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Simple hollow fiber liquid membrane based pre-concentration of silver for atomic absorption spectrometry

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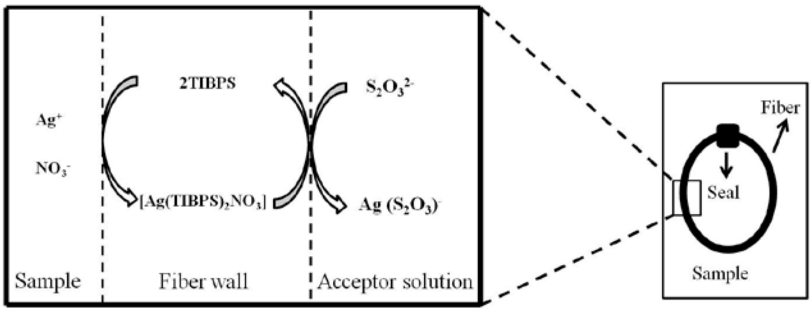
Table of contents entry

The presented hollow fiber supported liquid membrane improves and simplifies silver pre-concentration in natural water samples, allowing its determination at ultra-trace level using standard instrumental techniques as GFAAS.



Abstract

Silver pollution has gained attention in the last years because silver is being massively used as a bactericide in self-care, medical and textile products. Difficulties of Ag determination are associated with the very low concentrations in which it is normally found (ng L^{-1}) and the nature of sample matrix. Standard methods as liquid-liquid extraction (LLE) are regularly used. Alternatively, liquid phase micro-extraction (LPME) appears as an environmentally friendly tool for sample treatment that offers higher pre-concentration factors. This allows determining ultra-traces of silver using standard instrumental techniques as atomic absorption spectrometry. In this work, a hollow fiber LPME is proposed.

Silver pre-concentration has been conducted using tri-isobutylphosphine sulphide (TIBPS) as a carrier from the sample to an acceptor solution through a solvent placed in the fiber pores. Accurel-PP 50/280 fibers with an internal volume of 20 µL were used for 50 mL samples. After optimization, 0.1 M KNO_3 in the sample, 0.1 M TIBPS in dihexyl ether as the

organic phase and 1 M $Na_2S_2O_3$ in the acceptor solution were established. The system offers enrichment factors of 1053 times, a limit of detection of 1.76 ng L^{-1}. This method improves the limit of detection of the most recent liquid micro-extraction methods for silver pre-concentration coupled with GFAAS, being in this case comparable to ICP-MS detection based techniques.

Introduction

The environmental interest of heavy metals analysis is mainly supported by their high toxicity and in some cases easy bio-accumulability, even when they are present in very low concentrations. This is the case of silver [1], normally found in ng L^{-1} in pristine waters [2-3], but in μg L^{-1} for polluted ones [4]. Its toxicity and bio-accumulability are only exceeded by Hg [5]. Controlling its concentration in natural water courses has gained increasing attention due to its application as biocide for medical, self-care and laundry products, increasing silver loads to natural water courses in the last years [6,7].

Difficulties of silver analysis are associated with the nature of sample matrix and the very low concentrations it is normally found [3]. Therefore, extraction and pre-concentration steps are often required prior to instrumental determination [8]. Even then, very sensitive instrumental techniques as ICP-MS are needed for its quantification. In particular, liquid-liquid extraction (LLE) has been established as a reference method for silver pre-concentration [9]. This methodology is time-consuming and requires several steps and important amounts of solvents and reagents. For this reason flow injection systems, ionic exchange, bulk liquid membranes (BLM), and solid phase extraction (SPE) have been proposed as alternatives for sample treatment and silver pre-concentration prior ICP-MS determination [10-13].

Despite that the use of ICP-MS is currently widely extended it is not still available for all laboratory facilities. Therefore, new sample treatment methods that present higher pre-concentration capability are required to allow determining silver at the ng L^{-1} level using more easily available techniques as graphite furnace atomic absorption spectroscopy (GFAAS). In this respect, the potential of micro-extraction techniques for pre-concentration is based on a higher volume ratio between the sample and the finally measured solution [14]. Moreover, only a few micro-grams of reagents and solvents are needed, constituting a green alternative to traditional methods [14-17]. In particular, liquid phase micro-extraction has the advantage that the metal does not need to be eluted from the extractant prior to instrumental determination, because the extraction and back-extraction process is carried out in a single step [18].

