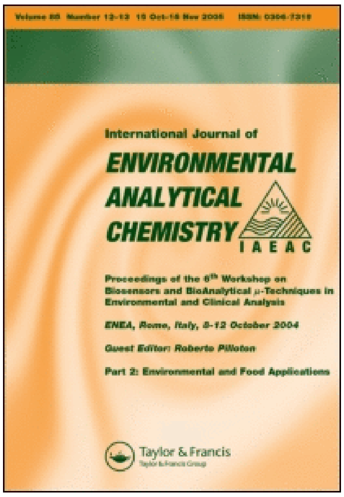

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Analysis of Silver in Freshwaters: Sample Preservation and Pre-Treatment Studies

K. C. Jones[a b]; P. J. Peterson[a]; B. E. Davies[c]
[a] Department of Biological Sciences, Chelsea College, University of London, London [b] Department of Environmental Sciences, University of Lancaster, Bailrigg, Lancaster [c] Department of Geography, University College of Wales, Penglais, Aberystwyth

To cite this Article Jones, K. C. , Peterson, P. J. and Davies, B. E.(1985) 'Analysis of Silver in Freshwaters: Sample Preservation and Pre-Treatment Studies', International Journal of Environmental Analytical Chemistry, 20: 3, 247 — 254
To link to this Article: DOI: 10.1080/03067318508077060
URL: http://dx.doi.org/10.1080/03067318508077060

Intern. J. Environ. Anal. Chem., 1985, Vol. 20, pp. 247–254
0306-7319/85/2004-0247 $18.50/0

Analysis of Silver in Freshwaters: Sample Preservation and Pre-Treatment Studies

K. C. JONES† and P. J. PETERSON
Department of Biological Sciences, Chelsea College, University of London, Hortensia Road, London SW10 0QT.

and

B. E. DAVIES
Department of Geography, University College of Wales, Penglais, Aberystwyth, SY23 3DB.

(*Received January 9, 1985*)

Losses of Ag from solution by adsorption on to borosilicate glass and polyethylene sample containers are reported. In distilled water over 80% of a 1 μg Ag l^{-1} solution may be adsorbed within 11 days. Acidification to 0.3 M HNO_3 satisfactorily preserved samples for this length of time and allowed direct analysis of Ag by graphite furnace atomic absorption spectrometry or pre-concentration by solvent extraction. Filtration through 0.45 μm membranes may bias the dissolved versus suspended partitioning of Ag in freshwaters in favour of the latter, by adsorption of soluble Ag.

KEY WORDS: Silver, freshwater, sample preservation, pretreatment studies.

INTRODUCTION

Silver usually occurs in natural freshwaters at μg l^{-1} concentrations or below, which are lower than those of elements ordinarily determined. Trace element analyses at these concentrations are frequently

---

†Present address: Department of Environmental Sciences, University of Lancaster, Bailrigg, Lancaster LA1 4YQ.

biased by losses of the analyte from solution by adsorption on to the sample collection vessels or filters. Various recommendations have been proposed to limit this problem but these have often been based on studies which used Ag concentrations unrepresentative of those found in natural waters.[1-3] High density polyethylene containers are usually recommended for the collection of field samples,[4,5] while in the laboratory, environmental samples are commonly stored in borosilicate glassware. An investigation was therefore undertaken to find the most appropriate sample preservation technique for these two container materials, using the radiotracer ^{110m}Ag. In addition, adsorption losses during filtration were investigated and the effect of this process on the interpretation of the "dissolved" versus "suspended" partitioning of Ag in water samples was assessed.

Ag concentrations determined directly in natural waters by graphite furnace atomic absorption spectrometry (GFAAS),[6] or following a solvent extraction scheme have been reported elsewhere.[7,8]

