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ARTICLE TYPE

# A novel spectrofluorometric method for the determination of arsenic in human hair using $Dy_2O_3$-doped $CeO_2$ nanoparticles

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The abstract should be a single paragraph which summarises the content of the article.

**This paper describes a simple and inexpensive method for the determination of arsenic in human hair samples based on spectrofluorometric detection. The applied $Dy_2O_3$-doped $CeO_2$ (DDC) nanoparticles were synthesized using microwave-induced combustion technique and subjected to the analytical samples containing As(V) species. At the optimum conditions (pH 6, DDC concentration 3 mg $L^{-1}$, and excitation/emission wavelengths 250 nm/352 nm), the fluorescence emission of DDC nanoparticles was diminished by increasing the As(V) concentration present in the medium. The co-existence ions present in hair were not interfered. A method for the speciation of As(III) and As(V) is also described. The method is validated using a well-known separation/spectrofluorometric method. There was no significant difference at the 95% confidence level between the results for the two methods. The proposed method is characterized by a wide analytical concentration range ($5.0\times10^{-8}$ –$1.0\times10^{-5}$ M), a detection limit for As(V) of $1\times10^{-8}$ mol $L^{-1}$ and relative standard deviation of 1.4%. The recoveries for the spiked amounts of As(V) was found to be 93.3 – 104.0%.**

***Keywords:*** *$Dy_2O_3$-doped $CeO_2$; nanoparticles; Arsenic; Fluorescence.*

## Introduction

Arsenic is a trace abundant element in the environment. Formerly, it was used in many industrial products, such as glass manufacture, pigment production, rodent poisons, insecticides, fungicides, medicines, printing, and tanning. Nowadays, application of arsenic products is limited owing to its toxic effects revealed in the recent years. However, previous applications of arsenic give rise to its spreading out in the environment and endanger of human health due to consumption of water or food contaminated with arsenic species [1]. It is reported that long term exposure to trace levels of arsenic causes chronic skin and cardiovascular disease [2]. Skin lesions, cancers and cardiovascular diseases are traceable to arsenic poisoning. Susceptibility to excessive amounts of arsenic causes gastrointestinal and cardiac damages [3]. Under the defense mechanism of body against diseases influenced of arsenic species, elevated amounts of arsenic may be found in tissues such as skin, hair and nails. It was detected that a large percentage of the population (30–40%) that is consuming arsenic-contaminated drinking water can have elevated arsenic levels in urine, hair and nails, while showing no noticeable clinical symptoms, such as skin lesions [4]. Hence, the trace determination of arsenic, especially in hair, nail and other biological tissues is of increasing importance in studies relevant especially to medicine, forensic, archaeology and nutrition. Human nails and hair have similar affinities for arsenic, but hair is more convenient to sample analysis than nails, and can identify chronic arsenic poisoning, provided that external contamination was excluded [5]. Retrospective studies suggested that arsenic in hair may be used as biomarker, even in samples that are many years old.

There are numerous analytical techniques available for the determination of total arsenic in biological materials, such as raman and infrared spectra methods [6,7], chemiluminescence analysis [8], inductively-coupled plasma-mass spectrometry (ICP-MS) [9], cathodic stripping voltammetry (CSV) [10], atomic absorption spectrometry [11,12], atomic fluorescence spectrometry [13], chromatography [14,15] and spectrophotometry [16]. Unfortunately, except that the last method, the other methods are troublesome, expensive, time consuming and requires highly trained personnel. The last one has also poor sensitivity and suffers from interference due to presence of other coexistence ions so that adequate detection limits are not obtained in treatment with many complicated samples. It is therefore necessary to develop simple new methods exhibiting high sensitivity and selectivity for ultra-trace determination of arsenic. The disquisitions on molecular fluorescence technique for the determination of arsenic have been rarely studied, and a few works correspond to assay arsenic species by molecular fluorescence technique has been reported

[17-19].

