Sequential Injection Analysis of Anionic Surfactants Using On-line Preconcentration Technique and a Microfluidic Polymer Chip with an Embedded Ion-Selective Electrode as a Detector

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ABSTRACT

A sequential injection analysis (SIA) system with on-line preconcentration technique using a microfluidic chip with an embedded anionic surfactant ion-selective electrode (AS-ISE) as a detector, was developed for the determination of anionic surfactants. Under the SIA system with no on-line preconcentration technique, the AS-ISE in the SIA system showed a linear relationship between peak heights and logarithmic concentrations of AS ion such as dodecylbenzene sulfonate (DBS) ion with a Nernstian slope of 60.4 mV decade⁻¹ in a concentration range from 3.0 × 10⁻⁶ to 1.0 × 10⁻³ mol dm⁻³. For the determination of trace levels of ASs, on-line preconcentration technique with solid-phase extraction process was incorporated into the SIA system. By using the on-line preconcentration technique in the SIA system, DBS ion in a concentration range from 1.0 × 10⁻⁷ to 3.0 × 10⁻⁶ mol dm⁻³ was successfully determined. The recovery for DBS ion added to river water samples was ca. 91–97% using on-line preconcentration technique in the SIA system. The result shows that the present SIA system with the on-line preconcentration technique can be applicable to the determination of the level of AS ion in river and tap water samples.

Keywords : Ion-Selective Electrode, Microfluidic Polymer Chip, Sequential Injection Analysis, Anionic Surfactant

1. Introduction

Anionic surfactant (AS) is widely used as base agents for detergents, and one of the sources of environmental pollution with the increase of its consumption. Solvent extraction-spectrophotometric methods have been widely used for the determination of ASs. However, harmful organic solvent should be used in the methods. Furthermore, the methods are very tedious and not applicable to colored samples. Therefore, development of simpler analytical methods for the determination of AS using no harmful organic solvent is required.

AS ion-selective electrodes (AS-ISe)s and AS-sensitive field-effect transistors (AS-FETs) are gaining attention as excellent analytical method for the determination of ASs, because AS-ISe and AS-FETs have high selectivity to AS, and the procedures of their analysis operation are very simple using no harmful organic solvent, and AS-ISe and AS-FETs are applicable to turbid and colored samples. The microfluidic chip technology is paid much attention in the field of chemistry and biochemistry because it has excellent advantages of lower consumption of reagents and lower sample volumes. Potentiometry using ISe and FETs has been considered to be one of an excellent detection method in microfluidic chips because the sensitivity of ISe and FETs does not change with their size and as the result, ISe and FETs are very easy to miniaturize with keeping the sensitivity. However, only a few studies using microfluidic chips with embedded miniaturized ISe and FETs as a detector have been reported. We have already developed a new microfluidic polymer chip with an embedded AS-FETs using a small-diameter wire as a template for the channel. On the other hand, in the flow analysis method of AS using our new microfluidic chip, introduction of sample solutions to the microfluidic chip must be performed manually and sample analysis time was very long (sample throughput: ca. 6 samples h⁻¹). Furthermore, the sensitivity of our new microfluidic chip was insufficient to determine AS in the environmental water.

Lately, many analytical methods using sequential injection analysis (SIA) have been reported in the environmental and clinical chemistry fields because the SIA system has the advantages of high sample throughput and automatic operations of every procedures and low consumption of a reagent, compared with batchwise analytical methods. Recently, ISe and FETs have been often used as a detector of SIA and microfluidic chips with embedded miniaturized ISe. Generally, AS in environmental water samples is not determined using AS-ISe because lower limit of Nernstian response of reported AS-ISe is order of approximately 10⁻⁶–10⁻⁵ mol dm⁻³. For the determination of trace levels of environmental pollutants, on-line preconcentration technique with solid-phase extraction process integrated with the SIA system was reported.

