Application of nanofilms for arsenic speciation using surface-enhanced Raman spectroscopy (SERS)

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ABSTRACT: The novel analytical method based on combination of “coffee ring” effect and Surface-enhanced Raman spectroscopy (SERS) has been developed for the speciation of thiolated arsenicals. The gold nanofilm (AuNF) has been fabricated by the coating of glass surface with 3-aminopropyltrimetoxysiloxane (APTMS) and citrate derived negatively charged gold nanoparticles. After the deposition of thioarsenicals buffer solution onto AuNF, following solvent evaporation, ring stamp was formed. Due to the difference in charges of molecules, DMMTA(V) and DMDTA(V) travelled different distances. Overall, the “coffee ring” effect has a decent potential for the speciation of arsenic compounds.

1 INTRODUCTION

The “coffee ring” effect has been previously employed primarily for the analytes preconcentration, however with proper glass surface modification it could have a potential for the separation of arsenic species. Dimethylmonothioarsinic acid (DMMTA(V)) and dimethyldithioarsinic acid (DMDTA(V)) are thioarsenicals that has been widely detected in animal urine after exposure to iAs(III) and DMA(V) (Fig. 1). Pentavalent thioarsenicals can bind to the proteins in contrast to iAs(III) and DMA(V), thus the toxicities of thioarsenicals are similar with that of iAs(III) and are much higher than those of DMA(V). So, high toxicity and protein binding capacity demonstrate that thioarsenicals might be the key arsenic metabolites related to the As overall toxicity. As a result, it is vital to develop a method that can precisely determine the exact amount of thioarsenicals in biological systems.

2 METHODS/EXPERIMENTAL

DMMTA(V) was synthesized according Cullen *et al.* (2016), the molar ratio of Na₂S/H₂SO₄/DMA was 1.6:1.6:1.

DMDTA(V) was synthesized by two different methods. The first method reported by Suzuki *et al.* (2004) provided the acidic form of DMDTA(V) in contrast to the second approach that has been described by Fricke *et al.* (2005) and allowed to synthesize the salt form of DMDTA(V). The molar ratio for these two methods of Na₂S/H₂SO₄/DMA(V) was 7.5:7.5:1.

The preparation of a gold nanofilm includes two stages, synthesis of citrate-coated gold and gold nanoparticles (AuNPs) and coating nanoparticles

Figure 1. The structures of Dimethylmonothioarsinic (DMMTA(V)) acid and dimethyldithioarsinic acid (DMDTA(V)).

onto silicon wafers. AuNPs were synthesized by Turkevich method. The fabrication of AuNF was performed by silanization of glass substrates by 3-aminopropyltrimetoxysiloxane (APTMS), following the deposition of negatively charged gold nanoparticles onto the positively charged amino groups silanized surface.

DMMTA(V) and DMDTA(V) solutions (10⁻⁴ M) solutions of thioarsenicals were prepared by dissolving thioarsenicals in buffer, following the deposition of 2 μL of DMMTA(V) and DMDTA(V) buffer solution onto the AuNF. Once the droplet was completely dried and a ring-shaped stain was formed on the AuNF, SERS signals were obtained from the center to the edge of the dried droplet.

3 RESULTS AND DISCUSSION

Raman spectra of solid thioarsenicals are shown in Figures 2 and Figures 3.

Since charged and neutral species would have various interactions with negatively charged SERS

Figure 2. Raman spectroscopy of DMMTA(V).

Figure 3. Raman spectroscopy of DMDTA(V).

Table 1. Raman vibrational frequencies of DMMTA(V) and DMDTA(V).

Arsenical	Assignment	Experimental Raman frequency (cm ⁻¹)
DMMTA(V)	As = S	469
	As – C	641
	As – O	643
DMDTA(V)	As – S	370,398
	As ÷ S	429
	s C – As – C	573,604
	a C – As – C	625

surface, their travelling distances might be different (Table 1). AuNF was applied for the separation of DMMTA(V) and DMDTA(V).

From the graph it is clear that As–S vibrations shift from 429 cm⁻¹ to 417 cm⁻¹ for DMDTA(V) and from 469 cm⁻¹ to 465 cm⁻¹ for DMMTA(V) respectively (Fig. 4), thus, thioarsenicals were adsorbed onto the AuNF and charge transfer between the molecules and AuNF surface occurred. However, it is not clear whether a capillary force that drawn thioarsenicals to the edges of evaporating droplet or attraction/repulsion interaction between analytes and the AuNF surface had the major impact onto the separation of thioarsenicals.

Figure 4. SERS of 10⁻⁴ M DMMTA(V) and DMDTA(V) buffer solution separated by "coffee ring" effect.

4 CONCLUSIONS

DMMTA(V) and DMDTA(V) were separated using "coffee ring" effect and identified by SERS. Nanofilms are versatile tools, facile to fabricate and easy to operate under necessary conditions. Overall, nanofilms had a decent potential for the separation of arsenic species.

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