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Online Arsenic Species Separation and Analysis of Arsenite, Arsenate, Monomethylarsenate, Dimethylarsonate and Arsenocholine Using Liquid Chromatography and Hydride Generation Atomic Fluorescence Spectrometry

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Authors' contributions

This work was carried out in collaboration of all authors. Authors TD, XY and JG designed the study and authors JG and XY performed the experiments and author YG helped in lab work. All authors read and approved the final manuscript.

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Method Article

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ABSTRACT

Aims: The purpose of this research was to establish a five-arsenic-species separation and analysis method including arsenite [As(III)], arsenate [As(V)], monomethylarsonate (MMA), dimethylarsonate (DMA) and arsenocholine (AsC) in water sample by liquid chromatography with hydride generation atomic fluorescence spectrometry (LC-HG-AFS).
Study Design: The Successful separation and detection for the five arsenic species can be achieved through changing the chromatographic columns and adjusting the compositions of mobile phase.
Place and Duration of Study: Study in the laboratory of College of Marine Science and Engineering at Tianjin University of Science & Technology between March 2014 and September 2014.

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Methodology: Firstly the effect of anion exchange chromatography was compared with that of reversed-phase ion-pair chromatography for separating the five arsenic species. Then reversed-phase ion-pair chromatography was selected in the next step because of its universality for separating these arsenic species by adjusting mobile phase.
Results: Effective separation was achieved within 10 min for all the five arsenic species by a single reversed-phase ion-pair chromatographic column eluted with 1 mmol/L diammonium hydrogen phosphate buffer [$(NH_4)_2HPO_4$] (pH=6.00) + 1% (v/v) CH_3OH + 5 mmol/L tetrabutyl ammonium bromide (TBAB). The concentration of arsenic compounds were determined by peak height. And the concentration of AsC, As(III), As(V), MMA, DMA were 250 μg/L, 100 μg/L, 100 μg/L, 100 μg/L, 100 μg/L respectively in this experiment.
Conclusion: The five arsenic species can be effectively separated and detected by hyphenated techniques (LC-HG-AFS).

Keywords: Arsenic species analysis; LC-HG-AFS; reversed-phase chromatography; hyphenated techniques.

1. INTRODUCTION

Elemental arsenic (As) is widespread in environment and organisms. Humans may be exposed to arsenic through different ways. It is well known that arsenic species have different toxicological properties dependent upon their oxidation states and chemical forms. Therefore, determination of total arsenic is not adequate for present analytical need. The actual toxicity levels for different arsenic compounds vary greatly and thus arsenic speciation analysis is particularly essential [1]. Usually, inorganic arsenic compounds are more toxic than organic arsenic, and arsenite [As(III)] is more toxic than arsenate [As(V)]. Generally, inorganic arsenic compounds are classified as carcinogenic [2]. While the organic arsenic forms have varying degrees of toxicity. For example, monomethylarsonate (MMA) and dimethylarsonate (DMA) exhibit a toxicity factor of one in four hundred that of the inorganic forms [3,4]. MMA and DMA are identified as possible cancer promoters [5]. However, arsenobetaine (AsB) and arsenocholine (AsC) are believed to be non-toxic [6].

The chromatographic hyphenated techniques are widely used for arsenic speciation analysis [7,8] such as the combination of liquid chromatography (LC) with inductively coupled plasma mass spectrometry (ICP-MS) [7-11], atomic absorption spectrometry (AAS) [12], inductively coupled plasma optical emission spectrometry (ICP-OES), hydride generation atomic fluorescence spectrometry (HG-AFS) [13-15], hydride generation dynamic reaction cell inductively coupled plasma mass spectrometer (HG-DRC-ICP-MS) [10] and so forth, among mentioned techniques LC-HG-AFS has the advantages of short warm-up time, short detection time and relatively high sensitivity [12].