Different organic ligands containing electron donor atoms have been used for silver complexation in extraction processes [19]. In particular, tri-isobutylphosphine sulphide (TIBPS) has been applied for separation of silver through supported liquid membranes [20] and its determination in the level of low µg L^{-1} by using BLM [21].

In this work, a liquid membrane, containing TIBPS as carrier, has been supported on a hollow fiber for liquid phase micro-extraction (HF-LPME). HF-LPME offers, better stability than other liquid-micro-extraction methods due to the use of a polymeric support [18,22]. Fiber pores are impregnated with the organic solution containing the carrier, the sample is in the outer part of the fiber and a few micro-liters of acceptor solution (receiving phase) are filling its internal volume [23, 24]. Therefore, the aim of this work is to obtain improved enrichment factors for silver pre-concentration, allowing the determination of ng L^{-1} of silver total concentration by atomic absorption. Thus, limits of detection can be improved without the requirement of highly sensitive techniques as ICP-MS, making ultra-trace analysis more accessible [10,12].

Materials and methods

Reagents and solutions

All reagents were used as received, without further purification. Toluene (99.5%, extra pure), potassium nitrate (99.0%, p.a.), sodium sulphite (99%, p.a.), sodium thiosulphate (98% p.a.), potassium thiocyanate (99%, p.a.), hydrochloric acid (37%, p.a.), nitric acid (65%, p.a.), palladium nitrate (10 g L^{-1}, matrix modifier for AAS), and ammonia (25%, p.a.) were obtained from Merck (Darmstadt, Germany). Dihexylether (97% GC, purum) and nitric acid (65%, trace analysis) were purchased from Fluka (Buchs, Switzerland), and diethylentriaminepentacetic acid (DTPA) was obtained from Sigma Aldrich (St. Louis, MO, USA). Tri-isobutyl phosphine sulphide (TIBPS) (Cyanex 471-X ©) was kindly provided by Cytec Industries In. (NJ, USA). Aqueous solutions of silver were prepared from a 1000 mg L^{-1} standard solution obtained from Merck (Darmstadt, Germany).

Apparatus

Membrane experiments were conducted employing polypropylene Accurel PP 50/280 capillary hollow fiber membranes (Membrana, Germany), with a 280 µm internal diameter, 50 µm wall thickness and 0.1 µm pore size. Syringes from BD Micro-Fine (Beckton Dickinson, USA) were used to fill the fibers with the acceptor solution. Glass beakers with screw cap were employed to keep the samples during the extraction process. Paraffin film was used to seal the ends of fibers. Atomic Absorption Spectrometer SolaarM, Thermo (United Kingdom) with flame atomizer (FAAS) and graphite furnace atomizer (GFAAS) was used for determination of silver in the acceptor solution.

Procedure of fibers preparation

Fibers were cut to 40 cm to contain 20 µL of acceptor solution and were immersed in 50 mL of sample in all cases. Taking into account the characteristics of the polymeric material, the first step of the set up was filling the fiber lumen with the acceptor solution; secondly the fiber pores were impregnated with the organic phase by immersion. Then, the ends of the fiber were sealed using paraffin film, making a loop with the fiber, due to its flexibility. After, it was immersed in the sample, with the help of tweezers, for silver extraction. All extractions were conducted at room temperature.

After extraction, paraffin film was removed from the ends of the fiber to recover the internal solution which was flushed by a syringe into a vial for further instrumental analysis. Silver concentration in the fiber was analyzed by atomic absorption spectroscopy by injection of the 20 µL of the acceptor solution.

Tri-isobutyl phosphine sulphide (TIBPS) is a chelating ligand which affinity for silver is not affected by the pH. The characterization of Ag-TIBPS complex can be found elsewhere [25]. Therefore, since the objective of this work is to analyze the total concentration of silver traces in natural waters, all samples were filtered through a 0.45 µm pore size filter and stored after acidification with HNO_3 before analysis. Thus, no pH adjustment or buffer was needed during extraction experiments, as previously observed for liquid-liquid extraction or bulk liquid membrane systems [21].

