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Journal of Chromatography A, 790 (1997) 1–8

JOURNAL OF CHROMATOGRAPHY A

On-line electrochemical detection of carbohydrates coupled with the periodate oxidation

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Received 14 April 1997; received in revised form 23 June 1997; accepted 26 June 1997

Abstract

A new concept of an amplified electrochemical detection of carbohydrates is proposed, where carbohydrates are oxidized by periodate ion (IO_4^-) in acidic solutions to yield iodate ion (IO_3^-) which would be electrochemically reduced into iodide ion (I^-) under suitable conditions. This scenario allows highly sensitive detection of carbohydrates, for example, as 30 electrons per aldohexose molecule. Our cyclic voltammetric study revealed that IO_3^- is reduced at much lower overpotentials than IO_4^- at gold, platinum and carbon-based electrodes despite the fact that the standard redox potential of the IO_3^-/I^- couple is more negative than that of the IO_4^-/I^- couple. In the electrochemical reduction of IO_3^-, I^- is considered to function as a mediator. Stable flow-through detection of IO_3^- in the presence of IO_4^- was realized at glassy carbon electrodes. This method was coupled with the IO_4^- oxidation of carbohydrates and the experimental conditions were partially optimized on a flow injection system. The IO_4^- oxidation-coupled electrochemical detection of carbohydrates was applied to ligand-exchange high-performance liquid chromatography in a post-column mode. Sub-nanomole order of carbohydrates were successfully detected on this system. © 1997 Elsevier Science B.V.

Keywords: Detection, LC; Electrochemical detection; Electrodes; Carbohydrates

1. Introduction

Electrochemical detection in high-performance liquid chromatography (HPLC) has been one of the most active and successful developments in electroanalytical chemistry [1,2]. However, carbohydrates, of which highly selective and sensitive detection is an attractive subject in analytical chemistry [3], are not generally electroactive at common electrodes. Thus, several efforts have been devoted to derivatization of carbohydrates into some electroactive species in pre- or post-column modes for constant-potential amperometric detection [4–7]. The methods, however, were only applicable to reducing carbohydrates due to the reaction specificity in the derivatization. On the other hand, direct amperometric detection methods for carbohydrates in alkaline solutions have been recently developed. One of the strategies concerns the convenient constant-potential amperometric detection at copper [8–12] or nickel electrodes [13,14] and the other is the pulsed amperometric detection at gold or platinum electrodes [15,16]. At copper electrodes glucose could be oxidized into formate with the transfer of 12 elec-

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0021-9673/97/$17.00
PII S0021-9673(97)00735-8

trons under suitable conditions [10]. Such large numbers of electrons allows the highly sensitive amperometric detection of carbohydrates and thus these direct electrochemical detection methods have been successfully utilized in practical HPLC [11,14–16] or capillary electrophoresis systems [17,18].

Periodate (IO_4^-) oxidation of carbohydrates is well known and is used in determination and structural analysis of carbohydrates [19–21]. Glucose, for example, is oxidized by IO_4^- with the transfer of 10 electrons, as shown by

$$C_6H_{12}O_6 + 5IO_4^- \rightarrow 5HCOOH + HCHO + 5IO_3^- \quad (1)$$

In conventional determination based on the IO_4^- oxidation, the quantities of IO_4^- consumed by carbohydrates are frequently determined by iodimetric titration [22,23] or spectrophotometry [24]. Some reports deal with the utilization of the IO_4^- oxidation in on-line [25] and off-line flow-through determination [26–29] of carbohydrates using potentiometry [25,26] or spectrophotometry [27–29]. The on-line potentiometric determination was based on the measurement of the IO_4^- consumption, but iodate ion (IO_3^-) as the product is inherently detected simultaneously. Therefore, the sensitivity was not satisfactory in spite of the large number of the transferred electrons in the reaction (Eq. (1)) as in the case of iodimetry. The spectrophotometric detection would be limited in sensitivity due to the low absorption coefficient and the spectrum overlapping of IO_4^- and IO_3^-. Although the spectrum overlapping was overcome by combination of some techniques for the separation of IO_4^- and IO_3^- [28,29], it would be difficult to utilize such off-line detection methods in HPLC systems.