Metal oxide nanoparticles have been exploited extensively for removing and determination of arsenic species from contaminated environmental and biological samples. Among the various metal oxide nanoparticles, rare earth ones benefit from some advantages, such as richness valence states, variable electronic structures, natural abundance and high stability in aqueous media [20-22]. The most abundant and least expensive of rare earth metal oxides is cerium oxide ($CeO_2$) exhibiting specific physical and chemical properties. Hence, it has been extensively used in fuel cells as electrolyte materials of solid oxide [23], as catalysts [24], UV shielding [25], and chemical mechanical planarization materials [26]. Cerium oxide has the lowest solubility in high concentrated acidic media among the rare earth metal oxides. On behalf of its high adsorption capacity, it has been used as an effective adsorbent for removal of harmful anions including fluoride [27], dichromate [28], and arsenate [29] in aqueous media. These favorite properties could be enhanced by incorporating the rare-earth trivalent cations into the cerium oxide nanoparticles structure. This phenomenon gives rise to obtain highly functionalized cerium oxide nanoparticles exhibiting quantum confinement effects and fluorescence emission. Among the rare earth oxides, $Dy_2O_3$ is highly insoluble and thermally stable so that used for glass, optic, and ceramic manufactures. In this paper, a molecular fluorometric method was developed for the determination of trace amounts of arsenic in hair samples. The method is based on the sensitive inhibition effect of As(V) on the fluorescence intensity of the colloidal $Dy_2O_3$-doped $CeO_2$ (DDC) nanoparticles. Under the optimum conditions, the fluorescence quenching of the DDC system is directly proportional to the concentration of As(V) present in the media. A favorable selectivity towards the As(V) species was observed since the fluorescence intensity of the nanoparticles system is hardly influenced by coexistent substances. Significant factors influencing on the determination and speciation of arsenic were also investigated. The proposed method was then applied for trace As(V) determination in hair samples.

## Materials and methods

### Instrumentation

All fluorescence spectra and fluorescence intensity measurements were done with a RF-5301PC spectrofluorometer (Shimadzu. Japan) equipped with a xenon discharge lamp and 1 cm quartz cell at room temperature (25 ± 2 °C). Adjusting the pH was conducted with a Corning model 125 pH-meter. A LBC24 model 285 W ultrasonic generator was used for contact with the material all of which had been used in the experiments. The zeta potential of the nanoparticles was measured by the Zetasizer (Nano-ZS) from Malvern Instrument. The morphology of the synthesized nanoparticles was investigated by transmission electron microscopy (TEM) using a Philips-CM10 HT-100KV model.

### Reagents and solutions

All chemicals were of analytical grade and used without further purification. $Na_2HAsO_4 .7H_2O$ and $NaAsO_2$ were purchased from Fluka (Buchs, Switzerland). The other chemicals were purchased from Merck (Darmstadt, Germany). All solutions were prepared with Ultra-pure distilled deionized water (DDW) obtained by a Milli-Q water purification system. All glassware was cleaned by soaking in 10% $HNO_3$ and washed carefully with DDW. Stock solutions of As(V) were prepared with concentration of 1000 mg $L^{-1}$. Working solutions from each one of the As(V) species were made up daily by appropriate dilutions. A colloidal solution of DDC nanoparticle with concentration of 30 mg $L^{-1}$ was prepared by sonication the mixture for 20 min. The buffering systems of HCl/KCl (pH 1–3), acetic acid/acetate (pH 3–5), Tris/HCl (pH 5–8), and $NH_4Cl/NH_3$ (pH 8–11) with concentration of 0.1 M were prepared to adjust the pH of the experimental solutions.