The mainly separating methods for arsenic speciation analysis reported in literatures were ion-exchange such as anion exchange chromatography and cation exchange chromatography [16-25] or reverse-phase ion-pair chromatography [26-31]. As(III), As(V), MMA and DMA contain an acidic group in their chemical structures with acid dissociation constant (pKa) ranging from 2.2 to 9.2 [32] and thus their ionization dependent on the pH of the mobile phase. AsC is permanently cationic in structure and independent of the pH, and thus AsC will not be retained in an anion-exchange column, in which As (III) only presents slight retention. As for reverse-phase ion-pair chromatography, rentention time of arsenic species will be changed by adjusting ion-pair reagents, organic modifiers (such as methanol or acetonitrile), ionic strength and pH of the mobile phase. The ion-pair reagents usually used include tetrabutylammonium (TBA, including hydroxide, phosphate and bromide), tetraethylammonium hydroxide (TEAH) and didoctyldimethylammonium bromide (DDAB). TBA+ is the common pairing cation for the separation of As(III), As(V), MMA and DMA. Therefore, in this paper, the separation and detection of five arsenic compounds including As(III), As(V), MMA, DMA and AsC in simple matrix were investigated based on the combination of LC with HG-AFS by using tetrabutylammonium bromide (TBAB) as ion-pair reagent and methanol as organic modifiers in the mobile phase.

2. EXPERIMENTAL DETAILS

2.1 Standard Solutions and Reagents

As(III) and AsC stock solutions were obtained from National Standard Substance Center of China. As(V), MMA and DMA were prepared by dissolving appropriate amounts of $Na_2HAsO_4 \cdot 7H_2O$, $CH_3AsO(ONa)_2 \cdot 6H_2O$ (Sigma-Aldrich, USA) and $(CH_3)_2AsO_2H$ (Acros, Belgium) in double deionized water (DDW). All chemical reagents used were at least analytical grade. DDW used throughout the work was purified to the resistivity of no less than 18 mΩ·cm.

Mobile phase was prepared using $(NH_4)_2HPO_4$, TBAB (tetrabutylammonium bromide) and CH_3OH. It was adjusted to pH equal to 6.00 with 10% formic acid and filtered through a 0.22 μm microporous membrane prior to use. Reducing reagent and oxidizing reagent were prepared daily by dissolving 20.00 g KBH_4 and 20.00 g $K_2S_2O_8$ in 1000 mL 0.5% KOH solution, respectively. Carrier solution was prepared by diluting 60 mL of concentrated hydrochloric acid to 1000 mL with DDW. The abbreviation of some compounds used in the experiment were listed in Table 1.

2.2 Analytical Procedures

A Venusil-MP C18 reverse-phase chromatographic column (4.6 mm×150 mm i.d., 5 μm) protected by a guard column CH-100 (4.6 mm × 10 mm i.d., 5 μm, Agela, USA) was used for the separation of arsenic species. Samples were introduced by a 7725i injection valve with 100.0 μL sample loop (Rheodyne, Japan). A LC-10AT high performance liquid pump (Shimadzu, Japan) was used to deliver mobile phase through an isocratic mode. The separated arsenic compounds were delivered into a SA-10 speciation analysis pretreatment device (Titian, China) for hydride generation. A peristaltic pump was used for the introduction of carrier solution (6% HCl), reducing reagent (2% KBH_4) and oxidizing reagent (2% $K_2S_2O_8$). Hydrides generated were eventually sent to an atomic fluorescence spectrometer (Titian, China). Instrumental operating parameters were given in Table 2.

3. RESULTS AND DISCUSSION

3.1 Ion-exchange Chromatography

Even though As(III), DMA, MMA and As(V) can be well separated by an anion exchange chromatographic column using 20 mmol/L $(NH_4)_2HPO_4$ (pH=6.20) as mobile phase [14], it was incapable of separating between AsC and As(III) at optimizing conditions. It may result from that AsC presents positive charge in most pH conditions, while As(III) mainly exists in the form of neutral molecule. Therefore, AsC and As(III) will be eluted at the same time in anion exchange chromatographic column in spite of the pH of the mobile phase is adjusted.

3.2 Reverse-Phase Ion-pair Chromatography

For the separation of arsenic species by reversed-phase ion-pair chromatography, a kind of counter ion and organic modifier (such as methanol or acetonitrile) need to be added to the mobile phase, and a secondary chemical equilibrium of the ion-pair formation is used to control the retention and selectivity [1]. Therefore, concentration and kinds of counter ion, organic modifier, ionic strength and pH of the mobile phase are necessary to be optimized so as to obtain the expected separation among different species. The chromatographic behaviors of these arsenic species can be predicted based on their pKa values. Accordingly, these species are expected to be eluted in the following order: AsC → As(III) → DMA → MMA → As(V).