In this paper, we propose the SIA system with on-line preconcentration technique for the determination of ASs using our microfluidic chip with an embedded AS-ISe as a detector.

2. Experimental

2.1 Chemicals

Tetrahexadecylammonium bromide (THAB) from Fluka was used as an anion exchanger for an AS-ISe. The purity of the THAB was more than 98%, according to the manufacturer’s specification. Poly (vinyl chloride) (PVC) (degree of polymerization: 1100) and sodium dodecylbenzenesulfonate (NaDBS) was obtained from Wako Pure Chemicals Co. 2-nitrophenyl octyl ether (NPOE) from Dojindo Laboratories was used as a plasticizer for an AS-ISe. All other reagents were of analytical grade.
2.2 Fabrications of an AS-ISE and microfluidic polymer chip integrated with the AS-ISE detector

An AS-ISE as an indicator electrode was fabricated in the similar manner as reported in the previous paper.\(^\text{30}\) A NPOE (2.00 g), THAB (0.0199 g) and 2.0 mL of 1.0 × 10\(^{-2}\) mol dm\(^{-3}\) NaDBS aqueous solution was pipetted into a test tube. Next, the mixed solution was shaken for 1 day at 30–50°C. After the NPOE phase and water phase were separated by centrifugation (30 min, 4000 rpm), the NPOE solution (1.0 g) and PVC powder (0.40 g) were dissolved in 10 mL of tetrahydrofuran (THF) in order to prepare sensing membrane solution of the AS-ISE. The AS-ISE was fabricated by coating the bare metal part of the BEAMEX-S wire (diameter of bare metal part: 0.65 mm, o.d. 1.45 mm, standard type irradiated polyethylene wire from Furukawa Electric Co., Ltd.) with the plasticized PVC membrane containing the THAB by dipping it into the above sensing membrane solution several times.\(^\text{32}\) The silver halide membrane (AgX, X: halide ion) type reference electrode becomes selective for X\(^-\) ions as the solubility product of AgX becomes lower, and it becomes less susceptible to interference from other anions.\(^\text{47}\) Since the solubility product of AgX is AgCl > AgSCN > AgBr > AgI, the AgI reference electrode is less susceptible to interference from anions than AgCl type reference electrode, or AgBr or AgSCN type reference electrodes. On the other hand, the potential response of the AS-ISE used in this work is based on the exchange equilibrium of the ion between the sample solution, and sensing membrane of the AS-ISE. Therefore, the potential response of the AS-ISE is interfered with ions having higher hydrophobicity. The more left anions on the sequence of the Hofmeister series (Cl\(^-\) > SCN\(^-\) > I\(^-\) > NO\(_3\)\(^-\) > N\(_3\)\(^-\) > Br\(^-\) > NO\(_2\)\(^-\) > Cl\(^-\) > SO\(_4\)\(^2-\), HCO\(_3\)\(^-\), HPtO\(_3\)\(^2--\), CH\(_3\)COO\(^-\), F\(^-\)) with higher hydrophobicity, interfere with the potential response of the AS-ISE more strongly.

From the viewpoint of selectivity of an AS-ISE, it would be desirable that a solution containing an ion on more right side of the sequence of SCN\(^-\) < I\(^-\) < Br\(^-\) < Cl\(^-\) is used as a carrier solution for the determination of a baseline potential, and an AgX electrode responsive to the ion is used as a reference electrode. From the above discussions, we used AgBr wire electrode as a reference electrode for applying our microfluidic chip-based SIA system to the determination of DBS\(^-\) ion, by considering interfering ions on the potential responses of AS-ISE and AgX type reference electrode.

The fabrication of the AgBr wire electrode as a reference electrode was fabricated by coating the bare metal part of the BEAMEX-S wire with an AgCl ink (BAS Co.) several times and drying for 5 min at 120°C and conditioning by 0.1 mol dm\(^{-3}\) NaBr solution for 2 days.