### Collection and preparation of hair samples

The proposed method was used for determination of arsenic in several natural hair samples from male and female barber shops in Birjand, Iran. All samples were kept in sealed plastic bags and stored at room temperature. The hair samples were washed once with acetone, twice with tap water, three times with DDW, and twice more with acetone, respectively. The hair samples were then dried in an oven at 70 °C for 20 min. The analysis was carried out on portions of 3-g of the dried hair samples. Each sample was treated with 6 ml of $HNO_3$–$HClO_4$ (4:1) mixture and heated for 2 h at 85 °C until a clear solution was obtained. The heating was gently followed till a moisture residue was remained. Subsequently, the residue was dissolved in 10 mL DDW and subjected to the experiments.

### Synthesis of Dy2O3-doped CeO2 nanoparticles

$Dy_2O_3$-doped $CeO_2$ nanoparticles (DDC) were synthesized through the following process. Initially, 0.01 mol of cerium nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$), and stoichiometric amounts of urea ($CO(NH_2)_2$) dissolved in minimum quantity of water were mixed with 0.55 mmol of dysprosium oxide ($Dy_2O_3$) dissolved in nitric acid (1M). The resultant mixture was placed in a domestic microwave oven (1000 W) that worked in a duty cycle power of 30%. The heating was followed for 15 min till a yellowish precipitate was appeared. During the combustion under the microwave radiation, an oxidation/reduction process was taken place in which DDC nanoparticles together with large amounts of gases ($O_2$, NO, $N_2$, $NH_3$, and HNCO) were produced. The residue was cooled to room temperature, and then washed several times with DDW to remove any possible ionic species. At last, the products were dried in an oven at 60 ºC overnight.

### Spectrofluorometric determination procedure

For the determination of As(V) species, 10 mL solution containing up to 7.5 μg ($1\times10^{-5}$ M) of As(V) ions was taken in a suitable vessel. After adjusting its pH to 6.0 by addition of 1 mL of the buffer solution, 1 mL of the colloidal solution of DDC nanoparticle was added to it and the mixture was sonicated for 20 min. The fluorescence intensity of the mixture was then recorded at 352 nm against the excitation wavelength of 250 nm. Both slit widths of excitation and emission were 5 nm. The quenching of fluorescence intensity influenced by the As(V) concentration are observed in Fig. 1.

## Results and discussion

### The synthesis process

The reaction temperature and heat duration influence on the phase structure and particle size of the $CeO_2$ nanoparticles products [30]. Generally, prolongation of the reaction time gives rise to increase the particle size. At low temperature or short reaction time, the crystal growth rate is lesser than the nucleation

formation rate resulting in small particle size formation. In such conditions, the particle size of the ceria nanoparticles formed is not naturally controllable. Hence, achievement to homogenous nanoparticles is not feasible. These synthesis routs lead to nanoparticles having surface defects and wide range size distribution, which is prejudicial to optical performance. Considering microwave-induced combustion has been recently used for the preparation of homogenous nanosized oxides, it was used for preparation of DDC nanoparticles. The microwave-induced combustion synthesis process involves the dissolution of the reactants in water followed by heating the solution in a microwave oven. The urea and metal nitrates decompose and generate flammable gases such as $NH_3$, HNCO, $O_2$, and NO. After the solution reaches the point of spontaneous combustion in which a solid residual becomes to form, it burns at the temperature over 500℃. Combustion is completed when all the flammable substances are consumed. The resulting material is a loose, highly friable substance exhibiting cavities and pores formed by the escaping gases during the combustion reaction. The whole process takes only a few minutes to yield DDC nanoparticles. To optimize Dy amount, the reaction temperature and heat duration, various Dy percent (5.2%, 11%, and 17.6%) duty cycle powers(10 – 50%), and reaction times (5 – 30 min) were examined. The experiments showed that 11% Dy, 30% duty cycle power and 15 min heat duration are sufficient to produce homogenous DDC nanoparticles. In such condition, the temperature yielded is in the range of 500 – 800℃.

