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# Simple and rapid method for screening of pyrophosphate using 6,6-ionene-stabilized gold and silver nanoparticles

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ABSTRACT

Desensitized ionene-stabilized gold and silver nanoparticles were prepared and applied as colorimetric probes for single-step determination of pyrophosphate at the relatively high concentration level. The approach is based on aggregation of the nanoparticles leading to the change in their absorption spectra and color of the solution. Due to both electrostatic and steric stabilization these nanoparticles show decreased sensitivity, which allows for simple and rapid direct single-step determination of pyrophosphate at the relatively high concentration level in real samples. Influence of different factors (the time of interaction, pH, the concentrations of pyrophosphate and the nanoparticles) on aggregation and analytical performance of the procedure was investigated. The method allows for the determination of pyrophosphate in the mass range of 90–150 μg and 45–150 μg with RSD of 2–5% by using gold and silver NPs, respectively. It has sharp dependence of the colorimetric response on the concentration of pyrophosphate, which makes it prospective for indicating deviations of the concentration regarding some declared value chosen within the above mentioned ranges using spectrophotometry or naked-eye detection. The method was applied to the analysis of baking powder sample, copper plating solution and samples of bread.



## 1. Introduction

Pyrophosphates are actively used in industry as food additives to increase the mass of muscle tissue and the yield of a final product. Also pyrophosphates improve organoleptic characteristics and product consistency, they stabilize the color and slow down the oxidative processes. This additive is widely used in canning of various meat products, seafoods and in the preparation of processed cheese. It may also be contained in some dairy products [1,2]. When excessive use of this additive, it can cause indigestion, as well as disorders related to an imbalance of phosphorus and calcium in the body. With increased use of this additive, deterioration of the calcium absorption may take place, resulting in deposition of phosphorus and calcium in kidneys, which contributes to the development of osteoporosis [3].

The traditional method for determination of pyrophosphate is titrimetry [4]. Electrochemical [1,5], chromatographic [6,7], biological [8,9] and spectrophotometric methods [10–12] have also been proposed for its determination. However, simple and fast spectrophotometric or naked-eye colorimetric procedures are of interest. One of the prospect ways to develop such a procedure can be based on the optical properties of gold and silver nanoparticles (AuNPs and AgNPs).

These nanoparticles have attracted the attention in the last two decades due to their unique properties [13–16]. The surface plasmon resonance (SPR) is one of the interesting characteristics of these nanoparticles, which gives them a peculiar optical behavior. As a result, AuNPs and AgNPs display intense colors and corresponding specific extinction bands in their UV–vis spectra (515–530 nm and 390–440 nm, respectively), which depend on the size, shape, dielectric environment and aggregation state of the nanoparticles. The aggregative stability and selectivity of NPs aggregation depends essentially on the type of a stabilizer and functionalizing additives used during their preparation. Hence, functionalizators/organic ligands play important role in tuning NPs applications [17–20]. Currently nanoparticles are widely used in analytical chemistry for spectrophotometric determination of metal cations [21–24], anions [25–28] and organic compounds [29–34]. However, the studies on the determination of anions are much rare than the others.