It was found that the separation of arsenic species by a Venusil MP C18 column allows baseline separation of AsC, As(III), DMA and MMA in DDW by eluting with 5.0 mmol/L $(NH_4)_2HPO_4$ (pH=5.30) + 1.0% CH_3OH + 10.0 mmol/L TBAB. However, MMA and As(V) were not sufficiently separated at the same conditions as shown in Fig. 1. Therefore, the mobile phase conditions were investigated so as to establish a methodology that was suitable for the separation and detection of As(III), DMA, MMA, As(V) and AsC in simple matrix.

3.2.1 CH_3OH

Increasing the concentration of CH_3OH in mobile phase will reduce its polarity, but high concentration of CH_3OH probably leads to an unstable current, even a flameout in the atomizer [10]. The effects of CH_3OH on the retention time of different arsenic species were thus investigated. The concentration of CH_3OH was changed from 0.1% to 3% (v/v) in 3 mmol/L $(NH_4)_2HPO_4$ buffer solution (pH=6.50) containing 5 mM TBAB, and the result was shown in Fig. 2. It was found that As(V) with the strongest retain

ability could be eluted within 7 min with larger difference of retention time between different arsenic species when the concentration of CH_3OH was 1%. In this condition, retention time of MMA, DMA, As(III) and AsC were 4.9, 4.3, 2.5 and 2.0 min respectively. Therefore, 1% CH_3OH was selected to carry out further experiments.

3.2.2 Diammonium hydrogen phosphate

Usually, the retention time of arsenic species with negative charge will increase with the ionic strength decreased in mobile phase when they were separated by reversed-phase ion-pair chromatography. Adding of $(NH_4)_2HPO_4$ in mobile phase will increase its ion strength, and meanwhile $(NH_4)_2HPO_4$ will compete with arsenic species to combine on stationary phase. As a result, retention time of arsenic species was decreased. As shown in Fig. 3 that the retention time of DMA, MMA and As(V) obviously decreased when the concentration of $(NH_4)_2HPO_4$ was increased in eluent of 1% CH_3OH + 5 mmol/L TBAB (pH=6.50). Therefore, in order to realize acceptable separation of different arsenic species and minimize analysis time, 1 mmol/L $(NH_4)_2HPO_4$ was finally selected. Thus the time taken for As(V), MMA, DMA, As(III) and AsC to travel through the column to the detector were 11.1, 7.0, 5.2, 2.5 and 2.0 min respectively.

3.2.3 pH of mobile phase

pH has important effect on the separation of arsenic species as it was behaved in Fig. 4. Arsenic species were separated and eluted by 1 mmol/L $(NH_4)_2HPO_4$ + 1% CH_3OH + 10 mmol/L TBAB at different pH value varying from 3.00 to 8.00. It was found that pH has slight influence on the separation of As(III) and AsC. The reason for this result can be explained by the pKa of As(III) which is 9.2 that is larger than the pH tested in the experiment [31]. As(III) is neutral molecule when its pKa is bigger than the tested pH. So As(III) could not be well separated from cationic AsC for its uncharged characteristics at this pH. However, situations were different for DMA, MMA and As(V). It was noticed that accepted separation was achieved at the pH near 6.00, Tetention time of As(V), MMA, DMA, As(III) and AsC were 12.0, 8.1, 6.0, 2.9 and 2.2 respectively. Thus pH=6.00 was selected for the subsequent investigation.

Table 1. Abbreviation of partial compounds used in the experiment

Full name of compounds	Abbreviation of compounds
$NaAsO_2$	As(III)
$AsHNa_2O_4$	As(V)
$Na_2HAsO_4 \cdot 7H_2O$	MMA
$CH_3AsO(ONa)_2 \cdot 6H_2O$	DMA
$(CH_3)_2AsO_2H$	AsC
$C_{16}H_{36}BrN$	TBAB

3.2.4 TBAB

Increasing the concentration of TBAB will be beneficial to the adsorption of large amount of TBAB on the stationary phase in reverse-phase chromatographic column. As a result, there are more chances for arsenic species to combine with TBA+ to form ion pairs, by which it will increase their retention time. Therefore, the retention time of DMA, MMA and As(V) will suffer from significant influence of the concentration of the counter ion as they have relatively smaller acid dissociation constants (pKa of DMA, MMA and As(V) are 6.2, 4.2, and 2.2) [31] (Fig. 5).