**Effect of DDC nanoparticles concentration**

The concentration of DDC nanoparticles is the main factor influencing not only on the fluorescence intensity, but also the sensitivity of assay. As shown in Fig. 2, with increasing the concentration of DDC nanoparticles more than 2.5 mg $L^{-1}$, the sensitivity is significantly reduced due to the nanoparticles aggregation process, which causes to self-quenching the fluorescence intensity observed. However, the low concentration of nanoparticles gives rise to exposure insufficient sites for the adsorption process, resulting in narrow linear range and low intensity. Accordingly, the DDC nanoparticles concentration of 2.5 mg $L^{-1}$ was selected as the optimum concentration for the future investigations.

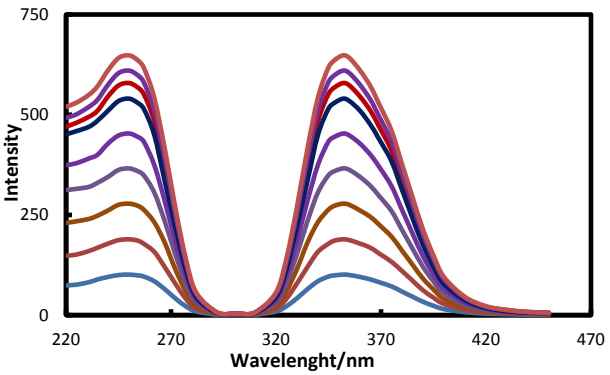


Fig 1. The fluorescence excitation (left) and emission (right) quenching of DDC nanoparticles upon addition of As(V) species at different concentration. The concentration of As(V) ions from top to bottom are: blank, 3.75, 37.5, 75, 225, 375.0, 487.5, 600, and 750 μg $L^{-1}$

**Effect of pH**

The pH of the solution plays an important role in the determination process. Decreasing pH of the solution helps to lay the protonation of arsenate ions and weakens their adsorption abilities. Hence, effects of pH on the fluorescence intensity of the aqueous DDC nanoparticles at the presence and absence of arsenate was investigated in the range of 1 – 11 with the same initial As(V) concentration and nanoparticle (375 μg $L^{-1}$, 2.5 mg $L^{-1}$, respectively).

On the other hand, considering the zeta potential, which is the overall charge of a particle acquires in a specific medium, the stability of the colloidal system influenced by the pH is necessary to investigate. The zeta potential of colloidal dispersions of DDC nanoparticles was measured in different pH media. As observed in Fig. 3, the zero point of zeta potential of the DDC nanoparticles was found to be at pH 4.2 in which the colloidal system is the least stable due to the absence of particle surface charges. Consequently, the surface of the mixed oxide should be positive at pH below 4, which is unfavorable for the formation of a defect-free surface. As depicted in Fig. 4, both $F_0$ and $F$ showed maximum values at pH 4 regardless the presence of As(V) species ($F_0$ and $F$ are the fluorescence intensity of the aqueous DDC nanoparticles at the absence and presence of As(V) species). By increasing pH of the solutions, $F$ more drastically decreased so that no intensity was observe at pH 6. On the other hand, the maximum difference between the nanoparticles fluorescence intensity ($F_0 - F$) was obtained at pH 6. Considering the dissociation constants of arsenic acid, $H_2AsO_4^-$ is the dominant form of As(V) species present at pH 6 competing with $OH^-$ to adsorb on DDC nanoparticles. Evidently, buffering the solutions at pH 6 prevents to compete $OH^-$ ions with As(V) species during the adsorption process. In addition, As(III) species cannot adsorb on the DDC nanoparticles since they are present as $H_3AsO_3$ form. In such condition, inorganic speciation of arsenic i.e. the determination of As(V) species at the presence of As(III) is feasible.

