

Use of gold as a routine and long term preservative for mercury in potable water, as determined by ICP-MS

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A study was made of the effects of storing both deionised and potable water spiked with mercury in both glass and poly(ethylene terephthalate) (PET) containers, using gold as a preservative. Bulk solutions of mercury at three different concentrations (0.5, 1.0 and 1.5 $\mu\text{g l}^{-1}$) were prepared separately in deionised (DI) water and locally obtained potable water. Individual glass and PET bottles containing gold, as gold chloride solution, were filled with these solutions and then analysed over a four week period, by ICP-MS. Details of the ICP-MS operational criteria are given in the text. The results show that there was little difference in mercury recovery from any of the solutions used when stored in either the glass or the PET containers during the study. The maximum/minimum recoveries for each system spiked at 1 $\mu\text{g l}^{-1}$ Hg were: glass–DI water 103/93%; glass–potable water, 106/96%; PET + gold–DI water, 103/97%; PET + gold–potable water, 106/99%. This establishes the effectiveness of gold as a preservative agent for mercury in potable water up to a concentration of 1.0 $\mu\text{g l}^{-1}$ Hg, adequately covering the range up to the Prescribed Concentration or Value (PCV) required by UK legislation. The effect of the gold on the analysis of other low concentration metals in potable water using ICP-MS was studied and recoveries ranging from 92–103% were obtained in its presence. The determination of mercury using the cold vapour fluorescence technique was affected by the presence of the gold chloride. All mercury containing solutions and standards were matrix matched to potable water by the addition of calcium, potassium and sodium salts.

Introduction

Mercury is one of the elements that must by law be monitored in potable water to ensure compliance with water quality regulations.¹ There is no specific regulation about the material of the container into which any sample is placed, but guidance is given in the Blue Book² where it is suggested that for mercury glass containers be used with acidified samples. Glass has its limitations in that it is fragile and heavy when compared to modern plastics. Previous work by Copeland *et al.*³ demonstrated that containers made from poly(ethylene terephthalate) (PET) can be used to store mercury samples, if preserved by potassium dichromate and nitric acid, performing as well as acidified glass containers.

A project to develop an analytical method for the determination of mercury in potable water by ICP-MS was successfully concluded by the authors.⁴ This project utilised gold as a preservative agent for mercury and results demonstrated that mercury in the standards and samples was stable for several weeks in glass containers. Having identified this fact an extension to the original project was undertaken to verify if this effect would occur when PET bottles were used. The results of this work comparing the storage of mercury containing samples in glass and PET bottles, pre-treated only with gold chloride solution, are described in this paper.

The advantage of using PET bottles, untreated other than with gold as the preservative, would offer many advantages over glass. They would obviously be lighter and more robust in use. Additionally as the gold solution is in more dilute nitric acid this offers less risk to the technician taking the sample than the mixture of concentrated nitric acid and potassium dichromate currently used. It is also possible to measure the concentration of the gold at the same time as the mercury, by ICP-MS, thus confirming that there is sufficient gold present to retain the mercury. Failure to sample correctly would then be detectable

as the gold concentration would be low, whilst the presence of the correct concentration of gold will reinforce the quality of the sampling. Using this scheme it is possible to simultaneously analyse for all metals of interest at low concentrations by ICP-MS.

The comparison of stability between glass and PET was made using solutions of mercury of three differing concentrations in both deionised water and potable water over twenty six days.

Procedure

Mercury standard solution (1 mg l^{-1}) was prepared by serial dilution of a 1000 mg l^{-1} , ICP standard (Merck, Poole, Dorset, UK) in 1% nitric acid (Aristar grade, Merck) in glass volumetric flasks.

Test solutions were prepared in bulk by adding mercury standard to both deionised and locally obtained potable water to give three different concentrations, 0.5, 1.0 and 1.5 $\mu\text{g l}^{-1}$ Hg in each matrix. All deionised water test solutions were matrix matched by the addition of calcium, sodium and potassium salts as shown in Table 1. All solutions were also spiked with various metals (from ICP standards) as described in Table 1, to reflect the severest situation where they are all at the Prescribed Concentration or Value (PCV). This would check the effect of their presence on the ICP-MS results. All solutions were spiked with rhodium (10 $\mu\text{g l}^{-1}$) as internal standard (IS).

