Rapid and Accurate Automatic Temperature Calibration of Disposable Screen-printed Heated Gold Electrodes

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Rapid and Accurate Automatic Temperature Calibration of Disposable Screen-printed Heated Gold Electrodes

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Abstract

Joule-heated electrodes have been used to enhance electrochemical analysis. Due to such direct heating, a steep temperature gradient is created near the electrode surface. The heating device that provides the high-frequency AC (50 kHz or more) has to be calibrated, in order to apply the desired temperature during analysis. The applied temperature of the working electrode influences both its electrical resistance and the electrochemical potential of a redox couple. Open circuit potentiometric (OCP) measurements were performed automatically with screen-printed gold loop electrodes (Au-LE), while applying 50 kHz AC heating pulses of increasing intensity provided by a ThermoLab® AC generator. Potentiometric temperature calibrations were performed using 5 mM equimolar ferri/ferrocyanide in 0.1 M of potassium chloride at 20 °C bulk temperature. Potential differences produced during each heat pulse were used to automatically calculate the electrode temperature using the

temperature coefficient of this redox couple (-1.6 mV/K). The electrode resistance values at each heating pulse were obtained by measuring the heating voltage and heating current. The automatic temperature calibration experiments with five Au-LEs were shown to be highly reproducible and precise, with an RSD for the temperature of 0.24% and 4% for resistance. The average margin error of OCP temperatures were ± 0.66 K at a 95% confidence level. The temperature coefficient (α) of electrical resistivity of the screen-printed gold layers was found to be 0.0025 $^{\circ}\text{C}^{-1}$, which is 27% lower than the theoretical value for gold metal. These findings were confirmed by DC resistance measurements using a potentiostat. Comparing the OCP temperature with the resistivity method, the temperature difference was about 0.94 $^{\circ}\text{C}$ (2.8%). Both methods enable quick, reproducible and accurate temperature calibration for disposable Au-LE, which were also used for trace mercury detection in lake water samples.

Keywords: Directly heated electrode; open circuit potentiometry; resistivity; automatic temperature calibration; gold electrode; mercury determination

1 Introduction

Heated electrodes have been used increasingly to enhance electrochemical analysis or for fundamental thermodynamic and kinetic studies of redox systems [1,2,3,4,5]. Due to direct electrical heating, a temperature gradient inside the bulk solution is created near the electrode surface. Thus, high temperature is only applied at the location, where electrochemistry takes place, i.e the electrode surface. The temperature of the bulk electrolyte can remain constant at room temperature or even below.

Heated electrodes have been applied for various chemical sensor applications. Stripping determinations of arsenic(V) by direct electrochemical reduction was conducted at a gold wire electrode [6]. Lead was determined by cathodic stripping of deposited PbO_2 at platinum micro-wire electrodes [7]. Mercury(II) [8], copper(II)

and arsenic(III) traces have been determined on gold micro-wire electrodes [9]. The latter article reported that the micro-stirring effect at a thin (25-micron diameter) gold wire resulted in a better signal enhancement compared with the use of a rotating disk electrode (RDE). Another focus of that article was a study of temperature effects upon deposition and multiple stripping scans of Hg, Cu, and As. Heated mercury film electrodes based on iridium and screen-printed carbon have been applied for cadmium and lead analysis [10, 11].

Beside micro-wires, also glassy carbon [12], pencil [13,14,15] electrodes and even carbon paste electrodes have been joule-heated directly [16,17].

In all of these cases, the temperature calibration plays a crucial role, i.e. it is essential to find the function between heating power (heating voltage or heating current) and electrode temperature in order to apply any desired temperature value. Most groups that studied directly and indirectly heated electrodes performed temperature calibrations based on ferro/ferricyanide as a redox couple for chronopotentiometry. This approach is therefore widely accepted [18, 19, 20]. A Pt100 resistance thermometer or a thermo-element cannot be attached to the directly heated electrode, because it would disturb the measurements, and secondly, it would most probably not display the correct temperature value due to problems with heat transfer and temperature gradients. Another alternative approach for directly heated electrodes is based on precise resistance measurements. For this “resistance method”, introduced by Gabrielli et al. [21], the heated electrode serves as its own resistance thermometer. Both the heating current through and the voltage drop across the heated electrode are being measured. The resistance is then calculated according to Ohm’s law. Since the temperature coefficient of electric resistivity is well-known for most metals, the temperature can be calculated using equation (1),

$$R = R_{20}[1 + \alpha(\theta - 20\text{ }^{\circ}\text{C})] \quad (1)$$

where R is the resistance of the heated electrode at the temperature θ , α is the temperature coefficient of the electrical resistivity, and R_{20} is the electrode resistance

at 20 °C. This method works well with micro-wire electrodes, because the geometry is very well defined and reproducible. The applied temperature of the electrode surface depends linearly on the heating power P , i.e. on electrode resistance R and the square of the current I of the (AC) heating pulses as described by eq. (2).

$$P = RI^2 \quad (2)$$

The second method relies on the temperature coefficient of the standard potential of a proper redox couple, in particular ferro/ferricyanide. According to the Nernst equation (3), with equimolar concentrations, we only have to deal with the temperature dependence of the standard potential or the standard entropy, respectively. The entire logarithmic term with gas constant R , temperature T , number of transferred electrons n , and Faraday constant F becomes zero.

$$E = E^o + \frac{RT}{nF} \ln \frac{[Fe(CN)_6^{3-}]}{[Fe(CN)_6^{4-}]} \quad (3)$$

Open circuit potentiometry (OCP) can be used to measure the potential shift, if both components of the redox couple are present at equimolar concentrations. By voltammetric determination of the half-wave potential it is possible, to work with only one such component [22].

Until now, heated electrodes of any kind have been used many times after manufacturing them and performing a single temperature calibration. In case of adjusting the heating current with micro-wire electrodes, it has been expected that the same temperature difference is achieved each time a certain heating current is applied, no matter how long the wire electrode is. It is, however, tedious to perform the OCP procedure in case of disposable sensor chips such as screen-printed electrodes. We have been using screen-printed gold-loop electrodes (Au-LE) once before to study the deposition of copper by means of time-of-flight secondary ion mass spectrometry (ToF-SIMS) [23]. That study revealed that there may be deep

pores in the sintered gold layer that can retain small volumes of electrolyte.

While OCP with ferro/ferricyanide has been used very successfully in aqueous electrolytes, it has turned out to be difficult in non-aqueous solutions because proper redox couples are hard to find [24]. Such a redox couple must be available and stable in both conjugate forms, soluble, and provide a sufficient temperature coefficient of the standard potential.

