reactor

Chien-Hou Wu[a], Jiunn-Hsiung Lian[a], Jia-Lin Wang[b], Jiunn-Guang Lo[a,*]

[a]*Department of Atomic Science, National Tsing Hua University, 101, Section 2, Kuang Fu Road, Hsinchu 300, Taiwan*

[b]*Department of Chemistry, National Central University, Chungli 320, Taiwan*

Abstract

A method for the analysis of six alkyl organoiodides (iodomethane, iodoethane, 1-iodopropane, 1-iodobutane, 1-iodopentane, 1-iodohexane) commonly found in acetic acid process was developed. In this method the target analytes were determined by high-performance liquid chromatography (HPLC) using a post-column photochemical reactor with electrochemical detection (ED) in less than 30 min. HPLC was performed in ODS C_{18} reversed-phase column (5 μm, 250×4.6 mm I.D.) under isocratic conditions with methanol–0.067 *M* acetate buffer (70:30, v/v), pH 6.2 as mobile phase at flow-rate 1.1 ml/min. Alkyl organoiodides, which are electrochemically inactive, were made oxidizable at potential of 120 mV after post-column irradiation with low-pressure mercury lamp in a knitted PTFE tube. The photoreactor was placed in an aluminum housing full of nitrogen in order to prevent from the interference of oxygen. The detection limit for most analytes was of the order of 1–2 μg/l. The HPLC–ED method with a post-column photochemical reactor has good precision and linearity and can be readily applied to the routine determination of alkyl organoiodides in real acetic acid samples.

Keywords: Detection, LC; Organoiodide compounds; Iodoalkanes; Halogenated compounds

1. Introduction

Alkyl organoiodides are widely employed as catalyst promoters of the Monsanto acetic acid process and found as byproducts in the catalytical cycle system [1–3]. The Monsanto process, an enormously successful solution-phase commercial process, accounts for approximately 60% of world acetic acid manufacturing capacity. The traditional distillation section of the plant by the Monsanto process has removed a considerable amount of alkyl organoiodides from the acetic acid product; nevertheless, the residues with ppb levels still remain and restrict their costs and usefulness. For example, trace alkyl organoiodides in raw acetic acid are strong catalyst (Rh or Pd) poisons for manufacturing of vinyl acetate. In order to evaluate the purity of acetic acid products and quantify trace amount of alkyl organoiodides in them, a sensitive analytical technique needs to be developed and devised to detect traces for chemical quality-control assays.

Typically, the analysis of organohalogens has been performed by using gas chromatographic methods with selective and sensitive detection obtained by using electron capture detection or mass spectrometry because of the volatile nature of most of

*Corresponding author. Tel.: +886-3-571-5131x1175; fax: +886-3-571-8649.

E-mail address: jglo@mx.nthu.edu.tw (J.-G. Lo).

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these compounds [4–7]. However, time-consuming sample cleanup procedures may be necessary prior to GC analysis, to avoid column overload with matrix materials or to remove potential interferents prior to the separation. In addition, the analysis of organohalogens which are insufficiently volatile for GC or thermally sensitive has been proven difficult [8]. To circumvent GC deficiencies, high-performance liquid chromatography methods have been applied for the trace determination of organohalogens.

Over the last 20 years photochemical reactors coupling HPLC with electrochemical detection (HPLC–ED) have been developed for improving the selectivity and sensitivity of electrochemical detection [9–14]. This approach, known as HPLC–photolysis-ED (HPLC–$h\nu$-ED), employs continuous, on-line UV photolysis by a low-pressure mercury lamp to generate relatively stable electrophores such as halides from nonelectroactive analytes such as organohalogens, following their separation on a reversed-phase LC column. The concept has been successfully applied for the trace determination of various classes of analytes; however, the number of the application in actual samples is rather limited. In this paper, our focus is centered on the analysis and determination of a series of alkyl organoiodides under different separation conditions. This work is aimed at establishing a simple and sensitive HPLC–$h\nu$-ED method for quality-control assays of real acetic acid samples.

