



Activated carbon-modified knotted reactor coupled to electrothermal atomic absorption spectrometry for sensitive determination of arsenic species in medicinal herbs and tea infusions



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ABSTRACT

A flow injection system based on a modified polytetrafluoroethylene (PTFE) knotted reactor (KR) was developed for arsenite [As(III)] and arsenate [As(V)] species preconcentration and determination by electrothermal atomic absorption spectrometry (ETAAS). Activated carbon (AC) was immobilized on the inner walls of a PTFE KR by a thermal treatment. A significant increase in analyte retention was obtained with the AC-modified KR (100%) as compared to the regular PTFE KR (25%). The preconcentration method involved the on-line formation of As(III)-ammonium pyrrolidinedithiocarbamate (As-APDC) complex, followed by its adsorption onto the inner walls of the AC-modified KR. After analyte retention, the complex was eluted with acetone directly into the graphite furnace of ETAAS. The parameters affecting the flow injection system were evaluated with a full central composite face centered design with three center points. Under optimum conditions, a preconcentration factor of 200 was obtained with 10 ml of sample. The detection limit was 4 ng L^{-1} and the relative standard deviation (RSD) for six replicate measurements at $0.2 \text{ } \mu\text{g L}^{-1}$ of As were 4.3% and 4.7% for As(III) and As(V), respectively. The developed methodology was highly selective towards As(III), while As(V), monomethylarsonic acid [MMA(V)] and dimethylarsinic [DMA(V)] were not retained in the AC-modified KR. The proposed method was successfully applied for As speciation analysis in infusions originated from medicinal herbs and tea.

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1. Introduction

The demand for rapid, selective, and sensitive methodologies for determination of arsenic (As) species is increasing as a consequence of its deleterious impact on human health [1]. Widely known as a toxic element, As may naturally occur in environmental compartments under different species, depending on the nature of the sample [2]. Both the toxicological behavior and biochemical activity of As depend on its chemical forms [3]. Therefore, determination of total As in a sample does not fulfill the understanding about the toxicological risks derived from this element in environmental and biological studies. Consequently, speciation analysis of As becomes highly necessary.

Tea (*Camellia sinensis*) is a popular non-alcoholic and healthy beverage widely consumed in the world [4]. Even when a regular consumption of infusions of medicinal herbs and tea may contribute to the daily dietary requirements of several essential elements [5,6], some

toxic metals and organic pollutants are ingested as well [7]. Specifically for As, its inorganic species, arsenite [As(III)] and arsenate [As(V)], which are much more toxic than the organic ones, generally predominate in infusion samples [8]. Therefore, considering the massive consumption of infusions in some countries [4], determination of As in infusions of tea and medicinal herbs is highly needed to evaluate As daily dietary intake [5]. Different instrumental techniques including atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES) [9], inductively coupled plasma mass spectrometry (ICP-MS) [10], and capillary electrophoresis (CE) [11] have been used to determine As levels in tea leaves and infusions. However, since the reported concentrations of total As in tea leaves are below 0.08 mg kg^{-1} , preconcentration methodologies are required prior its determination to achieve accurate, sensitive and reliable results [5].

Analytical methods for preconcentration and speciation of metals and metalloids are numerous and several devices have been used for analyte retention [12,13]. Among them, knotted reactors (KR) have been successfully employed in flow injection methodologies based on the sorption of metal complexes on the inner walls of these reactors [14]. Knotted reactors are open tubes made of fully knotted polytetrafluoroethylene (PTFE) tubing. Both the effect of centrifugal

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force generated by the steady change in flow direction due to the knots and the hydrophobic nature of PTFE surface allow the retention of analytes as precipitates [15]. Since lower back-pressures are observed in KR's compared to those observed in packed columns at similar flow rates, higher sample loading flow rates and elution efficiency can be obtained. Furthermore, a KR is easily manufactured without needing packing materials, offering an almost unlimited lifetime due to chemical inertness of PTFE. Additional advantages of KR's are: high stability under different sorption conditions, rapid mixing of sample and reagent solutions, low hydrodynamic impedance and minimum analyte dispersion, allowing high load sample rates and increased sample throughput [16]. Nevertheless, retention capacity of KR's is limited (usually lower than 30%), thus conditioning the enrichment factors obtained with on-line preconcentration methods using these reactors [17,18]. In fact, the use of regular PTFE KR's has been reported previously for preconcentration and determination of As(III) by ICP-MS [19], HG-AFS [20] and ETAAS [21]. However, the sensitivity enhancement factors obtained with these types of KR's has been low and ranged between 11 and 44.

The aim of the present work was the modification of the inner walls of a classical PTFE KR to solve one of its main drawbacks for analytes preconcentration: the low retention capacity. The modification of the inner walls of the KR was performed using activated carbon (AC), which is widely known for its excellent sorption capacity. Therefore, a novel on-line analytical methodology based on an AC-modified KR was developed for simple and highly selective preconcentration of As species. As(III) reacted with ammonium pyrrolidinedithiocarbamate (APDC) forming a precipitated complex which was adsorbed on the walls of the KR. An experimental design (CCD) was used for the optimization of the factors that influence the preconcentration of the formed complex. The complex was eluted with a few microliters of acetone directly into the graphite furnace of ETAAS for As determination. The performance of the AC-modified KR was evaluated under flow conditions with an on-line system coupled to ETAAS. The proposed methodology proved to be particularly useful to obtain quantitative information on inorganic As(III) and As(V) species concentrations in infusions of medicinal herbs and tea samples.