EXPERIMENTAL

Sample preservation studies

High density, wide-mouthed, screw top polyethylene bottles (0.55 l) were decontaminated by rinsing in 10% (v/v) HNO_3 for at least 48 h.[5] Grade A borosilicate glass volumetric flasks (0.1 l) were treated similarly. All containers were then rinsed thoroughly three times in double distilled water (DDW). Solutions containing ^{110m}Ag at a concentration of $1\,\mu g\,l^{-1}$ ($1\,\mu Ci\,l^{-1}$) were prepared in DDW, 0.3 M and 0.8 M HNO_3 (pH 2 and 1.3 respectively),[3,9-11] 0.001 M and 0.01 M ethylenediaminetetra acetic acid (EDTA)[1,2] and 0.01 M sodium thiosulphate ($Na_2S_2O_3$).[2] The DDW solution was stored in both light and darkened containers.[10] The solutions in glassware were made to volume while 0.25 l of solution was added to each of the polyethylene bottles. Each treatment was performed in triplicate. The solutions were assayed for ^{110m}Ag on a Packard Auto-Gamma 500 counting system at time intervals of 2, 4 and 6 hours, 1, 2, 3, 7, 14 and 21 days after the start of the experiment. After corrections for radioactive decay the percentage of ^{110m}Ag remaining in solution at each time interval was calculated.

Filtration studies

Millipore (0.45 μm, 47 mm diameter) filters were pre-treated in 2% (v/v) HNO_3 for 24 h and rinsed thoroughly in DDW. Solutions of $^{110m}AgNO_3$ for the experiment were prepared with pre-filtered DDW after passage through a Millipore all Pyrex glass vacuum filter unit with a male, standard-taper joint on a 1 l filter flask. The unit had previously been decontaminated by soaking with 10% HNO_3 for several days before use. The retention of soluble Ag by Millipore filters from various solutions containing 1 μg ^{110m}Ag l^{-1} was recorded. Filtration was carried out under a low vacuum.

RESULTS AND DISCUSSION

Sample preservation studies

The adsorption behaviour of Ag in both types of container was broadly similar for the media investigated (see Tables I and II). Adsorption appeared increasingly erratic with time in all cases. For example, after 21 days in DDW and borosilicate glass losses ranged between 59 and 87%. Adsorption over the container surface is commonly thought to be uniform in distribution. However, this is clearly not the case, as autoradiographs of the base of the polyethylene bottles used for storing DDW-^{110m}Ag show (see Figure 1). Considerable differences in the amount of Ag adsorbed by containers are also highlighted by the autoradiographs. Ag was rapidly lost from the DDW solutions, as much as 10% being adsorbed in 24 hours. Darkening of the polyethylene bottles reduced adsorption in the short term, but after three weeks losses were unacceptable. In borosilicate glass, losses to the surfaces of darkened flasks were higher than for clear containers and give no support to Struempler's[10] suggestion that Ag solutions should be stored in darkened vessels.

Acidification of the solutions in either of the HNO_3 preparations significantly reduced adsorption for at least 21 days at pH <2. These findings show good agreement with Struempler[10] who used a solution of 0.5 μg Ag l^{-1} in HNO_3 and found negligible adsorption following acidification; several other workers also recommend the acidification of samples as an aid to preservation.[11,12] In contrast, Schutz and Turekian[13] found no significant adsorption of Ag in

TABLE I

Percentage of ^{110m}Ag remaining in solution during storage in borosilicate glassware.

Treatment	Storage time 2 hours	4 hours	6 hours	1 day	2 days	3 days	8 days	14 days	21 days
Distilled water only	—	—	—	88.9 (82.4–95.0)	86.1 (76.4–93.5)	81.2 (70.1–90.8)	51.7 (44.9–60.8)	35.9 (25.8–44.4)	28.0 (13.3–41.4)
Distilled water darkened flask	88.4 (80.9–94.3)	87.0 (71.4–90.7)	80.4 (62.3–91.7)	80.7 (36.1–94.3)	55.9 (24.0–80.0)	55.1 (28.3–78.4)	34.0 (21.8–48.6)	26.6 (21.0–34.4)	22.2 (19.5–26.3)
0.3 M nitric acid	—	—	—	—	—	—	—	—	—
0.8 M nitric acid	—	—	—	—	—	—	—	—	—
0.001 M EDTA	—	—	90.3 (83.2–95.9)	92.9 (92.5–93.2)	89.7 (85.1–94.3)	88.6 (85.7–91.5)	71.4 (45.8–91.7)	48.7 (35.1–64.5)	35.2 (29.5–40.9)
0.01 M EDTA	—	—	94.1 (92.7–95.1)	93.1 (91.9–95.4)	86.6 (84.7–90.0)	85.5 (78.8–97.5)	57.7 (41.3–83.5)	50.2 (24.0–83.1)	46.4 (25.2–77.8)
0.01 M $Na_2S_2O_3$	—	—	—	—	—	—	—	—	—

At $t=0$, the solution contained 1 μg Ag.l^{-1}. The error on each aliquot due to pipetting and counting was ±5%. Hence only those values <95% of the $t=0$ count are shown. A dash (—) indicates a value lying within this 95–100% limit. The values shown are an average of 3 samples for each treatment, with duplicate aliquots taken from each. The range is shown in brackets.