Clean glass and PET bottles, 54 of each, were labelled to give sufficient individual containers for the trial period. The gold preservative (ICP standard, Merck) was added to every individual container to give 5 mg l^{-1} Au in the final volume. Each bottle was then filled with the pre-prepared mercury solutions in either deionised (DI) or potable water as described in Tables 5 and 6. The bottles were stored at the ambient

conditions in the laboratory until analysis. On the appropriate day one glass and one PET bottle, each containing one of the three differing concentrations, from the remaining pool of unopened bottles was selected. The bottles were unsealed and the contents analysed by ICP-MS, using a PE Sciex Elan 6000 (Perkin Elmer Ltd, Beaconsfield, UK). The details of the ICP-MS operation are given below. The use of unopened bottles was preferred to avoid the possibility of external contamination affecting the bottle contents once a bottle had been unsealed. Any contamination would have had a marked effect on the final results of the study, as the concentration of mercury being detected is small.

A separate multi-element spiked solution was prepared by the addition of a variety of metals from ICP standards (Merck) to potable water to give final concentrations close to the PCVs of the individual metals as described in Table 1. This solution was analysed by ICP-MS at the end of the study period to determine if the presence of the gold adversely affected the recovery of the other metals that require mandatory monitoring in potable water.

To complete the study, samples of both deionised and potable water containing gold at 5 mg l⁻¹ and mercury at differing concentrations were analysed using the cold vapour fluorescence technique on the PSA Merlin instrument (P.S. Analytical Ltd, Orpington, Kent, UK).

ICP-MS instrument operation

The PE Sciex Elan 6000 ICP-MS was used for the determination of mercury. Full optimisation was carried out weekly and the tuning and performance checks made daily using the solutions described below. Cerium and barium were used to monitor the formation of oxides and doubly charged ions. Operating criteria for the Elan 6000 are listed in Table 2. No analysis was done unless the instrument performance complied with the manufacturer's criteria.

Tuning solution

This solution consisted of ⁹Be, ²⁴Mg, ¹⁰²Rh, ²⁰⁸Pb and ²³⁸U, all at a concentration of 10 µg l⁻¹, matrix matched with Ca at 100 mg l⁻¹, Na at 30 mg l⁻¹ and K at 10 mg l⁻¹ in 1% nitric acid (Aristar).

Table 1 Concentrations of metals added to deionised and potable water test solutions^a

	Deionised water test solutions	Potable water test solutions
Ca	100 mg l ⁻¹	—
Na	30 mg l ⁻¹	—
K	10 mg l ⁻¹	—
Al	200	200
Fe	200	200
Cr	50	50
Mn	50	50
Ni	50	50
Pb	50	50
Ag	10	10
Cd	5	5
As	50	50
Se	10	10
Sb	10	10
Cu	3000	3000
Zn	5000	5000
Rh (IS)	10	10

^a Concentrations in µg l⁻¹ except where stated.

System optimisation solution

This solution consisted of the following metals, all at 10 µg l⁻¹ in 1% nitric (Aristar) acid: ³Li, ⁹Be, ²⁴Mg, ⁵⁹Co, ⁵⁸Ni, ¹⁰³Rh, ¹¹⁴In, ¹³⁷Ba, ¹⁴⁰Ce, ²⁰⁴Tl, ²⁰⁸Pb, ²¹³Bi, ²³⁸U, and matrix matched with Ca at 100 mg l⁻¹, Na at 30 mg l⁻¹ and K at 10 mg l⁻¹.

Calibration

Since the method is primarily for determination of Hg in drinking water the calibration standards were made using deionised water with comparable concentrations of Ca, Na, and K added, as found in drinking water. These are the major elements present in potable waters in concentrations that can cause matrix effects. The top calibration standard was selected at 1.2 µg l⁻¹ to cover the PCV as defined by UK legislation. All standards were spiked with 10 µg l⁻¹ Rh as an internal standard and 5 mg l⁻¹ Au. Table 3 shows the composition of the calibration standards used.

The performance of the analytical method for mercury undertaken to NS 30 specifications is given in abbreviated form in Table 4.