Selective determination of IO_3^- generated in the IO_4^- oxidation might be an alternative for carbohydrate analysis, which is the subject of this work. IO_3^- would be reduced electrochemically into iodide (I^-) with the uptake of six electrons at suitable electrode potentials.

$$IO_3^- + 6e^- + 6H^+ \rightarrow I^- + 3H_2O \quad (2)$$

Therefore, development of a selective amperometric determination of IO_3^- in the presence of IO_4^- will allow an extremely sensitive determination of carbohydrates. In the case of aldohexose, for example, the apparent number of the electrons could be enhanced to be 30 (=5 mol of IO_3^- per mol of aldohexose × 6e^- per mol of IO_3^-) in the amperometric detection, considering the reactions written by Eqs. (1) and (2). In this work, we attempted to investigate voltammetric behavior of IO_3^- and IO_4^- at several electrodes and amperometric detection of IO_3^- in flow-through analysis. The IO_3^- detection method has been coupled with the IO_4^- oxidation for the determination of carbohydrates in a flow injection analysis (FIA) system and a post-column ligand-exchange HPLC system.

2. Experimental

2.1. Reagents

All carbohydrate samples used were obtained from Wako and/or Aldrich. All other chemicals were of analytical grade quality and used as received. All sample and reagent solutions were prepared with triple-distilled water just before each experiment.

2.2. Apparatus and measurements

Cyclic voltammetry was performed on a Bioanalytical Systems (BAS) 50W electrochemical analyzer or a Hokuto Denko HA-501 potentiostat combined with a Hokuto Denko HB-104 function generator and a Graphtec WX-2400 *x–y* recorder with a three-electrode system. The potentials were referred to the Ag/AgCl/KCl(sat) electrode. A coiled platinum wire was used as the counter-electrode. The materials of working electrodes evaluated in cyclic voltammetry were gold (Au), platinum (Pt), glassy carbon, carbon paste (CP) and basal-plane pyrolytic graphite (BPG). These electrodes except BPG were purchased from BAS (3 mm in diameter) and polished with alumina powder (0.05 μm, Union Carbide, USA) and then sonicated in distilled water before use. BPG electrodes with a diameter of 5 mm were fabricated according to the literature [30] and the surface was just cleaved with a razor blade before use. The scan rate was fixed at 100 mV s^{-1}. All the voltammetric measurements were done in 5%

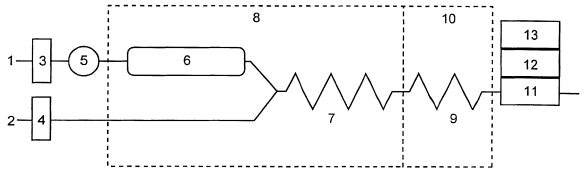

Fig. 1. Schematic diagram of an apparatus for HPLC. 1: Mobile phase (water), 2: reagent solution, 3: HPLC pump, 4: peristaltic pump, 5: injector, 6: separation column, 7: reaction coil, 8: column oven, 9: cooling coil, 10: water bath, 11: electrolytic thin-layer flow cell, 12: potentiostat and 13: recorder.

H_2SO_4 solution as the electrolysis solution at room temperature without deaeration.

FIA of IO_3^- was carried out using a Gilson Minipuls 2 peristaltic pump, Rheodine 7125 sample injector with a 20-μl loop, a Yanagimoto VMD-101 amperometric detector and a Yokogawa 3056 chart recorder. A PTFE tube with an inner diameter of 0.5 mm was used as the solution guide line. A thin-layer cell with a glassy carbon or Au working electrode, an Ag/AgCl/KCl(sat) reference electrode and a stainless-steel counter-electrode was purchased from BAS.

In the HPLC system for the detection of carbohydrates, a Shimadzu LC-6A pump and a Shimadzu CTO-6A column oven were combined with the above FIA system in a post-column mode. The schematic diagram of the HPLC system is given in Fig. 1. A Shimadzu Shim-pack SCR-101C HPLC column (10 μm packing, 30 cm×7.9 mm) was used for the ligand-exchange HPLC separation of carbohydrates, the mobile phase being distilled water. A post-column reaction coil for the IO_4^- oxidation was heated in the column oven and the reaction solution was cooled down within a coil immersed in a laboratory-made water-jacket type cooling bath in the front of the electrochemical cell.