TABLE II

Percentage of ^{110m}Ag remaining in solution during storage in polythene containers.

Treatment	Storage time								
	2 hours	4 hours	6 hours	1 day	2 days	3 days	7 days	14 days	21 days
Distilled water only	—	92.7 (91.0–93.9)	95.0 (93.5–97.8)	93.3 (93.1–93.6)	86.7 (81.7–91.3)	82.8 (72.0–88.7)	60.6 (46.3–73.4)	19.6 (10.4–37.3)	14.5 (4.9–32.8)
Distilled water, darkened flask	—	—	—	—	—	94.1 (90.8–98.2)	77.1 (72.9–80.9)	55.9 (47.5–66.3)	34.6 (20.8–45.1)
0.3 M nitric acid	—	—	—	—	—	—	—	—	—
0.8 M nitric acid	—	—	—	—	—	—	—	—	—
0.001 M EDTA	—	—	—	—	—	—	87.8 (84.4–94.2)	59.3 (42.9–91.5)	34.4 (7.9–87.1)
0.01 M EDTA	—	—	—	94.4 (92.4–96.4)	94.0 (93.3–95.0)	92.7 (90.4–95.3)	82.0 (77.5–86.9)	46.1 (22.2–59.4)	26.6 (2.9–44.0)
0.0 M $Na_2S_2O_3$	—	—	—	—	—	—	—	—	93.7 (93.1–94.2)

At $t=0$, the solution contained 1 $\mu g\,Ag.l^{-1}$. The error on each aliquot due to pipetting and counting was ±5%. Hence only those values <95% of the $t=0$ count are shown. A dash (—) indicates a value lying within this 95–100% limit. The values shown are an average of 3 samples for each treatment, with duplicate aliquots taken from each. The range is shown in brackets.

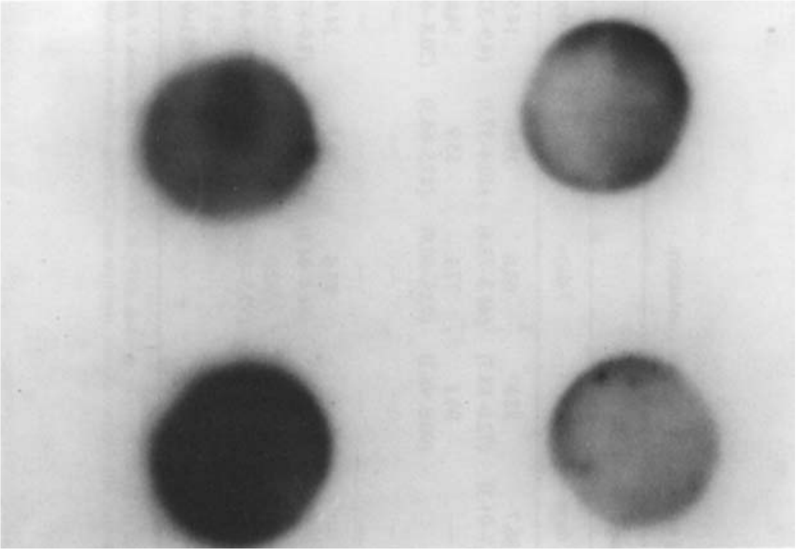

FIGURE 1 Autoradiographs of the base of polyethylene containers used for storing 1 μg ^{110m}Ag l^{-1} for 28 days.

seawater stored in pyrex glass bottles at its natural pH for up to 6 months. West *et al*[1,2] reported Ag losses of 20–30% onto borosilicate glass from a 0.01 M NaCl solution (pH 4.6), but only 7–10% from 0.1 M NaCl under the same conditions. This may explain the absence of Ag adsorption in non-acidified seawater mixtures,[11] either through competition for adsorption sites by Na^+ or by the formation of the soluble $AgCl_2^-$ ligand.

