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Arsenic(III) detection using electrochemical–chemical–chemical redox cycling at bare indium–tin oxide electrodes†

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Sensitive As(III) detection in ground water is of great importance for evaluating the quality of drinking water. We report a sensitive electrochemical method for As(III) detection based on electrochemical–chemical–chemical (ECC) redox cycling involving Ru(IV) [an oxidized species of $Ru^{III}(NH_3)_5NH_2^{2+}$], As(III), and tris(3-carboxyethyl)phosphine (TCEP). Electrochemical oxidation of $Ru^{III}(NH_3)_5NH_2^{2+}$ formed from $Ru^{III}(NH_3)_6^{3+}$ generates Ru(IV), which quickly oxidizes As(III). This electro-mediated oxidation of As(III) produces As(V), which is reduced back to As(III) by TCEP. Electrochemically generated Ru(IV) then reoxidizes As(III), allowing ECC redox cycling to occur at a high rate on bare indium-tin oxide (ITO) electrodes without modifying the surfaces with electrocatalytic materials. Because most interfering metal ions precipitate in a carbonate buffer, water samples are mixed with carbonate buffers prior to electrochemical measurements, rendering the effects of Cu^+, Cu^{2+}, Fe^{2+}, Fe^{3+}, and Pb^{2+} insignificant. The detection limit calculated by ECC redox cycling using a chronocoulogram is 1.2 μM, much lower than that obtained using only the electro-mediated oxidation of As(III) (90 μM).

Introduction

Arsenic species present in drinking water cause serious, acute, and chronic health effects because of their toxicity.[1–3] With prolonged exposure, even low concentrations of arsenic species can lead to skin lesions, peripheral neuropathy, diabetes, renal system effects, cardiovascular disease, and cancer.[4] Moreover, unlike organic species, it is not trivial to convert toxic arsenic species into non-toxic ones and to remove arsenic species from drinking water. It is therefore necessary to prevent exposure to arsenic-containing water. For this purpose, arsenic concentrations in drinking water, such as groundwater, should be frequently and accurately monitored, especially in the field. The World Health Organization (WHO) recommends arsenic concentrations of less than 10 μg L^{-1}, necessitating a sensitive method for its detection.[3]

Much effort has been devoted to developing sensitive methods for arsenic detection. The methods include atomic (absorption and fluorescence) spectrometry, (inductively coupled plasma) mass spectrometry, calorimetry, and electrochemical methods.[2,5] Occasionally combined with chromatographic separation, atomic and mass spectrometries enable

highly sensitive and accurate detection.[6] However, their practical application in the field is restricted due to their large size and high cost. On the other hand, electrochemical methods offer low cost and immediate applicability without emitting toxic AsH$_3$ gas.[3]

Electrochemical methods based on anodic or cathodic stripping voltammetry use Hg or Au, because the stripping of arsenic species from these electrodes is facile, providing very high signal-to-background ratios.[3] However, anodic stripping voltammetry suffers from the generation of hydrogen bubbles, which affects reproducibility.[7] Some electrochemical methods use the direct electrocatalytic oxidation of As(III) at electrodes modified with ruthenium oxide,[8] iridium oxide,[9,10] cobalt oxide,[11] or arsenite oxidase.[12] Although the operational procedure is simple, detection limits are relatively high and electrode modification is essential. Another electrochemical method involves the use of electro-mediated oxidation of As(III), although to date, only iodide (I$^-$) has been used as an electron mediator.[13–15]

The interference of electroactive metal ions (such as Cu^{2+}) in drinking water significantly impedes electrochemical detection of As(III).[3] In this paper, we report a selective and sensitive electrochemical detection method for As(III) based on electrochemical–chemical–chemical (ECC) redox cycling[16–18] involving Ru(IV) [Ru(NH$_3$)$_5$NH$_2^{3+}$, an oxidized species of Ru(NH$_3$)$_5$NH$_2^{2+}$], As(III), and tris(3-carboxyethyl)phosphine (TCEP). This ECC redox cycling is compared to the electro-mediated oxidation of As(III) by Ru(IV). The pH of the carbonate buffer as well as the

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concentrations of $Ru(NH_3)_6^{3+}$ (a source of $Ru(NH_3)_5NH_2^{2+}$) and TCEP are optimized, and the interfering effects of electroactive metal ions are then tested. Detection limits for As(III) in distilled and tap water, obtained using ECC redox cycling, are compared to those obtained by electro-mediated oxidation.

