Chemometrics and Intelligent Laboratory Systems 141 (2015) 88–93

Contents lists available at ScienceDirect

Chemometrics and Intelligent Laboratory Systems

journal homepage: www.elsevier.com/locate/chemolab

Determination of nanoparticles concentration by multivariate curve resolution

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ARTICLE INFO

Article history:
Received 26 April 2014
Received in revised form 9 December 2014
Accepted 13 December 2014
Available online 20 December 2014

Keywords:
Nanoparticles concentration
Spectrophotometry
Chemometrics
MCR-ALS

ABSTRACT

The use of multivariate curve resolution-alternating least square (MCR-ALS) for determination of nanoparticles concentration is proposed. The concentration of nanoparticles based on its reaction with a reagent such as a biomolecule, nanoparticles and etc was calculated. The reagent can be considered as an aggregating agent, capping agent and so on. To do so, titration of nanoparticle was achieved by adding variable amounts of reagent to a nanoparticle solution of unknown concentration. A reverse titration was also performed. The UV–Vis spectra of the solutions at different titration steps were recorded. After data collection, chemometrics approach was employed for data analysis. To use MCR-ALS as a quantitative tool, rotational and intensity ambiguities were removed employing unimodality, non-negativity, closure and equality constraints and simultaneous analysis of four spectroscopic titrations: three titrations of reagent by nanoparticles with different concentrations of reagent, and one titration of nanoparticles by reagent. The proposed method was firstly evaluated by simulated data. Then, the concentration of the laboratory-synthesized silver nanoparticles was determined using human serum albumin as reagent. The estimated concentration by the suggested method (1.24×10^{-8} M) was very close to that obtained by analysis of TEM images (1.19×10^{-8} M) with a relative error of 4.2%.

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1. Introduction

Over the past three decades, nanotechnology opens a new window to the various branches of sciences[1–7]. Many reviews on synthesis, characterization, properties and application of nanostructures were published in recent years[8–11]. But undoubtedly, in all branches of nanoscience especially in quantitative analysis, the first challenge is determining nanostructures concentration. For example, knowing the concentration of nanoparticles is essential to report the biological efficacy or toxicity levels of nanoparticles, and also to use them as analytical reagent for sensing purposes. Although instrument such as scanning mobility particle sizers[12], electrospray sources[13], and single-particle tracking microscopy[14] were utilized for determination of nanoparticles concentration, but these kinds of methods are sophisticated and costly. On the other hand, the methods such as quartz crystal microgravimetry [15], osmotic pressure measurement [16] and particle-impact electrochemistry[17] were introduced which are rather inexpensive but cannot be used for concentration determination of all kinds of nanoparticles. It seems that, introducing a new general method which is applicable routinely in all laboratories for all kinds of nanostructures is urgent.

A simple method which is used extensively in the literature and gives approximate concentration is based on the estimation of the average number of the atoms per each nanoparticle. The value of average number of the atoms per each particle can be calculated by using sizes of nanoparticles which can be obtained by light scattering methods such as dynamic light scattering (DLS) [18], X-ray diffraction (XRD) [19] or microscopic method such as atomic force microscopy (AFM) [20], transmission electron microscopy (TEM) [21], and scanning electron microscopy (SEM) [22]. Then, the concentration can be obtained by dividing the total number of precursor atoms to the number of the atoms per nanoparticles. This procedure is based on two major assumptions. At first, conversion of the precursor atoms to the nanoparticles is 100% completed and the second one is the equality of nanoparticles density to its bulk material.

Another method which can be used for determining metal nanoparticles and quantum dot concentration is plasma sources such as ICP-AES [23] and ICP-MS [24–26]. In these cases, the impurities such as precursor atoms of nanoparticles should be removed to obtain reliable results. This pretreatment is not easy in all cases, especially in case of small nanoparticles and quantum dots which cannot be separated easily from their precursor due to their very small sizes. Also, plasma sources are costly and complicated instruments and are not common-used equipments.

Alternatively, UV–Vis spectroscopy is known as a simple, convenient and powerful method which can be used for determination of nanoparticles concentration [27]. Based on Beer's law, if the molar extinction coefficient of the nanoparticles is known, the nanoparticles concentration can be calculated directly from its absorbance. But, the major drawback

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http://dx.doi.org/10.1016/j.chemolab.2014.12.004
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of this method is its requirement of the knowledge of molar extinction coefficient of the corresponding nanoparticles or quantum dots which is dependent on several parameters including nanoparticles size [28]. In 2003, Peng et al. introduced a method to obtain the molar extinction coefficient of CdSe, CdTe and CdS nanocrystals by using of their experimental/theoretical particle sizes [29]. Also, there are reports based on UV–Vis spectra of silver and gold nanoparticles for direct determination of size/concentration of these nanoparticles [30,31]. Totally, this method is limited to determination of the concentration of gold nanostructures, silver nanoparticles and just three kinds of quantum dots (i.e. CdSe, CdTe and CdS). Based on our knowledge, unfortunately, there is no general report on direct determination of molar absorption coefficient of the nanoparticles for determination of nanoparticles concentration. Another point which should be mentioned is peak broadening of corresponding UV–Vis spectra in nanoparticle solution which is due to the existence of size distribution in nanoparticle solutions (even with very narrow size distribution). Also, presence of another species such as initial precursors of nanoparticle synthesis may have influence on corresponding spectra of nanoparticles. In summary, these drawbacks can influence on application of UV–Vis spectroscopy for determination of nanoparticles concentrations.