Table 2. Instrumental parameters of LC and HG-AFS

System	Parameter	Value
LC	Sample volume	100.0 μL
	Flow rate	1.0 mL/min
	Mobile phase composition	1 mmol/L $(NH_4)_2HPO_4$ (pH 6.00) +1% CH_3OH+5 mmol/L TBAB
HG	Reducing reagent	2.0% KBH_4+ 0.5% KOH, 7.7 mL/min
	Oxidizing reagent	2.0%$K_2S_2O_8$+0.5%KOH, 7.7mL/min
	Carrier solution	6.0% HCl, 4.7 mL/min
AFS	Lamp current, /(mA)	90
	Negative high Voltage, /(V)	290
	Carrier gas (Ar), /(mL/min)	400
	Shielding gas (Ar), /(mL/min)	800

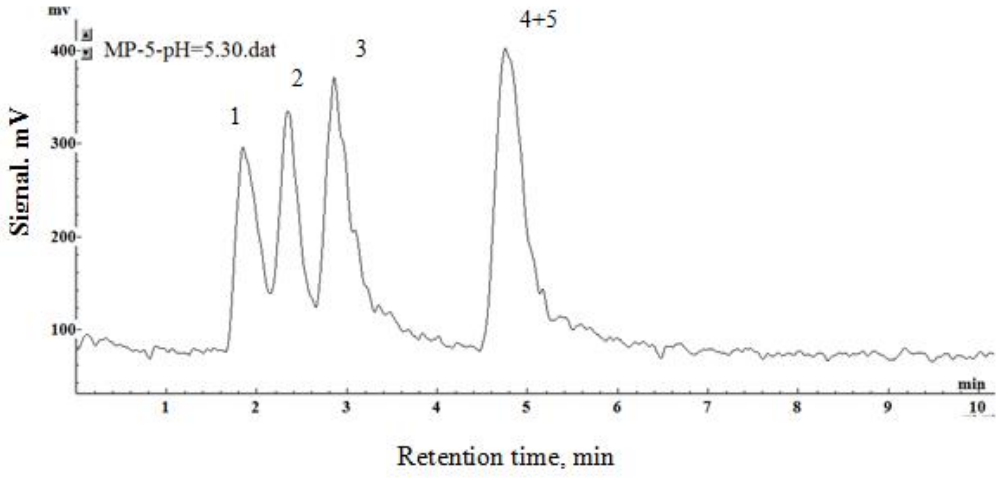

Fig. 1. Chromatogram of five arsenic species separated by a ion-pair reverse-phase chromatography using 5.0 mmol/L $(NH_4)_2HPO_4$ (pH=5.30) + 1.0% CH_3OH + 10.0 mmol/L TBAB
Peaks: 1, AsC; 2, As(III); 3, DMA; 4, MMA; 5, As(V)

