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Contributed Paper

Miniaturized Green Analytical Method for Determination of Silver Ions Using C-phycocyanin from Cyanobacteria as an Ecofriendly Reagent

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ABSTRACT

Green analytical chemistry methods have attracted increasing attention for sustainable development in analytical laboratories. Miniaturization of analytical devices and replacement of chemical regents with ecofriendly ones are key steps to realizing the objectives of green analytical chemistry. This work describes a microfluidic-based micro-flow injection analysis (μ-FIA) system for determination of silver ions (Ag^+) in water samples using C-phycocyanin extracted from cyanobacteria as a natural and safe colorimetric reagent. The μ-FIA system is comprised of a 30 × 30 square polymethylmethacrylate platform on which the microchannel architecture has been engraved with a CO_2 laser. The microchip was sandwiched between two polydimethylsiloxane sheets for packaging and to facilitate its integration with fiber optic spectrometer for signal monitoring, and a multi-syringe pump for delivery/manipulation of solutions. At optimized operating conditions, the system response was linear over the range 0.080–2.40 mg L^{-1} with a R^2 of 0.9996, and the detection limit was 25 μg L^{-1}. The developed method was applied to analysis of Ag^+ in drinking water, river water and wastes, and the results were comparable with those from the standard inductively coupled plasma optical emission spectrometry method. The outstanding features of this system are the low consumption of reagents by the microfluidic device, and the replacement of toxic reagents with natural, ecofriendly alternatives.

Keywords: microfluidic, micro-flow injection analysis, natural reagent, silver ion, C-phycocyanin, green analytical chemistry

1. INTRODUCTION

The growth of urbanization and industries worldwide has raised serious health concerns because large quantities of hazardous pollutants are released into the environment[1]. Heavy metal pollutants are discharged/emitted into the environment from various anthropogenic activities such as industry[2] and agriculture[3]. Although heavy metals occur naturally in the Earth's crust, the evolution of urbanization has increased the quantities of metals deposited onto the Earth's surface to several times the background levels from natural sources. These ions could damage environmental systems and impair human health when their levels exceed permissible limits[4].

Silver is classified as very toxic to the cells and functions[5] of some aquatic organisms, and might also damage some beneficial microbes[6]. There has been considerable evolution in the applications of silver in medicine, dentistry, photography, electronic and electrical uses, jewelry, coins, and mirrors[7]. Silver nanomaterials reportedly make up 30% of the total nanomaterials in consumer products[8]. Silver waste discharged into the environment is potentially harmful if not pretreated properly[9]. Depending on the surroundings, silver can exist as groups of particles, aggregates, or soluble ions[6]. Among these forms, free silver ions (Ag^+) are the most toxic form to aquatic organisms[10]. It can be produced by transformation of other forms of silver, and can be fatal even at low concentrations[11]. Silver salts are also used for antibacterial applications in some water purification processes[12]. To avoid toxicity issues, the release of silver waste into the environment should be controlled. The World Health Organization has suggested a limit of 0.1 mg L^{-1} Ag^+ contamination in drinking water[10]. To gauge if water meets this limit, the levels of Ag^+ should be monitored regularly in various water samples.

Several electroanalytical and spectrophotometric methods are available for the determination of Ag^+, including polarography, colorimetry, spectrography[13], flame atomic absorption spectrometry [14,15], graphite furnace atomic absorption spectrometry [16], inductively coupled plasma optical emission spectrometry [17], and inductively coupled plasma mass spectrometry [18]. Colorimetric technique needed reagent consumption and toxic chemical. However, most of these techniques used expensive equipment and huge instrument. Some spectrometric methods have been developed for determination of Ag^+ using colorimetric reagents such as dithizone[19,20], 2,3-naphthotriazole[21], and 2-mercaptopyridine *N*-oxide sodium reagent[22]. However, these reagents can be toxic to aquatic life.

Armenta et al.[23], first postulated the concept of green analytical chemistry (GAC) in 2008, and the idea has attracted the attention of many researchers. One of the 12 principles of GAC established by Gałuszka et al.[24], is the use of renewable sources of safe reagents. Natural products are good examples of reagents fulfilling GAC criteria. Numerous methods using natural reagents have been developed for determination of heavy metals. These include cyanidin extracted from red cabbage for the detection of Cu^{2+}, Pd^{2+}, Al^{3+}, and Fe^{3+} by the naked eye[25], determination of Hg^{2+} using chlorophyll extracted from peas leaves in a fluorometric method[26], and the use of a slippery elm leaf extract for spectrometric determination of Mo^{6+}[27].

