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Analysis of silica nanoparticles by capillary electrophoresis coupled to an evaporative light scattering detector



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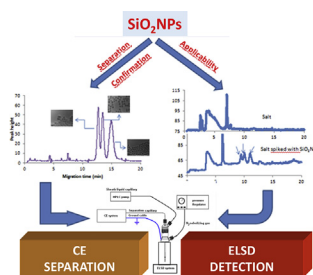
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HIGHLIGHTS

- Novel, simple and low expensive methodology to separate SiO₂NPs by size.
- Capillary electrophoresis – Evaporative light scattering arrangement.
- Separation of 20, 50 and 100 nm SiO₂NPs was achieved.
- Appropriate resolution and sensitivity.
- Identification of SiO₂NPs in salt samples.

GRAPHICAL ABSTRACT



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ABSTRACT

A simple and rapid methodology has been developed to identify and separate silica nanoparticles (SiO₂NPs) of different sizes in aqueous solution by capillary zone electrophoresis coupled to an evaporative light scattering detector (CE-ELSD). SiO₂NPs were separated using 3 mM ammonium acetate buffer, containing 1% methanol at pH 6.9. SiO₂NPs of 20, 50 and 100 nm were successfully separated under the optimum experimental conditions. CE coupled to ELSD has been proven to be an effective separation technique to determine particles with such small sizes, although the peaks are very close to each other, and it is a promising technique that may allow the separation of other types of nanoparticles. Confirmation by TEM and quantification of the SiO₂ content was also carried out by inductively coupled plasma-mass spectrometry (ICP-MS). The new method was applied to the analysis of real samples, in order to assess its ability to avoid matrix effects in the determination of SiO₂NPs in these kinds of samples.

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1. Introduction

In recent years, nanoscience and nanotechnology have become increasingly studied area due to the potential benefits that these areas have brought to various research topics and their application in numerous fields, such as sensors miniaturisation [1], chip fabrication [2], agriculture production [3], analytical assays [4] and

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the food industry [5,6]. However nanomaterials (NMs) may have a negative effect on the environment, and there are safety and toxicological concerns associated with these materials are of relevance. NMs encompass any type of material that meets the following two requirements according to The Royal Society of Chemistry [7]: larger surface area in relation to the same mass of material produced in a larger form, and quantum effects that dominate the behaviour of matter at the nanoscale. Nanoparticles (NPs) are three-dimensional nanomaterials with a size of less than 100 nm in at least one dimension [3]. It is at this scale that the physical, chemical, and biological properties of materials differ with respect to those at a larger scale [8]. NPs have had a significant impact in agriculture, particularly in relation to nanopesticides [9].

Silica nanoparticles (SiO₂NPs) are classified on the list of authorised food additives with the code E551 and, according to European legislation, maximum levels are dependent on the type of matrix in which they are contained [10]. Synthetic amorphous silica has been employed for many years in beer and wine clearance and it has also been used as an anti-caking agent to retain flow properties of powders and to thicken pastes. Silica has always been regarded as safe and it is approved for use as a food or animal feed ingredient [11]. Yamashita et al. [12] conducted several studies on the risks associated with SiO₂NPs. They found that SiO₂NPs with a diameter of less than 100 nm are likely to cause complications in pregnancy or consumptive coagulopathy in mice after systemic exposure. It was also proven that surface-modified SiO₂NPs were unlikely to induce undesired inflammatory responses *in vitro* and *in vivo*, thus suggesting that it might be possible to decrease adverse biological effects of nanomaterials and to enhance their safety by modifying their surface properties.

