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Practical considerations on detectability of electrically active nanoparticles in environmental samples

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Abstract. Environmental impact of nanotechnologies is among the most important global concerns because these technologies have introduced a completely new class of artificial pollutants with very diverse biological effects. Detection and characterization of nanoparticles in environmental samples requires highly sensitive methods and laboratory equipment. Recently introduced chronoamperometry of single nanoparticles has a potential to measure parameters of nanoparticles of different kinds, including organic and inorganic substances, metals and their oxides.

This paper reports practical considerations on factors limiting the level of detection (LOD) for the chronoamperometry of single nanoparticles, successfully used to characterize electrically active nanoparticles. The influence of two major sources of electrical current noise on LOD was studied. It was shown that electrochemical noise dominates over the noise of electronic components. The LOD for a typical laboratory potentiostat was calculated. The overall background current noise (root mean square value) for a typical ultra-low input current potentiostat is between 10^{-13} - 10^{-12} A, that allows detecting silver nanoparticles with radius of 10 - 15 nm, LOD for nanoparticles of α -Fe₂O₃ is 60-80 nm. The theoretical limit of minimum detectable size of nanoparticle is at least 10 times lower, but to achieve this limit very complicated technical issues should be resolved.

1. Introduction

Detecting and estimating the amount of nanoparticles in environmental samples is quite a challenging problem of great importance. It is a well known fact, that nanoparticles have both positive and negative biological activity, but uncontrollable releasing of artificial industrial nanomaterials could cause severe biological and environmental unbalance. For example, hematite (α -Fe₂O₃) is the most stable iron oxide in the Earth upper lithosphere [1], which is why it is widely spread and has a direct influence on the biosphere. According to several research, hematite is a vital source of iron for microorganisms and plants [2]. By measuring the amount of hematite particles and their chemical and structural conditions it is possible to monitor the remediation of ground water [3].

Research on nanoparticles have been gaining importance in recent years because of increasing amount of artificial nanomaterials could disturb the natural environmental balance. Studies have shown that artificial metal-based nanoparticles can cause cell membrane malfunction, have high cytotoxicity and can induce severe inflammatory response [4].

Artificial industrial nanoparticles are widely used in manufacturing of consumer products, that inevitably leads to dumping of substantial amount of the nanoparticles into environmental media via sewers, improperly utilized waste and soil [5][6]. Being released, the nanoparticles may enter rivers, lakes and other natural water reservoir, ending up in oceans [7][8]. Previously, researchers state that

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large amount of anthropogenic waste is dumped into aquatic systems [9]. Knowing the environmental load of agglomerated nanoparticles and their concentration in natural reservoirs could allow us to estimate the anthropogenic effect on aquatic systems [10].

Thus, it is important to develop new methods to measure the concentration of nanoparticles in environmental samples. Metal based nanoparticles are electrochemically active, so their size and concentration could be measured using an ultra low current chronoamperometry [11][3]. This paper focuses on the ultra low current chronoamperometric method of detecting metal-based nanoparticles and its practical limitations.

2. Electrochemical detection of nanoparticles

Electrochemical detection of nano-sized electrically active particles is a good alternative to more complex and expensive electronic microscopy, especially when it comes to studying environmental samples, taking, for instance, from natural water reservoirs. Recently, chronoamperometry of single nanoparticles (also called "nano-impacts") has been introduced [12]. The main advantage of the nano-impacts method is its ability to measure physical and chemical parameters of virtually any nanoparticles, including organic, metal and metal oxides. Since the introduction, this method has been used in many applications related to detection and measuring of nanoparticles [13].

The chronoamperometry of single nanoparticles (CSNps) can detect individual nanoparticles when they collide with a surface of an electrically charged electrode. The collision causes very small spike-like Faradic current, which amplitude depends on the size of the collided nanoparticle. The overall sensitivity and size resolution of this method is fully determined by the current noise in the measurement system. The excellent theoretical study of noise sources in picoampere-range electrochemical measurement systems and some practical recommendations are given in [14].

2.1. Background noise of a potentiostat



Figure 1. A simplified schematic of a potentiostat with the most important sources of noise. A1 is an transimpedance amplifier, built around an ultra low input current operational amplifier. A2 is a control amplifier, A3 is a voltage follower for the reference electrode. Ref, W and Aux are the reference, working and axillary electrodes, respectively. Rfb is a feedback resistor, Cfb is parasitic capacitance of the Rfb, R a-w in parallel with C a-w creates an equivalent impedance connected between the auxilary and working electrodes. Ic, Vc represent total current and voltage noise caused by the electrochemical cell, connecting cables and the printed circuit board (PCB). Cp is a parasitic input capacitor mostly formed by the distributed capacitance of PCB, A1 input pins and cables. Ia is the input current noise of the operational amplifier A1. Ir, Vr are the current and voltage thermal noise of the Rfb.