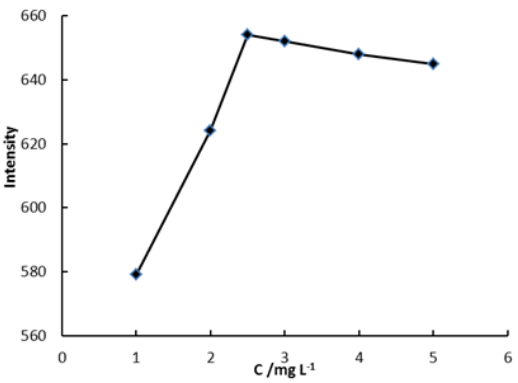


Fig. 2. Effect of the concentration of aqueous DDC nanoparticles ($C_{As(V)}$ : 7.5 μg $L^{-1}$) on fluorescence intensity

**Effect of solvent**

Usually, solvent properties influence on photoluminescence intensity. In some criteria, binding the analyte to surface of the nanoparticles facilitates at the medium with lower polarity. Hence, to study the effect of solvent on the adsorption of As(V) species, the DDC nanoparticles were dispersed in three different 50% mixed-solvents media including acetone, ethanol, and methanol at the presence of As(V) species with concentrations of 3.75 and 7.5 μg $L^{-1}$. According to the results present in Table 1, it

is clear that the maximum difference fluorescence intensity ($F_0 - F$) occurred in the absence of any organic solvent. Furthermore, the results showed that better linearity and higher sensitivity is feasible in aqueous media.

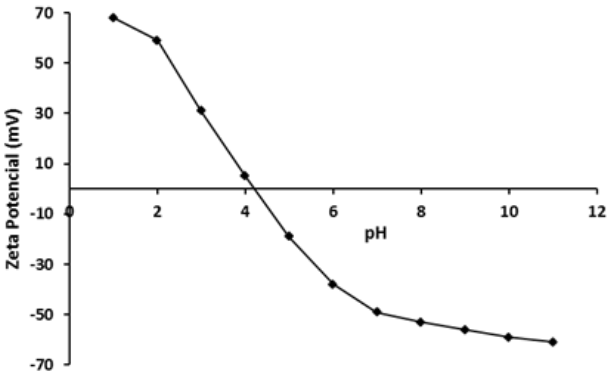


Fig.3. The zeta potential of DDC naoparticles dispersed in aquous media at various pH values

**Sonication time and persistence of fluorescence intensity of DDC nanoparticles**

The sonication time is the main parameters influencing on favorable dispersion of nanoparticles system either at the absence or presence of the target species. Hence, the effect of sonication time on fluorescence intensity of DDC nanoparticles either at the absence (*F0*) or presence (*F*) of As(V) species was investigated in the range of 5 – 60 min. Fig. 5a shows dispersion of the DDC nanoparticles with the concentration of 30 mg $L^{-1}$ in the solution after the sonication process. It is detected that the nanoparticles have been homogenously distributed in the entire of the solution so that the distribution has been extended to the nanoparticles in the range of 5 – 15 nm. The results showed that $F_0 - F$ reached to a maximum value with performance of 20 min sonication, as depicted in Fig. 5 b. After that, the fluorescence intensity of DDC nanoparticles regardless the presence of As(V) species was stable basically for 5 h at room temperature. In addition, the fluorescence intensity of DDC solution with concentration of 2.5 mg $L^{-1}$ exhibited remarkable stability as long as 3 days storage in dark glass bottle.

Table 1. The changes in Fluorescence intensity of DDC nanoparticles at the presence of As(V) species in three different solvent media

| *As(V) concentration ($\mu g\ L^{-1}$)* | *Fluorescence intensity* | | |
|---|---|---|---|
| | 100% Water | 50% Water/ethanol | 50% Water/methanol |
| 375 | 294 | 271 | 198 |
| 37.5 | 54 | 48 | 25 |

**Recovery of As(III) to As(V)**

Under the selected conditions described above, recoveries of As(III) and As(V) from a solution containing both types the species with equal concentration of 37.5 µg $L^{-1}$ were investigated. The determination of As(V) was carried out just according to the proposed method in treatment with 10 mL aliquot of the solution. To the similar aliquot of the solution, 1 mL of 10% $H_2O_2$ dissolved in 0.2 M HCl was added and it was shaken for a few minutes to oxidize the As(III) species. It was then boiled to remove the residual $H_2O_2$ content. After adjusting its pH and volume respectively to 6 and 10 mL, the solution was subjected to the As(V) determination process. The As(III) concentration was determined by subtracting As(V) concentration from the total arsenic content. The recovery of As(V) was found to be 103.2 ± 1.2%, whereas a value of 97.8 ±2.4% was obtained for As(III) species. This performance confirms feasibility of the method to determine inorganic arsenic species.