The use of flow injection and micro-flow injection analysis enables high sample throughput at reduced cost[23, 24, 27-29]. The use of natural reagents with these devices allows for development of convenient and sustainable GAC methods that use ecofriendly regents and release few (or no) hazardous wastes. The use of natural regents for detection of metal ions with flow systems has been reported in many publications, for instance, the detection of Fe^{3+} using guava leaf [30] and green tea extracts [31,32], and the determination of Al^{3+} using a reagent extracted from *Morinda citrifolia* root [33] and heartwood of *Caesalpinia sappan Linn*[34]. In addition, powdered lime and turmeric have been used as natural base

and indicator, respectively, in a sequential injection system for acetic acid determination[35].

In this article, we applied biotechnology and the lab-on-a-chip concept to design a GAC system for the determination of Ag^+. This was realized using C-phycocyanin (C-PC), which is a cyanobacteria extracted from *Oscillatoria* sp., as a natural colorimetric reagent in a microfluidic system fabricated on a chip. The system was integrated with optical spectroscopy via an optical fiber for signal monitoring. The developed miniaturized analytical system was applied to determination of Ag^+ ions in real water samples, and the accuracy was compared with that of ICP-OES.

2. MATERIALS AND METHODS

2.1 Reagents and Chemicals

All chemicals were of analytical-reagent grade or better. A stock solution of Ag^+ (1000 mg L^{-1}) was prepared by dissolving appropriate quantities of silver nitrate ($AgNO_3$) (Carlo Erba, France) in deionized water. The stock solution was kept in an amber bottle in a refrigerator. For construction of calibration graph, a series of standard Ag^+ solutions (0.010, 0.050, 0.080, 0.10, 0.20, 0.40, 0.80, 1.20, 1.60, 2.00, and 2.40 mg L^{-1} of Ag^+) were prepared daily from the stock solution by dilution with deionized water. Phosphate buffer solution (0.1 mol L^{-1}, pH 9.0) was prepared by dissolving 14.2 g of disodium hydrogen phosphate (Univar, USA) and adequate amounts of hydrochloric acid (Lab-scan, Ireland) in water.

Wet biomass of cyanobacteria *Oscillatoria* sp. was obtained from the Plankton and Algae Research Unit, Department of Biotechnology, Faculty of Science and Technology, Thammasat University. The C-PC was extracted using the freeze–thaw technique [36]. Briefly, the wet biomass was resuspended in 0.1 mol L^{-1} phosphate buffer (pH 7.0) to achieve a wet biomass volume fraction of 20%. The biomass suspension was subjected to five freeze–thaw cycles at 24 h intervals. Then, the solutions were centrifuged at 5000 rpm for 10 min., and analyzed for the C-PC concentration following the method of Bennett and Bogorad [37]. The concentration of C-PC in the crude extract was about 1.3 mg mL^{-1}. The crude extract was then aliquoted and kept at −20 °C for use throughout this research.

2.2 Design and Fabrication of the Microfluidic Chip

The microchannel architecture network was engraved onto a polymethymethacrylate chip (30 × 30 × 10 mm) with a CO_2 laser (Laser1325, CNCBro, China) at an etching rate of 100 μm s^{-1} at 20% power. The chip was sandwiched between two 1.5-mm thick polydimethylsiloxane sheets prepared by mixing a silicone elastomer (Sylgard 184, Dow Corning, USA) and a curing agent at a mass ratio of 10:1. The chip was connected to the samples and reagent via polytetrafluoroethylene tubing (0.5 mm i.d.) with two inlets and one outlet (Figure 1d). To enhance the mixing capacity [38], a split channel with 34 split zones was fabricated to increase the rate of the colorimetric reaction (Figure 1g).