Here, we introduce an accurate automatic temperature calibration approach based on potentiometry with ferro/ferricyanide. The new method was compared with resistivity-based measurements. Accuracy of the temperature of new Au-LE was compared and evaluated. The question was whether or not such electrodes are sufficiently alike enabling to apply one temperature calibration function for all sensors of a batch. Alternatively, a simple correction factor obtainable by a single resistance measurement could have been sufficient to apply one temperature calibration for all sensors of a batch. It turned out that not even the temperature coefficient of the resistivity for gold was applicable and constant for all the screen-printed electrodes. Therefore, we have developed a quick 10-min automatic calibration method that allows accuracy of better than 0.5 K. The automatic temperature calibration was then tested by analyzing mercury(II) in water samples allowing us to apply 60 °C and 70 °C, electrode temperature, during the deposition step.

2 Experimental

2.1 Instrumentation

Directly heated Au-LE sensor chips according to our design were screen-printed and delivered by DropSens (Spain) and used as working electrodes (WE). The reference electrode (RE) was a Ag/AgCl (3 M KCl) (Metrohm-Autolab, Switzerland). All measurements were performed inside a Faraday cage. All temperature calibrations were performed by means of a ThermoLab (Gensoric GmbH, Rostock, Germany)

equipped with EmStat3 potentiostat (PalmSens BV, The Netherlands) and a 50 kHz AC generator. Open-circuit potentiometry was performed for the temperature calibration using ThermoLab Tool software v.0.952 (Gensoric). A multimeter 570A-TrueRMS (Extech Instruments) was used to measure the heating voltage drop across the WE. Heating AC values were obtained by measuring the voltage drop across a 1 Ω serial precision resistor, purchased from Mouser Electronics® (Texas, USA), using a digital oscilloscope from Tectronic (30 MHz-500 MS/s). A differential oscilloscope probe GE8109 (1x attenuation) from Elditest Electronic was used to connect the digital oscilloscope to the 1 Ω precision resistor in the circuit.

SEM images were generated using a JEOL Ltd JSM-5600LV scanning electron microscope together with SEM User Interface (Version 3.02) software. Parameters included a working distance of 10 mm, with a spot-size of 30 +/-5, with an electron beam intensity of 10 keV.

EDX analysis was performed via the INCA x-ray microanalysis system with a INCA x-sight Si(Li) EDS detector probe (model No. 7388) and INCA s-stream pulse processor (from Oxford Instruments), incorporating the INCA Suite Software (Version 3.04). EDX analysis was performed with the above parameters excluding a working distance of 20 mm and a spot-size ranging from 50-80 depending on the image

Atomic force microscopy (AFM) images were obtained using an AIST-NT Reflection AFM (Novato, CA, USA) in combination with A OMEGA software (version 3.5.61). AFM images were taken using AC tapping mode with a single-crystal silicon cantilever. The cantilever manufacture frequency was 300 kHz at a force constant of 40 N/m. The conical tip height was 15 μm with ~8 nm radius.

Ion beam analysis was performed using Rutherford Backscattering Spectrometry (RBS) to determine the gold layer thickness in combination of XRUMP software. RBS analysis was performed using a RPEA 4.0 Dynamitron particle accelerator (^4He gas, with charge 1 and molecular state 1) at a high energy of 2.00 MeV.

2.2 Chemicals:

All chemicals used for the experiments were received from certified manufacturers and were of analytical grade. Sulfuric acid (0.5 M) was used as supporting electrolyte in all cyclic voltammetric cleaning procedures. All solutions were diluted as needed using distilled water. Automatic temperature calibration of each directly heated Au-LE chip was performed as described below by open circuit potentiometry in 5 mM equimolar ferri/ferrocyanide solution containing 0.1 M KCl as supporting electrolyte. Sulfuric acid was provided by Agros Organic (Belgium). Potassium hexacyanoferrate(III) was provided by Chem-Impex (Illinois, USA). Potassium hexacyanoferrate(II) trihydrate and potassium chloride were provided by Sigma-Aldrich (Germany). All solutions were prepared using distilled water from a Barnstead Mega-Pure® System ACS MP-11A.

2.3 Electrochemical cleaning of the gold loop electrode

Electrochemical cleaning was performed in a three-electrode electrochemical cell containing 20 mL of 0.5 M H_2SO_4 as supporting electrolyte. The Au-LE were scanned using cyclic voltammetry at a starting potential of -0.2 V, 1st vertex potential 1.5 V and 2nd vertex potential -0.2 V. A single cleaning step would last for a duration of 25 cycles and cleaning was repeated until changes in sequential voltammograms were deemed negligible or whether the voltammogram was comparable to a reference voltammogram. An approximate active area of 0.326 cm^2 of the Au-LE was calculated from the reduction peak and the conversion factor $480 \mu\text{C}/\text{cm}^2$ [25]. The Au-LE had a geometric surface area of 0.0924 cm^2 .

2.4 Automatic potentiometric temperature calibration

The automatic temperature calibration was performed by open-circuit potentiometric (OCP) measurements while applying five AC heating pulses of increasing intensity. The heating generator ThermoLab allowed to adjust “power steps”, an arbitrary unit. The electric resistance of the heated Au-LE was calculated for each applied power step by measuring both heating current and heating voltage during the automatic temperature calibration. The OCP calibration solution (5 mM ferri/ferro cyanide in 0.1 M KCl) was maintained at 20 °C during the automatic temperature calibration using an ANOVA circulating water bath.

2.5 Temperature calibration based on measurements of electric resistivity

The digital oscilloscope was used to measure the true RMS voltage drop (V) across a 1 Ω precision resistor connected in series with the Au-LE. This voltage drop was then used to calculate the heating current in the circuit using Ohm’s law (eq. 4),

$$I = U/R \quad (4)$$

where I is the heating current, and U the voltage drop across the resistor R.

The heating voltage (i.e. the voltage drop across the heated electrode) was measured in parallel to the Au-LE using the TrueRMS multimeter (Fig. 4B).

2.6 Stripping-voltammetry of mercury in water samples

Mercury trace determination was performed using square wave voltammetry (SWV) in water samples containing 0.1 M sulfuric acid and 0.01 M hydrochloric acid as supporting electrolyte. A glassy carbon electrode and a Ag/AgCl in 3 M KCl were used as counter and reference electrode respectively. The working electrode, Au-LE, was chemically cleaned before each analysis with 0.5 M sulfuric acid by cyclic voltammetry. A 0.7 V was applied as a conditioning potential for 60 s and a

deposition potential of 0.2 V for 120 s and an equilibrium time of 5 s before SWV measurements. Stripping measurements were performed from 0.2 V to 0.8 V with a step potential of 3 mV, an amplitude of 30 mV and a frequency of 20 Hz. All analyses were performed in presences of dissolved oxygen. The real water sample was collected from Black River Pond (Cherry Plain State Park, NY at 42° 37' 08" N and 73° 24' 41" W), filtrated using a filter system of 0.45 μm PES from CELLTREAT®. Filtrated water sample was then acidified with 69% nitric acid and stored at 4 °C. UV digestion treatment was conducted in quartz tubes containing 30 mL of the water sample containing 40 μL of 30% hydrogen peroxide. The quartz tube was sealed and irradiated for one hour with UV light.

