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Storage of natural water samples for total and reactive mercury analysis in PET bottles

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Poly(ethylene terephthalate) (PET) bottles used in commercially available mineral water were compared to Teflon bottles for sampling and storage of river water samples prior to mercury determination. The metal concentration was in the range 0.3–2.0 ng L^{-1} for the reactive species, and in the range 1–9 ng L^{-1} for total mercury. A paired *t*-test showed no significant difference in the results for both reactive ($p = 0.011$) and total Hg ($p = 0.024$). Storage time was studied for PET bottles, using synthetic samples spiked with 10 ng L^{-1} Hg^{2+} ions, using two different types of preservation: (a) by freezing at −18 °C, and (b) by the addition of BrCl solution. Both procedures yielded the same results up to the 14th day of storage (ANOVA, $p = 0.72$ for BrCl and $p = 0.12$ for freezing). The freezing procedure proved to be more suitable for longer storage times, *i.e.*, up to 40 d (significance level of 0.03, ANOVA).

Introduction

Mercury occurs at very low levels (sub-ppt) in natural waters and serious problems can arise in sampling and post-sampling procedures due to possible losses during storage time and from contamination caused by the release of mercury from the flask walls to the sample. Owing to the porous nature of some sampling vessels, mercury uptake from the surrounding atmosphere can also occur, especially when using polyethylene bottles.[1]

In respect of the conservative stability of mercury solutions, significant changes in the concentrations can occur as a function of the concentration level, the redox characteristics of the water, the nature of the sampling material container, the cleaning and pretreatment of the sampling devices, and the use of preservative.[2] These aspects are largely known and are well documented.[3] Official guidelines recommend the use of glass bottles for sampling and storage of water samples[4,5] since polyethylene bottles are inadequate for this purpose.[1,2] Actually, when working with waters showing low levels of mercury, it is common practice in the scientific community to use Teflon bottles for water sampling and short-term storage. Clean protocols for decontamination of sampling devices are well established too.[6–8]

The use of poly(ethylene terephthalate) (PET) bottles has been previously suggested[9] and has been validated for aqueous samples showing mercury levels of between 50 and 1500 ng L^{-1}, a range well above the typical mercury concentration levels found in slightly or non-impacted lakes and rivers, which are already monitored in different parts of the world.[10–15] The major aim of this work was to evaluate (and validate) the potential use of PET bottles for sampling and mid-term storage of non-impacted water samples, from both natural river and lake water samples collected in the Amazon region, as well as synthetic samples. There are some key advantages for using PET bottles instead Teflon or glass bottles; PET bottles are relatively inexpensive and can be discharged as recyclable plastic after use, thereby avoiding the timing consuming and labor intensive steps of cleaning the material for reuse, at the same time it assures undetectable levels of contamination either by leaching from the sampling vessels or by metal losses.[9]

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Experimental

Apparatus

The determination of mercury was carried out using a Brooks Rand (Seattle, WA) CVAFS (cold vapor atomic fluorescence spectrometer), using gold quartz-sand columns for the mercury pre-concentration. Hydrochloric acid was purified by a quartz sub-boiling mill and distilled water was treated in a MilliQ Plus (Molsheim, France) equipment. Alfa Aesar (Bethesda, MD) high density Teflon bottles and 500 mL commercially available mineral water PET bottles were used as the sampling and storage devices.

Mercury measurements

The determination of the reactive mercury was carried out according to the following procedure. To a 100 mL non-filtered water sample was added 2 mL of $SnCl_2$ solution (containing 20% w/v of $SnCl_2$ and 10% v/v concentrated HCl, bubbled with gold filtered argon for 45 min). This solution was then purged with argon (300 mL min^{-1}) for 15 min. The mercury released was amalgamated in a gold-sand column, desorbed by heating, and detected using CVAFS.[16] A detection limit of 0.04 ng L^{-1} (blank plus 3 times the standard deviation) was observed. For total mercury, 100 mL (or less) of sample were first wet-oxidized using a BrCl solution.[17]

Sampling vessel pre-treatment

The Teflon bottles were rinsed with MilliQ water, the soaked in hot (70 °C) 4 mol L^{-1} HCl for 48 h, washed with MilliQ water, and filled with sub-boiling distilled HCl containing 5 mL L^{-1} of the BrCl solution. After 24 h, the bottles were then rinsed several times with MilliQ water, dried in a class 100 fume hood, filled with 100 mL of high purity 0.1 mol L^{-1} HCl and wrapped in three plastic bags until sampling.[18] The preparation of the PET bottles was much simpler, consisting only of discharging the original mineral water, washing several times with MilliQ water, drying in a class 100 fume hood, filling with 100 mL of high purity 0.1 mol L^{-1} HCl, and finally wrapping in three plastic bags until sampling.