Typical picoampere-range current measurement system comprises an electrochemical cell and potentiostat with ultra low input bias current (figure 1). The theoretical limit of the total noise in the measurement system is given in [14]. The theoretical model includes the thermal noise generated by the



Figure 2. Power density spectrum of the flicker and thermal noise

feedback resistor (Rfb) and the voltage noise of the electrochemical cell. Although this model correctly estimates the lowest level of the overall thermal noise, in practice the measured level of the output noise is always higher because two other types of random fluctuations are not taken into account.

First of all, this is flicker (or 1/f) noise. Its power spectral density (PSD) decreases while frequency increases. The flicker noise dominates in low frequency range, while the PSD of thermal noise remains constant (figure 2). As a result, to achieve the theoretical sensitivity the spectrum range must be selected above the frequency corner of the given measurement system.

The second type of random fluctuations is Poisson noise (also called shot noise). This noise is a pulselike random signal with a Poisson statistical distribution. The shot noise rarely plays a significant role in electrochemical measurements, but if ultra low electrical current of $10^{-12} - 10^{-15}$ A has to be measured precisely, the shot noise can not be neglected (figure 3). Moreover, this type of noise could interfere with the single nanoparticle collision signal because they have very similar characteristics (amplitude and width).

Root mean square (r.m.s.) value of current associated with the Poisson noise is given by (1).

$$\sigma_i = \sqrt{2qI\Delta f} \tag{1}$$

where σ_i is the r.m.s. value of the shot noise, q - charge of electron, I - electrical current being measured, Δf - a bandwidth. For example, electrical current with mean value I=1.6e-15 A measured in bandwidth $\Delta f=250$ Hz produces shot noise with r.m.s. value $\sigma_i \approx 3.6e-16$ A, and the peak-to-peak value $\pm 3\sigma_i \approx 2.1e-15$. The relative r.m.s. error is 22 %, peak-to-peak amplitude of the noise exceeds the measuring current. Obviously, such high uncertainty can not be ignored.

Thus, the total current noise of the measurement system for registering the electrical current caused by collisions of a single nanoparticle with the working electrode, should include three most important sources of electrical noise: thermal noise of the feedback resistor, flicker and Poisson noise. With a reasonable suggestion that all sources of noise are non-correlated, the expected noise floor I_n of the potentiostat can be calculated from (2).

$$I_n = \sqrt{I_{therm}^2 + I_{1/f}^2 + I_{shot}^2}$$
(2)



Figure 3. Root mean square value of current shot noise on measuring current

where I_{therm} is the thermal current noise, $I_{1/f}$ - flicker current noise, I_{shot} - Poisson current noise. For instance, a laboratory potentiostat with Rfb=10 G, bandwidth 250 Hz and input bias current 10e-15 A has the corrected noise floor given by (3).

$$I_{therm} = \sqrt{4kTB/R} \approx \sqrt{4 \cdot 1.38^{-23} \cdot 298 \cdot 250/10G} \approx 2.0^{-14}A$$

$$I_{1/f} \approx 30^{-15}A$$

$$I_{shot} = \sqrt{2qI\Delta f} \approx \sqrt{2 \cdot 1.6^{-19} \cdot 10^{-15} \cdot 250} \approx 8.9^{-16}A$$

$$I_n = \sqrt{I_{therm}^2 + I_{1/f}^2 + I_{shot}^2} \approx 3.6^{-14}A$$
(3)

The corrected noise floor for this potentiostat is 1.8 times higher than the theoretical one. The thermal and Poisson noise, though fundamentally irreducible, can be easily estimated under given conditions. In contrast, the flicker noise mainly depends on electronic components the potenstiostat is built around, as well as on type and quality of the electrochemical working and reference electrodes. Unfortunately, the flicker noise in ultra low current electrochemical systems can not be predicted using fundamental physical properties, as a result, it should be determined experimentally.

2.2. Signal-to-noise ratio limit of nanoparticles detection

The detectability of nanoparticles for a certain potentiostat design depends on two major parameters:

- signal to noise ratio (S/N) of the measurement system;
- distribution of nanoparticles by their size and charge.

The concept of the limit of detection (LOD) has been discussed for a long time. There have been many statistical measures, introduced by several international organizations, including ISO and IUPAC, specifically to estimate the limit-of-detection (LOD) in analytical chemistry [15]. The commonly agreed approach to establish the lower limit of detection is based on a simple assumption [16]: the signal is detected if its amplitude is above the LOD calculated from the standard deviation Sx (4).

$$LOD = k \cdot Sx,$$

$$k \approx \frac{t_{f,1-\alpha}}{\sqrt{n}}$$
(4)

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where f is the number of degrees of freedom, n - the number of the averaged measurements, α - the maximum allowed probability of I type error. In case of chronoamperemetry $Sx \approx I_n$, n = 3, f = n - 1, $k \in [2..4]$, so the LOD is in the range from $7.2^{-14}A$, $\alpha = 0.05$ to $14.4^{-14}A$, $\alpha = 0.01$. It means that the laboratory potentiostat, mentioned above, can detect 95 % of nanoparticle impact events causing flow of at least $4.5 \cdot 10^5$ electrons per second. In order to catch 99 % of the impact events, they should produce twice as many electrons per second.