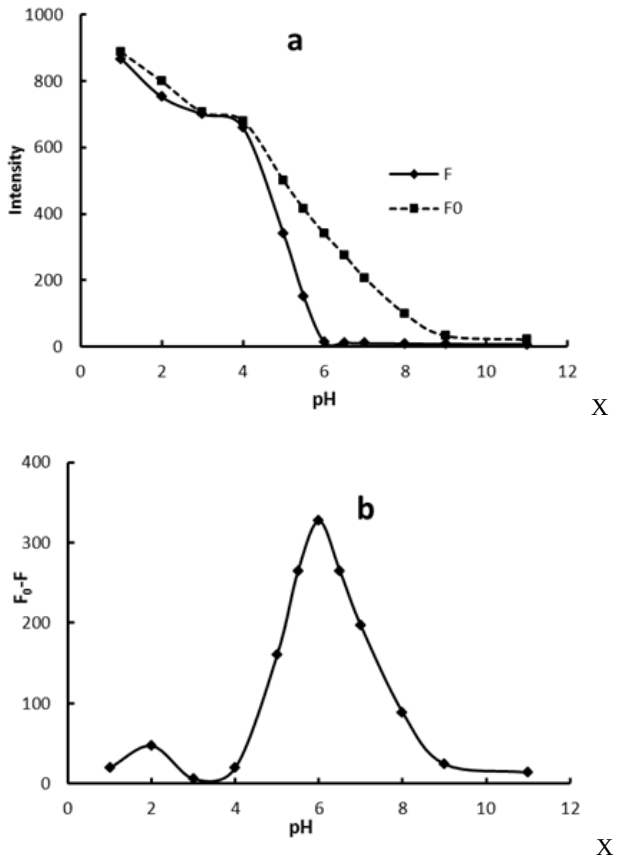


Fig. 4. $F_0$ and $F$ are the fluorescence intensity of the aqueous $Dy_2O_3$-doped $CeO_2$ without and at a given As(V) concentration (375 µg $L^{-1}$)

**Effect of co-existence substances**

To evaluate the usefulness of the method, the effects of co-existence ions which may be found in human hair were studied in treatment with a series of As(V) solutions with concentration of 37.5 µg $L^{-1}$ to which increasing amounts of interfering substances were added. The determination of As(V) was then carried out according to the procedures described in the experimental section. The tolerance limit was defined as the highest amount of foreign ions that produced an error not exceeding 10% in the determination of As(V) respect to the measuring alone. As detailed in Table 2, all the co-existence substances with this concentration level are not interfered. It is notable that some of the tolerable values are greater than that usually found in human

hair. This feature denotes on high capability of the proposed method to reliable determination of arsenic in either diseased or healthy human hair.