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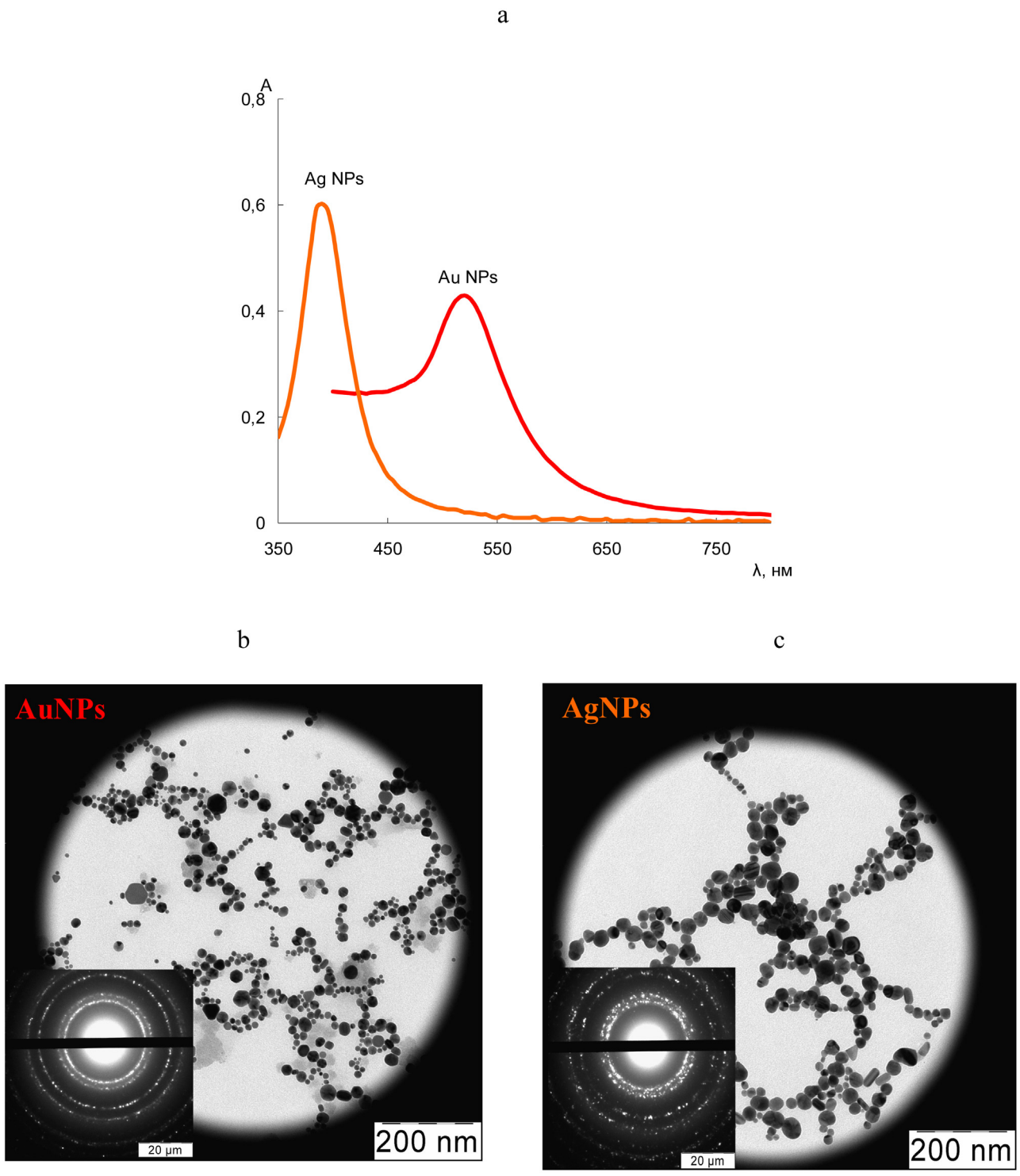


**Fig. 1.** Absorption spectra (a), TEM images and ED patterns (b, c) of the ionene-stabilized gold (b) and silver (c) NPs. (a) $c_{NPs} = 24\ \mu g\ mL^{-1}$.

In this study, we investigated the possibility of using gold and silver nanoparticles stabilized with 6,6-ionene for spectrophotometric determination of pyrophosphate based on their aggregation.

## 2. Materials and methods

### 2.1. Materials

Hydrogen tetrachloroaurate, silver nitrate, sodium borohydride, *N,N,N,N*,-tetramethylhexamethylenediamine, 1,6-dibromohexane, *N,N*-dimethylformamide, acetone, hydrochloric, nitric and phosphoric acid, sodium hydroxide, sodium sulfate, bromide, chloride, perchlorate, chlorate, fluoride, nitrate, phosphate and bicarbonate were used. All substances were at least of analytical grade. The substances stock solutions were prepared by dissolving their weighed portions in deionized water. 6,6-Ionene (poly(*N,N*-dimethyl hexamethyleneiminium bromide), $[-N(CH_3)_2{}^+Br^- -(CH_2)_6-]_n$) was synthesized according to the following procedure [35].

Equimolar solutions of *N,N,N,N*,-tetramethylhexamethylenediamine and 1,6-dibromohexane were mixed in *N,N*-