The chip design of a polymer-based microfluidic chip detector with the embedded AS-ISE and the AgBr wire electrode as a reference electrode was the same as that described in our previous paper.\(^\text{35}\) Diameter and effective length of a channel in the polymer-based microfluidic chip are 0.5 mm \(\phi\) and 4.0 cm, respectively. The distance between the AS-ISE and the AgBr wire electrode is 1.5 cm. The SIA system is composed of two syringe pumps (syringe pump 1 and syringe pump 2, Carvo X Calibur Pump, Tecan Japan Co.), two two-way port valves (V1, V2, Carvo Smart Valve, Tecan Japan Co.), two holding coils (i.d. 0.5 mm \(\times\) 480 cm), two six-port selection valves (SV 1 and SV 2, Carvo Smart Valve, Tecan Japan Co.), a polymer-based microfluidic polymer chip detector, a potentiometer (COM-20R, TOA-DKK) and a personal computer. After washing the teflon tubing and the microfluidic polymer chip with a carrier solution (1.0 × 10\(^{-2}\) mol dm\(^{-3}\) LiBr adjusted to pH 4.0 with a CH\(_3\)COOH–CH\(_3\)COONa buffer solution), 62 \(\mu\)L aliquot of a sample solution was aspirated into the holding coil 1. The syringe pump 1 was pushed up and the carrier and sample solutions in the holding coil 1 were moved forward to the microfluidic polymer chip detector via a port 5 of the selection valve. During this procedure, a sample solution plug in the holding coil 1 was overlapped with the carrier solution in the holding coil. Finally, the zones that are in the holding coil are directed to the microfluidic polymer chip detector. For the determination of trace levels of ASs, on-line preconcentration technique with solid-phase extraction process was integrated with the SIA system. After washing the teflon tubing and the microfluidic polymer chip with a carrier solution (1.0 × 10\(^{-2}\) mol dm\(^{-3}\) LiBr adjusted to pH 4.0 with a CH\(_3\)COOH–CH\(_3\)COONa buffer solution), 200 \(\mu\)L and 2500 \(\mu\)L aliquot of a sample solution were successively aspirated into the holding coil 1. The syringe pump 1 was pushed up and the carrier and sample solutions in the holding coil 1 were moved forward to the preconcentration column (i.d. 2.0 mm \(\times\) 2.0 cm) packed with Sep-Pak Plus PS-2 (Waters) via a port 6 of the selection valve 1. The syringe pump 2 was pushed up, and air and an eluent (acetonitrile, 75(v/v) %, 63 \(\mu\)L) in the holding coil 2 were moved forward to the preconcentration column via a port 1 of the selection valve 2 and the preconcentrated AS was eluted by the eluent. The eluted solution and the carrier solution were aspirated into the holding coil 1 and the zones that are in the holding coil 1 are directed to the microfluidic polymer chip detector.
The protocols of the experimental procedures shown indicated in Table 1 and 2 were performed by a personal computer using a software program (Pump Link, Tecan Japan Co.). During the sample solution was introduced into the AS-ISE detector in the microfluidic polymer chip, and measurement was aspirated into the holding coil at a volume of 83 to 125 µL, and was delivered to the detector with the carrier solution at a volume of 1188 µL. Since sample throughput increased as the flow rate of carrier solution increased to 4, 8, and 21 µL s⁻¹ with keeping Nernstian response in sensitivity of the AS−ISE detector to a DBS⁻ ion, we determined optimal flow rate of carrier solution to be 21 µL s⁻¹ by considering both sensitivity and sample throughput.

