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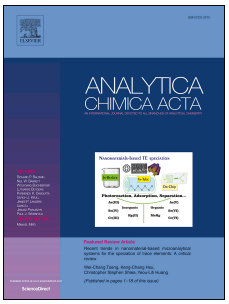

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Silver nanoparticles-based plasmonic assay for the determination of sugar content in food matrices

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Abstract

A simple colorimetric assay for sugars (monosaccharides, polyols and disaccharides) quantification based on silver nanoparticles (AgNPs) formation is proposed. Sugars are able to form AgNPs reducing Ag^+ and stabilizing the suspension. Since the driving force is not only chemical reduction, the optimized assay allows the determination of both "reducing" and "non-reducing" sugars with similar reactivity. The localized surface plasmon resonance (LSPR) absorption band with maximum wavelength centered at ≈ 430 nm (A_{430}) is used for the detection. Monosaccharides, disaccharides and polyols with different functional groups and structure have been investigated: D-(+)-glucose, D-(+)-galactose, D-(-)-fructose, sucrose, D-(+)-raffinose D-(+)-maltose, D-(+)-trehalose, D-mannitol, D-sorbitol, i-inositol, xylitol and D-(+)-xylose. The resulting AgNPs have been characterized by UV–Vis spectroscopy, dynamic light scattering (DLS) and transmission electron microscopy (TEM). The reactivity of monomers and polyols was found higher than the disaccharides. The AgNPs-based method was applied to the determination of the sugars content in soft drinks (n = 6) and apple extracts (n = 5). Sugars content (expressed as glucose equivalents) determined by the proposed assay resulted comparable to results obtained by ion chromatography (R = 0.994). Reproducibility (RSD ≤ 9.4 %) and recovery values (from 86.1% to 117.7 %) in food matrices were satisfactory. Moreover, the assay is selective vs. potentially interfering compounds found in food. Considering the assay time (10 min), the low cost of reagents, limited volumes of sample (5-100 μL), no use of organic solvents and low waste generation, this assay appears very promising for sugars content determination.

Keywords: silver nanoparticles; food sugars; metal nanoparticles; sugar assay; nanomaterials; spectrophotometric method.

1. Introduction

The evaluation of sugars content in foodstuff is an important issue in food quality control, both during processing and for the final product. Sugar content is a key parameter to define the sweetness and the caloric intake of food and, in many products, defines also the category of raw materials. Furthermore, several foods production are driven by sugars (e.g. fermentation, ethanol production, sugars hydrolysis, etc.) and their quantity becomes a key factor in the modulation and monitoring of the process.

In recent years, increasing attention has been devoted to sugars content in foods (in particular added sugars), and their potential impact on health, associated to their excessive intake; particularly in terms of insulin resistance and obesity, and the associated risk of developing diabetes and other chronic diseases [1,2]. Furthermore, the high intake of added sugars has adverse effects on cardiometabolic health [2]. Recently, systematic review and meta-analysis confirmed the global trends that most of the diet sugars intake results as added sugars [2,3]. In particular, in sales of beverages, despite the increasing trend to produce non-caloric beverages, a persistent trend to consume beverage with caloric sweeteners has been evidenced [3,4]. For these reasons, the determination of sugars content attracts considerable research efforts continuing to be a challenging analytical issue. Sugars are undoubtedly the most abundant components of the majority of foodstuff.

Several classical analytical methods to evaluate sugars content and characterize their composition have been optimized and routinely applied, recently flanked by emerging approaches. Among these, chromatography and capillary electrophoresis remain the most used techniques to characterize the sugars relative composition [5]. However, they require extensive sample preparation, and are time-consuming. Moreover, the aim of the analysis is often the total estimation of sugar/sugars content in food samples. Historically, the determination of total reducing sugars is performed by Fehling [6] reaction and other optical assays [7]. However, these methods are lengthy and require several steps (titrations at high temperature, precipitations, etc.).Moreover they are still non selective towards other reducing compounds.

A wide range of alternative methods and devices based on different principles have been proposed for rapid sugars content determination, such as standard hand-held refractometers, hydrometers, visible to near infrared spectroscopy, and electronic tongues [8]. In addition, optical and electrochemical enzymatic methods continue to be largely used in sugars analysis, particularly for applications in clinical field [9–11]. On the market, several enzymatic tests for sugars analysis in foods are also available. These assays exploit a combination of enzymatic reactions, with consequent issues of stability, selectivity, temperature of employment, conservation of reagents, etc.

In the last few years, metal nanoparticles (MNPs) have emerged as useful tool in food analysis, since their unique features allow their use in colorimetric or spectrophotometric detection[12–19]. Indeed, under the influence of electromagnetic radiation in the visible range, the electrons of surface atoms can easily move through vacant orbitals generating absorption at a

particular wavelength. This phenomenon is called localized surface plasmon resonance (LSPR) [13–19]. Recently, optical methods based on metal salts (metal source) reduction under the form of MNPs mediated by reducing agents appeared in the literature [12,19–26]. In particular, different methods for the evaluation of antioxidant capacity have been proposed[12,19–26], mainly based on the formation of gold nanoparticles (AuNPs)[23,24,27].

Recently, some application based on this principle has also been proposed for optical sugars evaluation. A proof of principle using an electrospun polyamide mesh containing Au salts was proposed by Scampicchio et al.[28] for visual evaluation of reducing sugars. Spectrophotometric assays based on the formation of AuNPs have been also proposed for glucose [29]. However, the proposed strategy is time consuming and requires high temperature to obtain AuNPs. Recently, an approach based on the interpretation of the AuNPs formation kinetics, has been proposed for the evaluation of xylitol [30].

Synthesis of AgNPs using different reducing compounds has been also reported [25], because of the great interest into the "green" synthesis of AgNPs used in nanomedicine and microbiological applications [19,31,32]. Among these, some example of AgNPs synthesis based on sugars have been reported [33,34], nevertheless none of them can be used for sugars contents evaluation. The proposed procedures work with high temperatures, long times, large volumes, high fixed concentration of single sugars. For these reasons, no one of these AgNPs syntheses is exploitable directly for food sugars contents determination.