2. Experimental

2.1. Chemicals and reagents

All chemicals were of analytical or reagent grade, or the highest purity available from several suppliers and were used as received. Iodomethane, iodoethane, 1-iodopropane, 1-iodobutane, 1-iodopentane, and 1-iodohexane were obtained from Aldrich (Milwaukee, WI, USA). Acetic acid and sodium acetate were obtained from Merck (Darmstadt, Germany). Methanol was purchased from Tedia (Fairfield, OH, USA). Doubly deionized water prepared with a Milli-ultrapure R/Q system (Millipore, Bedford, MA, USA) was used exclusively for all solutions ($\geq$18.2 MΩ cm resistivity).

The standard solutions of alkyl organoiodides were mixed with methanol and diluted to proper concentrations (each 4, 10, 20, 40, 100, and 250 ppb for iodine basis). They were all stored at 4 °C in amber bottles capped with PTFE-coated septa to prevent from effusion and photolysis before used. The solutions were stable for at least a week at 4 °C in amber bottles. Eluent pH was measured with a Radiometer Copenhagen PHM 82 standard pH meter and combination glass electrode (PHC2401). The pH of the acetate buffer was adjusted by mixing acetic acid with sodium acetate. Real samples of acetic acid were obtained from five local chemical manufacturers in Taiwan. They were analyzed once received and without any previous treatments or filtration.

2.2. HPLC instruments

The liquid chromatographic system consisted of the following components connected in series: a CCPD pump (Tosoh, Tokyo, Japan), a Rhenodyne (Cotati, CA, USA) Model 7125 injector, a reversed-phase chromatographic column, a laboratory-made photochemical reactor (described in the next paragraph), and an electrochemical detector (Shodex EC-1, Tokyo, Japan). Two columns were tested in this study: Hamilton polymeric PRP-1 (150×4.1 mm I.D., 5 μm particle size) and Waters Spherisorb S5-ODS-B (250×4.6 mm I.D., 5 μm particle size). We adopted the latter one with better matching polarity and reducing the tailing of peaks

2.3. Photochemical reactors

The irradiator was constructed with a low-pressure Hg discharge lamp (Model GPH10T$5_{1/2}$L-S400 from Voltarc Tubes, Waterbury, CT, USA) and a knitted open tubular (KOT) reactor composed of 0.5 mm I.D.×7.5 m×1.6 mm O.D. PTFE tubing (Cole-Parmer). The geometry of the KOT3 was developed by Selavka et al. [15] and its construction and optimization have been reported. The whole photochemical reactor was placed in an aluminum cylindrical holder (80 mm I.D.×340 mm O.D.) and full of nitrogen.

2.4. Analytical methods

The reversed-phase column (Waters Spherisorb S5-ODS-B) was operated under isocratic conditions with methanol–0.067 *M* acetate buffer (70:30, v/v), pH 6.2 as mobile phase at flow-rate 1.1 ml/min, corresponding to 80 s of irradiation in the photochemical reaction unit. The injection volume was 50 μl. The electrochemical detector was operated with the Ag working electrode at 120 mV (versus Ag/AgCl reference electrode). Qualitative information was obtained by switching the mercury lamp on and off response differences. Peak identification for each analyte was carried out by spiking with the known standard and the peak with increased height was identified. Recovery studies were performed by spiking the sample preparation with a known amount of standards. The recovery of the analyte was determined using the equation below:

$$\text{Recovery} = \left(\frac{C_{\text{determined}}}{C_{\text{spiked}}}\right) \cdot 100\% \quad (1)$$

where C_{spiked} is the known concentration of the standard sample injected and $C_{\text{determined}}$ is the concentration determined from the calibration curve of this specified analyte. In the optimal situation, the recovery is equal to 100%.