2. Experimental

2.1. Instrumentation

Measurements were performed with a PerkinElmer (Überlingen, Germany) Model 5100 ZL atomic absorption spectrometer equipped with a transversely heated graphite atomizer with a Zeeman-effect background correction system. An As electrodeless discharge lamp (EDL) operated at a current of 300 mA (modulated operation) and a wavelength of 193.7 nm with a spectral band pass of 0.7 nm was used. All measurements were made based on absorbance signals with an integration time of 5 s. Instrumental parameters are listed in Table 1. Gilson Minipuls 3 tygon-type pump tubing was used to carry the sample and APDC solution. The eluent (acetone) was carried using a silicone tube. The sample injection and the elution were performed using six-way rotary valve from Upchurch Scientific (Oak Harbor, WA, USA). The KR flow injection system is shown in Fig. 1. The modification of inner walls of KR and its morphological changes were observed by scanning electron microscopy (SEM) (LEO 1450 VP, Zeiss, Germany).

2.2. Reagents

All the reagents were of analytical grade and the presence of As was not detected within the working range. Stock standard solutions of inorganic As(V) and As(III) species (1000 mg L^{-1}) as sodium arsenate dibasic heptahydrate ($\text{Na}_2\text{HASO}_4 \cdot 7\text{H}_2\text{O}$) (99.998%) (Sigma-Aldrich, Milwaukee, WI, USA) and sodium metaarsenite (AsNaO_2) (99%) (Fluka, Buchs, Switzerland), respectively, were prepared in 0.1 mol L^{-1} HCl.

Table 1

Instrumental and experimental conditions for As determination.

Instrumental conditions				
Wavelength (nm)	193.7			
Spectral band width (nm)	0.7			
EDL lamp current (mA)	300			
Injection volume (μl)	50			
Matrix modifiers	5 $\mu\text{g Pd}$ [$\text{Pd}(\text{NO}_3)_2$] 3 $\mu\text{g Mg}$ [$\text{Mg}(\text{NO}_3)_2$]			
Graphite furnace temperature program				
Step	Temperature ($^{\circ}\text{C}$)	Ramp time (s)	Hold time (s)	Argon flow rate (ml min^{-1})
Drying	110	15	30	250
Pyrolysis	600	10	10	250
Atomization	2300	0	3	0
Cleaning	2400	1	2	250
Extraction conditions				
Sample volume (ml)	10			
APDC concentration (% w/v)	0.1			
HCl concentration (mol L^{-1})	0.01			
Eluent	Acetone			
Eluent volume (μl)	50			
Sample loading flow rate (ml min^{-1})	5.0			
APDC loading flow rate (ml min^{-1})	3.0			
Elution flow rate (ml min^{-1})	0.2			

Disodium methylarsenate ($\text{CH}_3\text{AsNa}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$) (MMA, 98%) (Fluka) and dimethylarsinic ($\text{C}_2\text{H}_7\text{AsO}_2$) (DMA, 98.6%) (Fluka) stock standard solutions (1000 mg L^{-1}) were prepared with ultrapure water and stored at 4°C in amber-colored HDPE bottles. Working solutions were prepared by diluting these stock solutions.

Hydrochloric acid (37%), purchased from Merck (Darmstadt, Germany), was used to guarantee acidic media in the samples and in As(III) standard solutions for optimization of the methodology. The chelating agent solution was prepared by dissolving APDC (Sigma-Aldrich, Milwaukee, WI, USA) in ultrapure water ($18 \text{ M}\Omega \text{ cm}$) (Milli-Q water purification system, Millipore, Paris, France). Potassium iodide >99% (Fluka, Buchs, Switzerland) was used as reductant. Activated carbon (Merck) of 35–50 mesh ASTM was used for modification of KR inner surface. A 1000 mg L^{-1} palladium nitrate solution [$\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (Fluka)] and 150 mg L^{-1} magnesium nitrate solution [$\text{Mg}(\text{NO}_3)_2$ (Merck)], both in 0.1% (v/v) HNO_3 (Mallinckrodt Baker, Phillipsburg, NJ, USA), were prepared and used as chemical modifiers. Methanol (Merck) and acetone (Merck) were used as eluents. A 10% (v/v) nitric acid solution was prepared in ultrapure water to be assayed as elution agent. All bottles used for storing samples and standard solutions and the glassware were washed in 10% (v/v) HNO_3 for 24 h and later rinsed with ultrapure water.

2.3. Fabrication of the AC-modified KR

The immobilization of AC was performed by filling a PTFE tube (0.51 mm i.d. and 120 cm length) with dry AC. The tube was extended vertically by attaching its endings with two clamps to a universal support stand, and a small micropipette tip was installed on the top of the PTFE tube to serve as a funnel using a desk tape. The dry AC material was poured into the PTFE tube while beating the outside in order to obtain a compact filling. Subsequently, the PTFE tube was heated in a muffle furnace for 5 h at 327°C . The PTFE tube used for this work was purchased from GRACE (Columbia, USA) and a melting point of 330°C is specified by the manufacturer. The muffle furnace had a temperature tolerance of $\pm 2^{\circ}\text{C}$. After heating time, the tube was cooled until room temperature was reached. Then, the tube was washed with a 0.1 mol L^{-1} HNO_3 solution at 1 ml min^{-1} in order to easily remove free AC particles not immobilized on PTFE surface. A SEM micrograph showing the modification of the inner section of the AC-modified KR is shown in Fig. 2.

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