In this paper we report for the first time the analytical determination of sugars in food samples using AgNPs. A rapid and simple one-step AgNPs-based colorimetric assay was developed, exploiting room temperature synthesis of AgNPs mediated by sugars (and polyols) commonly found in food. In order to compare the 'sugar' ability to form AgNPs, monosaccharides, disaccharides, and polyols were tested. The AgNPs-based colorimetric assay has been successfully applied to different kind of commercial soft drinks and apple extracts. The data obtained were found in good agreement with ion chromatography. The proposed AgNPs assay results simple to use, quick, selective, green, user friendly, and able to estimate significant sugars content in different foodstuff.

2. Materials and methods

2.1. Reagents, stock solutions, and reference compounds

All the chemicals were of analytical reagent grade. All the tested sugars: D-(+)-glucose, D-(+)-galactose, D-(-)-fructose, sucrose, D-(+)-raffinose pentahydrate, D-(+)-maltose monohydrate, D-(+)-trealose dihydrate, D-mannitol, D-sorbitol, i-inositol, xylitol, D-(+)-xylose were purchased from Sigma-Aldrich (St Louis, MO, USA). Cetyltrimethylammonium chloride (CTAC; 25% in water), ethylenediaminetetraacetic acid (EDTA), polyethylene glicol (PEG), cetyltrimethylammonium bromide (CTAB), silver nitrate ($AgNO_3$, > 99%), sodium hydroxide (NaOH), sodium phosphate monobasic monohydrate ($NaH_2PO_4 \cdot H_2O$), sodium phosphate dibasic anhydrous (Na_2HPO_4), ascorbic acid, and chlorogenic acid were purchased from

Sigma-Aldrich (St Louis, MO, USA). Stock solutions of sugar standards (in water) were prepared at a concentration of 1.0×10^{-2} mol L^{-1}, and stored at + 4°C in the dark. Glucose stock solutions were prepared 24 hours before use and stored at + 4°C in the dark to allow mutarotation. Milli-Q ultrapure (type 1) water (18.2 MΩ) was used for all the experiments and stock solutions preparation.

2.2. Samples

Different soft-drinks were purchased in local markets: peach tea, black tea, coconut water, gaseous, cedrata, and tonic water. Sparkling samples were degassed in an ultrasonic bath for 20 minutes. All the tested samples were centrifuged at 14.800 rpm for 10 minutes. The supernatant of each brand was recovered and kept at + 4 °C in the dark. Apple samples ('Golden Delicious' and 'Royal') were purchased in local supermarkets and extracted according to Neri et al. [35] with some modification. Each sample (5.0 g) was diluted with 20 mL of distilled water and ground with an Ultra-Turrax T18 basic homogenizer (IKAR Werke GmbH & Co. KG, Staufen, Germany) for 2 min. The homogenized solution was shaken for 20 min at + 4 °C and centrifuged at 5000 rpm for 10 min at 4 °C in a refrigerated ALC4237R centrifuge (ALC Intl., Cologno Monzese, Italy). Thus, the supernatant was filtered through a 0.45 μm nylon filter (MDI, Ambala, India). The supernatant was recovered and kept at + 4 °C in the dark until use. For each sample, pH was controlled before the analysis and after the addition in the reaction mix.

2.3. Apparatus

Mixing was carried out with a thermostated orbital shaker VDRL 711/CT from Asal (Florence, IT). Absorbance measurements were performed using a JENWAY 6400 Spectrophotometer from Barlworld Scientific (Staffordshire, UK). The transmission electron microscopy (TEM) measurements were carried out using a Philips CM12 (Philips Electronic Instruments, Mahwah, NJ, USA) transmission electron microscope. Before the TEM analysis, the AgNPs formed (without any dilution) have been drop casted (2μL) onto a Cu-support grid, and the solvent evaporated overnight at room temperature. Dynamic light scattering (DLS) particle size analyzer HPP-5001 (Malvern Instruments, Malvern, UK) was used for the AgNPs size determination, the AgNPs formed (without any dilution) have been allowed to equilibrate at 25 °C in the sample compartment 5 minutes and measured in polystyrene cuvettes. Sugars were determined by a Dionex (San Donato Milanese, Italy) ICS 3000 Ionic Chromatograph equipped with ICS 3000 SP pump and ICS 3000 ED detector.

2.4. AgNPs-based assay

The main reaction parameters of the AgNPs-based method were carefully studied: concentration of $AgNO_3$, capping agent, pH, temperature, and time. 5 μL of CTAC (1.0×10^{-3} mol L^{-1}), 25 μL of $AgNO_3$ aqueous solution (2.0×10^{-2} mol L^{-1}), and appropriate dilution of standard sugars or samples were added to deionized water. 10 μL of NaOH (5.0 mol L^{-1}) was finally added to trigger the reaction. Water volumes changed according to the sugar sample/standard volume employed, up to reach

the final volume of 500 μL. Reaction was started stirring for 10 min at 25° C in a thermostated orbital shaker. Finally, the reaction was blocked in ice for 10 min (to allow measures in series). The absorbance due to AgNPs formation was recorded at 430 nm. All measurements were carried out against the blank (reaction mix without standard or sample addition). Sugar content of real samples (soft drinks and apple extracts) was expressed as glucose equivalents (Glu. Eq), using the calibration curve obtained with standard solutions of glucose. Before analysis, samples were diluted in water (5-100 μL added to the reaction AgNPs mixture) as appropriate to fit the glucose calibration curve linear range. Useful absorbance values were fixed within 0.1-1.0 A_{430} against the blank. All the reagents involved in the reaction were used at room temperature.

2.5. Sugars reactivity and AgNPs characterization

End point reactivity was evaluated by plotting absorbance at 430 nm (A_{430}) of AgNPs plasmon band against sugar concentration. AgNPs formed upon sugars action (section 2.4) were characterized by UV-Vis spectra, TEM and DLS. Ultraviolet-visible (UV-Vis) spectra were recorded in the range 350 - 800 nm against the blank. TEM characterization was carried out by drop casting diluted sample solution on a carbon-coated copper grid that was then let dry at room temperature before measurements.