Efficiency of silver transport was conducted by means of its enrichment factor (EF), defined as the ratio of silver found in the acceptor solution ($[Ag]_a$) and initial silver concentration in the sample ($[Ag]_s$) (equation 1).

$$EF = \frac{[Ag_a]}{[Ag_s]} \qquad \text{Equation 1}$$

Instrumental determination

Determination of silver concentration in the acceptor solution was conducted by graphite furnace atomic absorption spectrometry. For optimization studies of Ag transport, donor phase containing 1 mg L^{-1} of silver was used, allowing Ag measurement by FAAS. During this study, the recovered 20 μL of acceptor solution were diluted to 1 mL to have enough sample as to measure by FAAS. Additionally, calibration standards were prepared with the same matrix as the acceptor solution samples from the fibers.

For analysis of real samples, atomization by graphite furnace was required and previous optimization of heating programs, the use of matrix modifiers, and selection of Zeeman or deuterium lamp background correction were carried out, using the analytical signal as response factor. In all cases, the recovered 20 μL of acceptor solution were directly injected in the graphite furnace from the fiber using a syringe.

Analytical features

The limit of detection for the proposed method was calculated as the average response of 10 independent blanks plus 3 times its standard deviation (S_b), for the whole method. In the case of the instrumental determination, the limit of detection was established from the calibration curve as the concentration that offers a signal equal to the average signal of 10 independent blanks plus 3 times its standard deviation [26].

In order to observe the effect of matrix effects on the pre-concentration of silver in real samples spiked and un-spiked samples were analyzed and the recovery of spiked concentration was evaluated as the difference between the analyzed and expected concentrations divided by the spiked silver. Finally, as a measurement of accuracy, the results obtained by the present method were compared with those obtained by a reference method in the case of silver analysis in natural waters as the liquid-liquid extraction with 1-pyrrolidine-dithiocarbamate/diethylammonium-diethyldithiocarbamate APDC/DDDC [9]. The recovery in this case was calculated as the percentage of silver analyzed by the proposed method in comparison with the reference. In all cases samples were stored at pH <2 using HNO_3 to keep the total concentration of silver in solution during storage.

Results and Discussion

Optimization of Ag transport:

Silver extraction using TIBPS is based on the formation of Ag-TIBPS complexes in the presence of NO_3^- to form two ion pairs, which are transportable from the sample to the organic phase [21]. As this is a solvating system, selection of the acceptor agent depends on the stability of Ag-Acceptor complexes in comparison with Ag-TIBPS complex. Notwithstanding, for HF-LPME also the polymeric support must be taken into account during optimization.

The first step of the process was selecting a convenient solvent for impregnation of the fiber pores. Evaluation of solvent suitability was conducted preparing 1 mol·L^{-1} solutions of TIBPS in different solvents and quantifying the yield of silver extraction from the sample into the fiber pores. In particular toluene [21], previously applied for silver transport in BLM systems and dihexyl ether, previously used in hollow fiber extraction were tested [27]. As a result, only dihexyl ether yielded quantitative extraction of silver after one hour, while extraction for toluene was negligible, due its poor stability on the fiber pores. Thus, dihexyl ether was selected for further experiments.

During optimization of carrier concentration and the stripping agent, experiments were conducted keeping a 0.1 mol L^{-1} NO_3^- in the sample and 4 hours of operation [21]. In the case of extractant concentration, different concentrations (0.1-1 mol L^{-1}) of TIBPS were applied as the liquid membrane to maximize extraction of silver from the sample, obtaining the higest yield at a concentration 0.5 mol L^{-1} TIBPS.

Selection of the acceptor agent was conducted on the base of the stability of complexes formed with Ag^+. Additionally, the formation of charged species in the acceptor phase was taken into account, in order to avoid back-extraction to the membrane. With this in mind, the suitability of different acceptors with different properties was evaluated. In this case, transport efficiency was studied measuring silver concentration in the acceptor solution. Firstly, the complexation capability of ligands such as NH_3, $S_2O_3^{2-}$, SO_3^{2-}, SCN^-, and DTPA was tested. Secondly, the use of acidic acceptors employing HCl and HNO_3 was studied. These experiments were run during 4 hours for an initial concentration of 1 mg L^{-1} of Ag^+ in the donor phase, and 0.5 mol L^{-1} TIBPS in the membrane. In the case of DTPA, NH_3, and the acidic acceptors transport yield was negligible. However, the use of sulphur-containing species offered better results, and different efficiency for Ag transport was observed in each case. As seen in figure 1 the best yield was achieved for $S_2O_3^{2-}$, its extraction profile being stabilized from 1 mol L^{-1}. These conditions were applied for the study of the optimum operation time.