3. Results and discussion

3.1. Separation of iodoalkanes

Displayed in Fig. 1 are chromatograms resulting

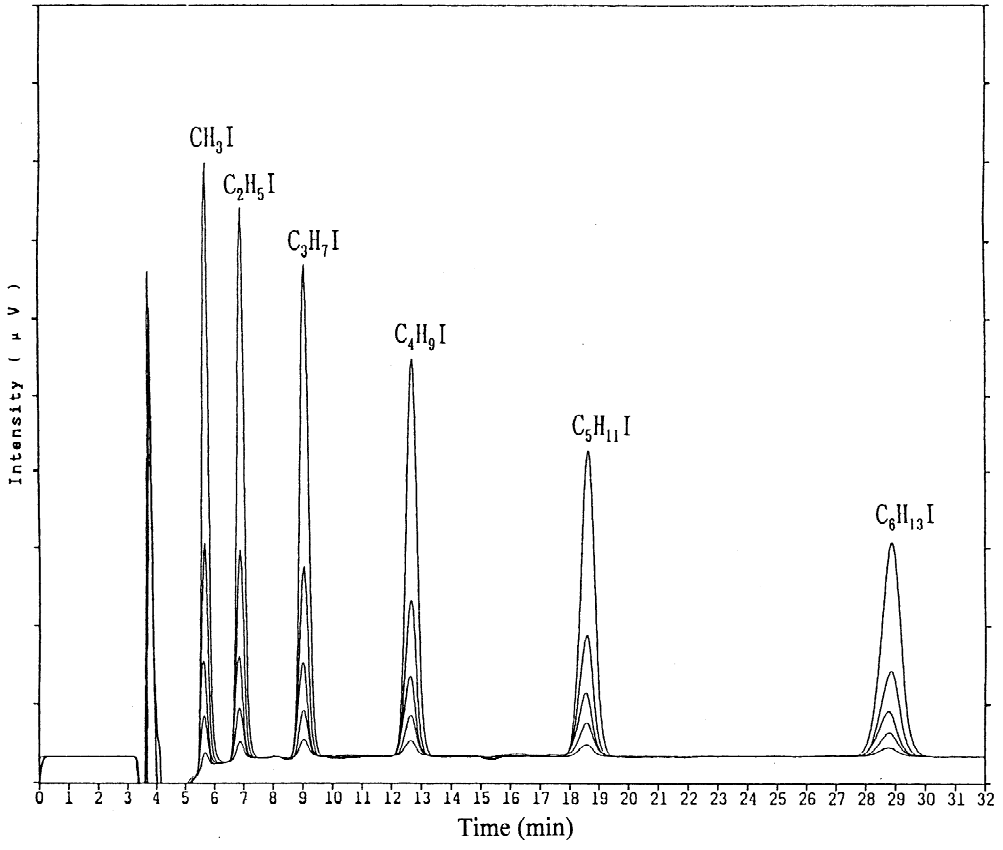

Fig. 1. Chromatograms of a mixture of six iodoalkane standards under five different concentrations 4, 10, 20, 40, and 100 ppb (for iodine basis) by using HPLC–*hν*-ED. Chromatographic conditions as in Section 2.4.

from the HPLC–$h\nu$-ED analytical method of the mixed iodoalkane standards. As expected, the most polar compound with the shortest alkyl group is eluted first, and the sequence of retention times parallels the increasing of hydrophobicity of iodoalkanes. To attain the optimization of separation, the effects of column, eluent composition, and flow-rate have been considered and studied in the following section. For maximum responses, the method also required optimization of the choice of lamp, the residence time of photolysis, and the ED potential used. Under the optimization of analytical method, response factors of organoalkanes were linear over two orders of magnitude.

3.2. Effect of eluent composition

It has been reported that iodinated organic compounds could be adequately resolved by using a C_{18} reversed-phase column and mobile phases containing methanol [10]. Fig. 2 shows the effects of mobile phase composition on the capacity factors (k') of six alkyl organoiodides in the reversed-phase column. The retention times of samples were dependent on the percentage of water in the mobile phase, increasing with diminishing methanol concentration. On the other hand, the greater the polarity with decreasing methanol concentration, the larger the capacity factor. Upon compromising these two factors, 70% MeOH in acetate buffer was chosen as the eluent.