2.3 Apparatus and Analytical Procedure

A schematic diagram of the developed μ-FIA device coupled with a spectroscopic detector is shown in Figure 1. The two inlets allow for introduction of deionized (DI) water as a carrier and the reagent (C-PC) into the microchip, and waste is discharge from the outlet. The channel is triangular geometry with a width of 250 μm (Figure 1h), depth of 450 μm (Figure 1g), length of 400 mm, and volume capacity of 23 μL. The channel network contains a 1.5-mm flow cell with a volume of 17 μL and path length of 1 cm. A multi-syringe pump (LSP 10-1B, Longer Pump, China) made of two 10-mL syringes (Nipro, Thailand) was applied to deliver the C-PC reagent and carrier (DI water) through 0.5-mm i.d. polytetrafluoroethylene tubing (VICI, USA) into the microfluidic device. The sample was injected into the carrier stream of DI water by a six-port valve (Ogawa, Japan). The colorimetric

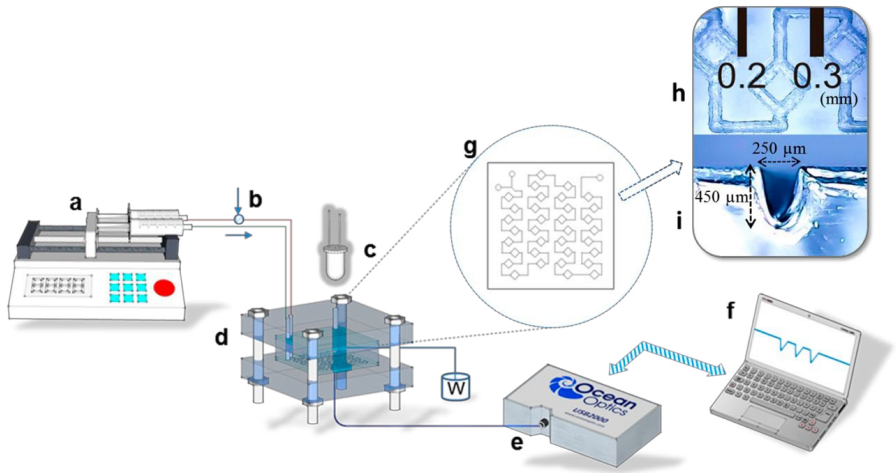

Figure 1. Graphical diagram represents microsystem components ; (a) Syringe pump, (b) Six-port valve, (c) White LED light source, (d) Microfluidic device, (e) Fiber optic – USB detector, (f) Computer, (g) the chip design and microchannel character; (h) microchannel dimension (50X), and (i) cross-section (200X) picture captured with a portable microscope.

reaction occurred inside the micro-reactor (split channels) and the solution then flowed to the detection area, which was connected to a fiber optic probe, USB2000 detector (OceanOptics, USA), equipped with a white LED light source. The wavelength was fixed at 617 nm for signal observation. OCEAN software (SpectraSuite) was used for data acquisition from the detector. The peak height was converted to positive peak and measured in the absorbance unit by eDAQ software (HBM, Germany). Three replicate injections were analyzed for each solution. The operating procedure of this µ-FIA system is demonstrated in the animation presented in the Supplement. For comparison, the samples were also analyzed by ICP-OES (Optima 8000, PerkinElmer, USA).

2.4 Sample Preparation

The performance of the developed analytical method was tested using different water samples. Three brands of commercial, bottled drinking water were obtained from a local Thai market, and 10 natural water samples were acquired from the Chao Phraya River (Pathumthani Province, Thailand). Each sample was filtered through filter paper (No.1, Whatman), stored in a polyethylene bottle at 4 °C, and analyzed within 1 h of collection. The last samples were collected from four waste bottles of chemistry laboratory of Thammasat University and diluted if necessary.

2.5 Study the Effect of Interferences

To examine the selectivity of the proposed method, samples were spiked with some cations and anions commonly present in water ; Mg^{2+}, Bi^{3+}, K^{+}, Fe^{3+}, NH_4^{+}, Al^{3+}, Mn^{2+}, Fe^{2+}, Zn^{2+}, Ni^{2+}, Ca^{2+}, Cu^{2+}, Pb^{2+}, Cr^{3+}, Hg^{2+}, SO_4^{2-}, ClO_3^{-} and SO_3^{2-}. A solution of Ag^{+} (0.10 mg L^{-1}) was mixed with solutions containing different concentrations of the above ions. An ion was considered to be an interfering species when an error greater than 5% was produced.