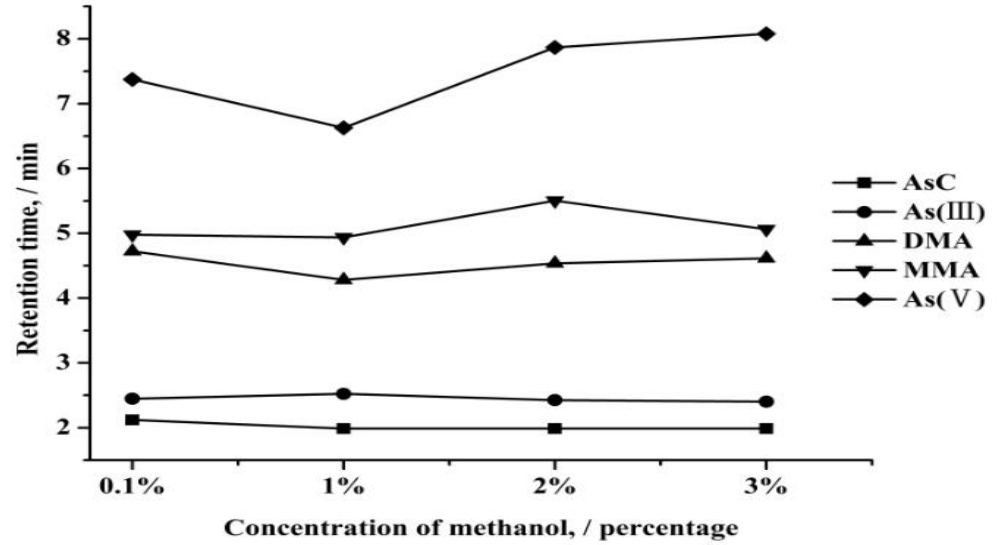

Fig. 2. Retention time of different arsenic species versus concentration of CH_3OH in mobile phase

However, it is just on the contrary for AsC and As(III) which are not easy to dissociate (pKa of AsC is 9.2). As shown in Fig. 5 that DMA, MMA and As(V) with relatively smaller acid dissociation constants cannot be well separated at high TBAB concentration when other conditions in mobile phase were constant. While at the same time AsC and As(III) can also not be well separated. In view of this situation and meanwhile in order to reduce the usage of reagents, 5 mmol/L TBAB in mobile phase of 1.0 mmol/L $(NH_4)_2HPO_4$ (pH=6.00) + 1.0% CH_3OH was finally chosen. Then the time taken for As(V), MMA, DMA, As(III) and AsC to travel through the column to the detector were 7.8, 4.8, 4.5, 2.3 and 2.0 min respectively.

AsC, As(III), DMA, MMA and As(V) were separated within 10 min by using an reserved-phase ion-pair chromatographic column at the optimized mobile phase that is 1 mmol/L $(NH_4)_2HPO_4$ (pH=6.00) + 1% CH_3OH + 5 mmol/L TBAB. The chromatogram was presented in Fig. 6.

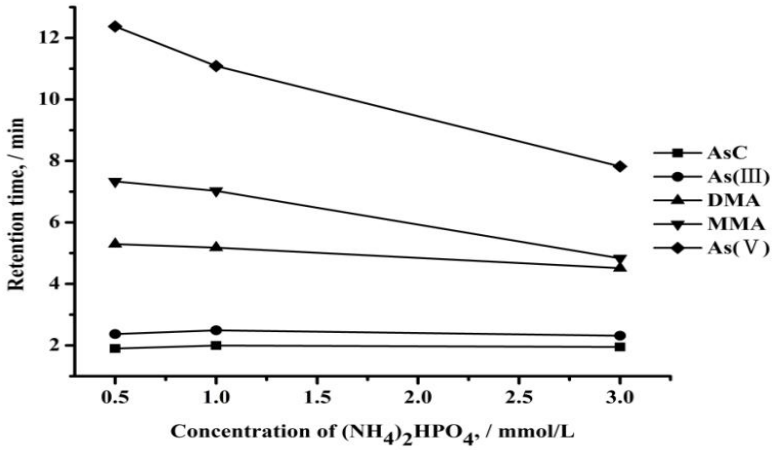

Fig. 3. Retention time of different arsenic species versus concentration of $(NH_4)_2HPO_4$ in mobile phase