3 Results and Discussion

3.1 Evaluation of gold electrode geometry and composition

Figure 1 displays topographical features of a new Au-LE after electrochemical cleaning by cyclic voltammetry in 0.5 M sulfuric acid. It was revealed through a point and ID function on the EDX, that the cluster-like protrusions on the Au surface were identified to be Au (Table 1). EDX analysis of the electrode surface further revealed that elements C, O and Al were present, including Au. Features shaped like “nodules” were suggested to be 95.83% Au and 4.17% C. It is highly unlikely that any carbon was incorporated in this structure and was most likely some unseen organic matter on the surface of the structure (carbon was found to be present for almost all gold surfaces analyzed and was interpreted the same way).

Figure 1 resolved thin black networks appearing largely throughout the surfaces. Such networks were deduced to be deep crevices or canyons in the Au surface. Analysis revealed the presence of aluminum and oxygen at 4.75% and 2.91% weight percentages respectively. Prior knowledge that the gold film was screen printed onto an alumina substrate, in combination with the EDX data that was obtained, support

that it is highly likely that such crevices are deep holes in the Au surface that reveal the alumina substrate. Reasons to why these channels are present are yet to be found, however they may be present due to damage.

Figure 1. SEM image of a Au Surface at x1000 magnification after electrochemical cleaning in 0.5 M H_2SO_4 using Cyclic Voltammetry; for 25 scans using a scan rate of 0.01 V/s between 0 and 1.4 V.

Area scans of two seemingly identical gold loop electrodes revealed similar quantities of C, O and Au (Table 1). However, the electrode surfaces are not of identical composition.

Table 1. Tabulated EDX results comparing electrodes A and B, after electrochemical cleaning in in 0.5 M H₂SO₄ using Cyclic Voltammetry; for 25 scans using a scan rate of 0.01 V/s and results allocated to the dark networks and nodule respectively.

Element	Electrodes A and B. Conditioned.							
	A		B		Dark network		Nodule	
	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %
C	2.90	32.06	1.93	23.28	2.87	22.73	4.17	41.62
O	0.33	2.74	0.39	3.55	2.91	17.28	-	-
Al	-	-	1.38	1.38	4.75	16.77	-	-
Au	96.77	65.19	97.43	71.79	89.47	43.22	95.83	58.38

Firstly, there was no appearance of Al on the spectra for electrode A, therefore it must be assumed that the occurrence of such canyons on this electrode is considerably less than on electrode B. Additionally, weight percentages of gold are 96.77% and 97.43% respectively for electrodes A and B. This can be interpreted in one of two ways: small quantities of gold oxide have formed over time on the electrode surfaces or different amounts of organic film remain present on the surface after electrochemical cleaning altering the percentages obtained. The latter is more likely, as larger differences in C weight percentages can be observed (2.90% and 1.93% for electrodes A and B respectively).

3.2 Atomic Force Microscopy and Rutherford Back-scattering Spectroscopy

AFM images were taken of the Au-LE sensor chip at the edge of the screen-printed gold layer in order to investigate the thickness of the gold layer. To differentiate the gold layer from the bare substrate surface, images were taken of each surface individually and later at the “boundary” between the bare ceramic substrate (Al₂O₃) and the gold layer. Topographic and phase mode images were recorded simultaneously in tapping mode with a resolution of 500×500 pixels. Individual surface images were recorded in a 25×25 μm² section (Fig. 2) at 0.3 Hz scanning frequency. The rim of the gold layer was recorded in a 50×50 μm² section at a

frequency of 0.2 Hz (Fig. 3).

Figure 2. AFM images of Au-LE of Al_2O_3 substrate and gold (Au) layers in a $25 \times 25 \mu\text{m}$ section at 0.3 Hz with a resolution of 500×500 pixels in different AFM modes: height (A,B), magnitude(C,D) and phase (E,F).

The gold surface was characterized by a much rougher appearance in comparison with the bare alumina surface. The thickness of the gold layer was determined by using the AFM image that covered the rim between the surfaces of both ceramic substrate and gold layer (Fig. 3) and measuring the height (z-scale) in different spots of this “boundary”. The average thickness was calculated to be $1.8 \mu\text{m}$.

Measurements by RBS revealed a gold layer of 600 nm thickness in average

(Fig. S1). The peculiar shape of the RBS spectrum for the gold layer suggests that its thickness is not very uniform across the electrode surface. Such non-uniformity may be caused by the formation of porous structures during gold thin film deposition or by the possibility of pre-existing micron scale features at the electrode surface.

Figure 3. (A) AFM height mode and (B) magnitude mode images of Au-LE of the “boundary” between gold layer and ceramic substrate Al₂O₃, of a 50x50 μm section at 0.2 Hz and 500x500 pixel resolution, (C) optical microscopy image of the boundary, and (D) thickness measurements of the gold layer (Z-scale) of selected areas, white lines of 25 nm in the height mode image, (A).

Measurements with a micrometer dial gauge did not indicate any thicker gold layers, in fact, the pointer of the dial gauge did not move significantly across the scale (smallest tick 1 micron).

These results indicate that the screen-printed and tempered gold ink formed a very

thin gold layer on top of considerably larger topologic features of the alumina substrate.

3.3 Open-Circuit Potentiometry

Figure 4A displays the OC potentiogram of an Au-LE sensor with five increasing heating pulses, which result in the increase of the electrode temperature.

Figure 4. (A) Open-circuit potentiogram of a Au-LE for temperature calibration averaging 5 points before the beginning and before the end of each pulse (as indicated by red arrows) as an automatic potential readout. (B) Circuit scheme of resistance measurement during temperature calibration.

Individual temperature calibrations were performed with five Au-LE, each with five repetitions (Table S1). We developed this new and quick automated temperature calibration procedure to improve reproducibility. Figure 5 illustrates the results of this automatic temperature calibration based on five different heating power settings. This technique called “Temperature Pulse Potentiometry” (TPP) as reported earlier [26,27,28] was performed manually until now. Figure 5A displays calculated potential

Figure 5. (A) Automatic Temperature Calibration with five heating power steps based on open-circuit potentiometry of five Au-LE using potential difference (vertical error bars) and calculated heated electrode temperature using the temperature coefficient of the redox couple (-1.60 mV/K). Quadratic relationship between (A) power step and (C) heating current with the heated electrode temperature and (B) between the heating current and the power step. (D) Linear fit of the electrode temperature against the square heat current.

differences between the points before the beginning and the end of each heat pulse. These potential differences were converted into temperature differences using the temperature coefficient -1.60 mV/K of ferri/ferrocyanide. The temperature calibration plot required a quadratic function as has been discussed earlier by Zerihun and Gründler [29]. Briefly, the reason can be found in the quadratic relationship between electric current and electric power. After the calibration and providing the ambient temperature value, the software calculates and applies the “proper power step” by means of the quadratic fit function, according to the desired electrode temperature. The automatic temperature calibration is very reproducible as demonstrated in Fig. 5

between the five electrodes, but also within the same chip. Table S2 lists the standard deviation and relative standard deviation between five electrodes. As the temperature increases, the deviation between electrodes increases as well. Occasionally that happened for one and the same electrode. Between the five Au-LE the lowest temperature deviation was at the lowest power step with a std. dev. of 0.18 K and RSD of 0.06%, due to the low electrode temperature. On the other hand, the highest temperature deviation was at the highest heat pulse with the std. dev. of 1.46 K and RSD of 0.45%. Deviation of electrode temperature for one and the same electrode varies from electrode to electrode. The lowest RSD at the lowest power step was 0.04% (Au-LE 2) and the highest 0.23% (Au-LE 5). For the highest power step the lowest RSD was 0.08% (Au-LE 1) and the highest 0.94% (Au-LE 4).