2.6. Recovery studies and evaluation of potential interferences

A mix of all the soft drink samples, was spiked with two different volumes of each standard sugar at 5×10^{-3} mol L^{-1}, in order to obtain solutions of 20/60 μmol L^{-1} and 200/400 μmol L^{-1}, for monosaccharides/polyols and for disaccharides, respectively. The fortified samples were separately subjected to the AgNPs-based assay and compared with the relative non-spiked samples, for the calculation of recoveries this formula has been employed: [(sugar concentration obtained with fortified sample - sugar concentration obtained with unfortified simple)/ sugar concentration added]*100. Potential interference effects of concomitant species commonly found in soft drinks and apple sugar extracts were also evaluated. Different amounts of the compounds, as suggested by the literature [29,36,37], were spiked in samples to evaluate under- and over-estimation on the AgNPs-based assay. The content of interfering compounds in apple samples was evaluated in parallel by HPLC.

2.7. Ion chromatography

Chromatographic analyses were conducted using a carbohydrates separation column (CarboPac PA20, 3 mm × 150 mm, Dionex) with a preguard column (CarboPac PA20, 3 mm × 30 mm, Dionex) according to Neri et al [38] with some modifications. 5.0×10^{-2} mol L^{-1} NaOH was used as mobile phase. Sugars detection was carried out using the time/potential waveform A, as recommended by the Dionex technical manual. A flow rate of 0.5 mL min^{-1}, a 35 min run at column temperature of 30 °C, and a volume injection of 10 µL were employed. Sugars identification and quantification were respectively achieved using retention times and the related sugar calibration curve.

3. Results and discussion

3.1 Study of the assay conditions and characterization of AgNPs obtained with standard sugars

The aim of the work was the development of a sugars-mediated single-pot optical assay based on AgNPs as signal transducers. Ideally, this should be simple, fast, and effective for a wide range of sugars. The formation of colloidal MNPs suspensions results from the concomitant reduction of the metal source and the stabilization of the MNPs produced [13–19,39,40]; at the same time their aggregation/collapse, and irreversible MNPs conformational changes with LSPR extinction band variation should be avoided [13–19,34,39,40]. Thus, a careful optimization of the reaction conditions is needed. Three sugars belonging to different chemical classes were selected and used for the optimization of the AgNPs-based assay: glucose (monosaccharide), sucrose (disaccharide), and xylitol (polyol).

The concentration of $AgNO_3$ was selected exploring a range between 2.0×10^{-4} and 1.5×10^{-3} mol L^{-1}. 1.0×10^{-3} mol L^{-1} $AgNO_3$ was eventually chosen since at this concentration the best signal/noise ratio (LSPR maximum absorbance/blank absorbance) was obtained.

The use of a capping agent is a key parameter to obtain sugars-mediated AgNPs formation in short times. It is well known that several capping agents may play the additional role of reducing agents, or contribute to the reduction of silver ions [17,39]. AgNPs formation in the presence of the capping agent starts quickly [41], by reducing the activation energy required to start the synthesis. Furthermore, it slows down the second growth phase, thus avoiding aggregation/collapse[34,39,40] and allowing the formation of stable and measurable AgNPs. Different amounts of EDTA, PEG, CTAB and CTAC were tested with the three standard sugars; the best signals were obtained with a final concentration of 8.0×10^{-3} mol L^{-1} of CTAC. The other capping agents resulted in either slow times of reaction or in turbidity of the solution.

The pH of the solutions is the other key parameter to be controlled, since it affects the ionization of carbohydrates, their reactivity towards silver (I) salt, and the final AgNPs stability in solution [41,42]. A 'micro-titration' in the reaction mixture was carried out to evaluate the pH influence on sugars reactivity. NaOH and phosphate buffer were used to obtain pH values from 10 to 14 and from 6 to 9, respectively. Alkaline reaction medium at pH 13 was found optimal for the AgNPs formation mediated by sugars. At lower pH, no silver nanoparticles formation was obtained while, at higher pH, the AgNPs formation occurs in an uncontrolled way, with and without sugars, resulting in a fast AgNPs collapse. At the selected pH value, the 12 investigated sugars (see below) are mainly in the dissociated state, according to their pKa (average sugars pKa = 12.7 ± 0.4). The high reactivity of sugars at alkaline pH can be attributed to higher reducing ability of unprotonated hydroxyl groups. At the same time, the increased charge of the sugars contributes to AgNPs stabilization in solution. The positive effect of alkaline conditions on sugar-mediated AuNPs formation has been already reported [26,29,33,42] as well as for the green synthesis of AgNPs [32,41,42].

Time and temperature were optimized in order to obtain the best selectivity in the shortest time. The compromise was found to be 10 min at 25 °C under constant stirring. Finally, the reaction was blocked in ice for 10 min. During the time/temperature optimization, the respective blank spectra obtained (reaction without sugars) were also recorded, to demonstrate the effective role of the sugars in the formation of AgNPs. Upon temperature and time increase, the excess of energy elicits the formation of AgNPs also in blank solution.

A typical example of the color evolution obtained by the AgNPs-based assay is reported in, Fig. 1A for glucose standards within 20-90 μM concentration range. The colorimetric trend finds a quantitative correlation with the plasmon spectra of Fig. 1B, recorded at the end-point of the reaction. Fig. 1C shows absorption spectra obtained for the disaccharide sucrose (Fig. 1C, blue line) and the polyol xylitol (Fig. 1C, red line). The absorbance maximum results for all the standards at $\lambda = 430 \pm 10$ ~~$\lambda = 425 \pm 10$~~ nm and colloidal solutions exhibited a characteristic yellow color indicative of AgNPs formation.