Multivariate curve resolution (MCR) techniques have also been applied in the analysis of spectral data from nano-materials [32–37] as well as their conventional biological and chemical applications [38–41]. Multivariate curve resolution-alternation least square (MCR-ALS) is known as a soft modeling chemometrics approach to obtain pure contribution of all components in a chemical process [42]. The reliable results can be obtained by the use of suitable constraints in each analysis. By spectroscopic monitoring of an evolutionary chemical process (e.g., complexation titrations, acid-base titrations, and reaction kinetic) following by MCR analyses, one can obtain pure spectra (molar absorptivity) and concentration of the species involved in the reaction [38]. Also, by proper elimination of rotational and intensity ambiguities, it is possible to use MCR-ALS for quantitative analysis as well as qualitative purposes [43,44]. In both cases, the analytical concentrations of the reagents should be known.

In this work, we investigated the ability of MCR-ALS analysis for quantitative analysis when the analytical concentration of one reagent (i.e., nanoparticles) is not known. To do so, the interaction of nanoparticles with a biomacromolecule such as bovine serum albumin (BSA) has been studied by UV–Vis spectrometry. Such interactions have been the subject of many studies in recent years. Rotational and intensity ambiguities were overcame utilizing natural constraints as well as simultaneous analysis of four experimental data matrices. At first, the molar absorption coefficient of nanoparticles was calculated using MCR-ALS analysis. Then, the concentration of nanoparticles was obtained by use of Beer's law. By using of this kind of interaction, the net molar absorption coefficient of nanoparticles without any interference of other species can be obtained. In fact, this method can apply selectivity for calculation of molar absorptivity. To test this method, both simulated and experimental data were analyzed. In case of experimental analysis, the data of interaction of Ag nanoparticles with BSA were analyzed and the obtained results were compared with other methods.

2. Theory

Finding the unknown concentration of a species is an old challenge in analytical chemistry. One of the basic solutions is determination of the unknown concentration based on the stoichiometric reaction of the analyte with a standard reagent such as those happened in classic volumetric titration. Herein, the concentration of nanoparticles was determined based on UV–Vis spectroscopic study of the stoichiometric reaction of the nanoparticles with a reagent but by using a chemometrics approach. Because, usually the product of reaction of a nanoparticles with a reagent has an overlapped absorbance spectra with that of initial nanoparticles, chemometrics approach can be used as a key to solve this problem. Suppose the reaction of nanoparticles (N) solution with a reagent (R) can be defined as Eq. (1).

$$rR + nN \leftrightarrows P \tag{1}$$

where, R is an absorptive reagent in measured wavelength range which in the presence of N can produce a complex or at least an associate product (P). The lowercase letters r and n represent stoichiometric ratio of R and N in the product, respectively. The species R can be an inorganic/organic ligand, a biomolecule, a drug molecule or even another kind of nanostructures. Also, the product (P) of the reaction is an absorptive species and its spectra may have strong spectral overlapping with other species. For example, P can be an aggregation product of N and R or even considered as a single nanoparticle which capped with several R species. The apparent equilibrium constant of the reaction is considered as follows

$$K_{app} = \frac{[P]}{[R]^r[N]^n} \tag{2}$$

In the above equilibrium (Eq. (1)), mass balance equation for R and N can be written as below

$$C_R = [R] + r[P] \tag{3}$$

$$C_N = [N] + n[P] \tag{4}$$

If all three species, i.e. R, N and P coexist in the solution, total absorbencies (A) at each wavelength λ (Eq. (3)) based on Beer's law can be defined as

$$A(\lambda) = \varepsilon_N(\lambda)[N] + \varepsilon_R(\lambda)[R] + \varepsilon_P(\lambda)[P] \tag{5}$$

where ε_N, ε_R and ε_P are the molar absorption coefficient of species N, R and P, respectively. By substituting Eqs. (3) and (4) in Eq. (5), the following equation can be obtained

$$A(\lambda) = \varepsilon_N(\lambda)(C_N - n[P]) + \varepsilon_R(\lambda)(C_R - r[P]) + \varepsilon_P(\lambda)[P] \tag{6}$$

In Eq. (6), if the stoichiometric coefficient of the reaction (i.e. r and n), equilibrium concentration of product ([P]) and molar absorption coefficient of P and R (i.e. $\varepsilon_P(\lambda)$, $\varepsilon_R(\lambda)$) are known, the initial concentration of N (C_N) and molar absorption coefficient of N are remained unknown. Knowing one, results in calculating another. To solve Eq. (6) for ε_N and C_N, MCR-ALS can be employed. Suppose an absorbance data matrix (**D**) for titration of R with N was constructed. In this matrix, each row is the corresponding spectra of the mixture at each titration points. So, the columns are the wavelengths and the rows are titration steps. By use of MCR-ALS algorithm, **D** matrix can be divided into two main submatrices, i.e., **C** and **S**.

$$\mathbf{D} = \mathbf{CS} + \mathbf{E} \tag{7}$$

C matrix includes the concentration profiles (or equilibrium concentrations) of the species in the mixture solution and **S** matrix includes the pure spectra of the species present in the equilibria mixtures at measured wavelengths range and **E** is the error matrix. If the results of MCR-ALS analysis were unique, in fact the **S** matrix is including of molar absorption coefficient of the species and can be used in quantitative analysis. For considered system (Eq. (1)), **D** matrix in Eq. (7) can be rewritten as below

$$\mathbf{D} = \mathbf{c}_R\mathbf{s}_R + \mathbf{c}_N\mathbf{s}_N + \mathbf{c}_P\mathbf{s}_P + \mathbf{E} \tag{8}$$

where $\mathbf{c}_N$ and $\mathbf{s}_N$ are the vectors of concentration profile and pure spectrum of nanoparticles (N). The same is applied for other terms in Eq. (8).

MCR-ALS is known as a soft model approach which attempts recovering of the true underlying contributions of the components in the

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