3. Results and discussion

3.1. Voltammetric response of IO_3^- and IO_4^-

Iodate ion (IO_3^-) exhibited a characteristic irreversible voltammogram at an Au and a glassy carbon electrode in 5% of H_2SO_4 as shown by the solid lines in Fig. 2. In the negative-going scan, the

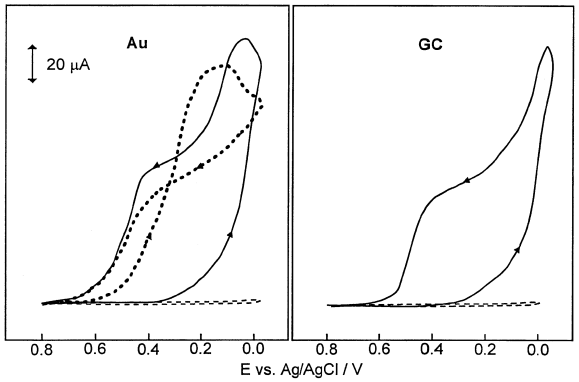

Fig. 2. Cyclic voltammograms of KIO_3 and KIO_4 in 5% H_2SO_4 at Au and glassy carbon electrodes at a scan rate of 100 mV s^{-1}. Solid line: 1 m*M* KIO_3 at bare Au and glassy carbon electrodes, broken line: 1 m*M* KIO_4 at bare Au and glassy carbon electrodes and dotted line: 1 m*M* KIO_3 at a KI-treated Au electrode.

electrochemical reduction started to arise at ca. 0.3 V (vs. Ag/AgCl) and the reduction current increased exponentially with the potential scan. In the reversed positive-going scan, two reduction waves appeared at ca. 0.05 V and 0.35 V and the reduction current was much larger than that of the cathodic wave. This means that the reduction of IO_3^- is accelerated with the electrolysis time. Such an electrolysis time-dependent increase in the reduction current was observed when the electrode potential was held at 0 V. These results suggest that the electrochemical reduction of IO_3^- is catalyzed by some electrode reaction product.

The mechanism for the electrochemical reduction of IO_3^- was initially proposed as follows [31].

$$IO_3^- + H^+ \rightarrow HIO_3 \quad \text{(fast)} \tag{3a}$$

$$HIO_3 + e^- \rightarrow HIO_3^- \quad \text{(slow)} \tag{3b}$$

$$HIO_3^- + 5e^- + 5H^+ \rightarrow I^- + 3H_2O \quad \text{(fast)} \tag{3c}$$

The electrochemical reduction is strongly irreversible and requires large overpotentials, as compared with the standard redox potential of the overall IO_3^-/I^- system (1.09 V vs. NHE, NHE = −0.197 V vs. Ag/AgCl) [32]. The slow reaction of Eq. (3b) would be responsible for the large overpotential. We considered the following mechanism for the electrolysis time-dependent acceleration of the IO_3^- reduction.

Once I^- is generated according to Eq. (3c), IO_3^- near the electrode surface is easily reduced by I^- to yield I_2 (or strictly speaking I_3^-), which is reversibly reduced at electrodes to regenerate I^-.

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O \quad (4a)$$

$$I_2 + 2e^- \rightleftarrows 2I^- \quad (4b)$$

That is, I^- serves as a mediator. It can be reasonably assumed that the electrochemically generated amount of I^- increases with the elapse of the electrolysis time, which causes an increase in the reduction rate of IO_3^-.