AgNPs produced by glucose, sucrose and xylitol were subjected to further characterization by TEM and DLS analysis to determine their morphology, size, and size distribution (Fig. 2). Samples analyzed have been selected within the linear absorbance range (~ 0.1 – 1.0 A_{430}). As shown in Fig. 2A-C, nanoparticles resulted homogeneous and monodispersed for all the sugars tested.

The average AgNPs diameter obtained by TEM analysis for glucose (Fig. 2A), sucrose (Fig. 2B), and xylitol (Fig. 2C) resulted within 10 nm in all the cases. On the other hand, the mean diameters calculated using DLS was 14, 16 and 12 nm for glucose, sucrose, and xylitol, respectively (Fig. 2D-F), confirming comparable size of AgNPs and their uniform distribution over the three classes of sugars. The slight overestimation of DLS data compared to TEM has been already reported for AuNPs formed with sugars, since larger size obtained can be attributed to the sugar shell enveloping the MNPs core [32]. In fact, also in this case, and independently of the sugar used, a core-shell structure [34] has been observed due to the presence of an external 'nanosized layer' on AgNPs surface (Fig. S1). The presence of surface sugar molecules is an indirect further proof of the interaction with NPs surface, and, thus of their role as stabilizers. No shell was present on AgNPs obtained without sugar in the same medium increasing reaction time and temperature (data not shown). In the case of sucrose, it has been found that considerably higher concentration of the sugar is required, compared to glucose and xylitol, to induce the AgNPs formation process. This behavior was also already reported in literature [33,43].

3.2 Evaluation of the different sugars reactivity

In order to investigate the practical applicability of the method, the reactivity of 12 carbohydrates belonging to different classes of sugars has been tested. In particular, monosaccharides, disaccharides and polyols with different functional groups and structures were taken into account: D-(+)-glucose, D-(+)-galactose, D-(-)-fructose, sucrose, D-(+)-raffinose D-(+)-maltose, D-(+)-trealose, D-mannitol, D-sorbitol, i-inositol, xylitol, and D-(+)-xylose. The correlation between LSPR maximum ab-

sorbance and sugars in terms of type and concentration has been evaluated. Fig. 3A-C reports the dose-response plots obtained with the tested sugars per class of molecules: monosaccharides (A), disaccharides (B), and polyols (C). In Table 1 analytical parameters as linear ranges, equations, and determination coefficients for all the sugars tested are reported. Furthermore, their relative reactivity (%) has been expressed taking glucose as reference compound (100% reactivity). This parameter has been calculated using the slope/concentration ratio at 50% of the linear range for each sugar, then normalized to glucose (see equation footnote of Table 1).

The wavelength maximum, resulted centered at $\lambda \approx 430 \pm 10$ nm in all the cases. All the tested sugars resulted able to form AgNPs and their formation, in the experimental conditions used, is linearly correlated to the sugar concentration in solution. Table 1 reports good analytical performances in terms of determination coefficients ($R^2 \geq 0.991$), repeatability (RSD ≤ 8.2, n = 3, intra-day) and dose-response fit slope reproducibility (RSD ≤ 11.2 %, n = 3, inter-day) for all the sugars tested. The limits of detection (LOD were calculated as 3.29σ / slope ratio, where σ is the standard deviation of the mean value for 10 blanks), resulted very similar for monosaccharides (LOD = $8.7 \pm 0.5 \times 10^{-6}$ mol L^{-1}) and polyols (LOD = $8.7 \pm 0.3 \times 10^{-6}$ mol L^{-1}) despite the marked chemical differences between the two classes. Therefore, we may conclude that compounds in the form of small and open structures (regardless of being reducing sugars or not) are the most active in reducing Ag (I) to AgNPs suspensions. Reactivity and linear response of monosaccharides and polyols was comparable (relative reactivity RSD = 9.2 %), despite the differences in functional groups and length of the carbonaceous structure (see Fig. 3 and Table 1). The ability of reducing monosaccharides to form MNPs is well-known [34,44]. However, despite polyols are not reducing carbohydrates, their ability to form MNPs has been also recently reported for analytical purposes [30,41,45].

On the contrary, two orders of magnitude lower of sensitivity was obtained for disaccharides (LOD = $1.2 \pm 0.1 \times 10^{-4}$ mol L^{-1}). This behavior has been already reported in the literature underlining that, compared to open structure carbohydrates, high sugar concentration and/or high temperature are required to elicit MNPs synthesis [32,33,42,43]. The suggested explanation for the reduced activity of disaccharides is based on the lower ability to form/growth/stabilize AgNPs [32,43]. Among the tested sugars, i-inositol and D-(+)-raffinose, a cyclic polyol and a trisaccharide, resulted both unable to form AgNPs. This behavior confirms that their reactivity in the developed assay conditions is strictly dependent on the sugar structure. The cyclic and bulky structures of these sugars likely fail to react, surround, and finally stabilize the NPs in solution. On the contrary, the other sugars (in particular open carbohydrate structures) can react and "coordinate" the AgNPs core forming a protective and stabilizing shell [34] (Fig. S1). The weak correlation with the reducing power of carbohydrates is also confirmed by the similar reactivity shown by disaccharides. In fact, only D-(+)-maltose is a reducing sugar, but it shows the same reactivity of D-(+)-trehalose and sucrose that are not reducing disaccharides (Table 1) with very similar structure.