Experimental section

Materials

All chemicals were obtained from Sigma-Aldrich, except sodium (meta)arsenite ($NaAsO_2$), which was purchased from Fluka, and used without further purification. Indium-tin oxide (ITO) electrodes were obtained from Corning (Daegu, Korea). Standard solutions of $NaAsO_2$, $Ru(NH_3)_6Cl_3$, and TCEP hydrochloride were prepared daily. A standard solution of $Ru(NH_3)_6^{3+}$ was prepared using distilled or tap water, because $Ru(NH_3)_6^{3+}$ slowly decomposes in basic carbonate buffer although it is stable in neutral water. Standard solutions of $NaAsO_2$ and TCEP were prepared in a carbonate buffer (100 mM). To prepare each solution, two to four out of five solutions [(i) carbonate buffer, (ii) carbonate buffer containing a different concentration of $NaAsO_2$, (iii) carbonate buffer containing 4 mM TCEP, (iv) water containing 40 μM $Ru(NH_3)_6^{3+}$, and (v) water containing no interfering salt, 40 μM CuCl, $CuSO_4$, $FeCl_2$, $FeCl_3$, or $Pb(NO_3)_2$] were mixed just before electrochemical measurements.

Electrochemical measurements

ITO electrodes were dipped into 1 M HCl at room temperature for 10 min.[19] The electrodes were then washed with water and dried under a stream of N_2 gas. The electrochemical experiment was performed using a CHI 405A instrument (CH instruments, USA) and an electrochemical cell consisting of an ITO working electrode, a Pt counter electrode, and an Ag/AgCl (3 M NaCl) reference electrode. All measurements were made at room temperature. The geometric area of the ITO electrode exposed to solution was *ca.* 0.28 cm².

Results and discussion

As(III) detection by electro-mediated oxidation and ECC redox cycling

In order to detect As(III) without modifying the electrode surfaces, bare ITO electrodes were used. Because the direct oxidation of As(III) proceeds very slowly at ITO electrodes, the electro-mediated oxidation of As(III) is required. In this study, two schemes were developed for comparison [(i) electro-mediated oxidation of As(III) by Ru(IV) (Fig. 1a) and (ii) ECC redox cycling[16–18] involving TCEP, As(III), and Ru(IV) (Fig. 1b)]. In Fig. 1a, the electrochemical oxidation of two Ru(III) complexes generates two Ru(IV) complexes, which then oxidize As(III) to As(V). Fig. 1b shows that, in addition to the electro-mediated oxidation of As(III), As(V) is reduced back to As(III) by TCEP and the redox cycling proceeds. ECC redox cycling allows higher anodic currents to be obtained. Another conceivable type of ECC redox cycling involves TCEP, As(III), and Ru(III) (Fig. 1c). In this case, two Ru(III) complexes oxidize As(III) to As(V). However,
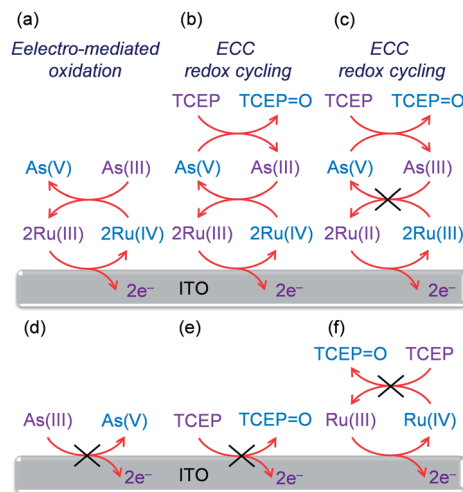

Fig. 1 Schematic representations of (a) electro-mediated oxidation of As(III) by $Ru(NH_3)_5NH_2^{3+}$ [Ru(IV)], (b) ECC redox cycling using TCEP, As(III), and Ru(IV), (c) ECC redox cycling using TCEP, As(III), and Ru(III), (d) direct oxidation of As(III), (e) direct oxidation of TCEP, and (f) unwanted electro-mediated oxidation of TCEP by Ru(IV).

this type of redox cycling is negligible because the reaction between $Ru(NH_3)_6^{3+}$ and As(III) is slow.