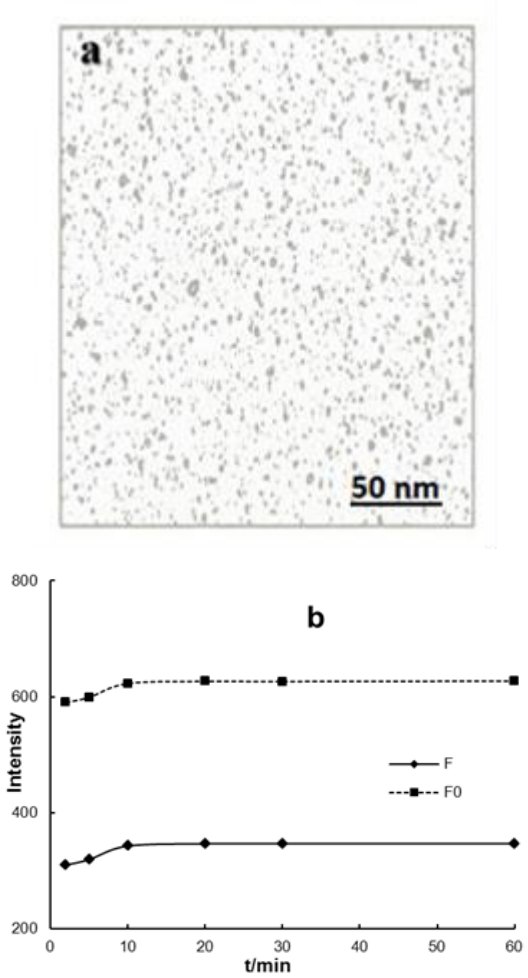


Fig 5. a: TEM image of the dispersed DDC nanoparticles after the sonication process; b: The relationship between the sonication time and fluorescence intensity of DDC nanoparticles at the absence ($F_0$) and presence (F) of As(V) species

**Analytical performance**

Under the optimal conditions, a linear relationship between the quenched fluorescence intensity of the DDC nanoparticles and concentration of the As(V) species present in the samples ($C_M$) was observed in the range of $5\times10^{-8}$ – $1\times10^{-5}$ M (3.75 – 750 µg $L^{-1}$). The linear regression equation was $F_0 - F = \Delta F = 5.42\times10^7\ C_M + 8.21$ with a correlation coefficient of $R^2$= 0.9992, where $C_M$ is the molar concentration of As(V) species. From seven blank solutions, the detection limit ($C_{DL}= 3\Delta F_{dL}m^{-1}$; $\Delta F_{dL}=\Delta F_B + 3S_B$, where $\Delta F_{dL}$ is the signal for detection limit, m is the slope of calibration curve, $\Delta F_B$ is the mean of blank signal and $S_B$ is the standard deviation of blank signal [31]) was obtained as 0.75 µg $L^{-1}$ ($1\times10^{-8}$ M). The relative standard deviation for seven determinations of 37.5 and 75.0 µg $L^{-1}$ of As(V) were 1.40% and 1.34%, respectively. The results indicated that the method has good precision.

Table 2. Tolerance of co-existence ions which may be found in human hair

| Foreign substance | Conc. ratio (Co-ex. ion/As(V) | Change of $\Delta F$(%) |
|---|---|---|
| $I^-$ | 50 | 2.09 |
| $SO_4^{2-}$ | 100 | 6.7 |
| $NO_3^-$ | 50 | 0.89 |
| $CO_3^{2-}$ | 50 | 0.53 |
| $HPO_4^{2-}$ | 1 | 9.09 |
| $Cr_2O_7^{2-}$ | 100 | 0.40 |
| $Cr^{3+}$ | 100 | -1.74 |
| $Zn^{2+}$ | 100 | 1.04 |
| $Cu^{2+}$ | 100 | 5.7 |
| $Ni^{2+}$ | 100 | 6.37 |
| $Pb^{2+}$ | 100 | 0.78 |
| $Co^{2+}$ | 100 | -2.01 |
| $Mn^{2+}$ | 100 | 4.7 |
| $Ca^{2+}$ | 100 | 0.9 |
| $Mg^{2+}$ | 100 | -7.57 |
| $Na^+$ | 100 | 4.5 |
| $K^+$ | 100 | -2.75 |
| $WO_4^{2-}$ | 25 | 5.9 |
| $SeO_3^{2-}$ | 25 | -8.5 |
| $Bi^{3+}$ | 25 | -9.9 |