Figure 6. (A) Resistance measurements of four Au-LE at five heating power steps during temperature calibration. (B) Directly heated electrode resistance at calculated heated electrode temperature of four Au-LE. Statistics after Q-test for heated electrode resistance measurements. Resistance values for Au-LE 1 were rejected after Q-test were $Q_{99\%} (5 \text{ values}) < Q_{\text{exp}}$ in each power step (Table S7).

The heated electrode resistance was determined as previously described using equation 4 and presented in Fig. 6. The temperature coefficient (α) was obtained from the resistance and temperature calibration plot and presented in Table S3. The electric resistivity was calculated for each heat pulse by its temperature dependence using equation 5, (Table S4),

$$\rho = \rho_{20} [1 + \alpha(\theta - 20^\circ\text{C})] \quad (5)$$

where ρ represent the resistivity at a particular temperature θ , ρ_{20} is the resistivity of gold metal at 20 °C ($2.44 \times 10^{-8} \Omega\text{m}$), and α is the temperature coefficient of the resistivity of gold at 20 °C obtained from experimental data. The temperature coefficient of the heated electrodes was calculated in each temperature calibration and compared to the literature value ($0.0034 \text{ }^\circ\text{C}^{-1}$) [30].

Figure 7. (A) Two-point temperature calibration of four Au-LE by OC potentiometry and the resistivity method. The measured resistance for the resistivity method was corrected by subtracting the resistance-offset contributed by the multimeter connectors. Electrode Au-LE 1 was rejected as an outlier after Q test (Table S7). **(B)** Electrode temperature comparison from open-circuit potentiometry of five electrodes and calculated temperature from equation 6, using the heated electrode resistance at each power step and the temperature coefficient α , from each temperature calibration method.

3.4 Two-point calibration with the electrode as a resistive thermometer

Figure 7A illustrates the two-point temperature calibration of four screen-printed electrodes comparing two different temperature calibrations: open-circuit potentiometry and electrode as a resistance thermometer. The OCP heated

electrode temperature and resistance were obtained from the automatic temperature calibration. The resistivity method of temperature calibration was performed by measuring the resistance of the Au-LE at two different temperatures of a water bath. An ice bath was used for the first point in the calibration at 0 °C, and the second point at 100 °C was measured using boiling water. The temperature coefficient of resistivity of the screen-printed gold layer obtained by the resistance method was 0.00237 °C⁻¹ with a RSD of 1.72%. This temperature coefficient is 30.4% lower than the literature value for gold. The value obtained by the resistance method was 2.62% lower than the one based on OCP measurements (0.00243 °C⁻¹). This temperature coefficient was used with eq. 6 to recalculate the electrode temperature. In Fig. 7B the temperatures were obtained by OCP method (black) and calculated using equation 6 and α values from the resistivity method (red).

Using the resistance of the heated electrode (Fig. 6) during the OCP and the two α values, from automatic temperature calibration and resistance thermometer technique, the electrode temperature was calculated for each heating pulse (Fig. 7B). These temperatures were calculated using rearranged equation (1),

$$\theta = 20\text{ °C} + \frac{R - R_{20}}{\alpha R_{20}} \quad (6)$$

where θ is the electrode temperature at a particular resistance R , whereas R_{20} is the resistance at 20 °C, and α is the temperature coefficient of the resistance (°C⁻¹).

The determination of a common conversion factor could minimize the time of the temperature calibration considerably by performing a two-point calibration for each single electrode chip. The Au-LE were dipped in both boiling water and ice bath and the two regarding resistance values was measured with a TrueRMS multimeter. Dixon's Q test was performed to test for outliers (Table S7). Au-LE 1 was rejected for the resistance measurements (Fig. 6 and 7) with a 99% confidence level after the Q test. The Q_{exp} average value for Au-LE resistance was 0.872 ($Q_{99\%}$ for five sample is 0.821).

The α value was calculated and presented in Table S6. These α values were then used to calculate the electrode temperature using equation 6 and compared with the temperature obtained from the automatic temperature calibration by OC potentiometry. It was observed that most of the time the calculated electrode temperature, with the α value from the resistance method, was slightly higher than the electrode temperature from the OC potentiometry (Fig. 7B).

Figure 6 illustrates the increase of the electrode resistance as the power step (A) and electrode temperature (B) increases. As mentioned before, the relation between the resistance and the power step, as well as with the heating current, both showed a quadratic relation. On the other hand, a linear relation was observed between electrode resistance and the electrode temperature. The experimental temperature coefficient α ($^{\circ}\text{C}^{-1}$), of each Au-LE was calculated from the slope of linear fit of the temperature calibration plot (Fig. 6B) and divided by the electrode resistance at 20 $^{\circ}\text{C}$. The α value ($^{\circ}\text{C}^{-1}$) was also obtained from an independent temperature calibration by controlling water temperature with ANOVA water bath, with a temperature range started at 20 $^{\circ}\text{C}$ to 60 $^{\circ}\text{C}$, and measuring the resistance with a multimeter. These values were compared with the temperature coefficient value of the resistivity of gold, 0.0034 $^{\circ}\text{C}^{-1}$ at 20 $^{\circ}\text{C}$, as shown in Table S10. The average temperature coefficient observed by the OCP method for the screen-printed gold electrode was, however, 0.00247 $^{\circ}\text{C}^{-1}$ with a RSD of 4.94%. Compared with the literature this α value is 27.4% lower. The Au-LE with the highest α value obtained was 0.00267 $^{\circ}\text{C}^{-1}$ which is still 21.6% below the literature value. Au-LE 1 and 5 had similar α values with very similar deviation from literature, 30.37% and 30.28% respectively. The two-point temperature calibration shown an average value of 0.00237 $^{\circ}\text{C}^{-1}$, which is also 30.42% lower. The independent temperature calibration by controlling the solution temperature by ANOVA water bath also showed a low temperature coefficient with 0.00238 $^{\circ}\text{C}^{-1}$ and 30% of deviation.