During the study of the kinetics of silver transport a maximum yield and minimum variability was obtained for 4 hours of operation (Figure 2), showing , while a decrease of the enrichment factor was observed for longer experiments. This could be related with partial loss of dihexylether in water leading to smaller enrichment factors and also with an increase of variability in silver extraction.

Finally, in order to improve the obtained Ag^{+} enrichment factor, the effect of the TIBPS concentration was re-optimized considering the complete three phases extraction process -for the optimized concentration of $S_2O_3^{2-}$, because an excessive concentration of the carrier in the membrane may slow down the metal transport [13]. As a result, transport yield varied from 0.05 to 0.5 mol L^{-1} TIBPS, being maximum at 0.1 mol L^{-1} offering a final enrichment factor of 1053±17 times (Figure 3).

Optimization of instrumental determination of silver by GFAAS

Different factors were optimized previous application of GFAAS for determination of silver in acceptor solutions containing 1 M $S_2O_3^{2-}$. In all cases 20 µL of sample were injected. In the case of background correction, the use of Zeeman Effect offered cleaner spectra than the deuterium lamp correction for the same heating conditions. As a consequence, better reproducibility and sensitivity was obtained.

Optimizing heating programs, ash and atomization steps were optimized in order to eliminate the $S_2O_3^{2-}$ matrix and to improve sensitivity. Matrix effect, in the absence of matrix modifier, was eliminated at ash temperature of 1300 ºC, being near to optimum silver atomization temperature of 1500 ºC in this case. This fact supports the use of $Pd(NO_3)_2$ as matrix modifier to allow the use of higher ash temperature without risk of Ag loss during this step. As a result, the use of 5µg of $Pd(NO_3)_2$ in combination with ash temperature 1300 ºC, atomization temperature 1800 ºC and Zeeman Effect as background correction, provided enough sensitivity and reproducibility to measure Ag at the required concentration level in the acceptor solution after extraction, giving a limit of detection for the instrumental determination by GFAAS of 0.25 µg L^{-1} (Figure 4). In these conditions the linear range for silver was 0.5-10 µg L^{-1} [26].

Application to real samples

Once the system was optimized, it was applied to several synthetic samples with silver concentrations 10 ng L^{-1} - 1 μg L^{-1}, showing that metal transport is not affected by its initial concentration. After study of the blanks an average value of 0.72 ng L^{-1} has been obtained.

For Ag ultra-traces determination, different synthetic samples as well as real spiked and un-spiked samples were analyzed. In all cases, final concentrations have been corrected by subtraction of the average value of the blank. In order to evaluate the capability of the proposed method for silver analysis in real samples, different types of water samples were analyzed. In particular, silver determination was conducted for samples of tap water and from the rivers Höje in Sweden and five independent samples from Guadalquivir in Spain (Table 1). Three replicates of each sample have been analyzed, and the results were in good agreement with those obtained with the reference method of liquid-liquid extraction with APDC/DDDC after comparison by a *t* test [9,26]. In the case of sample 5 from the Guadalquivir River (Table 1), the null hypothesis of *t* test cannot be accepted due to the small standard deviation obtained for the proposed method; however, as it can be observed, recovery is 109% and the result is in agreement with the reference technique. Therefore, the proposed method offers a clean, simple, and environmentally friendly alternative instead of the classical liquid-liquid extraction. Even more, 1000 times enrichment factors are obtained, appearing as the most efficient technique for Ag enrichment at the time, improving limit of detection and enrichment factors of the most recent alternatives for silver pre-concentration by liquid micro-extraction [31,32]. Consequently, natural water samples can be directly analyzed by standard techniques as graphite furnace atomic absorption spectrometry in the level of ng L^{-1}.

Additionally, the proposed method was compared with other recently published methods for pre-concentration of silver prior instrumental determination by GFAAS, ICP-MS, or anodic stripping dissolution voltammetry (ASDV). In all cases comparison was carried out against those methods that offer the lowest limit of detection (LOD) in their category. It is important to note that different criteria have been applied by different authors for the determination of LOD; therefore, the followed criterion has been specified in table 2 to establish comparisons. As it can be observed in table 2, the proposed HF-LPME method offers a lower limit of detection for silver compared with other methods with detection in GFAAS or ASDV, and it could be comparable with the majority of ICP-MS based methods.