It should be pointed out that for concentrations exceeding the linear range, longer times of reaction or higher temperatures used, the diameter of Ag nanoparticles increases leading to aggregation; a quick yellow-orange-brown-grey color transition is then observed with the formation of black and large aggregates visible by naked eye. This behavior has been observed for all the sugar tested. From the data reported, the main food sugars resulted to be detectable by the developed method (i-inositol and D-(+)-raffinose are not frequently found in food). In order to speed up and simplify the assay, the LSPR was taken at a fixed wavelength of 430 nm (A_{430}). To verify the robustness of this approximation, all the LSPRs obtained with the formed AgNPs (in the linear range), have been recorded. In all the cases a slight red-shift has been observed moving from low to high concentration of sugars; this behavior has been also observed in other works [13,16] coupled to a slight spectra peak broadening [17]. This red-shift is caused by an increase of the adsorbed layer around the MNPs [13,16,17] due to the increasing sugars shell around the AgNPs core [16]. This behavior has been already reported for AgNPs formed with increasing concentration of natural compounds [46–48]. In our conditions, the red shift was ≤ 18 nm (from the lower to the higher concentration) for all the tested sugars. The relative error, between A_{430} and the absorbance recorded at the LSPR maximum (A_{max}) for all the AgNPs formed by sugars, was not significant (relative error range of A_{430} vs. A_{max} form -2.7% to 1.7 %), confirming the suitability of the A_{430} nm taken for the analytical signal. The negligible error at A_{430} has been confirmed also by the glucose dose-response curve obtained plotting sugar concentration versus both A_{430} and A_{max}. The regression curves were $y = 0.0098 (\pm 4.2 \times 10^{-4}) x + 0.0639 (\pm 2.7 \times 10^{-3})$ and $y= 0.0100(\pm 7.3 \times 10^{-4}) x + 0.0539(\pm 5.4 \times 10^{-4})$, respectively, with a mean slope difference of 2%.

3.3 Real samples analysis

The proposed assay was applied to commercial soft drinks (peach tea, black tea, coconut water, gaseous, cedrata, and tonic water), and apple extracts. Samples were also tested in parallel by ion chromatography. Table 2 reports data obtained for 5 replicates of each sample. Data obtained by ion chromatography were expressed as the sum of glucose and fructose. Ion chromatography confirmed that the samples contain mainly glucose and fructose, and the relative results are thus expressed in Table 2 as their sum (Glu + Fru). Ion chromatography calibration curves displayed high correlation coefficients ($R^2 \geq 0.998$, n = 3) with very good reproducibility for all the samples (RSD ≤ 4.1, n = 3).

The AgNPs-based assay allowed the successful determination of sugars content in all the soft drink samples, as reported in Table 2. Noteworthy, this result was achieved despite the substantial diversity among samples, giving very good reproducibility (RSD ≤ 7.2, n = 5). To further explore the applicability of the method in natural samples, apple extracts have been also assayed, obtaining comparable reproducibility (RSD ≤ 9.4, n = 5). Also in this case, for all the samples analyzed, the LSPR maximum resulted at 430 ± 10 nm, giving average AgNPs around 10 nm and the typical yellow to orange colorimetric trend,

depending on the amount of reacted sample (Fig. S2). It should be noticed that the most added sweeteners (particularly in soft drinks) and the predominant sugars in natural products are sucrose, glucose, and fructose. The acidic pH of these drinks generally leads to the slow conversion of sucrose into its two constituent sugars: glucose and fructose, whereas in natural samples (apple extracts in this case), glucose and fructose naturally result the most representative sugars. However, to quantify accurately sucrose in samples with comparable amounts of monosaccharides (and polyols), a hydrolysis step should be performed.

Linear correlations between data obtained by AgNPs-based assay and the reference method are reported in Fig. S3, demonstrating very good results (R = 0.994). The relative error (%) for sugars concentrations quantified by the AgNPs-based assay with respect to ion chromatography has been between -14.3 and + 9.9 % (Table 2). These data show that there are no significant differences between the two determinations, demonstrating an excellent accuracy of the developed assay.

3.4 Recovery and interferents study

Despite the good results obtained on the samples, recovery tests and interferents studies were carried out in order to better understand the applicability of the colorimetric assay. The soft drink samples have been pooled (same volume) mixed and then fortified at two known sugar concentrations (2.0×10^{-5} and 6.0×10^{-5} mol L^{-1} for monosaccharides and polyols; 2.0×10^{-4} and 4.0×10^{-4} mol L^{-1} for disaccharides). The spectra of the mix of the soft drink samples, fortified with increasing concentrations of each sugar, exhibited the same absorbance peak around 430 nm (data not shown). Quantitative and reproducible recoveries, calculated on the relative sugar calibration curve, were obtained. Table 3 reports the estimation of recovery and the precision obtained. The fortified samples have been diluted 1:50 (v/v) to fit the linear range. RSDs (n = 3) obtained for all monosaccharides/polyols and disaccharides resulted ≤ 10.2% and ≤ 12.4%, respectively, with recovery values ranging from 86.1% to 117.7%, demonstrating that the method is suitable for sugars detection in real samples.

Selectivity vs. other compounds commonly present in the samples was also tested. In fact antioxidant compounds as polyphenols present in food can produce AuNPs [23,24], and AgNPs. Also ascorbic acid is naturally present in several soft drinks at low level [36], but used as additive, up to 0.05 g 100 mL^{-1} can be often found [29,37].

For the apple samples assayed the amount of ascorbic acid and total polyphenols has been determined via HPLC. Ascorbic acid was found in the $1.8 \times 10^{-3} – 2.0 \times 10^{-3}$ g 100 mL^{-1} range while polyphenols (mainly chlorogenic acid, and low amounts of catechins and phlorizin) were in the $1.0 \times 10^{-3} – 1.2 \times 10^{-3}$ g 100 mL^{-1} range. According to the amount of interferences found in the samples, different amounts of ascorbic acid (from 0.01 to 0.075 g 100 mL^{-1}) and chlorogenic acid (from 1.0 to 1.5 g 100 mL^{-1}).have been spiked. No interference was found following the optimized AgNPs-based assay procedure. Indeed, the ratio between sugars and antioxidant compounds, in natural samples, results strongly in favor of sugars at least of

500/1000 fold. This statement, was confirmed even for the studied soft drinks and apple extract sample. In conclusions, has been proved that a sugars/antioxidants ratio of 100-fold results totally interferents free.