The observed behavior of individual Au-LEs indicates two things: The arbitrary quantity “power step” used by the Thermalab software is proportional to the heating current, and the thickness and width of the screen-printed Au-LE is very reproducible

with occasional outliers. If a temperature accuracy of not better than 2 K was desired, then a few temperature calibrations of a few sensor chips would be representative for an entire lot of 100 sensors. On the other hand, the resistance, and thus, the active or heated length of the five Au-LE seems to vary by slightly higher degree (RSD 4%). For highest accuracy (0.5 K and better), the temperature calibration has to be performed individually with each Au-LE sensor chip. While the various Au-LE geometries, and thus, the individual electrical resistance, can be compensated by measuring the resistance at a given standard temperature (such as 20 °C), the temperature coefficient of electrical resistivity was also slightly different according to our experiments (RSD 4.9%, Table S2).

Figure 8. Left: Independent study of the temperature coefficient of electric resistivity using two independent methods. An Au-LE was immersed into a circulating bath (cryostat) filled with distilled water: Comparison of resistance values obtained at different temperatures using AutoLab PGSTAT12 and linear sweep from -20 to 20 mV (triangles), and (alternatively) a TrueRMS multimeter (balls). **Right:** AutoLab PGSTAT12 resistance measurements with error bars indicating the standard deviation.

3.5 Temperature coefficient of electrical resistivity of gold.

The ca. 30% deviation of the temperature coefficient of resistivity from the literature value for gold appeared to be very unusual. Therefore, the resistance measurements were also performed using the circulating bath of a cryostat to establish the desired

temperature, as measured by the internal electronic thermometer and digital display, and confirmed by a classical mercury thermometer (Fig. 8). A potentiostat was used to apply and accurately measure voltage and current. To do this with negligible heating effects, a linear sweep from -20 to +20 mV was applied. The resistance of the Au-LE at the given temperature was then obtained as the slope of this linear voltammogram (not shown). Separately from this, the resistance was also measured using a multimeter. The two additional clamp contacts resulted in an almost constant offset in resistance. The obtained temperature coefficient values for electrical resistance, however, were nearly identical.

Temperature coefficient of $0.002532\text{ }^{\circ}\text{C}^{-1}$ was obtained from the linear plot of R vs. ΔT ($R^2 = 0.99991$). There were few earlier reports on the effects of porosity upon temperature coefficients of the resistivity of sintered metals. Grootenhuis et al. investigated porous sintered bronze materials, and their data sets revealed a slight temperature dependency [31]. A table and graph based on their data set is being provided in the SI (Table. S11 and Fig. S5), and reveals a weak statistical correlation. Briefly, the temperature coefficient β of electric resistivity increased by 23%, when the density of sintered bronze specimen was diminished by 15%, and electric resistivity ρ decreased by 82%. The latter correlation may be considered significant, and can be expected. Due to the very low thickness of our screen-printed gold layer, and the relatively large roughness of the underlying alumina substrate, we could not calculate absolute values of the electric resistivity of our gold layers. All we can say at this time is that a decrease of α with increasing porosity could have been found before; however, Grootenhuis et al. did not pay attention to this; their data set is in this regard not very conclusive [31]. One possible explanation could be that thermal expansion of the sintered gold particles increases their contact areas, which makes the gold layer more compact, and thus, compensates for a small part of the increase of the electric resistivity of the gold metal. However, Koh and Fortini found that the temperature coefficients of both thermal conductivity and electrical resistivity are essentially independent of porosity, and even the matrix structure of the porous material could be neglected [32].

Very thin layers of gold have also been examined in the past with regard to their resistivity and the respective temperature dependence. A study of Sambles et al. suggests that with gold films of thickness between 35 and 889 nm, the temperature coefficient of resistivity increases between 20 and 300 K. Moreover, the temperature coefficient was essentially zero below 10 K at any film thickness and grain size (Fig. 3 in [33]). The authors cited surface scattering effects and grain boundaries as probable reasons. Such effects had already been observed earlier [34]. This probably explains fairly well why our thin screen-printed gold layers (<1 μm) can have a temperature coefficient of resistivity that is lower than the value for gold bulk materials.

3.6 Trace detection of mercury(II)

We have applied the disposable sensor for trace determination of mercury in various kinds of water samples. Similar to the more delicate gold micro-wire that we used earlier [8,9], the electrode heating during the deposition step greatly enhances sensitivity. This was also connected to improved detection limit. We have then used the new sensor to detect trace mercury in natural water samples collected at Cherry Park Lake, NY.

3.6.1 Temperature effect on stripping voltammetry of mercury(II)

Figure 9 depicts the effect of electrode heating upon the stripping-voltammetric response of 50 ppb Hg (II) in distilled water. Elevated electrode temperature (70 °C) during the conditioning and deposition steps, increased the Hg stripping peaks 28-fold.

Fig. 9. Temperature study of 50 ppb Hg (II) in distilled water using square wave voltammetry (SWV) in Au-LE by increasing electrode temperature. Analysis was performed in a quiescent solution of 0.1 M sulfuric acid containing 0.01 M hydrochloric acid.

Figure 10 illustrates the influence of analyte concentration ranging between 10 and 100 ppb, at two electrode temperatures, 23 °C, and 60 °C. The resulting calibration data and their prediction bands (95%) revealed a limit-of-detection (LOD), of 20.1 ppb at 23 °C and 9 ppb at 60 °C. The sensitivity of the calibration plot increased by a factor of 10. We also tested a lower concentration range, 1-10 ppb, exhibited in Fig. 11 at 23 °C and at 70 °C electrode temperature. The LOD was 6.4 ppb at 23 °C and 4.7 ppb at 70 °C. The sensitivity of the analysis increased by factor 5. A study with UV-treated distilled water (Fig. 12) revealed an increase in sensitivity by a factor 6 at 60 °C and by 9 at 70 °C. LODs under these conditions were 34, 7.4, and 9.1 ppb at 23, 60, and 70 °C electrode temperature, respectively. Again, electrode

heating was applied during conditioning and deposition steps only.

Fig. 10. Concentration study of Hg (II) using SWV in Au-LE. Standard addition of Hg (II) was done in an increment of 10 ppb. Blank value was obtained before the addition of Hg (II). Measurements were performed in a quiescent solution at room temperature, 23 °C (A), without applying a heating current to the electrode and compared with the ones taken at 60°C (B), electrode temperature. A 0.1 M sulfuric acid containing 0.01 M hydrochloric acid was used as supporting electrolyte. (C) Calibration curve of standard addition of Hg (II) at 23 °C (■) and 60 °C (●) of three trials. Prediction bands are shown with blue lines with a 95% confident.

