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Quantitative analysis of arsenic speciation in guano and ornithogenic sediments using microwave-assisted extraction followed by high-performance liquid chromatography coupled to hydride generation atomic fluorescence spectrometry

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ABSTRACT

Seabird guano is one of the main sources of nutrient fertilizers in remote coastal island areas, but guano-derived contaminants such as arsenic may cause serious threats to local ecosystems and public health issues. In this study, a new method was developed to analyze arsenic speciation in guano and ornithogenic sediments. Good extraction efficiencies of As(III) (arsenite), DMA (dimethylarsinate), MMA (monomethylarsonate) and As(V) (arsenate) were obtained by using 1.0 mol L^{-1} orthophosphoric acid and 0.1 mol L^{-1} ascorbic acid, followed by microwave-assisted extraction and high-performance liquid chromatography coupled to hydride generation atomic fluorescence spectrometry (HPLC-HG-AFS) detection. Under the optimized conditions, the extraction efficiencies of four arsenic species were over 80%. The relative standard deviations (RSDs) were 9.60, 6.15, 6.34 and 2.93% ($n = 7$), and the detection limits ($\mu g\ L^{-1}$) were 0.82, 2.38, 1.45 and 2.31 for As(III), DMA, MMA and As(V), respectively. This method was successfully used to determine arsenic speciation in the guano samples collected from the Xisha Islands of the South China Sea, and the results indicated that As(III) and As(V) were the dominant arsenic species in modern and ancient guano, respectively.

1. Introduction

The breeding activities of seabirds in maritime regions act as biovectors between marine and terrestrial ecosystems. It is well known that the input of seabird excreta to breeding colonies can significantly influence nutrient composition in neighboring soils and lacustrine sediments [1]. However, some studies have shown that seabirds can also transport large numbers of industrially produced contaminants to their nesting areas [2,3]. For example, intense seabird activities will cause an obvious enrichment of arsenic in soils and sediments adjacent to their colonies [3–6], and this may lead to potentially adverse effects on local ecosystems. According to previous studies, arsenic speciation is usually considered to play an important role in the toxicity and mobility of arsenicals [7]. Generally, inorganic arsenic species appear more noxious to organisms than organic species, and the toxicity of different arsenic speciation varies in the following order: As(III) > As(V) > DMA > MMA [8–10]. Along with the rapid development of environmental toxicology and arsenic epidemiology, arsenic speciation distributions in different environment samples have become the focus of intensive scientific research in recent decades. To our knowledge, however, most of the previous research on ornithogenic sediments and soils is concerned primarily with the distribution and geochemical characteristics of arsenic as a whole, and studies on arsenic speciation have rarely been conducted.

Many different methods have been used in the past for the analysis of arsenic speciation in environmental materials such as biotic tissues, water, soils and sediments (Table 1), whereas methods for the analysis of arsenic speciation in guano and ornithogenic sediments which have both biological and sedimentary characteristics had not yet been developed. Different extractants are employed in relation to specific environmental samples (Table 1), of which orthophosphoric acid is frequently used in extraction procedures applied to soils and sediments, and methanol in those extraction procedures applied to biotic tissues. Commonly, the extraction methods of arsenic speciation analysis include microwave digestion, water bath heating, mechanical oscillation and ultrasonic

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Table 1
Reported methods of arsenic speciation analysis for different environmental samples.