4. Conclusions

In this work for the first time AgNPs have been successfully employed to assess food sugars contents. Indeed, the AgNPs-based assay proposed demonstrates its wide exploitability both for single sugar determination and for the evaluation of mixtures of monosaccharides, polyols, and disaccharides in food samples. The ability of sugars and carbohydrates in reducing Au(III) and Ag(I) to MNPs is well-known. However, to the best of our knowledge, this is the first time that the AgNPs formation is used for quantitative purpose of determining sugars in real matrices with high analytical performances following a very easy protocol. The AgNPs-based assay here reported results fast, sensitive, one-step, and requires mild reaction conditions, representing undoubtedly a significant advancement vs. classical methods. Furthermore, it reacts with respect to a wide range of sugars commonly found in food and beverages. In conclusion, the AgNPs assay is able to quantify different classes of compounds individually and mixed, regardless of the sugar reducing ability and, without the use of enzymes, demonstrating very good sensitivity in particular towards monosaccharides and polyols. These features, make the AgNPs assay an excellent tool applicable by untrained personnel even in decentralized tests. Undoubtedly, the use of this strategy, with appropriate adaptations, in near future could be extended to other complex environmental or biological matrices.

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Tables

Table 1. Linear ranges, linear equations, determination coefficients, and relative reactivity obtained for different sugars by AgNPs-based colorimetric assay.

Sugars	Linear range (μM)	Linear equation (y=Abs. and x=μM)	L.eq. Slope Std. dev. (1/ μM)	L.eq.Intercept Std. dev. (Abs.)	Determination coefficient (R^2)	Relative reactivity (%) *vs*. glucose*
Monosacchrides						
Glucose	10 ÷ 90	y = 0.0098x + 0.0639	± 4.2E-04	± 2.7E-03	0.998	100.0 ± 4.3
Galactose	10 ÷ 90	y = 0.0091x + 0.0164	± 7.3E-04	± 1.3E-03	0.997	102.1 ± 8.2
Fructose	10 ÷ 90	y = 0.0101x + 0.0421	± 5.3E-04	± 2.2E-03	0.996	113.4 ± 5.9
Xylose	10 ÷ 90	y = 0.0103x + 0.0816	± 6.4E-04	± 5.1E-03	0.996	114.5 ± 7.1
Polyols						
Mannitol	20 ÷ 80	y = 0.0099x - 0.0275	± 8.1E-04	± 2.3E-03	0.994	111.1 ± 9.1
Sorbitol	20 ÷ 80	y = 0.0100x + 0.0319	± 4.4E-04	± 1.4E-03	0.999	112.2 ± 4.9
Xylitol	20 ÷ 100	y = 0.0094x - 0.0171	± 2.0E-04	± 3.6E-04	0.998	87.9 ± 1.8
Disaccharides						
Maltose	100 ÷ 900	y = 0.0008x + 0.2054	± 7.8E-05	± 2.0E-02	0.991	0.9 ± 0.1
Sucrose	100 ÷ 1000	y = 0.0006x + 0.1284	± 6.1E-05	± 1.3E-02	0.997	0.6 ± 0.1
Trehalose	100 ÷ 1000	y = 0.0007x + 0.1436	± 7.8E-05	± 1.6E-02	0.994	0.7 ± 0.1

*[(equation slope/ concentration 50% linear range)$_{standard}$ / (equation slope/ concentration 50% linear range)$_{glucose}$]x100, (n = 3 calibration curves).

Table 2. Data obtained by AgNPs-based assay and ion chromatography for soft drinks and apple extracts. Relative errors (%) of sugars concentrations detected AgNPs-based assay are referred to reference values determined by ion chromatography.

Sample	AgNPs assay (g 100 mL^{-1}, Glu. Eq.)	RSD (%, n = 5)	Ion chromatography (g 100 mL^{-1}, Glu + Fru)	RSD (%, n = 3)	AgNPs assay relative error (%)
Peach tea	3.0 ± 0.1	4.7	3.1 ± 0.1	2.7	+ 5.0
Black tea	3.6 ± 0.2	6.5	3.0 ± 0.1	3.6	- 14.3
Coconut water	4.7 ± 0.1	2.8	4.9 ± 0.0	1.0	+ 4.4
Gaseous	3.5 ± 0.2	7.2	3.5 ± 0.0	1.2	+ 0.9
Cedrata	9.4 ± 0.3	2.8	8.7 ± 0.8	9.0	- 6.6
Tonic water	6.1 ± 0.1	1.1	5.6 ± 0.1	2.1	- 8.0
Apple 1	1.7 ± 0.0	1.1	1.5 ± 0.0	1.1	- 10.2
Apple 2	1.1 ± 0.0	3.4	1.1 ± 0.0	1.8	0.0
Apple 3	3.3 ± 0.0	1.3	3.1 ± 0.1	3.1	- 4.6
Apple 4	2.4 ± 0.2	9.4	2.7 ± 0.1	4.1	+ 9.9
Apple 5	2.4 ± 0.0	0.7	2.3 ± 0.9	3.8	- 5.0

Table 3. Recovery and precision of the AgNPs-based assay, obtained for soft drink samples fortified with standard sugars.

Sugar	Spiked (μM)	Determined (μM)	Recovery (%)	RSD (%)	Spiked (μM)	Determined (μM)	Recovery (%)	RSD (%)
Glucose	20	21.3 ± 1.2	106.4	5.8	60	67.5 ± 4.9	112.5	7.2
Galactose	20	17.2 ± 1.6	86.1	9.1	60	60.6 ± 4.8	101.0	7.9
Fructose	20	23.2 ± 0.9	116.1	3.9	60	68.3 ± 3.0	113.8	4.5
Xylose	20	23.5± 1.8	117.7	7.8	60	61.6 ± 3.4	102.6	5.6
Mannitol	20	22.8 ± 1.8	114.3	7.9	60	59.8 ± 3.6	99.7	6.0
Sorbitol	20	18.5 ± 1.9	92.3	10.2	60	56.5 ±5.3	94.1	9.4
Xylitol	20	20.7 ± 0.4	103.5	2.1	60	56.3 ± 1.7	93.9	3.0
Maltose	200	218.3 ± 17.7	109.2	8.1	400	398.9 ± 35.5	99.7	8.9
Sucrose	200	194.0 ± 19.6	97.0	10.1	400	450.8 ± 35.6	112.7	7.9
Trehalose	200	205.6 ± 25. 5	102.8	12.4	400	421.1 ± 41.7	105.3	9.9

* mean value n = 3

Figure captions

Fig. 1. (**A**) Glucose solutions (20-90 μM) reacted in the optimized conditions; (**B**) corresponding absorbance spectra. (**C**) AgNPs spectra obtained using xylitol (20 and 60 μmol L^{-1}, red line) and sucrose (200 and 400 μmol L^{-1}, blue line).