3. Results and Discussion

3.1 Effect of the Ag^{+} on C-PC Absorbance

C-PC contained multiple chromophore with multiple electron donor and amino acid (Figure 2 a). To evaluate the effect of the Ag^{+} on

the C-PC absorbance, the fiber optic probe was used to scan the spectra over the wavelength range 435–685 nm before and after addition of Ag^+ in phosphate buffer (pH 9). A perceptible reduction in the C-PC absorption occurred as result of the coordination with Ag^+ (Figure 2 b). As work of Han et al.[39], after adding Ag^+, α-helix structure of C-PC is transformed to β-sheet/β-turn and the coordinated with Ag^+ through –NH and C=O region of billins and amino acid residues.

To accelerate the colorimetric reaction of C-PC with Ag^+, the design should incorporate integrated mixing enhancing elements within the microchannel configuration. In the present device, the split channel option was used to realize this objective. In the split zones, the velocity of the solution is half that in the normal channel. With the 34 split zones, the fluidic stream split and merge repeatedly 34 times along the microchannel network, which allows for many interactions in the micro-reactor. Optimization of the system parameters are described in the following sections.

3.2 System Optimization

The initial operating conditions were a flow rate of 200 μL min^{-1} and C-PC concentration of 130 mg L^{-1} in phosphate buffer (pH 9). The studied injection volume range for the samples and standards was 40–140 μL. The peak height (A) was observed to be increased as a function of injection volume between 40 and 100 μL and then reached equilibrium beyond 100 μL (Figure 3a). The split channel enhanced the dispersion and dilution of the sample/standard. The critical dispersion point was reached when 100 μL of Ag^+ solution (0.25 mg L^{-1}) was injected, and this

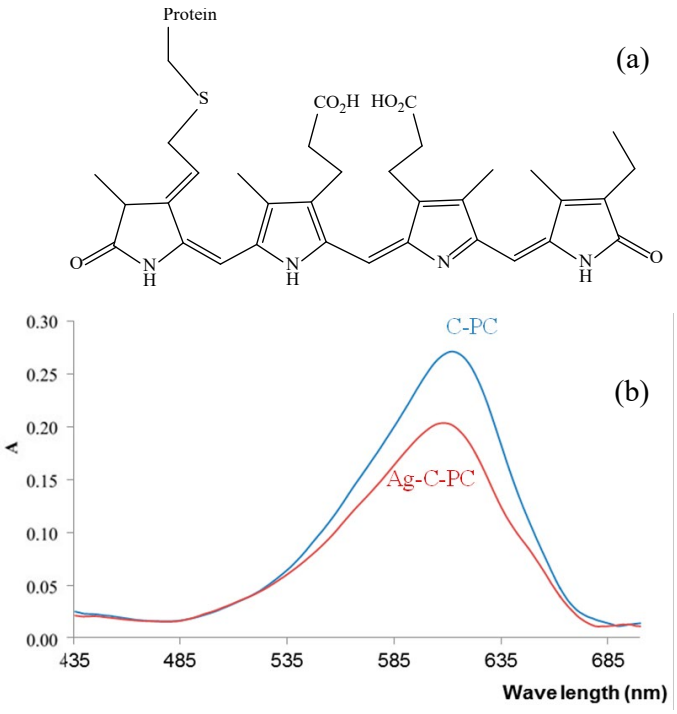

Figure 2. The structure of C-PC (a) and the absorbance spectra of solution of C-PC with and without Ag^+ (b). (Conditions: C-PC 130 mg L^{-1} in 0.1 M phosphate buffer pH 9 and concentration of Ag^+ was 2.5 mg L^{-1}).