Table 1 Comparative results obtained for reactive ($Hg_{reactive}$) and total mercury (Hg_{total}) in water samples collected in the Amazon region using both PET and Teflon bottles

		$Hg_{reactive}$/ng L^{-1}		Hg_{total}/ng L^{-1}	
Sampling site	Date	PET	Teflon	PET	Teflon
Iara Lake	02/16/98	1.35 ± 0.15	1.35 ± 0.04	8.79 ± 0.65	8.36 ± 0.65
Panacarica R.	02/17/98	0.30 ± 0.01	0.32 ± 0.02	1.69 ± 0.05	1.78 ± 0.14
Panacarica R.	02/17/98	0.32 ± 0.07	0.36 ± 0.01	1.89 ± 0.05	2.16 ± 0.19
Maependi R.	19/02/98	1.45 ± 0.04	1.51 ± 0.08	6.18 ± 0.09	6.73 ± 0.10
Maependi R.	20/02/98	1.50 ± 0.28	2.07 ± 0.04	5.92 ± 0.34	7.37 ± 0.28
Maependi R.	20/02/98	1.23 ± 0.06	1.43 ± 0.15	6.21 ± 0.17	6.79 ± 0.09
Maependi R.	20/02/98	1.28 ± 0.05	1.70 ± 0.01	5.53 ± 0.10	6.27 ± 0.31
Maependi R.	20/02/98	1.19 ± 0.01	1.34 ± 0.01	8.83 ± 0.31	9.44 ± 0.19
Maependi R.	20/02/98	2.07 ± 0.06	2.33 ± 0.01	6.64 ± 0.31	6.90 ± 0.56
Maependi R.	20/02/98	1.67 ± 0.06	2.32 ± 0.32	7.07 ± 0.05	7.22 ± 0.14

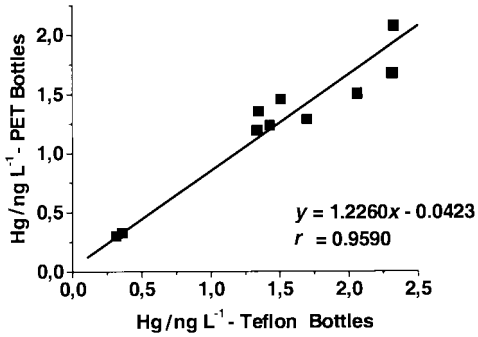

Fig. 1 Comparative results obtained for reactive mercury in river water samples collected and preserved in Teflon and PET bottles.

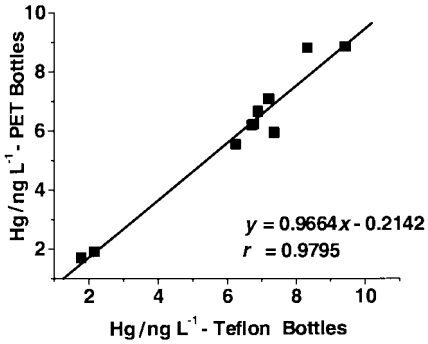

Fig. 2 Comparative results obtained for total mercury in river water samples collected and preserved in Teflon and PET bottles.

Bottles comparison

For comparison of the analytical results obtained using both types of bottles, 10 different river water samples from the Negro River Basin (Amazon), were collected, frozen, transported and analyzed in duplicate for reactive Hg, and in triplicate for total Hg. To further investigate the stability of the water samples kept in the PET bottles, synthetic (MilliQ ultra-pure water) samples containing 10 ng L^{-1} of total Hg were preserved both at −18 °C and by the addition of 1.0 mL L^{-1} of BrCl solution. These were then analyzed 0, 3, 7, 14, 28 and 40 d after spiking with mercury. Three bottles were analyzed in triplicate at each time.