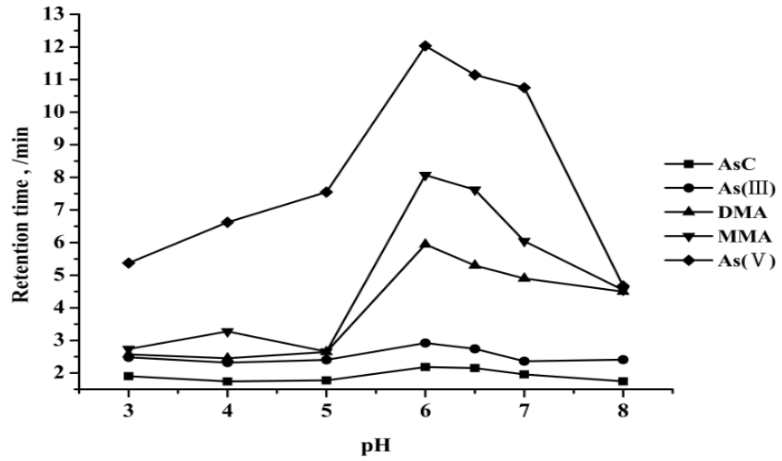

Fig. 4. Retention time of different arsenic species versus pH of mobile phase

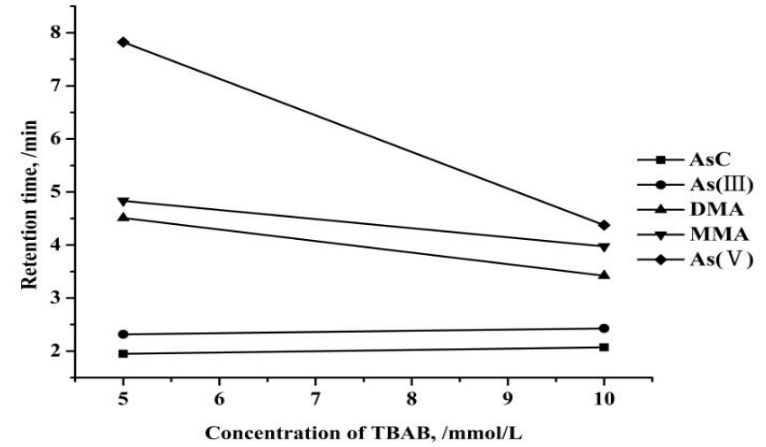

Fig. 5. Retention time of different arsenic species versus concentration of TBAB in mobile phase

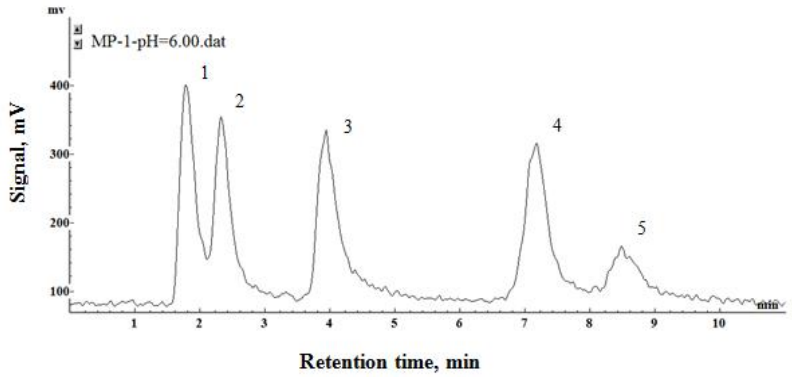

Fig. 6. Chromatogram of five arsenic species separated by ion-pair reverse-phase chromatography using 1.0 mmol/L $(NH_4)_2HPO_4$ (pH=6.00) + 1.0% CH3OH + 5.0 mmol/L TBAB
Peaks: 1, AsC; 2, As(III); 3, DMA; 4, MMA; 5, As(V)

4. CONCLUSION

A method for the separation and determination of five arsenic species in simple matrix was developed by using a Venusil-MP C18 reverse-phase chromatographic column eluted with 1 mmol/L $(NH_4)_2HPO_4$ (pH=6.00) + 1% CH_3OH + 5 mmol/L TBAB and detected by HG-AFS. It was found that AsC and As(III) were not easy to be separated for their electrical properties in solution. Meanwhile, the retention time of AsC and As(III) does not vary greatly with the change of concentration of CH_3OH, $(NH_4)_2HPO_4$ and TBAB in mobile phase. While pH of the mobile phase will lead to certain influence on their retention time. Five arsenic species were finally separated within 10 min by a reversed-phase ion-pair chromatographic column at the optimizing eluting conditions. Compared with the combination of anion exchange chromatography with inductively coupled plasma mass spectrometry (ICP-MS) reported in the earlier articles, the method here showed better separation results and less cost. This method provided a possibility for the separation and determination of AsC, As(III), DMA, MMA and As(V) in samples with simple matrix. The detection method may be applied to real samples such as sea water, urine or fish so that kinds and concentration of arsenic species in these samples could be determined.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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