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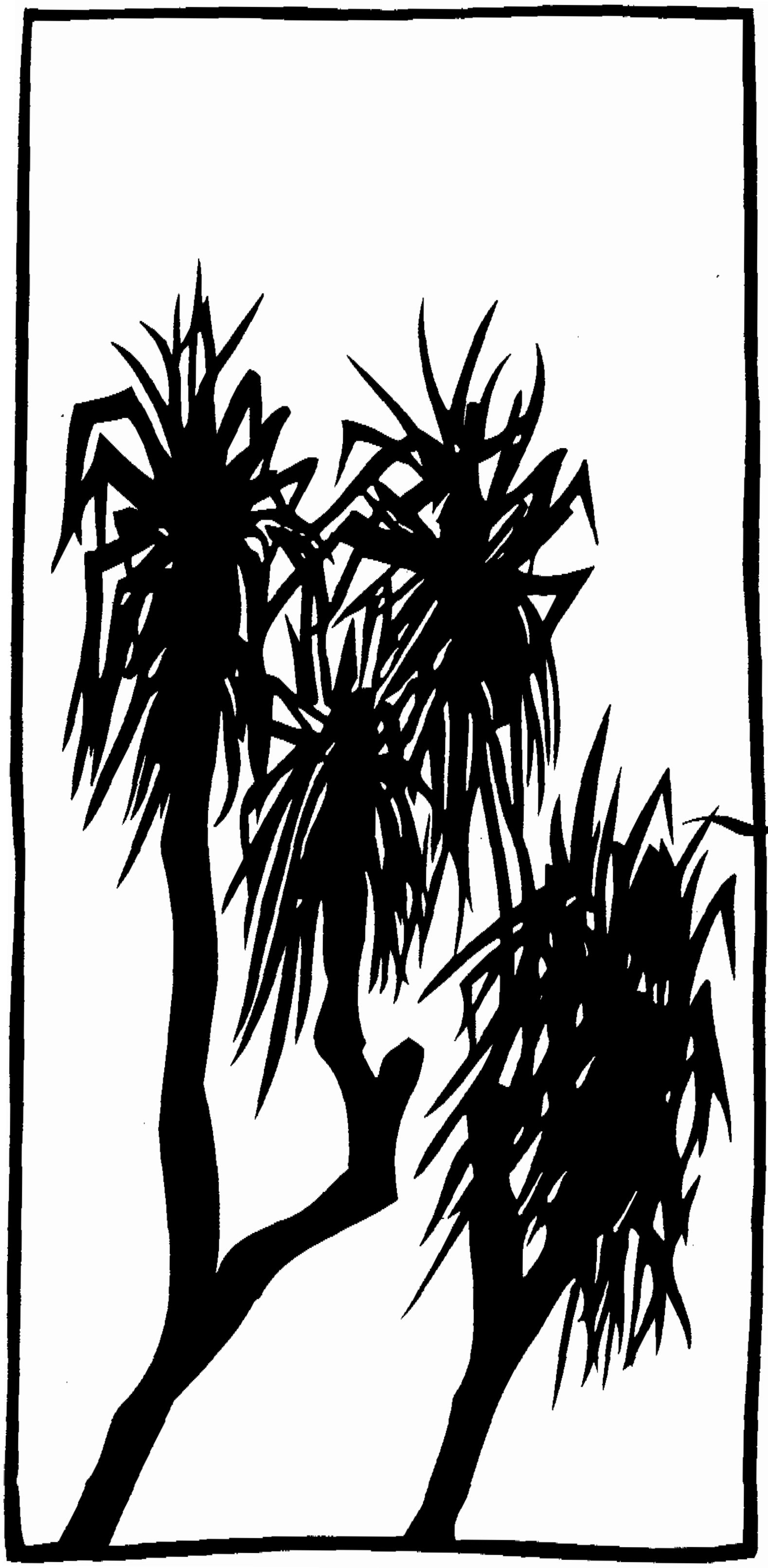

The extent of contamination of samples for carbon analysis by contact with plastic surfaces

Adam Speers
Christopher leGras

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supervising scientist

THE EXTENT OF CONTAMINATION OF SAMPLES FOR CARBON ANALYSIS BY CONTACT WITH PLASTIC SURFACES

Adam Speers and Christopher leGras

Abstract

Keywords: carbon determination, plastic containers, contamination potential

This report describes the effects of storage in plastic bottles, and filtration, on samples for analysis of total organic carbon. The sample containers used were made from high density polyethylene (HDPE). Polycarbonate filtration apparatus with neoprene gaskets were used, together with polycarbonate and nylon <0.45 µm membranes. High-purity water was prepared using Millipore Super-Q equipment.

Six experiments were performed on notionally blank samples (n=10). Unfiltered, unacidified Super-Q water was stored at 4°C for 24 hours and 7 days; unfiltered Super-Q water was acidified 1% v/v with Aristar HNO_3 and stored at 4°C for 24 hours and 7 days; and unacidified Super-Q water was filtered (<0.45 µm) through polycarbonate and nylon membranes, then acidified as above and stored for 24 hours before analysis. The highest concentration observed, in the unfiltered, acidified sample stored for 7 days, was 0.11 mg/L. Statistical analyses were performed on pairs of treatments, using the Student's t distribution. These showed that all treatments, except filtration through a polycarbonate membrane, yielded mean values which were significantly different from a Super-Q water blank stored in a glass container ($p<0.05$).