3.6.2 Determination of mercury in real samples of lake water

Samples of fresh water from rivers and lakes contain dissolved organic matter (DOM) that binds many heavy metal ions such as by formation of complexes with humic acids. In voltammetry, these compounds are usually removed using UV sample pretreatment. We tested whether the effects of elevated electrode temperature would also lead to improved sensitivity and accuracy of the standard addition method. This was investigated with water samples from Black River Pond spiked with 20 and 100 ppb Hg(II), respectively. The electrode heating during the conditioning and deposition steps resulted in a significant signal increase as demonstrated in Fig. 13. At the lower spiked concentration (20 ppb), the current peak signal increased approximately 30 times, when a higher temperature electrode (70

°C) was applied.

Fig. 11. Concentration study of Hg (II) in distilled water using SWV in Au-LE. Standard addition of Hg (II) was done in an increment of 1 ppb. Measurements were performed in a quiescent solution at room temperature, 23 °C (A), and at 70 °C (B) electrode temperature during deposition step. (C) Calibration curve of standard addition of Hg (II) at 23 °C (■) and 70 °C (▲) of three trials.

At the higher spiked concentrations (100 ppb), the stripping signal only increased ten times upon applying 70 °C electrode temperature during conditioning and deposition. The behavior of the sample spiked with 20 ppb indicated that this amount is being bound by matrix components, notwithstanding the UV treatment, and that only at elevated temperature above 50 °C, the mercury(II) would be released and available for reduction and deposition.

After that we investigated the effect of mercury(II) concentration upon stripping response after UV treatment of the Black River Pond water sample. Figure 14 reveals an increase in sensitivity of approximate factor 5.5 and 7 after applying 60 and 70 °C, respectively. Interestingly, up to 30 ppb mercury(II) were bound by the remaining sample matrix to be released only at elevated electrode temperature of 60 or 70 °C during conditioning and deposition. The precision of the stripping-voltammetric signal was also significantly improved by heating the electrode with RSD values no higher than 10 and 6% at 60 and 70 °C, respectively. The mercury concentrations in the lake water samples were determined by five standard additions

of Hg(II) with increments of 10 ppb. We obtained 6.50, 0.49, and 0.63 ppb Hg(II) at 23, 60, and 70 °C electrode temperature, respectively.

Fig. 12. Concentration study of Hg (II) in distilled water after UV digestion using SWV in Au-LE. Standard addition of Hg (II) was done in an increment of 10 ppb. Measurements were performed in a quiescent solution at room temperature, 23°C (A), 60°C (B) and 70°C (C) electrode temperature during deposition step. (D) Calibration curve of standard additions of Hg (II) at 23°C (■) 60°C (●) and 70°C (▲) of three trials.

The recovery rate of mercury(II) in the Black River Pond water sample after UV treatment was determined spiking 20, 30 and 40 ppb applying equation 7. Calculated concentration was obtained from a calibration plot of Hg(II) after UV treatment and the signal obtained after the spiked the pond water sample. The concentration of Hg(II) in pond water at each temperature was considered for the calculation of the percentage of recovery after each addition.

Fig. 13. Temperature study in Black River Pond water sample with UV treatment after addition of 20 and 100 ppb of Hg (II) using SWV in Au-LE by increasing electrode temperature. The analysis was performed in a quiescent solution of 0.1 M sulfuric acid containing 0.01 M hydrochloric acid.

$$\%R = \frac{[B]-[A]}{[S]} \times 100\% \quad \text{eq. 7}$$

Equation 7 shows how the percent of recovery was obtained for each spike and electrode temperature, where B is the concentration measured in the spiked sample, or calculated concentration, using a calibration curve of Hg(II) standard after UV treatment, [A] is the concentration in the original pond water sample obtained by standard addition at each electrode temperature after UV treatment and S amount added as a spike.

Table 2. Recovery rates for mercury(II) spiked in Black River Pond water after UV treatment

(Sample) + Spike added	Determined Concentration (ppb)			% Recovery rate		
	23 °C	60°C	70 °C	23 °C	60°C	70 °C
Pond sample + 20 ppb added	13.71	17.51	18.29	36.05	85.07	88.32
Pond sample + 30 ppb added	16.90	28.97	27.50	34.69	94.92	89.55
Pond sample + 40 ppb added	34.75	40.26	37.13	70.64	99.43	91.24

Fig. 14. Concentration study of Hg(II) in Black River Pond water sample with UV treatment using SWV in Au-LE. Standard addition of Hg(II) was done in an increment of 10 ppb. Measurements were performed in a quiescent solution at room temperature, 23°C (A), 60°C (B) and 70°C (C) electrode temperature during deposition step. (D) Calibration curve of standard additions of Hg(II) at 23°C (■) 60°C (●) and 70°C (▲) of three trials.

Finally, a test with the filtered original lake water sample indicated that mercury traces can also be detected without any further preparation in presence of the full sample matrix. Figure 15 demonstrates that at 70 °C, signals of mercury became clearly visible from 10 ppb; however, for accurate quantitation, even higher electrode temperatures will be needed that require a much smoother gold electrode surface in order to prevent the formation of air bubbles, which limit the reproducibility.

Fig. 15. Concentration study of Hg(II) in Black River Pond water sample without UV treatment using SWV in Au-LE. Standard addition of Hg(II) was done in increments of 10 ppb. Measurements were performed in a quiescent solution at room temperature, 23°C (left) and 70°C (right) electrode temperature during deposition step.

4 Conclusions

In this study, we aimed at a quick and accurate temperature calibration method for disposable heated gold electrodes based on screen-printed sensor chips. Comparison of five different Au-LE chips revealed deviations (RSD ca. 4 %) in electric resistance of the screen-printed gold-loops that would require an individual calibration of each single sensor chip. Then we investigated whether a simple correction factor would allow for compensation of the different resistance values. It turned out, however, that even the temperature coefficient of electric resistivity of the gold layers was changing significantly (RSD ca. 4 %). The temperature coefficient was determined to be $0.00247\text{ }^{\circ}\text{C}^{-1}$, which is 27% lower than the established value for gold around 20 °C.

We therefore developed an automatic calibration protocol, enabled by a software tool and automatic AC heating generator that is based on temperature pulse potentiometry and a well-investigated redox couple. The known temperature

coefficient of the standard redox potential of ferro/ferricyanide (-1.6 mV/K) was used to calculate the electrode temperature. The calculated temperature values were very precise with RSD no higher than 0.4% for a given electrode and 0.2% between the five electrodes. On the other hand, the margin error with a 95% confidence level were no higher than $\pm 1 \text{ K}$ within the same Au-LE and $\pm 0.7 \text{ K}$ between the five chips. An alternative two-point calibration is based on the measurement of the electric resistance of the Au-LE at two fixed temperatures that are easy to maintain: 0°C in an ice bath and 100°C in boiling water in order to determine the two parameters R_0 and α . This resistance temperature calibration approach method allows usage of the disposable Au-LE sensors even in organic solvents where OCP measurements are difficult. Both, the new automatic potentiometric and the two-point temperature calibration methods take no longer than 10 min., and allows for highly accurate temperature adjustment ($\pm 0.7 \text{ K}$).