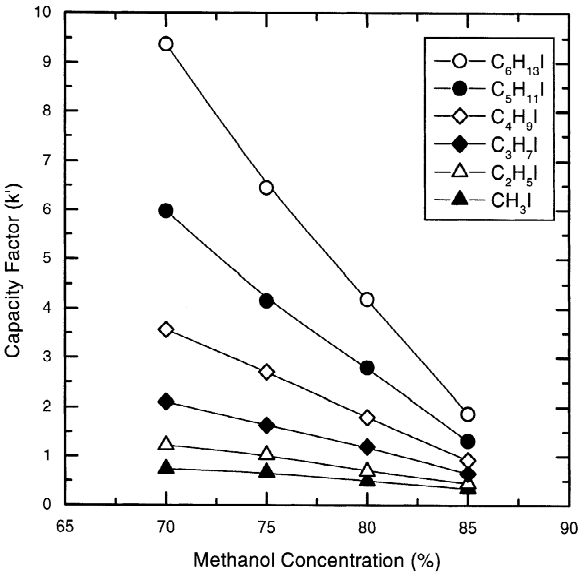

Fig. 2. Effects of methanol concentration on capacity factor (k'). Symbols: (▲) iodomethane; (△) iodoethane; (♦) 1-iodopropane; (◇) 1-iodobutane; (●) 1-iodopentane; (○) 1-iodohexane. Other conditions as in Section 2.4.

The mobile phase conditions were composed of methanol (MeOH)–20 m*M* solutions of sodium acetate (NaOAc) (70:30, v/v) because aqueous methanol–acetate buffer offered the lowest background current at the electrochemical detector with inherent baseline stability [12]. Since pH may affect the stability of iodide, a careful manipulation of pH can sometimes assist in resolving peaks that are difficult to separate. The optimal pH was found to be at 6.2.

There was no noticeable effect for the resolution varying the flow-rate from 0.8 to 1.5 ml/min. The flow-rate was set at 1.1 ml/min to maintain suitable residence time of analytes between 1.0 and 3.5 min in the 7.5-m KOT tubing.

3.3. Optimization of the photoreactor

The optimization of post-column photochemical reactor was controlled by adjusting the choice of lamp and the photoreactor device, most of which employed PTFE tubing as the reaction coils. A low-pressure Hg discharge lamp was a suitable light source for the photochemical dissociation of the C–I bond since all iodoalkanes exhibited a major absorption band close to the emission line of Hg at 254 nm. Useful qualitative information could be obtained by switching the lamp on and off. Although excess radiation powers may further reduce band broadening and improve signal-to-noise ratio by decreasing the length of the reaction coil [16], a fixed power of Hg tube lamp was used in the study.

Several postcolumn reactors have been constructed and their performances have been compared to each others [15,17–19]. PTFE tubing was applied in the study because it is the most commonly used and by far the simplest photoreactor with good performance. The use of appropriately designed knitted open tubular reactors can reduce the extra-column band-broadening to negligible values [15]. The signal versus the length of the KOT3 reactor is shown in Fig. 3. The signals increased with increasing the

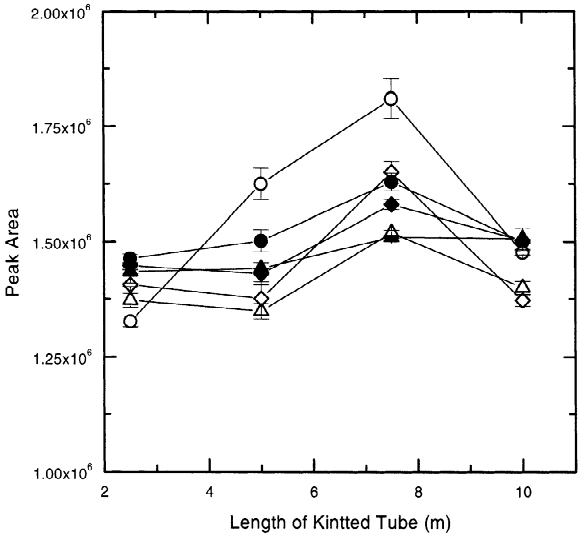

Fig. 3. Effects of reaction coil length on peak area. Notations as in Fig. 2. Each standard is at 10 ppb (for iodine base). Other conditions as in Section 2.4.