On the other hand, IO_4^- was found to be electrochemically inactive at Au and glassy carbon electrodes within the potential range examined, as shown by the broken lines in Fig. 2. Votammetric behavior of IO_3^- and IO_4^- at a Pt electrode was very similar to that at the Au electrode, while voltammetric behavior observed at CP and BPG electrodes was similar to that at a glassy carbon electrode. The behavior is in marked contrast with that observed at a dropping mercury (Hg) electrode, where IO_4^- gave well-defined two reduction waves: the first one at 0.35 V (vs. SCE, SCE = 0.045 V vs. Ag/AgCl) was assigned to the two-electron reduction of IO_4^- into IO_3^- and the second one at -0.25 V was assigned to the subsequent six-electron reduction of IO_3^- to I^- [33]. Such sequential reduction of IO_4^- might be expected considering the fact that the standard redox potential of the IO_4^-/IO_3^- (or strictly speaking H_5IO_6/IO_3^- [34]) couple (ca. 1.6 V vs. NHE [32]) is much more positive than that of the IO_3^-/I^- couple (1.09 V), although the large overpotentials are required even at Hg electrodes for the reduction of IO_4^-. It is noteworthy that Hg electrodes require much larger overpotential for the reduction of IO_3^- than noble metal (Au and Pt) or carbon electrodes. Therefore, we can conclude that the heterogeneous electron transfer rate constants of IO_3^- are relatively large at the noble metal and carbon electrodes in comparison with Hg electrodes, while those of IO_4^- are negligibly small.

Such kinetic properties of IO_3^- and IO_4^- at the noble metal or carbon electrodes are suitable for selective determination of IO_3^- in the presence of IO_4^-, which is the case of the IO_4^- oxidation of carbohydrates. However, it would be important for the sensitive detection of IO_3^- to realize diffusion-controlled reduction. In order to increase the heterogeneous reduction rate constant of IO_3^-, we attempted to modify Au electrodes with I_2 or I^- considering the role of the I_2/I^- couple in the electrode process of IO_3^- described above. It is generally accepted that relatively stable Au–I bonding is formed between Au and iodine species (I_2 or I^-) under appropriate conditions [35–38]. Thus, we fabricated potassium iodide (KI)-treated Au electrodes: a well-polished Au electrode was dipped into a 1 m*M* KI solution for 30 min and then rinsed thoroughly with distilled water. The KI-treated Au electrode exhibited a drastic change in cyclic voltammograms of IO_3^-, as shown by the dotted line in Fig. 2. The cathodic wave shifted by ca. 0.3 V in the direction of the positive potential and gave a reduction peak around 0.15 V. We also performed an I_2-vapor treatment of Au electrodes: a bare Au electrode and I_2 powder were left standing under reduced pressure in a closed vessel for overnight at room temperature and then the electrode was rinsed with distilled water. The I_2-treated Au electrode gave voltammograms very similar to those at the KI-treated electrode. In contrast, IO_4^- remained inert at KI- and I_2-treated Au electrodes in the potential range investigated. Similar KI- and I_2-treatment was attempted for glassy carbon electrodes. However, such treatments were not effective for glassy carbon electrodes: practically no change was observed in cyclic voltammograms of IO_3^- and IO_4^-. On the other hand, I^- in solution reacted with IO_4^- as well as IO_3^- to yield I_2 (cf., Eq. (4a)). These results indicate that the Au–I species on the electrodes plays an important role in selective facilitation of the electrochemical reduction of IO_3^-. In addition, the appearance of the cathodic peak at the iodine-modified Au electrode suggests that the reduction of IO_3^- is close to diffusion-control in nature at potentials more negative than 0.1 V.

3.2. Flow-through detection of IO_3^- and carbohydrates

Electrochemical behavior of IO_3^- and IO_4^- was also investigated on an FIA system using the thin-layer cell with glassy carbon and Au electrodes. A 20 μl portion of 5 m*M* KIO_3 solution was subjected

to FIA, in which 5 m*M* of KIO_4 solution containing 20% H_2SO_4 solution was used as the reagent solution at a flow-rate of 0.1 ml min^{-1}, while the carrier phase (water) was pumped at a flow-rate of 0.5 ml min^{-1} (the final concentrations of KIO_4 and H_2SO_4 being 0.83 m*M* and 3.3%, respectively). KIO_3 gave stable response at the bare glassy carbon electrode. In contrast to the cyclic voltammetric results, however, the background current due to the reduction of IO_4^- was also observed on the FIA system. Similar behavior was observed at the bare Au electrode, but the ratio of the peak height to the background current (*P*/*B* ratio) was smaller than that of the glassy carbon electrode. We also attempted FIA of IO_3^- at iodine-modified Au electrodes, where the bare Au electrode was treated with KI solution or I_2 vapor as described in Section 3.1. As expected from the above voltammetric results, the intensity of the reductive detection of IO_3^- at the iodine-modified Au electrode was initially larger about 100-times than that at the bare glassy carbon electrode at 0.1 V. However, the current intensity at the iodine-modified Au electrode was not reproducible in run-to-run analysis and decreased with time. Most probably, the Au–I bonding would not be so stable under the present conditions, although such instability was not observed in the cyclic voltammetric experiments. Therefore, the bare glassy carbon electrode was used in the following experiments at the sacrifice of the sensitivity.