3. Results and Discussion

3.1 Effect of sample volume on sensitivity to DBS⁻ ion with no preconcentration system

In order to examine the effect of sample volume on sensitivity (peak height) of the AS−ISE detector to a DBS⁻ ion, a sample solution was introduced into the microfluidic polymer chip by the SIA technique. In the first case, the sample solution was aspirated into the holding coil at a volume of 42 to 125 µL, and was delivered to the detector with the carrier solution at a volume of 1125 to 1208 µL. Therefore, the sum of the volume of the carrier solution and that of the sample solution was 1250 µL. In the next case, the sample solution was aspirated into the holding coil at a volume of 83 to 208 µL, and was delivered to the detector with the carrier solution at a volume of 2292 to 2417 µL. Therefore, in the case, the sum of the volume of the carrier solution and that of the sample solution was 2500 µL. As a result, it was found that when the volume of the carrier solution is 1188 µL and the volume of the sample solution is 62 µL, the sensitivity of the AS−ISE detector to a DBS⁻ ion was closest to Nernstian response. Effect of flow rate of carrier solution introduced into AS−ISE detector on sample throughput of DBS⁻ ion was examined when the volume of the carrier solution is 1188 µL and the volume of the sample solution is 62 µL. Since sample throughput increased as the flow rate of carrier solution increased to 4, 8, and 21 µL s⁻¹ with keeping Nernstian response in sensitivity of the AS−ISE detector to a DBS⁻ ion, we determined optimal flow rate of carrier solution to be 21 µL s⁻¹ by considering both sensitivity and sample throughput.

3.2 Calibration curve for DBS⁻ ion obtained by using a microfluidic polymer chip with an embedded AS−ISE with no on-line preconcentration technique in the SIA system

Figure 2 shows calibration peaks for DBS⁻ ion obtained under the optimal conditions described above. A linear relationship (r² = 0.9892) was found to exist between peak heights and logarithmic concentration of DBS⁻ ion with a Nernstian slope of 60.4 mV decade⁻¹ in a concentration range from 3.0 × 10⁻⁶ to 1.0 × 10⁻² mol dm⁻³ under the optimal conditions described above. The relative standard deviations of the peak heights examined by 3 injections of the 1.0 × 10⁻⁵ and 1.0 × 10⁻³ mol dm⁻³ DBS⁻ ions were 6.0 and 4.4%, respectively. Sample throughput for the determination of DBS⁻ ion was around 20 samples h⁻¹. Embedded

### Table 1. Protocols of the experimental procedures with no on-line preconcentration system.

| Step | Position of two-way port valve | Position of selection valve | Flow rate /µL s⁻¹ | Volume /µL | Flow direction | Event |
|------|---------------------------------|-----------------------------|------------------|------------|----------------|-------|
| 1    | D                               | —                           | 67               | 1188       | R              | Aspiration of carrier solution |
| 2    | C                               | 1–3(SV1)                    | 67               | 62         | R              | Aspiration of sample solution into the holding coil 1 |
| 3    | C                               | 5(SV1)                      | 21               | 1250       | F              | Propelling a mixture of carrier and sample solutions in the holding coil to the microfluidic polymer chip, and measurement |
| 4    | A                               | —                           | 67               | 1188       | R              | Aspiration of carrier solution |
| 5    | B                               | 4–5(SV2)                    | 67               | 62         | R              | Aspiration of sample solution into the holding coil 2 |
| 6    | B                               | 2(SV2)                      | 21               | 1250       | F              | Propelling a mixture of carrier and sample solutions in the holding coil 2 to the microfluidic polymer chip, and measurement |

R: reverse, F: forward to the DBS⁻-ISE detector.