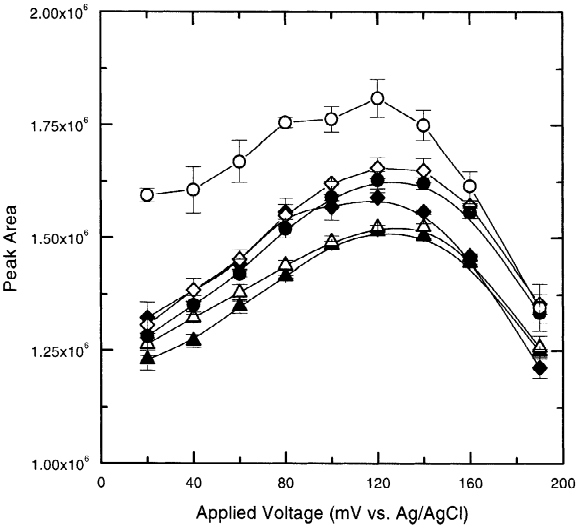

Fig. 4. Effects of applied voltage on the ED response. Notations as in Fig. 2. Each standard is at 10 ppb (for iodine base). Other conditions as in Section 2.4.

length of tubing in the initial region, and then decreased gradually afterwards. Similar to previous observation [10], the profile indicates that initial photolytic generation of iodide ion is followed by a competing photolytic process that destroys iodide. Therefore, an optimal length of knitted tube was determined to be around 7.5 m, which corresponded to the residence time around 80 s at the flow-rate 1.1 ml/min. In order to prevent from the interference of oxygen and improve durability, the whole photochemical reactor was placed in an aluminum cylindrical holder full of nitrogen.

3.4. Electrochemical detector

Fig. 4 shows the changes of the ED response at various applied voltage. The signals for all analytes increased initially with increasing applied voltage, and then decreased gradually afterwards. A number of reports have demonstrated that iodides may be electrochemically oxidized under the proper pH and eluent conditions, and using the proper electrode [20,21]. ED response is primarily due to anionic iodide but may be influenced by the presence of solvolyzed cationic photofragments [11]. At higher applied voltage, the formation of oxidizable nucleophilic products or the formation of iodine from iodide may enhance and decrease the electrochemical response. The optimum applied voltage was in the range 120 mV in this system. The conductivity detector was an alternative choice and evaluated in the study. However, the detection limit for each analyte was at the ppm level, which was too insensitive to be a useful technique for the analysis of trace organoiodides.

3.5. Precision, linearity, detection limit, and recovery

Three runs were used to establish the error bars in Figs. 3 and 4. The precisions (expressed in terms of relative standard deviation, RSD) for the six analytes are fairly good for the migration times (RSD$<$ 1.4%). The RSDs for the peak areas are typically less than 4%. The linearities and method detection limits of the present method for the six selected analytes that might be present in acetic samples are summarized in Table 1. Calibration curves were constructed by performing the standard solutions containing a mixture of the six analytes with known concentrations ranging from 4 to 410 μg/l. The data points from calibration curves were subjected to the least-squares regression analysis and the linearity of

Table 1
Linearities, method detection limits (MDL), and recoveries of the mixed iodoalkane standards analyzed by HPLC–$h\nu$-ED