Drinking water may contain electroactive metal ions, which interfere with the accurate measurement of As(III). The removal of these ions by precipitation is therefore required prior to electrochemical determination of As(III). Many metal ions precipitate out of basic solutions or solutions containing multivalent anions. In basic solutions, $As(OH)_3$ is formed with a K_{sp} of 2.1×10^{-1}, implying that its precipitation is negligible.[20] Moreover, soluble $As(OH)_2CO_3^-$ is formed in solutions containing carbonates, which are the most abundant anions in ground water. The K_{sp} values of $CuCO_3$, $FeCO_3$, and $PbCO_3$ are 2.3×10^{-10}, 3.07×10^{-11}, and 1.46×10^{-13}, respectively.[20] With a concentration of carbonate buffer of 50 mM, the equilibrium concentration of CO_3^{2-} at pH 9 is *ca.* 2.5 mM because the pK_{a2} of H_2CO_3 is 10.329.[21] In this solution, the solubility of Cu^{2+}, Fe^{2+}, and Pb^{2+} is *ca.* 9.2×10^{-8}, 1.2×10^{-8}, and 5.8×10^{-11} M, respectively. Therefore, most of the Cu^{2+}, Fe^{2+}, and Pb^{2+} in water can be removed by precipitation from an aqueous carbonate buffer.

The cyclic voltammograms depicted in Fig. 2 were obtained in carbonate solutions with four different pH values. In a
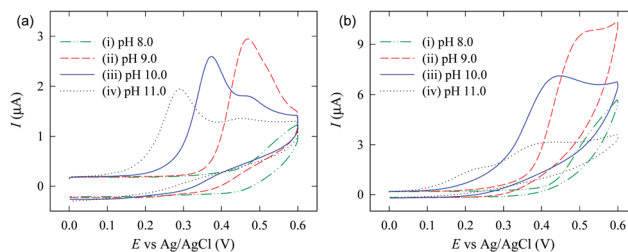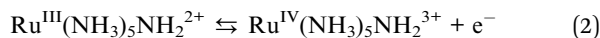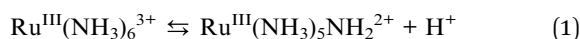

Fig. 2 Cyclic voltammograms obtained at bare ITO electrodes (at a scan rate of 50 mV s⁻¹) in carbonate buffers (50 mM) at four different pH values containing (a) 10 μM $Ru(NH_3)_6^{3+}$ or (b) 10 μM $Ru(NH_3)_6^{3+}$, 10 μM As(III), and 1.0 mM TCEP.

solution containing only $Ru(NH_3)_6^{3+}$ (Fig. 1a), the anodic peak potential decreased with increasing pH (Fig. 2a). In a solution containing $Ru(NH_3)_6^{3+}$, As(III), and TCEP (Fig. 1b), the anodic onset potential also decreased with increasing pH (Fig. 2b), although the voltammogram shows the highest anodic current at 0.5 V at pH 9. It is advantageous to use a pH value near 7, because $Ru(NH_3)_6^{3+}$ is stable in neutral solutions but slowly decomposes in basic solutions. Therefore, a carbonate buffer of pH 9 was selected for As(III) detection.