### Table 2. Protocols of the experimental procedures with on-line preconcentration system.

| Step | Position of two-way port valve | Position of selection valve | Flow rate /µL s⁻¹ | Volume /µL | Flow direction | Event |
|------|---------------------------------|-----------------------------|------------------|------------|----------------|-------|
| 1    | D                               | —                           | 67               | 2500       | R              | Aspiration of carrier solution |
| 2    | C                               | 4 (SV1)                     | 42               | 200        | R              | Aspiration of air into the holding coil 1 |
| 3    | C                               | 1–3(SV1)                    | 42               | 2500       | R              | Aspiration of sample solution into the holding coil 1 |
| 4    | C                               | 6(SV1)                      | 21               | 2500       | F              | Propelling air and sample solutions in the holding coil 1 to preconcentration column |
| 5    | A                               | —                           | 67               | 2500       | R              | Aspiration of carrier solution |
| 6    | B                               | 3 (SV2)                     | 42               | 200        | R              | Aspiration of air into the holding coil 2 |
| 7    | B                               | 6 (SV2)                     | 42               | 63         | R              | Aspiration of eluent (acetonitrile) into the holding coil 2 |
| 8    | B                               | 1(SV2)                      | 4                | 63         | F              | Propelling air and eluent in the holding coil 2 to preconcentration column |
| 9    | C                               | 6(SV1)                      | 42               | 63         | R              | Aspiration of the eluted solution into the holding coil 1 |
| 10   | C                               | 5(SV1)                      | 21               | 2500       | F              | Propelling the eluted solution and carrier solution in the holding coil 1 to the microfluidic polymer chip, and measurement |

R: reverse, F: forward to the DBS⁻-ISE detector.
Table 3. Effect of coexisting ions in the sample solution on the determination of 2.0 × 10⁻⁵ mol dm⁻³ DBS⁻ ion.

| Coexisting inorganic electrolytes | Concentration of coexisting ions / mol dm⁻³ | Relative peak height* |
|----------------------------------|---------------------------------------------|-----------------------|
| None                             | 100                                         | 100                   |
| KNO₃                             | 2.0 × 10⁻³                                  | 97                    |
| Na₂SO₄                           | 2.0 × 10⁻³                                  | 100                   |
| Na₂CO₃                           | 2.0 × 10⁻³                                  | 100                   |
| KCl                              | 2.0 × 10⁻³                                  | 98                    |
| NaBr                             | 2.0 × 10⁻³                                  | 98                    |
| NaSCN                            | 2.0 × 10⁻³                                  | 91                    |
| NaI                              | 2.0 × 10⁻³                                  | 78                    |

*The peak height was expressed as relative value to that in case of absence of coexisting ions.

AS⁻ ISE in the microfluidic polymer chip shows a Nernstian response to anionic surfactants other than DBS⁻ ion such as dodecylsulfate and di-2-ethylhexyl sulfosuccinate in the same concentration range as that to DBS⁻ ion. This fact means that total ASs in real samples such as environmental water are determined by the embedded AS⁻ ISE in the microfluidic polymer chip.

3.3 Effect of coexisting ions in the sample solution on the determination of DBS⁻ ion

Real samples such as environmental water contain inorganic ions. Therefore, the effect of these coexisting species on the determination of AS⁻ ion should be examined in order to apply the present method to the determination of AS⁻ in real samples. The effects of coexisting ions on the determination of 2.0 × 10⁻⁵ mol dm⁻³ DBS⁻ ion are shown in Table 3. Table 3 indicates that the coexistences of Cl⁻ ion, NO₃⁻ ion, CO₃²⁻ ion, SO₄²⁻ ion and Br⁻ ion at 100 times excess to DBS⁻ ion did not interfere with the determination of DBS⁻ ion. However, the coexistences of SCN⁻ ion and I⁻ ion at 100 times excess to DBS⁻ ion interfered with the determination of DBS⁻ ion with an error of −9%, −22%, respectively.

In the previous paper,¹¹ we reported that the anionic surfactant-FET based on the same sensing membrane as that used throughout this work, shows excellently selective for the DBS⁻ ion over small inorganic anions. For example, selectivity coefficient values (log Kᵢᵢᵃᵣₑ⁽ₑₓᵢᵢ⁾) for I⁻ and SCN⁻ ion are −3.46, −3.07, respectively. From the result, interference by SCN⁻ and I⁻ ions on the determination of DBS⁻ ion is not due to sensing membrane of AS-ISE.

