

1-1-2012

Improved rinsing procedure for samples containing sulfide and organic interferences in determination of arsenic by voltammetry

Paul Lewtas

Magdalena Wajrak
Edith Cowan University

Follow this and additional works at: <https://ro.ecu.edu.au/ecuworks2012>



Part of the [Environmental Sciences Commons](#)

This is an Accepted Manuscript of an article published by Taylor & Francis in Proceedings of International Congress on Arsenic in the Environment on 22-27 July 2012: Lewtas, P. , & Wajrak, M. (2012). Improved rinsing procedure for samples containing sulfide and organic interferences in determination of arsenic by voltammetry. Proceedings of International Congress on Arsenic in the Environment, As 2012. (pp. 400-401). Cairns, Queensland. CRC Press. Available [here](#)

This Conference Proceeding is posted at Research Online.
<https://ro.ecu.edu.au/ecuworks2012/201>

Improved rinsing procedure for samples containing sulfide and organic interferences in determination of arsenic by voltammetry

P. Lewtas

Edith Cowan University, School of Natural Sciences, Perth, Western Australia

Cogent Environmental, Cambridge, UK

M. Wajrak

Edith Cowan University, School of Natural Sciences, Perth, Western Australia

ABSTRACT: As part of an ongoing investigation into As analysis by anodic stripping voltammetry (ASV), it was found that strong rinsing regimes in between samples could reduce the cumulative effect of organic and sulfide interferences. Longer term effects of this rinsing procedure on the measurement response have been investigated and the procedure optimized to give more a stable response over multiple sample analyses.

1 INTRODUCTION

Arsenic (As) contamination of waters due to both natural and industrial sources is a widespread problem. Anodic Stripping Voltammetry (ASV) is one of the few analytical methods sensitive enough to analyse As at the low levels required for environmental regulations. It also has the advantage of being able to speciate between As(III) and As(V) (Mays et al. 2009), but can suffer from interferences, particularly organics and sulfide.

A detailed investigation is currently underway into the effects of various interferences on As analysis by ASV, with a view to developing improved sample pretreatment methods for field analysis. As part of this investigation, significant carryover effects were seen when analysing clean solutions after analysis of sulfide containing solutions. It was necessary for the continuation of the project to develop an interim rinsing procedure to prevent residual organic and sulfide contamination from one test solution affecting the response of the following test solution.

This paper will present some preliminary results stemming from these investigations.

2 EQUIPMENT, MATERIALS AND METHODS

All measurements were carried out using a PDV6000plus portable voltammetric heavy metals analyser (Cogent Environmental, UK).

Analytic grade reagents were used throughout. Triton X was used to represent general organic interferences and daily made stock 100 ppm sulfide solutions were prepared by dissolving solid sodium sulfide in deionised water.

Gold film electrodes were prepared daily by polishing the carbon substrate with aluminium oxide emulsion and plating the gold film from a solution of 40 ppm Au in 0.1M HCl at -500 mV. A solution of 50 ppb As was then analysed 5 times to sensitise the electrode.

Solid gold working electrodes were prepared daily by polishing the carbon substrate with aluminium oxide emulsion and performing 10x voltammetric sweeps in 0.1M H₂SO₄. A solution of 50 ppb As was then analysed 5 times to sensitise the electrode.

A stock solution of 7 ppb As in 0.25M HCl was made and 20 mL aliquots from this were analysed as test solutions. Each test solution was analysed 4 times with the mean value recorded. Parameters used for the solid gold electrode were as per the manufacturer's instructions.

3 RESULTS

Initial testing to determine the levels of sulfide and organics showed significant carryover from the triton-X or sulfide containing solutions to the following interferent free standard solution following standard rinsing with deionised water (Figure 1). As

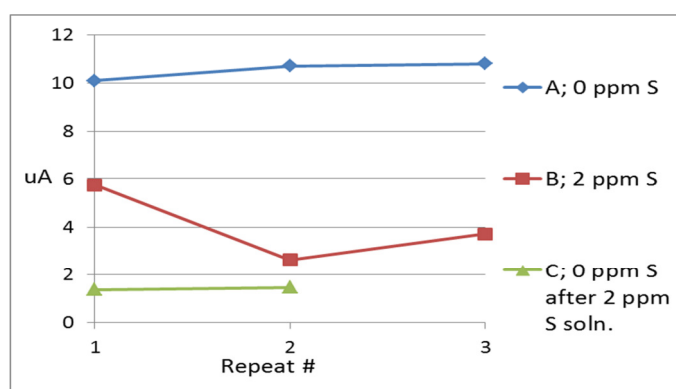


Figure 1 Initial test on effect of residual sulfide interference without NaOH-DI-HCl/KMnO₄ rinse on following solutions

described in our previous work (Lewtas et al. 2010), rinsing with a mix of 1M NaOH, deionised water and HCl/KMnO₄ solutions greatly reduced these effects, so this was applied to the current problem.

This method initially worked well in recovering response, as can be seen by the results in Figure 2. However, more rigorous long term testing of this procedure revealed some longer term negative effects on stability as seen in Figure 3. In particular, although initially more stable than the solid gold electrode, the gold film electrode sensitivity dropped significantly after analysing just 5 samples and visible gold film damage was seen after analysing less than ten samples. The solid gold electrode was not so easily damaged, although in this case, a significant trend of increasing response was seen with each new solution.