Fig. 3 shows hydrodynamic voltammograms of 5 m*M* KIO_3 at the glassy carbon electrode, in which the peak current reflecting the reduction of IO_3^- was measured by subtracting the background current. The peak height of KIO_3 as well as the background current increased with the negative shift of the electrode potential. Judging from Fig. 3, the reduction of IO_3^- did not attain the diffusion-limiting until −0.4 V. The *P*/*B* ratio exhibited the highest value at ca. 0.2 V, at which the electrode potential was set in the following (Fig. 3, inset).

Next, FIA analysis of carbohydrates was performed by the combination of the IO_4^- oxidation and the flow-through detection of IO_3^-. The FIA system used was identical with that illustrated in Fig. 1 except the separation column, which was removed in order to minimize the analytical time. Using glucose (0.1 m*M*, 20 μl) as a model sample, effects of

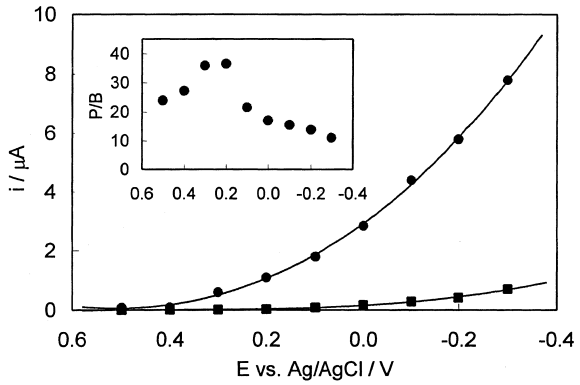

Fig. 3. Peak current of 5 m*M* KIO_3 (20 μl injection) (●) and background currents (■) as function of the electrode potential in FIA method using a glassy carbon electrode as the working electrode. The reagent solution: 5 m*M* KIO_4 in 20% H_2SO_4 at a flow-rate of 0.1 ml min^{-1}; the carrier phase: water at a flow-rate of 0.5 ml min^{-1}. The peak current was measured after subtraction of the background current. The inset represents the electrode potential dependence of the peak current ratio against the background current (*P*/*B* ratio).

several factors on the current signal were investigated, where the flow-rate of the reagent solution (KIO_4 in 20% H_2SO_4 solution) for the post-column reaction was fixed at 0.1 ml min^{-1}. The results are depicted in Fig. 4. With decreasing the flow-rate of the mobile phase (water), the signal intensity increased (Fig. 4, panel a). The increase in the peak height at low flow-rates is ascribed to the reduced factor of the dilution by the mobile phase volume and the increased resident time in the reaction coil and the electrochemical cell. All these changes are suitable for the IO_4^- oxidation and/or the electrochemical detection of IO_3^-. However, the decreasing in the flow-rate causes an increasing of the analytical time and the peak broadening. Then the flow-rate of the mobile phase was limited to 0.5 ml min^{-1} considering practical separation in HPLC. In order to increase the rate of the IO_4^- oxidation, the concentration of KIO_4 in the reagent solution was increased. Although increased concentrations of KIO_4 resulted in an increase in the peak height, the background current also increased. The maximum *P*/*B* ratio was attained at 5 m*M* in KIO_4 (Fig. 4b) and then we selected 5 m*M* as the KIO_4 concentration in the reagent solution. Although higher concentrations of H_2SO_4 are also useful to accelerate