Investigations of the screen-printed gold layer by SEM and AFM revealed porosity and low thickness which, however, may not explain why the temperature coefficient of electric resistivity was apparently altered in different electrode layers, and was much different from the literature value of gold. Rather, this phenomenon can probably be explained by surface scattering effects that have been described already for nm scale metal films. [33, 34]

Mercury analysis was significantly improved with SWV stripping signals that increased five to ten times upon heating the Au-LE during the deposition step compared to measurements at room temperature (23°C). Lower LOD values were also obtained when up to 70°C electrode temperature was applied. This observation indicates that the micro-stirring effect created by the temperature gradient at the surface of the electrode enhances the electrochemical signal. At this point the UV sample preparation of lake water cannot completely be avoided; however, we believe that interferences with dissolved organic matter can be overcome by even higher electrode temperature replacing the classical UV sample preparation altogether.

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Rapid and Accurate Automatic Temperature Calibration of Disposable Screen-printed Heated Gold Electrodes

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Supplementary Information

Fig. S1. Rutherford backscattering spectrometry (RBS) of Au-LE. Helium (2+) beam was placed on top of the gold electrode. The spectrum shows both layers in the Au-LE, the ceramic substrate and a gold layer on top. XRUMP simulation of a gold layer with a thickness of 4000 Å indicates that the thickness of Au is approximately 400 nm for this measurement. However, the thickness cannot be accurately determined since each layer is not well defined. Measurement of three different sensors shown an average thickness of 600 nm.

Fig. S2. Rutherford Back-scattering Spectroscopy (RBS) spectrum of Al₂O₃ substrate. XRUMP simulation shown the presence of carbon, oxygen and aluminum with traces of zinc and tin.

Fig. S3. Rutherford Back-scattering Spectroscopy (RBS) spectrum of Al₂O₃ substrate and gold layers in Au-LE individually. XRUMP showed a composition of oxygen and aluminum (ceramic substrate) and gold on the surface of the substrate.

Fig. S4. Gold loop screen-printed electrode (DropSens®).

Table S1. Data obtained from the temperature calibration of five electrodes by Open-Circuit Potentiometry. Individual temperature calibrations were performed with five Au-LE, each with five repetitions.

Power Step	ΔE (mV)					
	Au-LE 1	Au-LE 2	Au-LE 3	Au-LE 4	Au-LE 5	Average
100	-2.824	-2.784	-2.924	-2.924	-2.210	-2.733
200	-9.958	-9.968	-9.866	-9.866	-9.106	-9.753
300	-19.807	-20.279	-19.602	-19.602	-18.539	-19.566
400	-31.746	-33.443	-31.148	-31.148	-29.412	-31.380
500	-45.504	-48.224	-45.657	-45.657	-41.960	-45.400
Power Step	Electrode Temperature (K)					
	Au-LE 1	Au-LE 2	Au-LE 3	Au-LE 4	Au-LE 5	Average
100	298.77	298.74	298.83	298.59	298.38	294.81
200	303.22	303.23	303.17	302.54	302.69	299.12
300	309.38	309.67	309.25	308.76	308.59	305.28
400	316.84	317.90	316.47	316.18	315.38	312.70
500	325.44	327.14	325.54	324.39	323.22	321.30
Power Step	Electrode Resistance (Ω)					
	Au-LE 1	Au-LE 2	Au-LE 3	Au-SPE 4	Au-LE 5	Average
100	2.23	2.05	2.02	2.06	2.05	2.08
200	2.25	2.08	2.05	2.08	2.08	2.11
300	2.29	2.11	2.08	2.10	2.10	2.13
400	2.32	2.16	2.11	2.14	2.13	2.17
500	2.37	2.21	2.16	2.18	2.17	2.22
Power Step	Heating Current (A)					
	Au-LE 1	Au-LE 2	Au-LE 3	Au-LE 4	Au-LE 5	Average
100	0.270	0.285	0.293	0.283	0.275	0.281
200	0.524	0.546	0.562	0.548	0.539	0.544
300	0.772	0.805	0.825	0.815	0.800	0.803
400	1.012	1.056	1.074	1.064	1.046	1.050
500	1.244	1.296	1.328	1.316	1.286	1.294
Power Step	Electrical Resistivity ρ (Ωm)					
	Au-LE 1	Au-LE 2	Au-LE 3	Au-LE 4	Au-LE 5	Average
100	2.451E-08	2.451E-08	2.451E-08	2.449E-08	2.448E-08	2.45E-08
200	2.480E-08	2.480E-08	2.477E-08	2.473E-08	2.474E-08	2.48E-08
300	2.521E-08	2.521E-08	2.514E-08	2.509E-08	2.509E-08	2.51E-08
400	2.574E-08	2.574E-08	2.557E-08	2.553E-08	2.549E-08	2.56E-08
500	2.634E-08	2.634E-08	2.611E-08	2.602E-08	2.595E-08	2.62E-08

Table S2. Standard deviation and relative standard deviation between five electrodes. Individual temperature calibrations were performed with five Au-LE, each with five repetitions

Power Step	Std. Dev.					RSD (%)				
	T (K)	ΔE (mV)	R (Ω)	I (A)	ρ (Ωm)	T (K)	ΔE (mV)	R (Ω)	I (A)	ρ (Ωm)
100	0.18	0.30	0.083	0.009	1.35E-11	0.06	10.93	4.01	3.19	0.06
200	0.33	0.36	0.084	0.014	3.45E-11	0.11	3.74	3.97	2.58	0.14
300	0.45	0.64	0.087	0.020	6.26E-11	0.15	3.26	4.08	2.51	0.25
400	0.93	1.45	0.085	0.024	1.20E-10	0.30	4.61	3.93	2.27	0.47
500	1.46	2.23	0.088	0.032	1.78E-10	0.45	4.92	3.98	2.51	0.68

Table S3. Temperature coefficient (α) from the resistance and temperature calibration plot from OCP method. Theoretical value of temperature coefficient for gold metal used was 0.0034 $^{\circ}C^{-1}$.

Au-LE	R _{20°C} (Ω)	Slope ($\Omega/^{\circ}C$)	α ($^{\circ}C^{-1}$) _{ocp}	% Error of α at each Au-LE
1	2.22	0.00526	0.00237	30.37
2	2.04	0.00545	0.00267	21.59
3	2.02	0.00494	0.00245	27.93
4	2.04	0.00507	0.00248	26.92
5	2.04	0.00484	0.00237	30.28
Average	2.07	0.00511	0.00247	
Std. Dev.	0.0841	0.000246	0.000122	
RSD (%)	4.06	4.81	4.94	
% Error	-	-	27.42	

Table S4. Electrical resistivity ρ (Ωm), of five Au-LE at each heat pulse during OCP temperature calibration. Equation 5 was used to calculate ρ (Ωm) using the temperature coefficient α ($^{\circ}C^{-1}$) obtained from the same method.