Capillary Electrophoresis (CE) is considered to be a useful technique for the evaluation and analysis of NPs. Numerous studies have shown that CE can be effectively used to determine sizes of NPs such as quantum dots [13], AuNPs [14] and various NPs from metal oxides such as hematite (Fe₂O₃NPs) [15,16] and silica (SiO₂NPs) [17]. CE combined with diode-array detection can be used for visual and size analysis of NPs. However, in some cases this methodology lacks a low LOD. In order to make the most of its advantages for the detection of NPs a combined CE-ELSD approach has recently been developed. Zhou et al. [18] developed a microfluidic ELSD (μ ELSD) method coupled with pressurized capillary liquid chromatography (pCEC) for the analysis of active components in traditional Chinese medicine extracts. Another approach, developed by our research group, consisted of a customised combination of CE and ELSD [19] and this method was applied to size separation and detection of AuNPs [20]. Recently, Barahona et al. [21] reported an asymmetric flow field-flow fractionation (AF4) coupled to multi-angle light scattering (MALS) inductively coupled plasma mass spectrometry (ICP-MS) for the simultaneous size determination and quantification of silica nanoparticles (SiO₂NPs). However, this methodology was time-consuming and very expensive owing to the high cost of the instrumentation. These shortcomings can be circumvented by developing a simple, accessible, economical and reliable technique for the separation and detection of SiO₂NPs. A simple method based on the use of CE-ELSD is proposed as an alternative and a powerful tool for the separation, characterisation and quantification of SiO₂NPs. To the best of our knowledge, this is the first example in which this combination has been reported to achieve the objectives outlined above. CE-ELSD analysis of NPs, as proposed in this article, offers significant advantages, related to the use of low cost instrumentation, low sample volumes, low waste volumes, and good analytical performance. This method was validated for its application to the analysis of salt samples, in which it was possible to separate SiO₂NPs of 20, 50 and 100 nm.

2. Experimental

2.1. Material and reagents

Non-functionalised NanoXact™ silica nanoparticles of different sizes (20, 50, 80, 100 nm) were purchased from NanoComposix (USA), all as aqueous solution. Sodium hydroxide pellets (SigmaUltra, minimum 98%), silicon standard for ICP, and rhodium ICP-MS standard were obtained from Sigma Aldrich (USA). Ammonium acetate (Bioxta, $\geq 98\%$) was obtained from Sigma Aldrich (The Netherlands). All liquid reagents employed for analyses were of analytical grade: methanol, isopropyl alcohol, hydrochloric acid and acetonitrile. Deionised water was obtained from a Milli-Q purification system (Millipore, Bedford, MA, USA).

2.2. Instrumentation

Electrophoretic analyses were carried out on an Agilent Model G1600AX (Palo Alto, CA, USA) CE instrument equipped with a diode array detector. An uncoated fused silica capillary (100 cm long and 50 μ m id) (Beckman, Fullerton, CA) was used. The make-up flow of sheath liquid was delivered by an Agilent 1100 isocratic pump, which was operated at a 1:100 split ratio. An evaporative light-scattering detector equipped with a new interface, as described below, and an additional pressure regulator (0–2500 mbar) (Ingeniería Analítica, Spain) to connect with the CE instrument was used. The CE-ELSD instrument was controlled using Rev.B.04.01–481 3D-CE/MSD ChemStation software (Agilent Technologies). The experimental variables are listed in Table 1. The diameters and size statistics were obtained using a JOEL 2011 transmission electron microscope operating at 200 kV and equipped with an Orius Digital Camera (2 \times 2 MPi) from Gatan. Nanoparticles were prepared by dispersing the samples in acetone and depositing a drop onto a holey-carbon Cu grid (Agar). The Si content was determined on an ICP-MS Thermo Fischer Scientific X Series^{II} system (Thermo Fisher, Bremen, Germany). Spectroscopic properties and the hydrodynamic diameter/Zeta potential were obtained on a secoman spectrometer and Malvern Zetasizer Nano ZS respectively.

2.3. Preparation of SiO₂ NPs samples prior to determination by ICP-MS and CE-ELSD

According to the results obtained by Pestel et al. [22] and confirmed by Barahona et al. [21], the direct quantification of SiO₂NPs is possible and reliable in the size range considered in this work. These authors pointed out that atomisation was complete with monodisperse SiO₂ colloids with particle diameters of less than 500 nm. For quantification, the ICP-MS device was used in standard mode, and data for ²⁹Si and ¹⁰³Rh were acquired with a standard torch (injection diameter 1.6 mm), nickel cones, Scott nebulisation chamber (refrigeration at 2 °C), acquisition time of 10 ms and values for plasma gas, make-up and nebuliser flow of 16, 0.73 and 0.9 L min⁻¹, respectively.

A calibration curve was used in order to quantify the Si content and this curve was developed using silicon standards for ICP and Rhodium ICP-MS as an internal standard [21]. The range of the calibration curve for the quantitation of samples was between 1 and 120 μ g L⁻¹ of Si and samples were prepared in deionised water. The reported values are the average of three measurements (see Table 2). Samples were sonicated for 10 min prior to CE-ELSD determination.

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