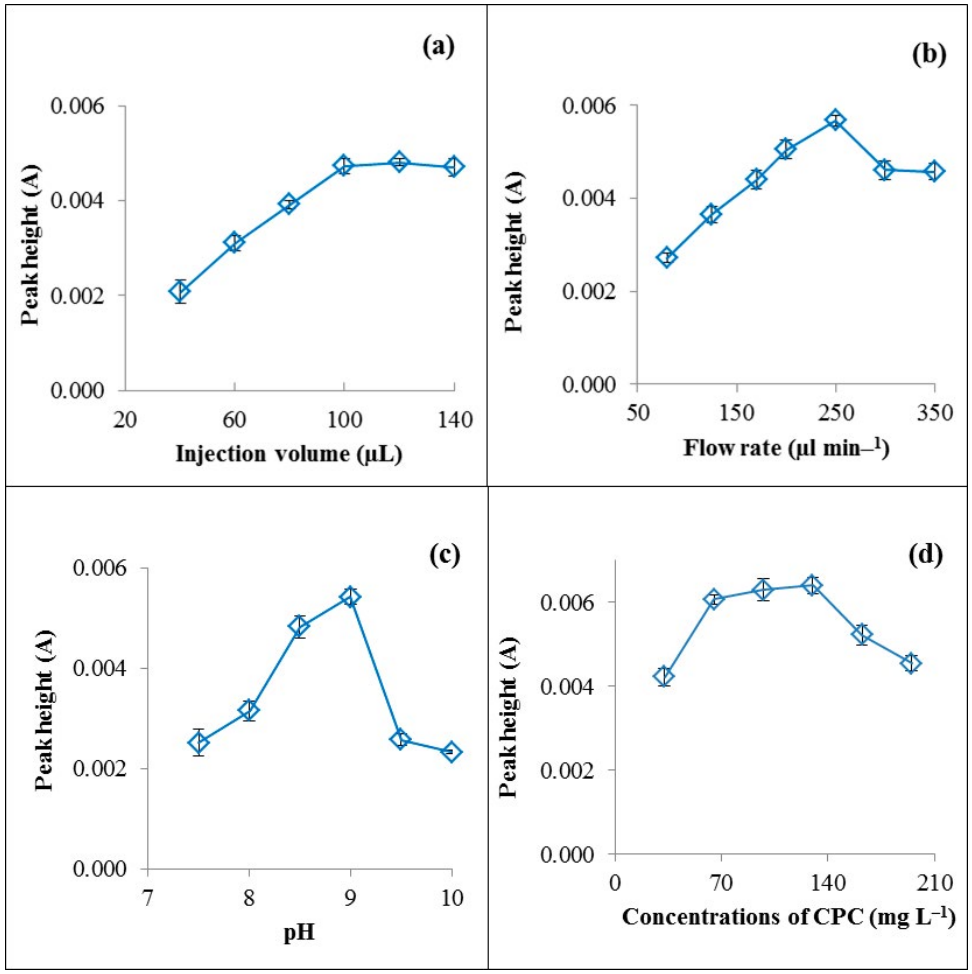

Figure 3. The effects of Injection volume of sample/standard (a), Flow rates (b), pH of C-PC solution (c), and C-PC concentration on the sensitivities of the proposed system (d).

volume was chosen for use in all subsequent experiments.

The flow rate is a critical parameter that influences the reaction and mixing capacity. Its effect was investigated in the range of 80–350 µL min^{-1}. The maximum peak height was obtained at 250 µL min^{-1} (Figure 3b). At lower flow rates, the signal decreased because of the lower mixing and reaction capacity. Meanwhile, slow flow rates extended the time per analysis, and high flow rates led to incomplete reactions, which reduced the quantity of product passing through the flow cell. Consequently, the signal intensity was greatly reduced and a large volume of waste was generated. Therefore, 250 µL min^{-1} was used as the optimum flow rate in consequent experiments.

Carboxyl groups in the C-PC reagent are more likely to form in alkaline media, which means the signal is dependent on the pH in the alkaline range. Therefore, the effect of pH was examined between 7.5 and 10.0 using phosphate buffer adjusting pH by adding 1 mol L^{-1} sodium hydroxide or hydrochloric acid. The maximum

signal was obtained at pH 9.0, and this pH value was selected as an optimum in the following experiments (Figure 3c).

The effect of buffer strength was also investigated, and it was found that 0.1 mol L^{-1} disodium hydrogen phosphate gave the highest signal. At higher buffer concentrations, the buffer viscosity increased leading to a reduction in the interaction of the analyte and reagent in the microfluidic channel[40]. The influence of C-PC concentration was also explored, and the optimum concentration of the colorimetric reagent was 130 mg L^{-1} (Figure 3d). Moreover, the stability of C-PC was studied for 4 hours, it was found that the absorbance of 130 mg L^{-1} of C-PC was decreased more than 5% after 3 Hrs. Therefore, the working C-PC was freshly prepared prior to use.