Fig. 3a shows cyclic voltammograms obtained in (i) carbonate buffer, (ii) carbonate buffer containing As(III), (iii) carbonate buffer containing TCEP, and (iv) carbonate buffer containing As(III) and TCEP. All four voltammograms are similar, indicating that direct oxidation of As(III) and TCEP at ITO electrodes is slow (Fig. 1d and e). The electrooxidation of $Ru(NH_3)_6^{3+}$ (actually $Ru(NH_3)_5NH_2^{2+}$) occurs readily in basic solutions. Accordingly, in curve i of Fig. 3b, the anodic peak potential appeared at *ca.* 0.46 V. In basic solutions, $Ru(NH_3)_6^{3+}$ is believed to undergo the following reactions:[22,23]

$$Ru^{III}(NH_3)_6^{3+} \leftrightarrows Ru^{III}(NH_3)_5NH_2^{2+} + H^+ \quad (1)$$

$$Ru^{III}(NH_3)_5NH_2^{2+} \leftrightarrows Ru^{IV}(NH_3)_5NH_2^{3+} + e^- \quad (2)$$

$$Ru^{IV}(NH_3)_5NH_2^{3+} \rightarrow \text{decomposition} \quad (3)$$

Further electrooxidation of $Ru^{IV}(NH_3)_5NH_2^{3+}$ can also occur.[22,23] The second peaks in curves iii and iv of Fig. 2a are related to further electrooxidation of $Ru^{IV}(NH_3)_5NH_2^{3+}$. However, in curve ii of Fig. 2a obtained at pH 9, the second peak was not observed in the given potential range, indicating that further electrooxidation of $Ru^{IV}(NH_3)_5NH_2^{3+}$ was not significant. The decomposition of unstable $Ru^{IV}(NH_3)_5NH_2^{3+}$ is responsible for the irreversible behavior of the cyclic voltammograms shown in Fig. 2a.[22] Although the formal potential of $Ru(NH_3)_6^{3+}/Ru(NH_3)_6^{2+}$ is independent of the pH, the electrooxidation of $Ru(NH_3)_6^{3+}$ (actually $Ru(NH_3)_5NH_2^{2+}$) is pH-dependent because H^+ is involved in eqn (1) prior to electrooxidation of eqn (2).

The oxidation of $Ru(NH_3)_5NH_2^{2+}$ in the presence of As(III) (curve ii of Fig. 3b) began at a more positive potential than it did

in its absence (curve i of Fig. 3b). This potential shift is responsible for the oxidation of As(III) mediated by $Ru(NH_3)_5NH_2^{2+}$. Interestingly, the anodic peak current in a solution containing $Ru(NH_3)_6^{3+}$ and TCEP (curve iii of Fig. 3b) was smaller than it was in a solution containing $Ru(NH_3)_6^{3+}$ (curve i of Fig. 3b), although the anodic onset potential was lower. This result indicates that the unwanted electro-mediated oxidation of TECP by $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_5NH_2^{2+}$ was insignificant (Fig. 1f). The anodic currents in a solution containing $Ru(NH_3)_6^{3+}$, As(III), and TCEP (curve iv of Fig. 3b) were much higher than those in a solution containing $Ru(NH_3)_6^{3+}$ and TCEP (curve iii of Fig. 3b), indicating that ECC redox cycling occurs in the presence of As(III).

Then, the concentrations of $Ru(NH_3)_6^{3+}$ and TCEP were optimized. The use of a low concentration of $Ru(NH_3)_6^{3+}$ is required to obtain low background levels, whereas the use of a high concentration of $Ru(NH_3)_6^{3+}$ is required to obtain high signal levels. In Fig. S1a of the ESI,† the anodic peak current of $Ru(NH_3)_6^{3+}$ increased with increasing the concentration of $Ru(NH_3)_6^{3+}$. It is important to note that $Ru(NH_3)_6^{3+}$ can adsorb onto ITO electrodes in amounts that vary with the electrolyte concentration and the type of ion present in aqueous solutions. When low concentrations of $Ru(NH_3)_6^{3+}$ were used, the contribution of adsorbed $Ru(NH_3)_5NH_2^{2+}$ to the electrochemical signals was significant and it became difficult to obtain reproducible signals in both electro-mediated oxidation of As(III) and ECC redox cycling. To overcome this problem, 10 μM $Ru(NH_3)_6^{3+}$ was chosen. Fig. S1b of the ESI† shows that a prominent electrochemical signal due to ECC redox cycling was obtained from a solution containing 10 μM $Ru(NH_3)_6^{3+}$, 10 μM As(III), and 1 mM TCEP. Although the electrochemical oxidation of TCEP at the ITO electrode was insignificant in solutions containing 0.1 and 1 mM TCEP, it was considerable in solutions containing 3 and 10 mM TCEP (Fig. S1c of the ESI†). In the solution containing 1 mM TCEP, the anodic onset potential was lower than it was in solutions containing 3 and 10 mM TCEP (Fig. S1d of the ESI†). Therefore, 1 mM TCEP was chosen for ECC redox cycling.