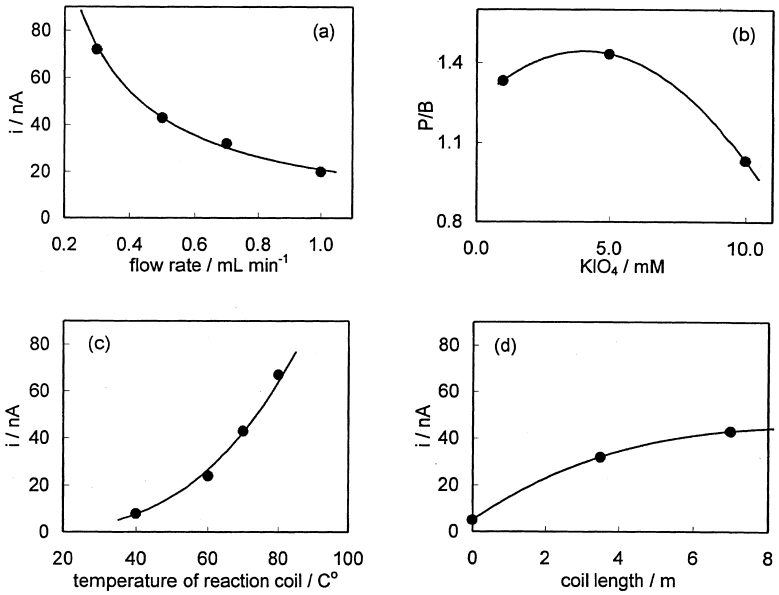

Fig. 4. Peak current of glucose (0.1 m*M*, 20 μl) as functions of (a) the flow-rate of the mobile phase (water), (c) the temperature of the column oven and (d) the length of the reaction coil and (b) the *P*/*B* ratio as a function of the concentration of KIO_4 in the reagent solution, detected at 0.20 V vs. Ag/AgCl by the FIA method on the system illustrated in Fig. 1 except the separation column which was removed. Other conditions are as follows unless otherwise noted; the flow-rate of mobile phase (water): 0.5 ml min^{-1}, the reagent solution: 5 m*M* KIO_4 in 20% H_2SO_4; the flow-rate of the reagent solution: 0.1 ml min^{-1}, the column oven temperature for reaction: 70°C and the length of reaction coil: 7 m.

the rate of the IO_4^- oxidation [39], 20% of H_2SO_4 was used as the maximum in the present on-line system. The peak height was exponentially increased with elevating temperature of the column oven (Fig. 4c). However, bubble was evolved above 80°C within the guideline tube. Thus, the column oven was kept at 70°C. Elongation of the reaction coil was effective in improving the signal intensity up to about 7 m (Fig. 4d), at which the length was fixed in the following.

Under the optimized conditions, the amperometric responses for various carbohydrates (2 nmol each) were measured. The result is summarized in Table 1 as relative values of the response compared with the sorbitol response. Table 1 also shows relative expected values, which were calculated by assuming the complete IO_4^- oxidation of the carbohydrates. The ratios of the experimental values to the expected ones would reflect the reactivity of carbohydrates toward IO_4^-. Sorbitol was the most reactive among the samples examined, while di- or trisaccharides exhibited relatively low reactivity.

Table 1
Relative intensities of responses for various carbohydrates in FIA[a]

Species	Compounds[b]	Relative intensity	
		Experimental[c]	Expected[c]
Aldopentose	Xylose	58	80
	Arabinose	61	80
Aldohexose	Glucose	58	100
	Mannose	49	100
	Galactose	84	100
Ketohexose	Fructose	39	80
Deoxysugar	Rhamnose	66	80
	Sorbitol	100	100
	Mannitol	70	100
Disaccharide	Lactose	25	100
	Maltose	46	220
Trisaccharide	Raffinose	109	360

[a] All conditions are the same as those given in Fig. 4.
[b] 2 nmol each (0.1 m*M*×20 μl).
[c] Relative value of the response against the sorbitol response, which is defined as 100.