Conclusion

Difficulties in silver determination are associated to its low concentrations and matrix effects during instrumental determination. In order to avoid tedious methods for sample preparation and very sensitive and expensive instrumental techniques, liquid phase micro-extraction offers a simple alternative for silver pre-concentration.

In particular, hollow fiber liquid phase micro-extraction using tri-isobutylphosphine sulphide as a carrier allows obtaining a pre-concentration factor of 1053 times. This permits determination of silver in the ng L^{-1} level by GFAAS, offering results comparable with ICP-MS based techniques, promoting a reduction of cost and in agreement with principles of Green Chemistry.

Acknowledgments

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Tables and and figure captions

Table 1. Analysis of silver in real samples using HF-LPME in comparison with the reference method of LLE with APDC/DDDC [9].

Table 2. Comparison of the limit of the detection of the proposed method with other methods based on GFAAS, ICP-MS and ASDV instrumental determination.

Figure 1. Enrichment factor *vs* concentration of sulphur containing reagent in acceptor solution. ♦ Na_2SO_3, ■ KSCN, ▲ $Na_2S_2O_3$. Fixed concentration of $[NO_3^-]$= 0.1 M, [TIBPS]= 0.5 M.

Figure 2. Optimization of the experiment time. Fixed concentration of $[NO_3^-]$= 0.1 M, [TIBPS]= 0.5 M, $[S_2O_3^{2-}]$= 1 M.

Figure 3. Second optimization of TIBPS. . Fixed concentration of $[NO_3^-]$= 0.1 M, $[S_2O_3^{2-}]$= 1 M. Experiment time of 4h.

Figure 4. Optimization of ash and atomization temperature for GFAAS determination of silver in the acceptor solution. ♦ Ash temperature, ■ Atomization temperature

Table 1

Sample		$C_{Analyzed}$ (ng L^{-1})	RSD (%)	$C_{Expected}$	Recovery (%)	t[3]
Synthetic		10.0	9.5	10[1]	100.5	
Tap		3.4	5.7			
Tap (spiked)		15.6	11.6	13.4[1]	86.0	
Höje river (Sweden)		9.2	13.6			
Höje river (Sweden) (spiked)		22.1	5.2	19.3[1]	83.1	
Guadalquivir River (Spain)	Sample1	1.8	4.5	1.9[2]	97.1	-2.1
	Sample 2	2.0	7.1	2.1[2]	92.6	-1.2
	Sample 3	4.0	3.2	4.2[2]	95.1	-2.7
	Sample 4	4.4	2.1	4.3[2]	100.7	1.9
	Sample 5	2.7	0.9	2.4[2]	109.0	19.2

[1] Expected concentration for spiked samples

[2] Analyzed by Liquid-liquid extraction with APDC/DDDC and ICP-MS determination [9]

[3] Critical value of *t* = 4.30 , n=3, α=0.05 [26]

Table 2

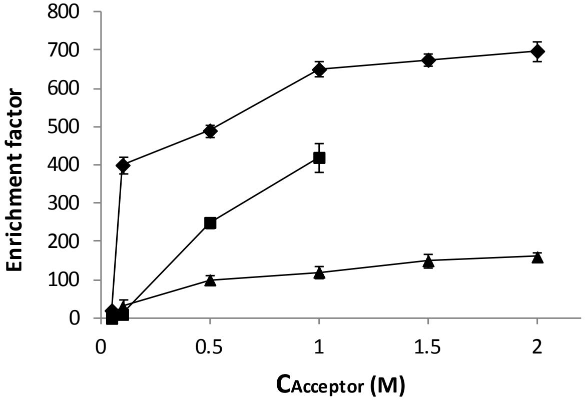
Method	**Limit of detection (ng L^{-1})**	**Reference**
Ionic liquid dispersive liquid-liquid micro-extraction/GFAAS	2.6^1	[16]
Carbon paste nanotube/Anodic stripping voltammetry	192^1	[28]
ICP-MS	3^1	[29]
Cloud point extraction/GFAAS	3^1	[30]
Solid phase extraction/ICP-MS	0.07^2	[12**]**
This method	1.16^3	

[1] Calculated as 3 Sb/m, were Sb is the standard deviation of 10 replicates of the blank and m the slope of the calibration curve.