To determine the effect of interfering electroactive metal ions, ECC redox cycling was conducted in their presence (Fig. 4). The difference between the cyclic voltammograms obtained in the presence and absence of a metal ion was found to be insignificant. This observation is best explained by the low K_{sp} values for metal carbonates in carbonate solutions, which results in the precipitation of interfering metal ions.

Reason for ECC redox cycling involving As(III)

Two kinds of electron-transfer reactions are involved in the redox cycling shown in Fig. 5a: outer-sphere reactions and inner-sphere reactions.[17] P, R_I, and R_{II} are reduced forms, and Q, O_I, and O_{II} are oxidized forms. In As(III) detection, P and Q represent As(III) and As(V), respectively. In order to generate the redox cycling in the presence of P or Q in Fig. 5a, the direct electron transfer between O_I and R_{II} in Fig. 5a should be slow. The electron-transfer reaction between a species that mainly undergoes an inner-sphere reaction (ISR-philic species) and a
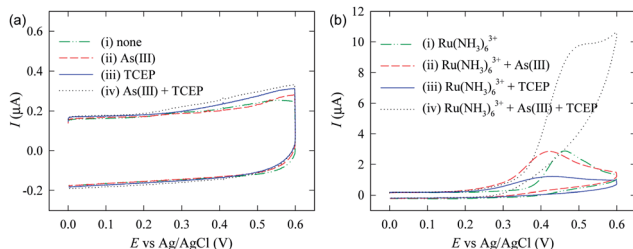

Fig. 3 Cyclic voltammograms obtained at bare ITO electrodes (at a scan rate of 50 mV s^{-1}) in carbonate buffers (pH 9, 50 mM) containing (a) (i) nothing else, (ii) 10 μM As(III), (iii) 1.0 mM TCEP, (iv) 10 μM As(III) and 1.0 mM TCEP, and (b) (i) 10 μM $Ru(NH_3)_6^{3+}$, (ii) 10 μM $Ru(NH_3)_6^{3+}$ and 10 μM As(III), (iii) 10 μM $Ru(NH_3)_6^{3+}$ and 1.0 mM TCEP, or (iv) 10 μM $Ru(NH_3)_6^{3+}$, 10 μM As(III), and 1.0 mM TCEP.
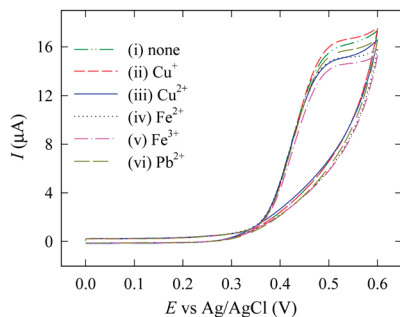
Fig. 4 Cyclic voltammograms obtained at bare ITO electrodes (at a scan rate of 50 mV s^{-1}) in carbonate buffers (pH 9, 50 mM) containing 10 μM Ru(NH$_3$)$_6$$^{3+}$, 10 μM As(III), and 1.0 mM TCEP, and (i) no interfering salt, (ii) 10 μM CuCl, (iii) 10 μM CuSO$_4$, (iv) 10 μM FeCl$_2$, (v) 10 μM FeCl$_3$, or (vi) 10 μM Pb(NO$_3$)$_2$.

ions exist in many different forms in aqueous solutions: HAsO$_2$ and AsO$_2$$^-$ are prevailing As(III) species, and HAsO$_4$$^{2-}$ accounts for much of the As(v).[10] The redox reaction between As(v) and As(III) can be expressed as follows:[24]

$$HAsO_4^{2-} + 4H^+ + 2e^- \leftrightarrows HAsO_2 + 2H_2O,$$
$$E^0 = 0.881 - 0.1182 \times pH \text{ V (vs. SHE)} \quad (4)$$