Power Step	Electrical Resistivity, ρ , (Ωm)							
	Au-LE 1	Au-LE 2	Au-LE 3	Au-LE 4	Au-LE 5	Average	Std. Dev.	RSD (%)
100	2.451E-08	2.451E-08	2.451E-08	2.449E-08	2.448E-08	2.45E-08	1.35E-11	0.06
200	2.480E-08	2.480E-08	2.477E-08	2.473E-08	2.474E-08	2.48E-08	3.45E-11	0.14
300	2.521E-08	2.521E-08	2.514E-08	2.509E-08	2.509E-08	2.51E-08	6.26E-11	0.25
400	2.574E-08	2.574E-08	2.557E-08	2.553E-08	2.549E-08	2.56E-08	1.20E-10	0.47
500	2.634E-08	2.634E-08	2.611E-08	2.602E-08	2.595E-08	2.62E-08	1.78E-10	0.68

Table S5. Electrode resistance of two-point temperature calibration by resistivity method. Resistance at room temperature (23.8 °C) is also provided.

Temperature (°C)	Electrode Resistance (Ω)					Std. Dev. (between Au-LE)
	Au-LE 1	Au-LE 2	Au-LE 3	Au-LE 4	Au-LE 5	
0	2.27	2.09	2.07	2.08	2.09	0.09
100.4	2.82	2.62	2.59	2.60	2.61	0.10
23.8	2.41	2.23	2.20	2.22	2.22	0.09

Table S6. Temperature coefficient α of two-point temperature calibration by resistivity method. Theoretical value of temperature coefficient for gold metal is 0.0034 °C⁻¹.

Au-LE	R _{20°C} (Ω)	Slope ($\Omega/^{\circ}\text{C}$)	α ($^{\circ}\text{C}^{-1}$)	% Error of α at each Au-LE
1	2.38	0.00547	0.00230	32.48
2	2.20	0.00527	0.00239	29.61
3	2.17	0.00520	0.00239	29.65
4	2.19	0.00517	0.00236	30.46
5	2.19	0.00523	0.00238	29.91
Average	2.23	0.005268	0.00237	
Std. Dev.	0.0871	0.0001188	4.078E-05	
RSD (%)	3.91	2.26	1.72	
% Error	-	-	30.42	

*Two-point temperature calibration by OCP of five heated electrode, not shown in table S6, had a slope of 0.00504 $\Omega/^{\circ}\text{C}$, R_{20°C} was 2.07 Ω , α equal to 0.00243 and 28.55% error.

**After Q-test, and Au-LE 1 resistance values were rejected, for the two-point resistive method calibration the slope was 0.00522 $\Omega/^{\circ}\text{C}$, R_{20°C} was 2.19 Ω , α equal to 0.00239 and 29.80% error. Two-point OCP calibration the slope was 0.00497 $\Omega/^{\circ}\text{C}$, R_{20°C} was 2.04 Ω , α equal to 0.00244 and 28.27% error.

Table S7. Dixon's Q-test of OCP resistance measurements at each power step of five Au-LE. Q_{exp} for Au-LE 1 was higher than the $Q_{\text{table (99\%)}}$ and increased at each power step, therefor Au-LE 1 resistance measurements were rejected for statistical purposes. $Q_{\text{table, 99\%}}$ confident, was 0.821.

Power Step	Q_{exp}
100	0.836
200	0.846
300	0.895
400	0.895
500	0.888
Average	0.872

Table S8. Independent temperature calibration of Au-LE by controlling bulk temperature with ANOVA water bath. Trials were repeated in triplicates for each electrode. Theoretical value of temperature coefficient for gold metal is 0.0034 C^{-1} .

Temperature (°C)	Electrode Resistance (Ω)					Std. Dev. (between Au-LE)
	Au-LE 1	Au-LE 2	Au-LE 3	Au-LE 4	Au-LE 5	
20.17	2.39	2.20	2.18	2.20	2.20	0.0873
29.73	2.44	2.25	2.23	2.24	2.25	0.0898
39.70	2.50	2.31	2.29	2.31	2.30	0.0891
49.93	2.56	2.37	2.34	2.35	2.35	0.0934
59.33	2.61	2.42	2.39	2.39	2.40	0.0930

Table S9. Temperature coefficient α of independent calibration by bulk temperature controlling with ANOVA water bath. Theoretical value of temperature coefficient for gold metal is $0.0034\text{ }^{\circ}\text{C}^{-1}$.

Au-LE	$R_{20^{\circ}\text{C}}$ (Ω)	Slope ($\Omega/^{\circ}\text{C}$)	α ($^{\circ}\text{C}^{-1}$)	% Error of α at each Au-LE
1	2.39	0.00558	0.00233	31.33
2	2.20	0.00548	0.00249	26.85
3	2.18	0.00534	0.00245	27.95
4	2.20	0.00504	0.00229	32.62
5	2.20	0.00514	0.00234	31.28
Average	2.23	0.005316	0.00238	
Std. Dev.	0.0873	0.0002260	8.397E-05	
RSD (%)	3.91	4.25	3.53	
% Error	-	-	30.01	

Table S10. Comparison of temperature coefficient α obtained by OCP and resistivity method, respectively.

Method	Open-Circuit Potentiometry	Resistivity (two-point calibration)	Resistivity (Bulk temperature controlled by ANOVA water bath)
Au-LE	α ($^{\circ}\text{C}^{-1}$)		
1	0.00237	0.00230	0.00233
2	0.00267	0.00239	0.00249
3	0.00245	0.00239	0.00245
4	0.00248	0.00236	0.00229
5	0.00237	0.00238	0.00234
Average	0.00247	0.00237	0.00238
Std. Dev.	0.000122	4.078E-05	8.397E-05
RSD (%)	4.94	1.72	3.53
% Error	27.42	30.42	30.01

Table S11. Values of electrical resistivity ρ at 20 °C and temperature coefficient β of sintered porous bronze alloy made from 89% Cu and 11% Sn powder reported by Grootenhuis et.al. [31].

Density (g/cm³)	ρ at 20°C ($\mu\Omega\cdot\text{cm}$)	β (°C⁻¹)	Grade of alloy	Particle diameter (cm)
5.50	60.1	0.00047	E1	0.04000
5.55	81.5	0.00057	C1	0.01275
5.75	52.0	0.00053	D1	0.02113
5.85	57.1	0.00070	B1'	0.00493
6.30	38.5	0.00059	B1	0.00493
6.45	33.0	0.00061	A1	0.00133

Figure S5. (A) Electrical resistivity ρ and (B) temperature coefficient β of sintered porous bronze alloy material made from 89% Cu and 11% Sn powder by metallurgy methods with different densities. Densities varies according to its particle size diameter. Graphs were plotted using the data set from Table S11.

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