3.3. Application to HPLC

Finally, we constructed a post-column mode HPLC system as illustrated in Fig. 1 under the conditions optimized in the above FIA analysis. A separation of a carbohydrate mixture is depicted in Fig. 5. The shape of the peaks was somewhat broadened, most probably due to the long reaction coil. The pump pulsation due to the peristaltic action was also observed, which might be reduced by using pulse damper. The linearity between the peak height and the sample concentration was guaranteed in the total concentration range at least from 0.4 to 20 nmol at a 20-μl injection. The relative standard deviation of the analysis was 0.82% in run-to-run analysis of 10 nmol glucose ($n=10$). The detection limit of glucose on this HPLC system was 250 pmol at a signal-to-noise ratio of three and it is more than one-order in magnitude lower than the other on-line or off-line FIA methods utilizing the IO_4^- oxidation reported so far [26,28,29].

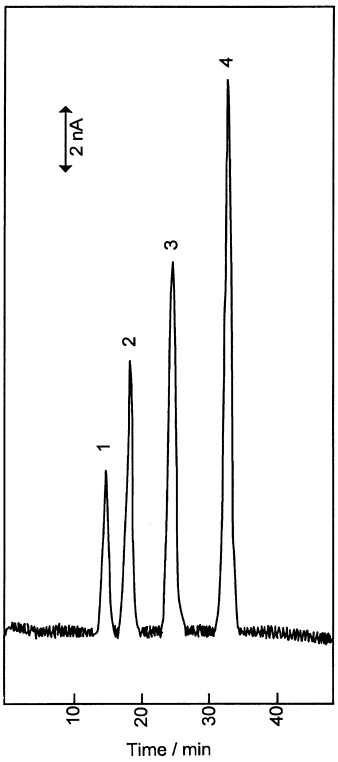

Fig. 5. Ligand-exchange chromatogram of a sample mixture of carbohydrates (1 nmol each) detected on the post-column HPLC system illustrated in Fig. 1 under the conditions given in Fig. 4. Peaks: (1) maltose, (2) glucose, (3) fructose and (4) sorbitol.

4. Conclusions

In this work, we have proposed a new concept of the reductive amperometric determination of carbohydrates based on the IO_4^- oxidation, in which the product IO_3^- is electrochemically reduced into I^-. The advantage of this concept is the current amplification: aldohexose, for example, could be detected as a 30-electron reduction as the maximum. In order to realize the concept, selective detection of IO_3^- in the presence of excess amount of IO_4^- is essential. Although the standard redox potential of the IO_3^-/I^- couple is more negative than that of the IO_4^-/I^- couple, our cyclic voltammetric experiments suggested that selective reduction of IO_3^- in the presence of IO_4^- is possible utilizing the preferable kinetic property of IO_3^- over that of IO_4^- at some electrodes, especially at iodine-modified Au electrodes. Unfortunately, the iodine-modified Au electrode fabricated here was not acceptable for use in the stable flow-through detection. Our proposed idea was in part realized using glassy carbon electrodes and the method was applied to the carbohydrate analysis in ligand-exchange HPLC separation. This is the first case of the utilization of the IO_4^- oxidation in HPLC analyses of carbohydrates. However, we could not attain complete selectivity of IO_3^- against IO_4^- and diffusion-controlled detection of IO_3^- under the flow-through conditions. In addition, the IO_4^- oxidation of carbohydrates did not go to completion under the present conditions. These would be responsible for the result that the present HPLC detection method for carbohydrates was inferior in sensitivity to the direct oxidation method in alkaline conditions [11,14–16]. Further improvement of the sensitivity is expected by further investigation concerning development of stable IO_3^--selective electrodes and improvement of the devices and/or optimization of the post-column reaction conditions. Related study is in progress.

Acknowledgements

This work was supported in part by a Grant-in-Aid

for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan.