PSA Merlin operation

The instrument was calibrated using standard solutions of mercury in 1% nitric acid in deionised water at concentrations of 1.0 and 2.0 µg l⁻¹. The standards were separately prepared,

Table 2 PE Sciex Elan 6000 ICP-MS operational settings

Sweeps/Reading	65
Reading/Replicate	1
Number of replicates	3
Tuning file	Default.tun
Optimisation file	Default.dac
Scan mode	Peak hopping
MCA	1
Dwell time	25.0 ms
Integration time	1625.0 ms
Detector mode	Dual
Auto lens	On
Spectral peak processing	Average
Signal profile processing	Average
Curve type	Linear through zero
Rh 103	Internal standard
Standard 1	Blank
Standard 2	0.6 µg l ⁻¹ Hg
Standard 3	1.20 µg l ⁻¹ Hg
Sample flush time	30 s
Sample flush speed	48 rpm
Read delay	60 s
Read delay between standards	60 s
Wash time between standards	1 s, 60 s, 120 s
Wash speed	48 rpm
Wash solution	5 mg l ⁻¹ Au in 1% nitric acid
Nebuliser gas flow	1.0 l min ⁻¹
Rf power	1025 W

Table 3 ICP-MS Calibration solutions

	Blank	Standard 1	Standard 2
Hg	—	0.6 µg l ⁻¹	1.20 µg l ⁻¹
Ca	100 mg l ⁻¹	100 mg l ⁻¹	100 mg l ⁻¹
Na	30 mg l ⁻¹	30 mg l ⁻¹	30 mg l ⁻¹
K	10 mg l ⁻¹	10 mg l ⁻¹	10 mg l ⁻¹
Rh	10 µg l ⁻¹	10 µg l ⁻¹	10 µg l ⁻¹
Au	5 mg l ⁻¹	5 mg l ⁻¹	5 mg l ⁻¹

Table 4 Validation results for mercury stabilised with gold using ICP-MS. Results in $\mu\text{g l}^{-1}$ ^{202}Hg

	Blank	0.12 $\mu\text{g l}^{-1}$ (10% PCV) Standard	1.08 $\mu\text{g l}^{-1}$ (90% PCV) Standard	Potable tap water	Spiked tap to 1.0 $\mu\text{g l}^{-1}$ (PCV)
Mean	0.0038	0.1137	1.0671	0.0070	0.9905
<i>F</i> value	1.8800	9.8573	13.0287	3.3602	40.0015
<i>s_w</i> (within)	0.0064	0.0030	0.0089	0.0039	0.0084
<i>s_b</i> (between)		0.0064	0.0218	0.0043	0.0370
<i>s_t</i> (total)		0.0071	0.0236	0.0058	0.0379
RSD		6.2	2.2	82.7	3.8
Estimated degrees of freedom		13	13	17	12
LOD		0.032 $\mu\text{g l}^{-1}$			
Recovery		99.05%			

Table 5 Results from stability trial in PET bottles

	Spiked potable water			Spiked deionised water		
	Concentration $\text{Hg}/\mu\text{g l}^{-1}$			Concentration $\text{Hg}/\mu\text{g l}^{-1}$		
Spiked to:	0.5	1.0	1.5	0.5	1.0	1.5
Day 1	0.51	1.03	1.67	0.51	1.01	1.50
Day 4	0.50	1.03	1.62	0.50	1.00	1.50
Day 5	0.49	0.99	1.52	0.50	0.98	1.47
Day 6	0.51	1.03	1.59	0.50	1.00	1.49
Day 11	0.49	1.00	1.53	0.48	0.99	1.50
Day 12	0.52	1.06	1.64	0.51	0.97	1.50
Day 13	0.52	1.06	1.58	0.52	1.03	1.56
Day 25	0.52	1.00	1.49	0.49	0.97	1.47
Day 26	0.50	1.00	1.56	0.51	1.03	1.53

Table 6 Results from stability trial in glass bottles

	Spiked potable water			Spiked deionised water		
	Concentration $\text{Hg}/\mu\text{g l}^{-1}$			Concentration $\text{Hg}/\mu\text{g l}^{-1}$		
Spiked to:	0.5	1.0	1.5	0.5	1.0	1.5
Day 1	0.52	1.06	1.61	0.50	1.00	1.59
Day 4	0.50	1.02	1.58	0.48	0.99	1.61
Day 5	0.49	1.00	1.50	0.48	0.98	1.69
Day 6	0.50	1.01	1.53	0.49	0.96	1.59
Day 11	0.47	1.03	1.47	0.45	0.93	1.50
Day 12	0.51	1.04	1.58	0.49	0.97	1.50
Day 13	0.50	1.05	1.52	0.49	1.0	1.59
Day 25	0.49	0.96	1.45	0.46	0.95	1.52
Day 26	0.50	1.04	1.56	0.51	1.03	1.62

one set without gold and the other with gold added to 5 mg l^{-1} .

A series of alternating blanks and Analytical Quality Control (AQC) standards, 1.0 $\mu\text{g l}^{-1}$ Hg in 1% nitric acid, was then run following calibration with the standards containing gold.