Since solubility product of AgX is decreased at sequence as AgCl > AgSCN > AgBr > AgI, the potential response of the AgBr type reference electrode is seriously interfered with the I⁻ ion, which is a constituent ion of AgI having solubility product much lower than that of AgBr. On the other hand, the solubility product of AgSCN is at most twice that of AgBr. Therefore, degree of interference from SCN⁻ ion on the potential response of the AgBr type reference electrode is much lower than that from I⁻ ion.

From the result, interference by SCN⁻ and I⁻ ions on the determination of DBS⁻ ion is due to that the potential response of the AgBr type reference electrode is seriously interfered with the I⁻ ion and SCN⁻ ion.

3.4 Effect of a nonionic surfactant in the sample solution on the determination of DBS⁻ ion

Real samples such as environmental water often contain nonionic surfactants. Therefore, the effect of a nonionic surfactant on the determination of AS⁻ ion should be examined in order to apply the present method to the determination of AS⁻ in real samples. The effects of Triton X-100 as a nonionic surfactant on the determination of 5.0 × 10⁻⁵ mol dm⁻³ DBS⁻ ion are shown in Table 4. Table 4 indicates that the coexistence of Triton X-100 at 10 times excess to DBS⁻ ion did not interfere with the determination of DBS⁻ ion with an error of less than 5%.

3.5 Effect of flow rate of a sample solution introduced into the preconcentration column on the enrichment factor of AS

A 1250 µL of 1.0 × 10⁻⁶ mol dm⁻³ NaDBS solution at several flow rate was introduced into the preconcentration column and it was eluted with 63 µL of 75 wt% acetonitrile. In this case, the NaDBS solution is concentrated to the 20-fold concentration theoretically. Table 5 shows the effect of flow rate of the sample solution introduced into the preconcentration column on the enrichment factor of AS. The flow rate was changed to 4, 8, 21 and 33 µL s⁻¹. The enrichment factor of AS more than 90%, compared with theoretical that of AS, was obtained at the flow rate of 4 µL s⁻¹ and 21 µL s⁻¹. Considering sample throughput, we used 21 µL s⁻¹ as the flow rate of AS introduced into the preconcentration column.

3.6 Effect of volume of sample solution introduced into the preconcentration column on the enrichment factor of AS

A 1.0 × 10⁻⁶ mol dm⁻³ NaDBS solution at several volumes was introduced into the preconcentration column and it was eluted with
and on-line preconcentration technique in the SIA system. DBS

63 µL of 75 (v/v) % acetonitrile. Table 6 shows the effect of volume of sample solution introduced into the preconcentration column on the enrichment factor of AS. The volume of the sample solution was changed to 1250, 2500, 3750 and 5000 µL. In case that the sample solution is 1250 µL and 2500 µL, the maximum enrichment factor of AS close to 90% was obtained, compared with theoretical that of AS. Considering detection sensitivity of AS, we used 2500 µL as the volume of sample solution introduced into the preconcentration column.

3.7 Calibration curve for DBS⁻ ion obtained by using a microfluidic polymer chip with an embedded AS⁻ ISE and on-line preconcentration technique in the SIA system.

Figure 3 shows typical calibration peaks for DBS⁻ ion obtained by using a microfluidic polymer chip with an embedded AS⁻ ISE and on-line preconcentration technique in the SIA system. DBS⁻ ion in the concentration range from 1.0 × 10⁻⁶ to 3.0 × 10⁻⁴ mol dm⁻³ was determined at sampling rate with one sample per 15 minutes including preconcentration time and elution time. Figure 4 shows calibration curves for DBS⁻ ion obtained with on-line preconcentration system (A) and with no on-line preconcentration system (B). By using the on-line preconcentration technique in the SIA system, DBS⁻ ion in a concentration range from 1.0 × 10⁻⁷ to 3.0 × 10⁻⁴ mol dm⁻³ with a Nernstian slope of 63.5 mV decade⁻¹, which was lower concentration range than that in Nernstian response of the ISE detector with no on-line preconcentration system, was successfully determined. A sample solution was concentrated to about 40 times by utilizing on-line preconcentration system. Sample throughput for the determination of DBS⁻ ion was around 4 samples h⁻¹.