**Analytical application**

To examine applicability of the method, As(V) content of male and female hair samples was determined as discussed in the experimental section. Five replicate samples were prepared for each of the products and the experiments were repeated at least three times. For comparison, the samples were also analyzed using a well-defined method for determination of As(V) species in which arsenate ions after extraction with Amberlite IRA-410, were subjected to L-cysteine capped CdS quantum dots (QDs) and the fluorescence quenching of the QDs due to reduction of As(V) by L-cysteine was considered as a signal relevant to As(V) concentration [32]. In addition, to ensure from reliability of the circumstance, fixed amounts of As(V) were spiked to both series of the samples. The results obtained from the both methods are shown in Table 3. As it is observed, no significant differences were observed using the F and *t* tests at 95% confidence level between the two methods.

**Conclusion**

Microwave-assisted heating method has been successfully used for the preparation of DDC nanoparticles. Based on the quenching of fluorescence intensity of DDC nanoparticles, a simple spectrofluorometric method for the determination of trace quantities of arsenic with spread dynamic range and the trace level of detection limit was suggested. The method was found to be fast and convenient for ultra-trace determination of As(V) ions. Due to high stability of DDC nanoparticles and simple preparation of its colloidal solution, the proposed method can be employed in many laboratories. The significant characteristic future of this work is that the accuracy, selectivity, sensitivity, and linearity in spite of its simplicity are excellent. Application of the proposed method on determination of arsenic in hair samples attended to acceptable results since favorable recoveries were

obtained by spiking As(V) ions to the samples.

Table 3. Determination of As(V) in human hair samples. The results are mean of three measurements ± standard deviation.

| *Human hair sample* | *As(V) Spiked* ($\mu g\ L^{-1}$) | *Proposed method* | | *Reference method [32*[a] | | | |
|---|---|---|---|---|---|---|---|
| | | As(V) found ($\mu g\ L^{-1}$) | Recovery (%) | As(V) found ($\mu g\ L^{-1}$) | Recovery (%) | *F*-test[a] | *t*-test[b] |
| Female 1 | – | 29.7±0.8 | – | 28.5±0.7 | – | 1.00 | 2.77 |
| | 7.5 | 37.5±0.9 | 104.0 | 36.2±0.7 | 105 | 1.96 | 2.81 |
| Female 2 | – | 39.0±0.5 | – | 38.2±0.6 | – | 1.44 | 2.52 |
| | 37.5 | 75.0±1.2 | 96.0 | 77.4±1.3 | 104 | 1.17 | 0.86 |
| Male 1 | – | 15.5±0.7 | – | 14.7±0.7 | – | 1.78 | 1.98 |
| | 7.5 | 22.5±0.5 | 95.3 | 22.1±0.4 | 99 | 1.00 | 1.39 |
| Male 2 | – | 19.8±0.5 | – | 20.3±0.3 | – | 2.78 | 2.17 |
| | 37.5 | 56.2±0.8 | 97.0 | 55.8±0.7 | 95 | 1.31 | 0.92 |

[b] Tabulated *F*-value at 95% confidence level is 6.39.

[c] Tabulated *t*-value at 95% confidence level is 2.78.

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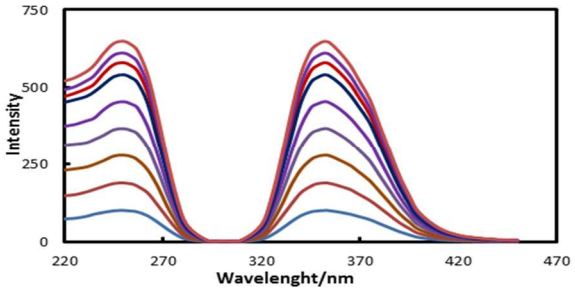
**Colour graphic:**




**Highlighting the novelty of the work:**

This paper describes a novel spectrofluorometric method for the determination of arsenic in human hair using $Dy_2O_3$-doped $CeO_2$ nanoparticles.