Complexing Ag with EDTA was effective in retaining the metal in solution over short periods (up to 3 days at 0.001 M EDTA in polyethylene), but was ineffective over anything longer than a week. These findings are at variance with those of West *et al*[14] who used EDTA as a preservative for up to 10 days. Sodium thiosulphate was as effective as acidification in preventing adsorption, but has the disadvantage of hampering direct analysis for Ag by GFAAS.[6]

Other workers have suggested freezing samples to preserve them, but this is impractical in the field when collecting large volumes (>0.5 l). There is also some evidence that freezing may produce erratic results. Sheaffer *et al*[15] found that in acidified samples (pH 1.5), supposedly frozen at −20°C, solutions of Ag retained an unfrozen core which contained most of the Ag originally present in the whole sample.

Acidification to pH <2 clearly seems the most efficient and practical method of sample preservation for Ag; it can readily be achieved in the field following filtration and has also proved a satisfactory method for the preservation of other metals, notably Cd, Cu, Pb and Zn.[4,7,10,11] Soluble metal contents may then be determined directly by GFAAS[6] or following solvent preconcentration with ammonium-1-pyrrolidine dithiocarbamate/methyl isobutyl ketone (APDC/MIBK).[8]

Filtration studies

The distinction between the "dissolved" (soluble, filtrable) and "particulate" (suspended, non-filtrable) components in waters has come to be accepted as those fractions which pass through or are retained by a filter with nominal pore size of 0.45 μm. However, the results presented in Table III suggest that the filtration process may itself bias the interpretation of data on the dissolved versus suspended partitioning of Ag. Adsorption of soluble Ag by the filters increases the proportion of total water Ag measured in the suspended phase. Some soluble Ag was retained on the filter from all the solutions tested, but this effect was most marked at high pH. Trace losses of Cd and Cu during filtration have also been reported.[16]

TABLE III

Percentage of ^{110m}Ag (added as $^{110m}AgNO_3$) retained by acid rinsed 0.45 μm Millipore filters from solutions of 1 μg Ag.l^{-1} (each value is mean of 3 analyses; 0.5 l passed through each filter).

	% retained
Double distilled water, buffered to pH 2	3
Double distilled water, buffered to pH 3	3
Double distilled water, buffered to pH 4.4	10
Double distilled water, buffered to pH 6	24
Double distilled water, buffered to pH 7	27
River Ystwyth water ("soft" water) pH 5.8	11
Chelsea College tapwater ("hard" water) pH 6.5	9

Acknowledgements

The authors are grateful to the Welsh Office for financial support during this work.

References

1. F. K. West, P. W. West and F. A. Iddings, *Anal Chem.* **38,** 1566 (1966).
2. F. K. West, P. W. West and F. A. Iddings, *Anal. Chim. Acta* **37**, 112 (1967).
3. W. Dyck, *Anal. Chem.* **40,** 454 (1968).
4. G. Batley and D. Gardner, *Wat. Res.* **11,** 745 (1977).
5. S. J. de Mora and R. M. Harrison, *Wat. Res.* **17,** 723 (1983).
6. K. C. Jones, P. J. Peterson and B. E. Davies, *Geoderma* **33,** 157 (1984).
7. K. C. Jones, P. J. Peterson and B. E. Davies, *Wat. Air Soil Pollut* **24,** 329 (1985).
8. K. C. Jones, *Environmental Aspects of Silver in Wales*, Unpublished Ph.D. Thesis, University of London (1984).
9. T. T. Chao, E. A. Jenne and L. M. Heppting, *US Geol. Survey Prof. Paper* 600-*D*, *D*13–*D*15 (1968).
10. A. W. Struempler, *Anal. Chem.* **45,** 2251 (1973).
11. R. Massee, F. J. M. J. Maessen and J. J. M. De Goeij, *Anal. Chim. Acta* **127**, 181 (1981).
12. D. E. Robertson, *Anal. Chim. Acta* **42,** 533 (1968).
13. D. F. Schutz and K. K. Turekian, *Geochim. Cosmochim. Acta* **29,** 259 (1965).
14. F. W. West, P. W. West and T. V. Ramakrishna, *Environ. Sci. Technol.* **1,** 717 (1967).
15. J. D. Sheaffer, G. D. Mulvey and R. K. Skogerboe, *Anal. Chem.* **50,** 1239 (1978).
16. J. Gardiner, *Wat. Res.,* **8,** 157 (1974).