References

[1] P.T. Kissinger, in P.T. Kissinger and W.R. Heineman (Editors), Laboratory Techniques in Electroanalytical Chemistry, Marcel Dekker, New York, 1984, p. 611.
[2] M. Warner, Anal. Chem. 66 (1994) 601A.
[3] R. Giese and S. Honda (Editors), Chromatographic and Electrophoretic Analyses of Carbohydrates; J. Chromatogr. A, Vol. 720 (1996).
[4] S. Honda, E. Akao, S. Suzuki, M. Okuda, K. Kakehi, J. Nakamura, Anal. Biochem. 180 (1989) 351.
[5] N. Watanabe, M. Inoue, Anal. Chem. 55 (1983) 1016.
[6] S. Honda, T. Konishi, S. Suzuki, J. Chromatogr. 299 (1984) 245.
[7] Y. Takata, G. Muto, Anal. Chem. 45 (1973) 1864.
[8] P. Luo, F. Zhang, R.P. Baldwin, Anal. Chem. 63 (1991) 169.
[9] T. Ueda, R. Michell, F. Kitamura, A. Nakamoto, J. Chromatogr. 592 (1992) 229.
[10] K. Kano, M. Torimura, Y. Esaka, M. Goto, T. Ueda, Electroanal. Chem. 372 (1994) 137.
[11] K. Kano, K. Takagi, K. Inoue, T. Ikeda, T. Ueda, J. Chromatogr. A 721 (1996) 53.
[12] J.M. Zadeii, J. Marioli, T. Kuwana, Anal. Chem. 63 (1991) 649.
[13] R.E. Reim, R.M. Van Effen, Anal. Chem. 58 (1986) 3203.
[14] P.F. Luo, T. Kuwana, Anal. Chem. 66 (1994) 2775.
[15] D.C. Johnson, Nature (London) 321 (1986) 451.
[16] D.C. Johnson, W.R. LaCourse, Anal. Chem. 62 (1990) 589A.
[17] T.J. O'Shea, S.M. Lunte, W.R. LaCourse, Anal. Chem. 65 (1993) 948.
[18] J. Ye, R.P. Baldwin, Anal. Chem. 65 (1993) 3525.
[19] J.R. Dyer, in D. Glick (Editor), Methods of Biochemical Analysis, Vol. III, Interscience, London, 1956, p. 111.
[20] G. Dryhurst, Periodate Oxidation of Diol and Other Functional Groups, Pergamon Press, London, 1966.
[21] S. Fujibayashi, Tanpakushitu Kakusan Koso, Bessatsu (in Japanese) 11 (1963) 136.
[22] M.L. Malaprade, Compt. Rend. 186 (1928) 392.
[23] M.L. Malaprade, Bull. Soc. Chem. France 43 (1928) 43.
[24] J.S. Dixon, D. Lipkin, Anal. Chem. 26 (1954) 1092.
[25] E.P. Diamandis, T.P. Hadjiioannou, Analyst 107 (1982) 1471.
[26] S. Honda, K. Sudo, K. Kakehi, K. Takiura, Anal. Chim. Acta 77 (1975) 274.
[27] S. Honda, K. Adachi, K. Kakehi, K. Takiura, Anal. Chim. Acta 78 (1975) 492.
[28] S. Honda, W. Wakasa, M. Terao, K. Kahehi, J. Chromatogr. 177 (1979) 109.
[29] S. Honda, K. Suzuki, K. Kakehi, Anal. Biochem. 177 (1989) 62.
[30] K. Kano, T. Konse, T. Kubota, Bull. Chem. Soc. Jpn. 58 (1985) 1879.
[31] Y.M. Temerk, M.M. Kamel and M.E. Ahmed, Bull. Soc. Chim. France, 1984, I-260.
[32] J.A. Dean (Editor), Lange's Handbook of Chemistry, McGraw-Hill, New York, 12th ed., 1979, Section 6, p. 10.
[33] R.H. Coe, L.B. Rogers, J. Am. Chem. Soc. 70 (1948) 3276.
[34] W.M. Latimer, Oxidation Potentials, Prentice-Hall, Englewood Cliffs, 2nd ed., 1952, p. 66.
[35] J.F. Rodrigues, T. Mebrahte, M.P. Soriaga, J. Electroanal. Chem. 233 (1987) 283.
[36] P. Gao, M.J. Weaver, J. Phys. Chem. 90 (1986) 4057.
[37] B.G. Bravo, S.L. Michelhaugh, M.P. Soriaga, I. Villegas, D.W. Suggs, J.L. Stickney, J. Phys. Chem. 95 (1991) 5245.
[38] X. Gao, M.J. Weaver, J. Am. Chem. Soc. 114 (1992) 8544.
[39] R. Criegee, Angew. Chem. 53 (1940) 321.