Although the signal-to-noise limit of detection gives a reasonable estimation of the lowest electrical current detectable by a certain potentiostat, there is no direct way of converting the measured current value into the size of nanoparticles. The nano-impact spikes have the duration in range of milliseconds [17]. Roughly, the detectable electrical charge, released within a certain period of time ms, can be found through (5).

$$Q_{impact} = \frac{LOD \cdot t_{impact}}{q};$$

$$Q_{impact} = \frac{7.2^{-14} \cdot 10^{-3}}{1.6 \cdot 10^{-19}} \approx 450e^{-}; t_{impact} = 10^{-3}s;$$

$$Q_{impact} = \frac{7.2^{-14} \cdot 4 \cdot 10^{-3}}{1.6 \cdot 10^{-19}} \approx 1800e^{-}; t_{impact} = 4 \cdot 10^{-3}s.$$
(5)

These values of Q_{impact} correspond to silver spherical nanoparticles with radii from 1.1 to 1.4 nm. The detectable nanoparticles of α -Fe₂O₃ would have size from 6.4 to 8.1 nm.

This LOD does not take into account a parasitic input capacitor of a potentiostat (Cp in figure 1). This capacitor should be small enough in order to the electrical current caused by the nanopartile impacts can charge the Cp to voltage above the voltage noise of the transimpedance amplifier (A1). Typical amplitude of the voltage noise is around 10 μ V, thus the overall value of the Cp should be below several picofarads (6).

$$Vcp = \frac{Q_{impact}}{Cp};$$

$$Cp = \frac{Q_{impact}}{Vcp} < \frac{450 \cdot 1.6 \cdot 10^{-19}}{10^{-6}} \approx 7.2^{-12}F$$
(6)

2.3. Noise of an electrochemical cell

The background noise of a potentiostat establishes the lowest possible level of detection for a given measurement system. The sources of electrochemical noise can be modelled with an equivalent resistor R_{a-w} and capacitor C_{a-w} connected between the auxiliary and working electrodes (figure 1). A source of voltage noise V_c in series with R_{a-w} and C_{a-w} adds frequency depended current noise [14].

$$I_{cell} = \sqrt{\left(\frac{V_c}{R_{a-w}}\right)^2 + \left(2\pi f C_{a-w} V_c\right)^2} \tag{7}$$

where $V_c = \sqrt{4kTR_c\Delta f}$ is the root mean square value of the thermal voltage noise, R_c is the equivalent resistance of the electrochemical cell, Δf - frequency bandwidth. Typical value of R_c for microelectrodebased measurement systems is in the range from 10^6 to 10^8 Ohm. Consequently, the thermal voltage noise in bandwidth Δf =250 Hz has the r.m.s. value from $2 \cdot 10^{-6}$ to $20 \cdot 10^{-6}$ V. The values of R_{a-w} and C_{a-w} depend on the surface area of the working and auxiliary electrodes, distance between them, temperature, conductivity and electrical permeability of the solution. Carefully designed and built electrochemical cell with microelectrodes could have value of C_{a-w} reduced down to several picofarads, although it is not a simple and straightforward process. The value of R_{a-w} has an optimum for a given operational

amplifier A1 with the input voltage noise v_n and current noise i_n . The optimum value of $R_{a-w} = \frac{v_n}{i_n}$, for electrometric-grade amplifiers $v_n \approx 10^{-8}$ V, $i_n \approx 10^{-15}$ A, thus the optimal value of $R_{a-w} \approx 10^7$ Ohm. Eventually, the total current noise I_{cell} of the electrochemical cell is in range from 10^{-12} to 10^{-13} A.

After including the I_{cell} into (3), the overall background noise of the whole measurement system is in the range from 10^{-12} to 10^{-13} . These results are in good agreement with the reported in [14] $I_n = 0.23$ pA, 250 Hz frequency bandwidth. The LOD of the whole measurement system now becomes 10 times higher. Nevertheless, the size resolution of the CSNps method still remains exceptional.

3. Conclusion

The chronoamperometry of single nanoparticles has a great potential for detecting electrically active nanoparticles. Theoretically, this method has size resolution comparable to a scanning electronic microscope, but the measurement systems are significantly smaller and cheaper. Moreover, preparation of samples is quite simple requiring only basic chemicals and equipment. These facts make CSNps very attractive to monitor pollution of environmental samples with nanoparticles of different kinds. The theoretical limit of detection seems very impressive. In practice, however, the limit has not been achieved yet, mainly because there are no commercially available potentiostats with ultra low input current along with low current noise, wide bandwidth, high slew rate and extremely low input capacitance combined all together.

One more issue that has to be resolved, is relatively high background noise of electrochemical cells with microelectrodes. The exact processes underlying collisions of nanoparticles with a working electrode are not well studied. Understanding the intimate mechanisms of nanoparticle collisions allows creating of a new class of laboratory equipment for environmental monitoring.

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