[2] Calculated as 3Sb of the blank of the method were Sb is the standard deviation of 10 times replicates of the blank for the whole method.

[3] Calculated as the the average of 10 blanks of the method + $3S_b$, for the whole method .

Figure 1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200
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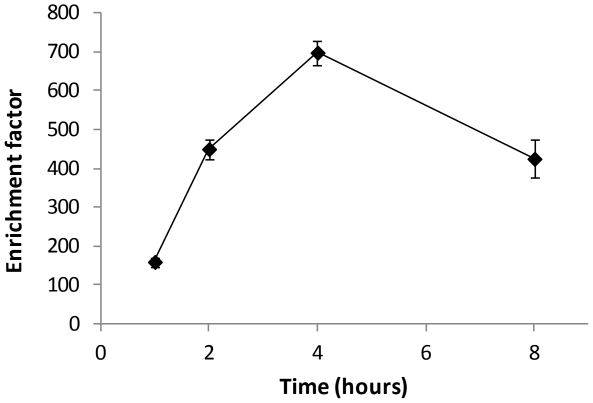
0.5
1
1.5
2
CAcceptor (M)

Figure 2


Enrichment factor
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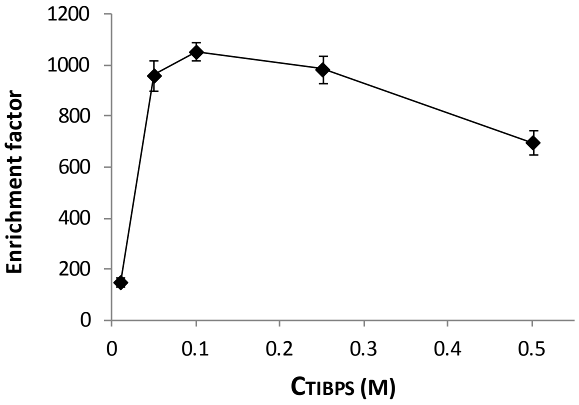
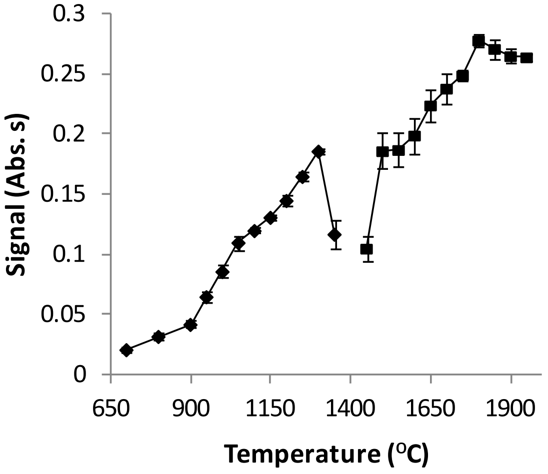
600
500
400
300
200
100
0
0
2
4
6
8
Time (hours)

Figure 3



1200
1000
800
600
400
200
0
Enrichment factor
0
0.1
0.2
0.3
0.4
0.5
CTIBPS (M)

Figure 4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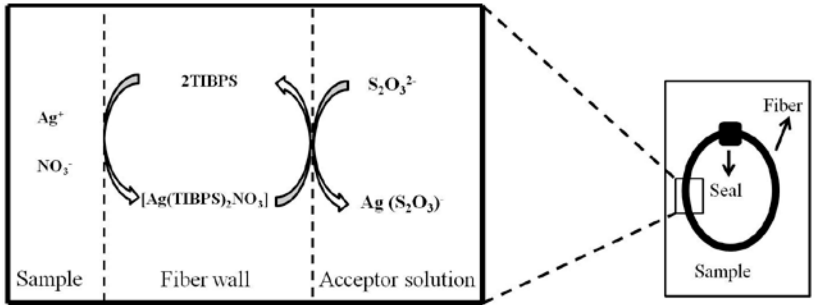
0.2
0.15
0.1
0.05
0
Signal (Abs. s)
650
900
1150
1400
1650
1900
Temperature (°C)

Graphical abstract



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