Selenium, an essential micronutrient commonly found in aqueous environments in the form of selenate, \( \text{SeO}_4^{2-} \), and/or selenite, \( \text{SeO}_3^{2-} \), requires monitoring and control given its toxicity when ingested beyond prescribed levels.\(^1\) Whereas the electrochemical reduction of \( \text{SeO}_3^{2-} \) can be effected with relative ease, \( \text{SeO}_4^{2-} \) is considerably more inert, requiring harsh conditions for its conversion to a selenium species of lower oxidation state.\(^2,3\) This communication describes a new tactic that allows purified \( \text{SeO}_4^{2-} \) to be reduced on polycrystalline Au, Au(poly), in acidic solutions containing \( \text{Cu}^{2+} \) at room temperature without prior pretreatment, allowing its direct detection and removal. The first step in the process involves formation of a thin layer of copper selenide, Cu\(_x\)Se, in the Cu underpotential deposition, UPD, region of Au(poly). In a subsequent step, Cu in the layer is oxidatively stripped, leaving behind an adsorbed layer of elemental Se, which undergoes oxidation at higher potentials generating \( \text{SeO}_3^{2-} \). Additional studies involving purified \( \text{SeO}_4^{2-} \) provided strong evidence that earlier reports claiming direct reduction of \( \text{SeO}_4^{2-} \) were likely compromised by the presence of trace \( \text{SeO}_3^{2-} \) in the as purified selenate salts.\(^4-8\)

**Experimental**

Fresh 0.1 M \( \text{HClO}_4 \) solutions were prepared before each experiment using high purity concentrated \( \text{HClO}_4 \) (Sigma Aldrich/Fluka, TraceSelect) and ultrapure water (UPW) supplied by an EASYpure UV system (Barnstead-Thermolyne Corp). Two types of sodium selenate of different purities were obtained from Alfa Aesar, i.e. 99.9% (decahydrate), and 99.8% (anhydrous), containing, respectively, less than 0.01% and 0.15% selenite by mass, to be denoted hereafter as HP and LP, respectively. Sodium selenite, rated at 44–48% selenium by mass, was purchased from Acros Organics. Copper (II) perchlorate hexahydrate was supplied by Aldrich (98%). Sodium selenite, \( \text{Na}_2\text{SeO}_3 \), present as an impurity in commercial HP \( \text{Na}_2\text{SeO}_4 \), was removed using the method reported by Gruebel et al.\(^9\) with slight modifications (see Supporting Information).

The glassware was cleaned by soaking overnight in a 9:1 mixture of concentrated \( \text{H}_2\text{SO}_4:30\% \text{H}_2\text{O}_2 \) (oxidizing and corrosive, handle with care), followed by rinsing with large amounts of UPW, and subsequently boiled in UPW three times. The carbon counter electrode was rinsed with UPW, and the \( \text{H}_2 \) bubble reversible hydrogen reference electrode (RHE) was filled with fresh neat electrolyte before each experiment. Two Au working electrodes were used: a Au wire (Alfa Aesar, Premion, 99.999%) and Au rotating disk electrode, RDE (Pine Instrument Company, \( r_{\text{disk}} = 0.25 \text{ cm} \)). The wire was cleaned by flame-annealing in a gas flame, and then immersed while hot into UPW, whereas the RDE was first placed in a 0.1 M \( \text{HClO}_4 \) solution overnight. Subsequently, both types of electrodes were transferred to the electrochemical cell filled with 0.1 M \( \text{HClO}_4 \), which was then deaerated for 10 min with \( \text{N}_2 \) (Airgas, High Purity 4.8 grade). Prior to experiments, both types of Au electrodes were cycled linearly in this electrolyte between 0.0 and 1.85 V at a rate \( v = 0.2 \text{ V/s} \) for ca. 15 min, sufficient for the electrode to exhibit voltammetry characteristics of clean Au(poly).\(^10\) At this stage, aliquots of concentrated analyte solutions were added to the solution to yield the desired final concentrations. All electrochemical measurements were performed with an Autolab potentiostat (Metrohm) equipped with a true linear potential scan module (Scan250).

The actual areas of the Au working electrodes were determined from CVs in 0.5 M \( \text{H}_2\text{SO}_4 \) assuming a charge density of 400 \( \mu \text{C/cm}^2 \) for the formation of Au oxide between 1.25 and 1.7 V vs RHE,\(^11\) yielding for the Au RDE a roughness factor of 1.4.

**Results and Discussion**

In agreement with earlier claims in the literature,\(^4\) the cyclic voltammogram of the Au(poly) wire in 0.1 M \( \text{HClO}_4 \) containing 1 mM \( \text{Na}_2\text{SeO}_3 \) (LP) (black curve, Fig. 1), displayed redox peaks centered at 1.2 and 0.6 V in the scans toward positive and negative potentials, respectively. Both peaks disappeared, however, when the same experiment was carried out using \( \text{Na}_2\text{SeO}_4 \) solutions purified by the method specified in the Supporting Information (red curve), indicating that \( \text{SeO}_3^{2-} \) does not undergo reduction on Au(poly) in 0.1 M \( \text{HClO}_4 \). In fact, the features observed for commercial \( \text{Na}_2\text{SeO}_4 \) (see black curve, Fig. 1) could be largely reproduced in 0.1 M \( \text{HClO}_4 \) (blue curve, Fig. 1), containing 1.5 \( \mu \text{M} \text{Na}_2\text{SeO}_3 \). The peaks observed using as received \( \text{Na}_2\text{SeO}_4 \) can be ascribed to the reduction of \( \text{SeO}_3^{2-} \) to yield adsorbed elemental Se (peak at 0.6 V), which is then reportedly re-oxidized back to adsorbed \( \text{SeO}_3^{2-} \) at ca. 1.2 V.\(^12-15\) This clearly indicates that earlier results published in the literature claiming a direct electroreduction of \( \text{SeO}_3^{2-} \) were almost certainly compromised by \( \text{SeO}_4^{2-} \) contamination in the commercial selenate employed.\(^4,8\)