Compound	Retention time[a] (min)	Calibration formula[b]	Concentration range (ppb)	Correlation coefficient	MDL[c] (ppb)	Recovery[d] (%)
CH_3I	5.67±0.08	$y = 1.24 \times 10^5 x - 3.39 \times 10^4$	4–110	0.9994	1.8	104±6
C_2H_5I	6.87±0.07	$y = 1.25 \times 10^5 x - 4.41 \times 10^4$	5–130	0.9997	1.5	97±5
C_3H_7I	9.05±0.06	$y = 1.24 \times 10^5 x - 6.76 \times 10^4$	5–140	0.9999	1.5	98±4
C_4H_9I	12.67±0.06	$y = 1.21 \times 10^5 x - 5.36 \times 10^4$	6–360	0.9993	1.9	95±5
$C_5H_{11}I$	18.59±0.08	$y = 1.13 \times 10^5 x - 3.06 \times 10^4$	6–390	0.9991	1.9	102±6
$C_6H_{13}I$	28.79±0.07	$y = 1.02 \times 10^5 x + 4.03 \times 10^3$	7–410	0.9999	0.6	99±3

[a] Mean±standard deviation ($n=5$).
[b] x is concentration of iodoalkane in μg/l and y is peak area in μV s ($n=5$).
[c] MDL were determined as recommended by the US Environmental Protection Agency and were calculated as three times the standard deviation of eight replicate measurements at 1.0 μg/l for all sample analytes ($n=8$).
[d] Mean±standard deviation ($n=8$). Recoveries were determined using Eq. (1), where C_{spiked} is at 10 μg/l for all sample analytes.

the present method was good as suggested by the square of correlation coefficients being better than 0.999. The method detection limits (MDLs) were calculated as three times the standard deviation of 8 replicate measurements at 1.0 μg/l, close to blank concentration [22,23]. The MDL for the determination of all iodoalkane compounds can be down to ppb level, with the same order as previous report [10]. To ensure the accuracy of the calibration and the stability of the system, the recoveries of the analytes were evaluated. The average recoveries of all the analytes determined from eight replicate experiments were listed in Table 1, ranging from 95 to 104%. This indicated the validity of the calibration established in this study.

3.6. Analysis of real samples

Five acetic acid samples from local chemical manufacturers were analyzed to demonstrate the practical applicability of the present HPLC–$h\nu$-ED method. Approximately 100 ml of acetic acid solutions were collected by the HPLC–$h\nu$-ED method according to the procedure and the method described. Depending on the manufacturing process, the finished product may contain various amounts of alkyl organoiodides. Depicted in Fig. 5 are representative chromatograms of one acetic acid sample (sample 5). The selectivity of the conditions with the photochemical reactor on/off can be used to confirm the identification of iodoalkanes. One unknown peak occurring at 20.0 min can be speculated by the correlation of Kovats retention index and the quantity estimated by interpolation [24].

Results of the five acetic acid samples are listed in Table 2. The contents of the impurities present in the five samples vary. While sample 1 was the highest purity among five real samples and this method could not detect any impurities with iodine atom, the other samples had more than two impurities present. The concentrations of the impurities present in sample 5 were higher compared to the other samples; however, the actual amount was minute, constituting only less than 32 μg/l by iodine atom basis. The samples contain at least 99.9% acetic acid, thus analyzing its impurity is a challenging problem. The present method provides a very sensitive means for checking the purity of acetic acid samples.

4. Conclusions

A highly sensitive, reproducible, and selective determination of alkyl organoiodides was performed using a post-column photochemical reactor with an electrochemical detector. The HPLC–$h\nu$-ED method was successfully applied to the analysis of alkyl organoiodides in real acetic acid samples. The new method developed has good precision and linearity. The sensitivity for detecting impurity in acetic acid commercial products is in the ppb range.