At pH 9, E^0 is −0.1828 V, which corresponds to *ca.* −0.4 V *vs.* Ag/AgCl. The formal potential of Ru^{III}(NH$_3$)$_6$$^{3+}$/Ru^{II}(NH$_3$)$_6$$^{2+}$ is *ca.* −0.14 V,[17,18] the formal potential of Ru^{IV}(NH$_3$)$_5$NH$_2$$^{3+}$/Ru^{III}(NH$_3$)$_5NH_2$$^{2+}$ is higher than that of Ru^{III}(NH$_3$)$_6$$^{3+}$/Ru^{II}(NH$_3$)$_6$$^{2+}$,[22] and the formal potential of TCEP = O/TCEP is less than −0.4 V.[17,18] Accordingly, it seems that in thermodynamic terms, two ECC redox cycling schemes are possible (Fig. 5b). As(III) might not readily undergo an outer-sphere reaction. It is expected that the redox reaction between ISR-philic As(III) and OSR-philic Ru(NH$_3$)$_6$$^{3+}$ is slow. Accordingly, the ECC redox cycling involving TCEP, As(III), and Ru(III) (Fig. 1b) is either slow or does not occur at all (Fig. 1c and 5b). However,
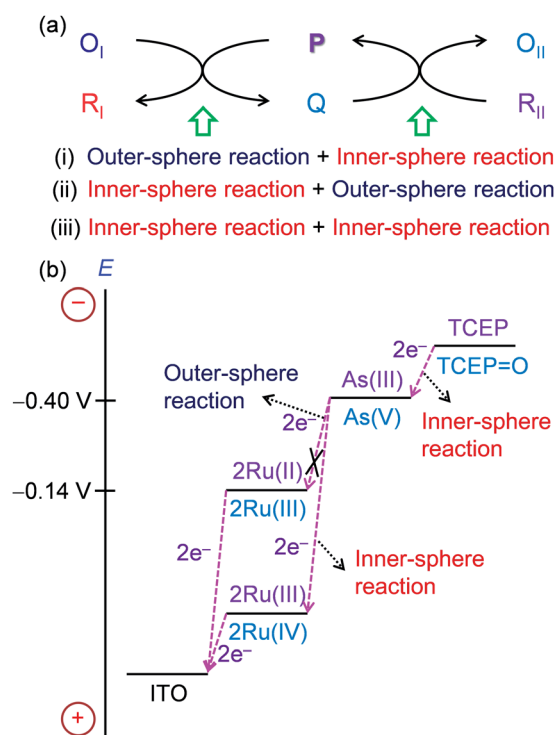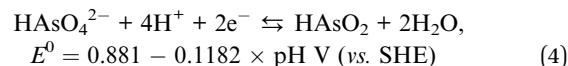

Fig. 5 Schematic representations of (a) the redox cycling involving O$_I$, P or Q, and R$_{II}$ and (b) the relative positions of the electrode potentials and the formal potentials of redox couples involved in two possible ECC redox cycling schemes. P, R$_I$, and R$_{II}$ are reduced forms, and Q, O$_I$, and O$_{II}$ are oxidized forms. In As(III) detection, P and Q represent As(III) and As(v), respectively.
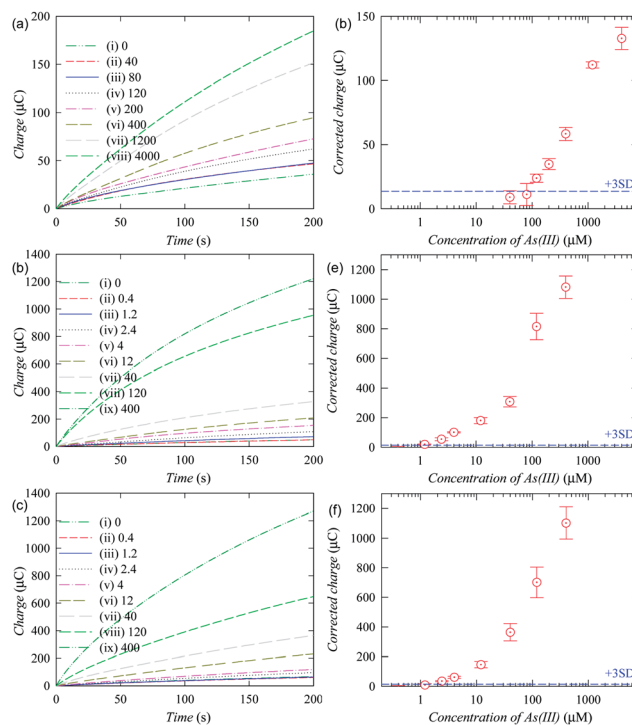