3.3 Method Validation

The developed system was calibrated under the optimum conditions (Section 3.2), using a series of Ag^+ standards. The results showed good linearity over the concentration range 0.080–2.40 mg L^{-1} Ag^+ with R^2 = 0.9996. The limit of detection (LOD, $3S_b$/slope) and limit of quantitation (LOQ, 10 S_b/slope) were calculated using the linear regression, where S_b is the standard deviation of y-intercept. This method gave LOD and LOQ of 25 and 80 µg L^{-1} of Ag^+, respectively. The system repeatability was assessed using 10 replicate injections of a 0.10 mg L^{-1} Ag^+ standard solution. The percentage relative standard deviation (%RSD) was 4.48. The reproducibility of the proposed system was studied using 10 solutions of 130 mg L^{-1} of C-PC. The results showed that %RSD of 0.10 mg L^{-1} Ag^+ was 6.03. The sampling frequency or sample throughput of the developed method was 33 samples per hour.

The accuracy of this proposed system was studied by spiking drinking water, river water and laboratory waste samples with 0.080, 0.10, 0.50, and 1.0 mg L^{-1} Ag^+ solutions. The recovery percentage ranges were 100–105, 95–110 and 98-112 for the drinking water, river water samples and laboratory waste samples, respectively (Table 1).

Table 1. Analytical features of the microfluidics system for determination of Ag^+.

Linearity study		**Results**		
-Range (mg L^{-1})		0.080 – 2.40		
-Slope±S_m [a]		0.02035 ±0.00014		
-Intercept±S_b [a]		0.00042 ±0.00017		
-R^2		0.9996		
-Limit of detection (µg L^{-1})		25		
-Limit of quantitation (µg L^{-1})		80		
Precision, %RSD				
-Repeatability (%)		4.5		
-Reproducibility (%)		6.0		
Ag^+ added (mg L^{-1})	0.080	0.10	0.50	1.0
% Recovery ± SD (n=3)				
- drinking water	100 ± 5	105 ± 6	103 ± 3	101 ± 3
- river water	110 ± 6	102 ± 4	95 ± 7	96±3
- laboratory waste	112 ± 6	107 ± 6	106 ± 4	98 ± 4

[a] S_m and S_b are the standard deviations of the slope and intercept, respectively.

Table 2. Tolerance limits for interfering ions in the determination of Ag^{+}.

Interferences	Tolerance ratio (C_{ions}/C_{Ag^+})
Mg^{2+}, Bi^{3+}, K^{+}, Fe^{3+}, NH_4^{+}, SO_4^{2-}, ClO_3^{-}	100
Al^{3+}, Mn^{2+}, Fe^{2+}, Zn^{2+}, Ni^{2+}, Ca^{2+}, SO_3^{2-}	20
Cu^{2+}, Pb^{2+}, Cr^{3+}, Hg^{2+}	10

Table 3. Determination of Ag^{+} in laboratory waste samples (3-replicate analysis).

Number	Determined value (mg L^{-1})	
	The proposed	ICP-OES
1	5.17 ± 0.37	5.21 ± 0.10
2	10.35 ± 0.43	9.70 ± 0.31
3	0.56 ± 0.05	0.45 ± 0.03
4	7.06 ± 0.10	6.82 ± 0.12

3.4 Effect of Interferences

The effect of interferences for Ag^{+} analysis was studied and it was found that the only ions that interfered with Ag^{+} detection were Cu^{2+}, Pb^{2+}, Cr^{3+} and Hg^{2+} (Table 2). These metals may compete with Ag^{+} in the reaction with C-PC [41], leading to a notable interference when their concentrations exceed 1 mg L^{-1}. However, the levels of these ions in water samples are usually relatively low. Some anions with high concentration may interfere the analysis such as SO_3^{2-} because it played a role of reduction of Ag^{+} and led to decrease the binding with C-PC.

3.5 Application of the Proposed System to Determination of Ag^{+} in Real Samples

The proposed system was applied to determine Ag^{+} in some samples with three replicate analysis. The amount of Ag^{+} was not detectable in drinking waters (n=3) and river waters (n=10) samples by this proposed method and ICP-OES. However, it was found in laboratory waste samples (n=4) in the range 0.56-10.35 mg L^{-1} as shown in Table 3. There was no significant difference between the concentrations obtained by the two methods at the 95% confidence level using paired t-test, and the t-statistic was 1.63.

4. Conclusions

The developed μFIA system reported in this work has employed the miniaturization concept and green colorimetric reagent (C-PC extracted from Cyanobacteria) to minimizes the amount and toxicity of the generated wastes from the analytical method. This is an authentic GAC approach for determination of Ag^{+} in different sample matrices. Moreover, the method is simple, cost-effective, and safe.

Conflicts of Interest

There are no conflicts to declare.

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