Results and discussion

The results obtained from the stability trial are given in Tables 5 and 6. It is recognised that the results from the solutions containing 1.5 $\mu\text{g l}^{-1}$ Hg are outside the calibration range used for mercury determination by ICP-MS. However they were originally included to indicate whether there was suppression of the preservative effect beyond the PCV value of 1 $\mu\text{g l}^{-1}$ Hg. It was deemed that the trials would be conducted using the previously validated method for mercury analysis by ICP-MS,⁴ which is calibrated to 1.2 $\mu\text{g l}^{-1}$ Hg. These results have been presented because it is known that the instrument response is linear beyond the top standard and also that they clearly show

Table 7 Recovery of a variety of metals of interest in potable water that contains Au and Hg

Element	Spiked to/ $\mu\text{g l}^{-1}$	Recovered/ $\mu\text{g l}^{-1}$
Al	200	198
Fe	200	193
Cr	50	47.9
Mn	50	49.2
Ni	50	48.5
Pb	50	51.6
Ag	10	10.1
Cd	5	5.03
As	50	50.3
Se	10	9.85
Sb	10	9.16
Cu	3000	2920
Zn	5000	4850

Table 8 Effect of the presence of gold on the calibration of the PSA Merlin analyser

	Without addition of Au	With addition of Au
Standards	Emission counts	Emission counts
Blank	0.000	0.668
1.0 $\mu\text{g l}^{-1}$ Hg	43.00	34.36
2.0 $\mu\text{g l}^{-1}$ Hg	89.00	62.76
	$r = 0.9998$	$r = 0.9988$

that the efficiency of the gold as a preservative is not limited to the calibration range.

The recovery rates from both the glass bottles and the gold–PET combination show that there is virtually no loss of mercury from the solution over the trial period. The method performance obtained from the analytical validation for the determination of mercury by ICP-MS is given in Table 4, and will account for most of the variation found in the results.

The results demonstrate that there is no effect shown upon the efficiency of the gold as a preserving agent by the presence of the other included metals at their PCV concentrations.

The data in Table 7 show that there is no noticeable effect on the recovery of the other metals of interest in potable water due to the presence of the gold at 5 mg l^{-1} . The Drinking Water Inspectorate (DWI) have defined the acceptable range of recovery for these metals as 95–105% in potable water at the PCV values. The other metals have been previously validated in this matrix and all show compliance with the analytical criteria detailed in the Guidance on Safeguarding the Quality of Public Water Supplies,⁵ that generally defines the DWI Analytical Quality criteria.

The performance of the cold vapour fluorescence technique was significantly affected by the presence of the gold. Table 8 shows that the presence of gold suppresses signal response of

Table 9 Consecutive blank and 1.0 µg l⁻¹ Hg AQC standard analysis for Hg spiked solution with 5 mg l⁻¹ gold using PSA atomic fluorescence technique

Samples	Concentration
AQC	1.009
Blank	0.018
AQC	0.980
Blank	0.016
AQC	1.015
Blank	0.000
AQC	0.969
Blank	0.000
AQC	1.013
Blank	0.004
Target AQC value 1.00 µg l ⁻¹	

the standards by about 50%, but that a workable straight line graph can still be obtained as indicated by the linear correlation coefficients. The performance of the instrument when analysing the short blank–AQC series, Table 9, indicates that despite the loss of signal reasonable results can be obtained from this instrument when analysing mercury containing samples. It is not known if the performance shown would comply with DWI analytical criteria.

Conclusion

This work has demonstrated that it is possible to preserve mercury in drinking water samples by using gold chloride addition to PET sample bottles prior to sampling. Drinking water samples preserved in this manner can then be analysed by

ICP-MS for mercury at the same time as the other metals of interest for compliance purposes.

The use of one PET bottle to sample water for all metals of interest to the DWI, significantly improves the efficiency of the analysing laboratory as the complete suite of metals can be determined simultaneously by ICP-MS. The fall back position of using the cold vapour fluorescence technique (PSA Merlin) is possible but would need to pass performance criteria, after full validation, on gold preserved samples before its use could be sanctioned.

The addition of gold will also be of use in confirming the quality of the sampling as the dose rate for any container should be 5 mg l⁻¹, and this can be measured con-currently. The lightness and robustness of the PET material will also be beneficial to the samplers resulting in fewer broken bottles. The gold chloride solution will pose virtually no hazard to either the samplers or householders from whose homes the samples are taken.

References

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