3.8 Application of the SIA system for the determination of DBS⁻ ion in real water samples.

Table 7 presents the results of a recovery test for DBS⁻ ion added to tap water and river water samples, obtained by using a calibration curve of the AS⁻ ISE detector and on-line preconcentration technique in the present SIA system. Environmental water samples, such as a tap water, and a river water, were filtered by a membrane filter (HAWP04700, Millipore) prior to use. For all of the tap water and river water samples examined in this work, the recovery of DBS⁻ ion was roughly 91–97%. The result indicates that there is little matrix effect on the determination of DBS⁻ ion in tap water and river water samples. The results mean that the present SIA system with on-line preconcentration technique is applicable for the determination of AS⁻ ion in tap water and river water samples.

| Table 5. Effect of flow rate of sample solution introduced into the preconcentration column on the enrichment factor of AS. |
|---|---|---|---|---|
| Flow rate of sample solution introduced into the preconcentration column/µL s⁻¹ | 4 | 8 | 21 | 33 |
| Enrichment factor of AS/% (n = 3) | 93.7 ± 2.9 | 85.5 ± 5.1 | 91.9 ± 1.2 | 70.0 ± 5.2 |

* A 1250 µL of 1.0 × 10⁻⁶ mol dm⁻³ NaDBS solution at several flow rate was introduced into the preconcentration column and it was eluted with 63 µL of 75 wt% acetonitrile.

| Table 6. Effect of volume of sample solution introduced into the preconcentration column on the enrichment factor of AS. |
|---|---|---|---|---|
| Volume of sample solution introduced into the preconcentration column/µL | 1250 | 2500 | 3750 | 5000 |
| Enrichment factor of AS/% (n = 3) | 88.3 ± 2.1 | 88.6 ± 5.7 | 80.8 ± 4.9 | 72.7 ± 3.0 |

* A 1.0 × 10⁻⁶ mol dm⁻³ NaDBS solution at several volumes was introduced into the preconcentration column and it was eluted with 63 µL of 75 (v/v) % acetonitrile.
Table 7. Recovery tests of DBS\(^{-}\) ion added to several environmental samples.

| Sample          | Added /μmol dm\(^{-3}\) | Found /μmol dm\(^{-3}\) | Recovery /\% |
|-----------------|--------------------------|--------------------------|--------------|
| River water 1   |                          |                          |              |
| (1.25-fold dilution) | 0.50                    | 0.77                     | 93.9         |
|                 | 1.00                     | 1.23                     | 93.3         |
| River water 2   |                          |                          |              |
| (1.25-fold dilution) | 0.50                    | 0.68                     | 96.8         |
|                 | 1.00                     | 1.16                     | 96.0         |
| Tap water       |                          |                          |              |
| (1.25-fold dilution) | 0.50                    | 0.20                     |              |

River water 1: Ayase river, Saitama, Japan. River water 2: Zenpukuji river, Tokyo, Japan. Tap water: Shibaura Institute of Technology, Tokyo, Japan.

4. Conclusions

A new plastic microfluidic polymer chip with an embedded DBS\(^{-}\)-ISE and AgBr wire electrode as a reference electrode was used as a detector for determination of DBS\(^{-}\) ion in a SIA system with a new on-line preconcentration technique. The present SIA system with on-line preconcentration technique offers the advantages of much increased sensitivity for anionic surfactants, as well as more automated operations compared with other analytical methods. Determination concentration range of AS\(^{-}\) ion with the present SIA system sufficiently satisfies the limits (200 ppb, ca. 5.7 × 10\(^{-11}\) mol dm\(^{-3}\)) permitted in Japan for drinking water. The present SIA system is useful for the determination of AS\(^{-}\) ion in tap water and river water samples.

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