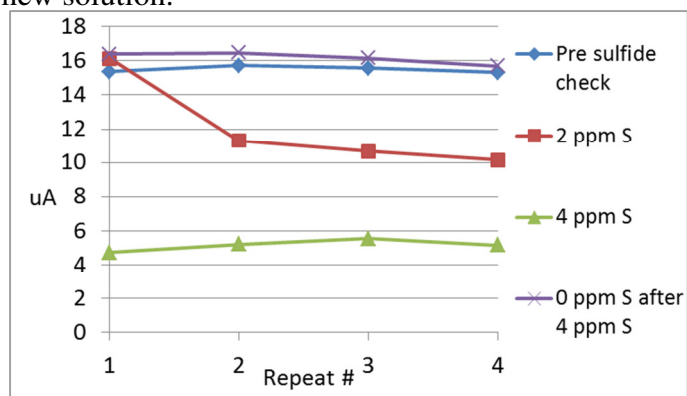


Figure 2 Test of rinsing NaOH-DI-HCl/KMnO₄ rinsing regime showing good peak recovery for clean solution after sulfide containing solutions.

the NaOH and the HCl/KMnO₄ rinsing solutions. 8 sample solutions were then analysed with the NaOH –DI- HCl/KMnO₄ rinse carried out between samples as further validation with results shown in Figure 4. A significant improvement in stability was seen at a level very near the final value shown in for the solid gold electrode in Figure 3 (approx. 16 uA), indicat-

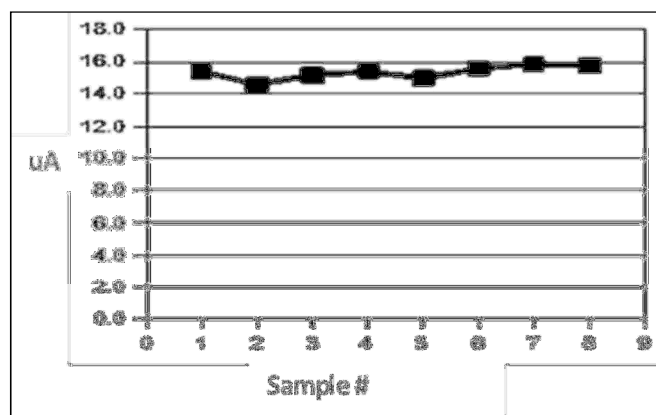


Figure 4 Stability of 8 test standard solutions using NaOH-DI-HCl/KMnO₄ rinse after Working electrode pretreatment with 5 minutes in 1M NaOH followed by 5 minutes in HCl/KMnO₄ at the start of the day.

ing that an equilibrium value would eventually have been reached without the 5 minute conditioning steps in the NaOH and the HCl/KMnO₄ solutions.

4 DISCUSSION

Comparison of Figures 1 and 2 show the effectiveness of the NaOH – DI – HCl/KMnO₄ rinsing step in reducing carryover interferences. The results shown in Figure 4 support the hypothesis that the increase in response with each analysed solution seen for solid gold in Figure 3 was due to an effect of the NaOH – DI – HCl/KMnO₄ rinse cycle increasing sensitivity, possibly due to working electrode oxidation. This data, though limited, should be of use to future studies in establishing reliable baseline values for interferences from organics and sulfides.

REFERENCES

Mays, D. E. & Hussam, A. 2009. Voltammetric methods for determination and speciation of inorganic arsenic in the environment-A review. *Analytica Chimica Acta* 646: 6-16

Lewtas, P, Fujikawa, Y., Sugahara, M., Hamasaki, T., Yoneda, D, 2010. Field analysis of arsenic by voltammetry – practical techniques for reduction of interferences. In J. S. Jean, J. Bundschuh, P. Bhattacharya (eds.), *Arsenic in Geosphere and Human Diseases*. CRC Press, The Netherlands.

Salaun, P., Planer-Friedrich, B. & van den Berg, C.M.G. 2007. Arsenic speciation in water and seawater by anodic stripping voltammetry with a gold microelectrode. *Analytica Chimica Acta* 585: 312–322

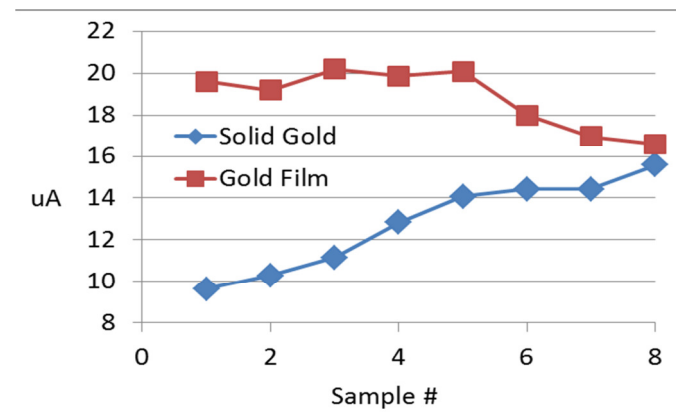


Figure 3 Long term effects of NaOH – DI – HCl/KMnO₄ rinsing at Au film electrode (top) & solid gold electrode (bottom). Note the greater initial sensitivity and stability of the gold film electrode.

This increasing response of the solid gold electrode was surmised to be mainly due to the continuing oxidation of the gold electrode surface by the KMnO₄ since increased oxidation of the working electrode has previously been shown to increase response of analysed metals (Salaun et al. 2007). It was also considered possible that the NaOH rinsing step could be a factor, possibly due to a cleaning effect of the electrode surface. To test this hypothesis, at the start of the next day's work the usual electrode pretreatment was followed by a 5 minute mix in both