A series of experiments were then carried out in purified 1 mM \( \text{Na}_2\text{SeO}_4 \) in 0.1 M \( \text{HClO}_4 \) containing 1.2 mM Cu\((\text{ClO}_4)_2 \) using the Au RDE rotating at \( \omega = 1500 \text{ rpm} \). For these measurements, the potential of the disk was poised at two different values, \( E_{\text{hold}} \), in the UPD Cu regime, i.e. \( E_{\text{hold}} = 0.325 \text{ (Panel A)} \) and 0.425 V vs RHE (Panel C) for different periods of time, \( t_{\text{hold}} \) (red, 100 (blue) and 1000 s (green), and then scanned anodically at a rate \( v = 0.1 \text{ V/s} \). As shown by these data, all linear scans displayed the same oxidation peak at 1.15 V found in Fig. 1. This feature was not observed, however, when only purified 1 mM \( \text{Na}_2\text{SeO}_4 \) (dashed black, Panel A) or 1.2 mM Cu\((\text{ClO}_4)_2 \)

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(magenta, Panel A) were individually added to 0.1 M HClO₄, even for \( t_{\text{hold}} = 1000 \) s. Inspection of the data revealed an increase in the magnitude of the peak with \( t_{\text{hold}} \), or decreases in \( E_{\text{hold}} \), consistent with a potential dependent, kinetically controlled reduction process. Similar oxidation features were reported on Au(poly) following reduction of SeO₄²⁻ from Cu(II)-containing solutions and assigned to the stripping of Cu from one or more forms of copper selenide (peaks below \( 0.7 \) V),[16,17] leaving behind adsorbed Se, which is then oxidized at 1.15 V yielding adsorbed SeO₃²⁻ as discussed before.[18] It may be concluded that UPD Cu promotes the reduction of SeO₄²⁻ to yield Cu₄Se and that the features below \( 0.7 \) V can be assigned to the stripping of Cu from this layer to yield elemental Se. The charge under the peak at 1.15 V was determined for each of the solid curves in Panel A, Fig. 2, by integrating the current between 1.05–1.3 V and then subtracting contributions due to the interfacial capacitance of Au(poly) measured during an anodic scan initiated at 0.7 V. This quantity, denoted as \( q_{\text{Se}} \), provides a measure of the amount of adsorbed Se, and yielded values of 33, 135, and 358 \( \mu \)C cm⁻² for \( t_{\text{hold}} = 10, 100 \) and 1000 s, respectively. Formation of Cu₄Se and Cu₄Se in bulk form from SeO₃²⁻ and Cu(II) would be thermodynamically favored below 0.522 and 0.488 V, respectively, but the \( q_{\text{Se}} \) values are too small to account for Se coverages on Au(poly) much in excess of a monolayer. In short, a bulk deposit of copper selenide is not formed.

An experiment carried out under the same conditions as those in Panel A, Fig. 2, in which the concentration of Na₂SeO₄ was reduced by two orders of magnitude (see Panel B, Fig. 2) yielded values of \( q_{\text{Se}} \) only 3, 1.5 and 1.37 times smaller than in Panel A, for \( t_{\text{hold}} = 10, 100 \) and 1000 s, respectively. Prompted by these results, systematic measurements were performed using purified Na₂SeO₄ at concentrations in the range 9.48 to 56.88 nM, yielding, for fixed \( t_{\text{hold}} \), linear correlations between \( q_{\text{Se}} \) and \( [\text{SeO}_4^{2-}] \), illustrating the power of this method for analytical applications. As shown in Fig. 3, the lowest concentration detected was 0.75 ppb Se, which is well below the 50 ppb maximum contaminant level established by the US Environmental Protection Agency for drinking water.

### Summary

Underpotential deposited Cu on Au(poly) in 0.1 M HClO₄ has been found to reduce solution phase SeO₄²⁻ to yield a thin layer of Cu₄Se, which upon subsequent oxidation produces sequentially a layer of elemental Se and adsorbed SeO₃²⁻ at more positive potentials. This novel method not only offers great advantages over those reported in the literature in that it avoids harsh and/or complex procedures for chemical reduction of SeO₄²⁻ prior to electrochemical assay,[2,3] but also displays high enough sensitivity to allow detection of SeO₄²⁻ down to the sub ppb range. Evidence was also presented suggesting previous claims of direct reduction of SeO₄²⁻ were compromised by the presence of SeO₃²⁻ impurities.[4,8] Investigation into mechanistic aspects of this UPD-mediated process and its potential value from an...
analytical and remediation viewpoint are currently under investigation using spectroscopic and microgravimetric techniques, the results of which will be reported in due course.

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