Sample	Arsenic species	Extractants	Extraction method	Detection means	Extraction efficiency (%)	RSD (%)	DL ($\mu g\,L^{-1}$)	References
Sediments	As(III), As(V)	1 mM PO_4 solution	Shaking	HPLC-HG-AAS	<5	<4	0.8	[11]
Sediments	As(III), As(V), DMA, MMA	0.3 M H_3PO_4 0.3 M $(NH_4)_2C_2O_4$	Microwave digestion	HPLC-HG-ICP-MS	>90	—	—	[12]
Soils, sediments	As(III), As(V), DMA, MMA	1 M H_3PO_4	Microwave digestion	HPLC-ICP-MS	60–80	4–10	1.3–1.7	[13]
Soils	As(III), As(V), DMA, MMA, AsB, AsC	Purified water	Shaking	HPLC-ICP-MS	5–12	1.4–2.8	0.033–0.217	[14]
Bivalves, bird eggs	As(III), As(V), DMA, MMA, AsB	Methanol/water (1:1)	Ultrasonic bath	HPLC-UV-HG-AFS HPLC-UV-HG-ICP-MS	59–96	AFS:7.8–11.7 MS:16.6–20.2	AFS:0.3 MS:0.3	[15]
Sediments Seawater, freshwater		0.4 M $HONH_3Cl$ —	Heating —					
Soils	As(III), As(V), DMA, MMA	1 M H_3PO_4 + 0.1 M ascorbic acid	Microwave digestion	LC-UV-HG-ICP-MS	60.0–101	0.8–4.7	0.03–0.12	[16]
Rice, fish, chicken	As(III), As(V), DMA, MMA, AsB	Methanol/water (1:1)	Ultrasonic bath	HPLC-ICP-MS	75–96	<4	1.1–5.4	[17]
Soils		1 M H_3PO_4	Heating		>95			
Moso bamboo shoots	As(III), As(V), DMA, MMA, TMAO	Methanol/water (1:1)	Ultrasonic bath	CT–HG–AAS	61.1–69.2	<7	0.030–0.080	[18]
Soils	As(III), As(V), DMA, MMA	0.5 M phosphate buffer	Microwave digestion	HPLC-HG-AFS	94.4–101.2	—	2.76–7.37	[19]
Rice, straw	As(III), As(V), DMA, MMA, AsB	α-Amylase solution	Ultrasonic bath	HPLC-ICP-MS	71.8–104.5	<5	0.0127–0.0196	[20]
Soils		1 M H_3PO_4	Ultrasonic bath		92.3–100.0			
Chinese herbal medicines	As(III), As(V), DMA, MMA	1% HNO_3	Microwave digestion	HPLC-ICP-MS	48–160	—	0.065–0.080	[21]

Note: "—" means not mentioned; AsB and AsC represent arsenobetaine and arsenocholine, respectively.

baths (Table 1). Microwave digestion is widely used to analyze soils and sediments because of its convenience and efficacy. After pretreatment, HPLC-HG-ICP-MS and HPLC-HG-AFS are commonly applied as part of detecting arsenic speciation (Table 1). Comparatively speaking, AFS is more convenient and inexpensive than ICP-MS, and the detection capabilities of AFS stand comparison with ICP-MS. Therefore, HPLC-HG-AFS has become increasingly popular in arsenic speciation analysis because of the above-mentioned advantages.

The main purpose of this study is to develop a proper method for arsenic speciation analysis in guano and ornithogenic sediments from remote regions such as the Xisha Archipelago in the South China Sea, and Antarctica. Orthophosphoric acid is used in the extraction process, followed by microwave digestion and HPLC-HG-AFS detection. Speciation analysis of arsenic will advance our knowledge of arsenic transformation and possible environmental toxicology in guano and ornithogenic sediments. Moreover, it may also allow an understanding of the geochemical cycle of arsenic within seabird habitats.

2. Materials and methods

2.1. Sample collection

The Xisha Archipelago (15°47′–17°08′ N, 110°10′–112°55′ E), located in the central South China Sea, consists of the eastern Xuande and southwestern Yongle groups of islands, islets and reefs. Most of the Xisha Islands are covered with lush vegetation, which provides good nesting habitats for seabirds [22]. As a result of increasing levels of human-induced disturbance, both bird diversity and population have decreased sharply in recent years on most of these islands. At present, seabirds are almost extinct on most of the islets except for on Dongdao Island, part of the Xuande Group. Due to a relatively high annual mean temperature (~26 °C) all year round, average annual evaporation levels (~2400 mm) are far higher than average rainfall (~1500 mm), leading to a relatively dry environment in the Xisha area [23]. Because of the archipelago's particular geographic position and climatic conditions, guano samples have been well preserved in coral sand sediments. All the guano samples used in this study were collected during an expedition to the islands in 2008. Ancient guano samples GJ3 and CH1 were collected on the Guangjin and Chenhang islands of the Yongle Group, respectively. A modern guano sample was collected from Dongdao Island, in the Xuande Group. Details of the guano sample collection were reported by Xu et al. [6] and Chen et al. [24]. Sediment profile MB6 influenced by penguin dropping was collected at Cape Bird in the Ross Sea region of East Antarctica, and details of the sample collection were reported by Nie et al. [25]. All the samples were kept at −20 °C until in-depth studies of them could be made. Prior to chemical analysis, they were air-dried, grounded with a mortar and pestle and then passed through a 200-mesh sieve.

2.2. Standards and reagents

Arsenite stock standard solution was purchased from National Institute of Metrology (China). Standards of arsenate, dimethylarsinate and monomethylarsonate were purchased from Dr Ehrenstorfer GmbH (Germany), and their stock standard solutions (containing 100 $mg\,L^{-1}$ of arsenic) were prepared using deionized water. All stock solutions were kept in the dark at a constant