Fig. 2. (A-C) TEM micrographs of AgNPs obtained with (**A**) glucose (**B**), sucrose, and (**C**) xylitol; (**D-F**) experimental estimation of particles size obtained by DLS on AgNPs obtained with (**D**) glucose, (**E**) sucrose and (**F**) xylitol.

Fig. 3. Dose-response plots obtained with increasing concentration of different sugars, by reading the absorbance at 425 nm. (**A**) monosaccharides: D-(+)-glucose, D-(-)-fructose, D-(+)-galactose, and D-(+)-xylose; (**B**) disaccharides: sucrose, D-(+)-maltose, and D-(+)-trehalose; (**C**) polyols: D-mannitol, D-sorbitol, and xylitol.

Figures

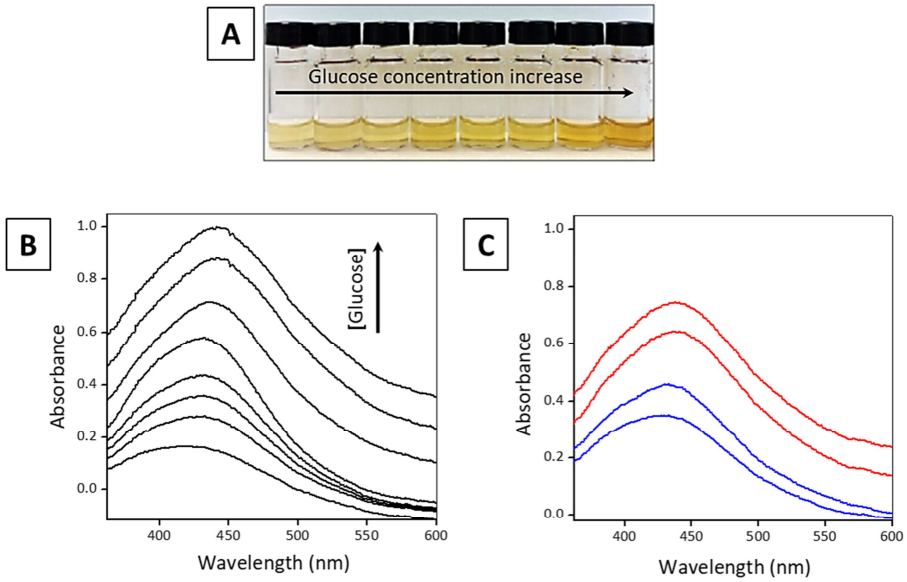


Fig.1.

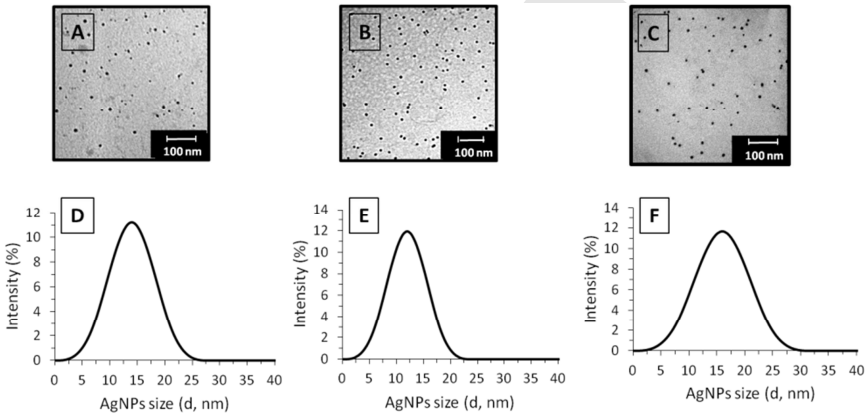


Fig.2.