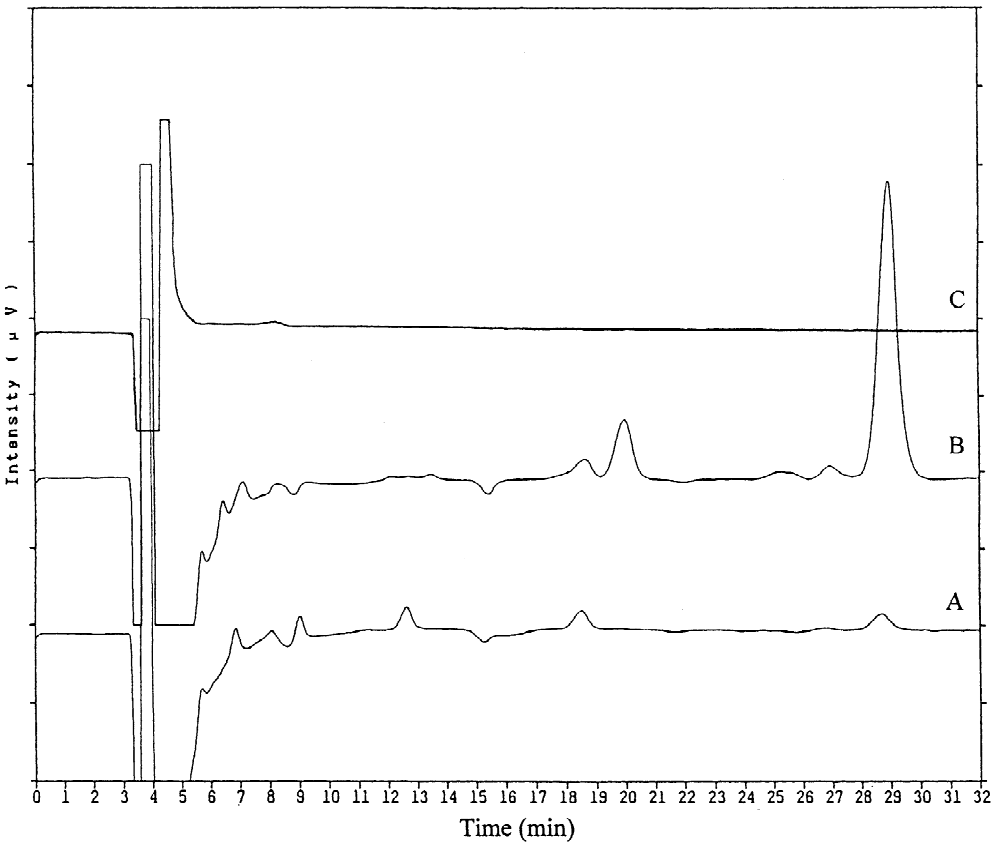

Fig. 5. (A) Chromatogram of a mixture of six iodoalkane standards at 1 ppb (for iodine basis) by using HPLC–$h\nu$-ED. (B) Chromatogram of HPLC–$h\nu$-ED assay for real sample 5. (C) Chromatogram of HPLC–ED assay for real sample 5 (lamp off). Chromatographic conditions as in Section 2.4.

Table 2
Contents of the alkyl organoiodides in real samples (μg/l)[a]

Compound	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
CH_3I	ND[b]	1.00[c]	1.00[c]	1.00[c]	1.00[c]
C_2H_5I	ND	4.82±0.12	2.79±0.08	2.70±0.09	2.16±0.05
C_3H_7I	ND	2.90±0.10	ND	ND	ND
C_4H_9I	ND	ND	2.23±0.05	ND	ND
$C_5H_{11}I$	ND	ND	ND	ND	2.98±0.07
$C_6H_{13}I$	ND	ND	ND	13.64±0.15	39.74±0.29
RI unknown	ND	2.67±0.08[d]	ND	ND	6.51±0.15[e]
Total contents of iodine	ND	8.60±0.22	4.70±0.10	11.26±0.16	32.50±0.35

[a] Mean±standard deviation ($n=6$).
[b] ND: not detectable.
[c] The average values are below limit of detection.
[d] The molecular mass of the unknown peak occurring at a retention time of 26.83 min was estimated as 210 g/mol by the correlation of Kovats retention index [24]. One iodine atom attached to each unknown molecule was assumed.
[e] The molecular masses of the unknown peak occurring at a retention time of 20.00 min was estimated as 200 g/mol. One iodine atom attached to each unknown molecule was assumed.

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