Fig. 6 Chronocoulograms obtained at bare ITO electrodes with various concentrations of As(III) in (a and b) distilled water and (c) tap water. Electro-mediated oxidation of As(III) occurs in a and ECC redox cycling occurs in (b) and (c). The final solutions contained a carbonate buffer (pH 9, 50 mM). (d–f) Calibration plots: the concentration dependence of the charge at 200 s in panels (a), (b), and (c). The concentrations of As(III) represent initial concentrations, and the As(III) solutions were diluted four-fold prior to electrochemical measurement. Each concentration-dependent experiment was carried out with three different electrodes for the same sample. The data were subtracted from the mean value obtained from seven measurements, at zero concentration. The dashed line corresponds to 3 times the standard deviation (SD) of the charge at a concentration of zero. The error bars represent the SD of three measurements.

species that mainly undergoes an outer-sphere reaction (OSR-philic species) and the electron-transfer reaction between an ISR-philic species and another ISR-philic species are likely to be slow.[17] Accordingly, three pairs of O$_I$ and R$_{II}$ in Fig. 5a may be possible in obtaining a slow electron-transfer reaction between O$_I$ and R$_{II}$: (i) OSR-philic O$_I$ and ISR-philic R$_{II}$, (ii) ISR-philic O$_I$ and OSR-philic R$_{II}$, and (iii) ISR-philic O$_I$ and ISR-philic R$_{II}$.

Fig. 5b represents the relative positions of the electrode potentials and the formal potentials of redox couples. Arsenic

because $Ru^{IV}(NH_3)_5NH_2^{3+}$ is unstable and reactive,[22,23] it may readily undergo an inner-sphere reaction with ISR-philic As(III). Consequently, the ECC redox cycling involving TCEP, As(III), and Ru(IV) (Fig. 1b and 5b) occurs.

As(III) detection in water

As(III) detection was carried out in either distilled or tap water. Chronocoulometry (Fig. 6) was used to obtain concentration-dependent data. The charges at 200 s in chronocoulograms were used to draw calibration plots and to determine detection limits. Fig. 6a and b are obtained using distilled water. The detection limits for the electro-mediated oxidation of As(III) and the ECC redox cycling were calculated and *ca.* 90 and 1.2 μM, respectively. ECC redox cycling gave rise to lower As(III) detection limits than did the electro-mediated oxidation. The detection limit for the ECC redox cycling obtained with tap water was *ca.* 1.5 μM, which was similar to those obtained with distilled water.

Conclusions

We have developed a sensitive electrochemical method for As(III) detection that is appealing for practical applications in the field. The method is based on ECC redox cycling involving Ru(IV), As(III), and TCEP at bare ITO electrodes. The ECC redox cycling allows higher anodic currents than the electro-mediated oxidation. Because $Ru^{IV}(NH_3)_5NH_2^{3+}$ is unstable, it may readily undergo an inner-sphere reaction with ISR-philic As(III). Adding a carbonate buffer to the water prior to the measurement allows low electrochemical interference by Cu^+, Cu^{2+}, Fe^{2+}, Fe^{3+}, and Pb^{2+}. The calculated detection limit obtained using the ECC redox cycling from a chronocoulogram is 1.2 μM, which is much lower than that obtained using only the electro-mediated oxidation of As(III) (90 μM).

Acknowledgements

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