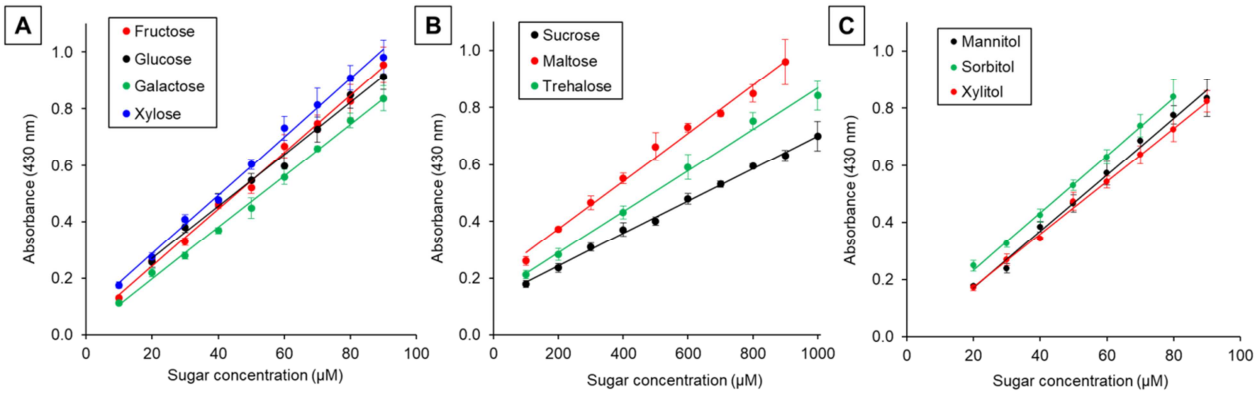
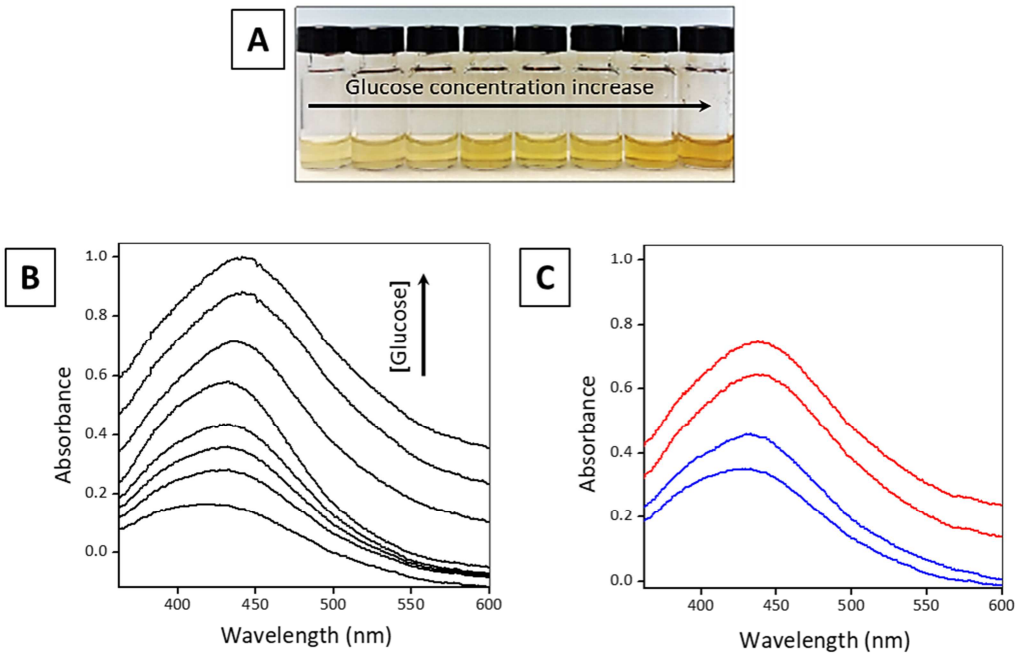
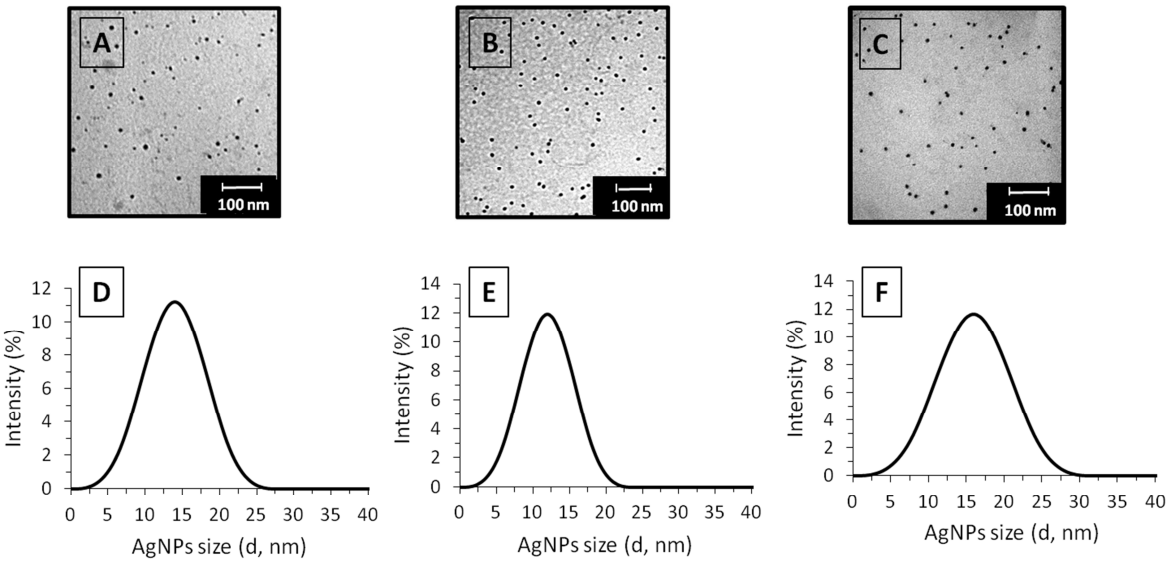
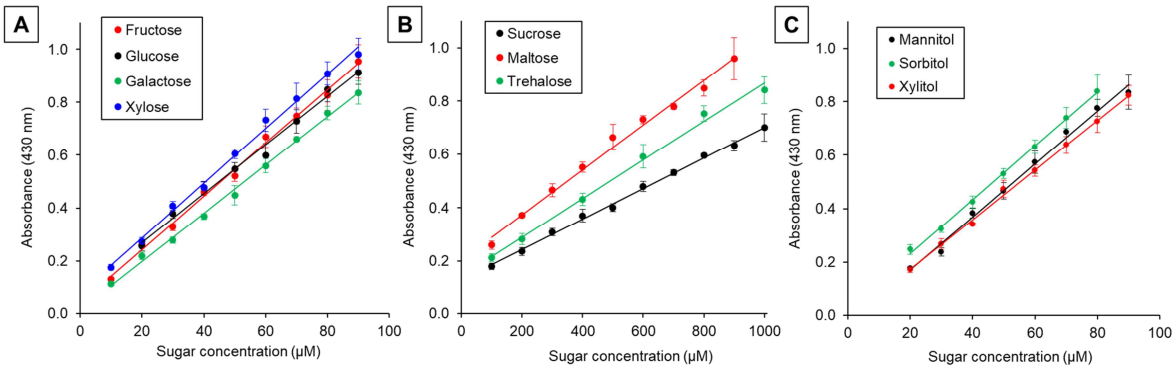


Fig.3.







Highlights

- Silver nanoparticles (AgNPs) were employed to estimate food sugars content
- A fast and simple silver nanoparticles colorimetric assay is proposed
- The ability to form AgNPs was tested and compared for different sugars
- The method was exhaustively applied for the determination of sugars in food samples
- The data obtained were found in good agreement with ion chromatography