Results and discussion

The results obtained for the 10 different water samples collected from three different sites at the Negro River Basin are presented in Table 1. The total mercury concentration varied in the range 1–9 ng L^{-1}, while the concentration of reactive mercury varied between 0.3 and 2.0 ng L^{-1}. In this analytical comparison of the two types of bottles, the paired *t*-test for the Amazonian river water samples (Fig. 1 and 2) showed no significant difference in the results for both reactive (p = 0.011) and total Hg (p = 0.024). These results fully demonstrate the potential of using

Table 2 Comparative results obtained for total mercury (Hg_{total}) stored in PET bottles and preserved by freezing (−18 °C) and using BrCl at room temperature

		Hg_{total}/ng L^{-1}	
Time/d	Bottle	−18 °C	Room temperature with BrCl[a]
0	1	9.91 ± 0.22	
	2	10.53 ± 0.57	
	3	10.72 ± 0.68	
	Mean	10.38 ± 0.91	
3	4	10.91 ± 0.82	10.05 ± 0.37
	5	9.93 ± 0.26	10.29 ± 0.42
	6	10.24 ± 0.73	10.82 ± 0.84
	Mean	10.36 ± 1.13	10.39 ± 0.54
7	7	10.36 ± 0.49	10.25 ± 0.31
	8	10.62 ± 0.23	10.30 ± 0.38
	9	10.56 ± 0.40	10.49 ± 0.15
	Mean	10.51 ± 0.67	10.34 ± 0.51
14	10	9.76 ± 0.07	9.64 ± 0.55
	11	9.89 ± 0.09	9.85 ± 0.12
	12	9.74 ± 0.08	10.69 ± 0.42
	Mean	9.80 ± 0.14	10.06 ± 0.70
28	13	9.51 ± 0.45	7.99 ± 0.07
	14	9.67 ± 0.32	8.10 ± 0.32
	15	10.06 ± 0.46	8.14 ± 0.27
	Mean	9.75 ± 0.72	8.08 ± 0.18
40	16	10.03 ± 0.22	9.39 ± 0.22
	17	9.40 ± 0.12	8.55 ± 0.26
	18	9.87 ± 0.36	8.19 ± 0.11
	Mean	9.77 ± 0.44	8.71 ± 0.36

[a] Each bottle was analyzed in triplicate.

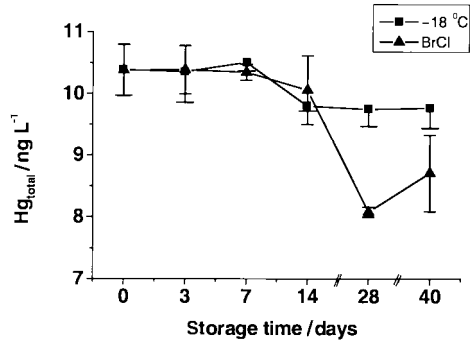

Fig. 3 Mercury concentration in synthetic samples preserved by freezing at −18 °C and at room temperature by the addition of BrCl in PET bottles.

PET bottles for both sampling and preservation of waters showing ppt mercury levels.

In a second part of this evaluation, a synthetic solution containing approximately 10 ng L^{-1} of total mercury was prepared directly in PET bottles, followed by two different types of storage: (a) freezing at −18 °C, and (b) room temperature preservation using BrCl addition. The results obtained in these complementary experiments are shown in Table 2 and Fig. 3. In respect of the recovery of mercury in samples preserved in PET bottles (Fig 3), both procedures yielded the same results up to the 14th day of storage (ANOVA, $p = 0.72$ for BrCl and $p = 0.12$ for freezing). At the end of 40 d, the freezing storage procedure showed no changes with respect to the initial mercury concentration fixed at the beginning of the experiment (significance level of 0.03, ANOVA).

Conclusions

The comparative results obtained for total and reactive mercury in aqueous samples both sampled and stored in Teflon and PET bottles showed no significant differences. When ultra-pure water was spiked with mercury at a concentration of 10 ng L^{-1}, short-term storage (up to 14 d) can be accomplished using either freezing at −18 °C or by the addition of the oxidizing agent BrCl in PET bottles. However, for longer periods of storage (up to 40 d), freezing is the recommended procedure.

The possibility of using PET bottles instead of glass or Teflon poses a tremendous advantage not only in direct costs, but also in that the sampling bottles are the same ones used for mineral water, they are widely available commercially in different volume sizes, and cost at least 100 times less than Teflon. Indirectly, the use of PET bottles for mercury sampling and storage dispenses with the need for tedious, labor and time-consuming pre-treatment, such as acid soaking, at the same time, being much lighter than both glass and Teflon, the costs related to sample transportation drop markedly.

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