Three experiments were performed on samples containing 25 mg/L dissolved organic carbon. The treatments were: a sample prepared using glass apparatus and analysed immediately; samples stored in HDPE bottles for 7 days at 4°C, and samples acidified as above and stored for 7 days at 4°C. Statistical analysis using the F distribution demonstrated that no significant differences existed among the samples. This implies that carbon contamination, and adsorption and oxidative degradation losses are minimal. However, close examination of the data suggests that a small degree of carbon contamination, similar to that found in the blanks, may occur.

The glass vials used in the autosampler require only simple rinsing in Super-Q water as a cleaning procedure.

Introduction

The APHA (1992) Standard Method for the analysis of total organic carbon (TOC) specifies that samples be collected, transported and stored in glass containers. These containers require special preparation, are relatively expensive, and potentially hazardous due to their fragility, especially in field situations. Where a number of analytes are required for samples, the conventional approach to collection and storage for TOC necessitates the acquisition and handling of parallel subsamples. Rigorous attention to sample preparation mandates the use, for example, of all-glass filtration apparatus. This is exactly the opposite requirement to that for heavy-metal analyses. Where large numbers of samples need to be analysed, the logistical constraints imposed by these parallel protocols becomes onerous, and in extreme cases impractical.

For these reasons, we describe here series of experiments which sought to determine the extent to which TOC contamination of samples ensues from the use of plastic bottles (high density polyethylene), filtration apparatus (polycarbonate) and filtration membranes (polycarbonate and nylon). We used samples, based on high-purity water, which were notionally free from organic carbon. An additional set of experiments, using unfiltered solutions that nominally contained 25 mg/L TOC, aimed to determine whether adsorptive losses of analyte occurred, and whether acidification with HNO_3 (APHA specifies HCl or H_2SO_4) caused oxidative degradation. Both experiments used samples stored for a week before analysis.

Sample bottle preparation was similar to that used to prepare sample bottles for general analytes, but particularly heavy metals. Use of a general preparative procedure was designed to avoid resource diversion in support of a multitude of cleaning protocols.

Experimental

Equipment and Reagents

All carbon analyses were performed using an OIC Model 700 TOC Analyser with dedicated autosampling module. Borosilicate glass screw-topped vials (10 mL capacity) were used with the autosampler. Samples were stored in 60 mL Nalgene high density polyethylene (HDPE) bottles (c/n 2002-0002). Sartorius filtration apparatus (polycarbonate with neoprene gasket) were used with Nuclepore 47 mm <0.4 μm polycarbonate membranes (c/n 111107). For syringe-assisted filtration, a Terumo polycarbonate syringe was used with Alltech disposable 25 mm cartridges (c/n 2359). The <0.45 μm Nylon 66 membrane and 1 μm glass prefilter were contained within a polypropylene housing.

All samples were prepared using Millipore Super-Q water, Aristar HNO_3 and Analar potassium hydrogen phthalate. All other reagents were Analar grade.

Procedures

Sample bottles and caps were prepared by soaking in 3% v/v Analar HNO_3 for 2 days, followed by copious rinsing with Super-Q water. The bottles were left filled with Super-Q water until use (about 1 week).

Unfiltered, unacidified samples were prepared by filling 10 emptied and rinsed bottles to the neck and storing them in a refrigerator for one or seven days. Acidified samples were prepared in the same way, with 600 μL of Aristar HNO_3 added with a dispensing pipette. The pipette tips were stored soaking in 10% v/v Analar HNO_3 before use. Filtered samples were acidified (1% v/v Aristar HNO_3) after filtration. Sartorius filtration apparatus and Nuclepore membranes were stored in 1% v/v Analar HNO_3 and washed copiously with Super-Q water before use. The syringe used for syringe-assisted filtration was washed in Super-Q water before use. Filter cartridges were not washed, but the first 5 mL of sample was run to waste before an aliquot was collected. A new filter membrane or cartridge was used for each of the ten samples.

Samples containing a nominal concentration of 25 mg/L TOC were prepared by dilution of a stock solution of potassium hydrogen phthalate (KHP) (1000 mg/L C; prepared from the compound dried at 110°C). The two treatments involved storage for 7 days of acidified (1% v/v Aristar HNO_3) and unacidified samples (n=10) at 4°C.

All samples were prepared at a time so that they could be determined in the same batch, thereby eliminating inter-run variations among experiments.

To determine TOC, a sample aliquot of 1020 μL was acidified with 200 μL of 5% v/v phosphoric acid and purged with nitrogen. This step allows determination of total inorganic carbon, if required. The acidified sample was mixed with 1000 μL of sodium persulfate solution (100 g/L) at 100°C and purged with nitrogen. The carbon dioxide produced was measured by non-dispersive infrared spectrometry. The TOC analyser was calibrated using a 25 mg/L solution of inorganic C. A stock solution (1000 mg/L C) was prepared from oven dried (110°C) anhydrous sodium carbonate, and the calibration standard prepared by dilution of this. Observed organic carbon concentrations are corrected for small variations in the recovery of TOC, compared with the inorganic calibration standard, by use of a SPEX (US EPA) Demand reference water. The product information for this material discloses that it is prepared from D-glucose and L-glutamic acid. Its certificate value (20.4±2.0 mg/L) was previously confirmed by comparison with a TOC (potassium hydrogen phthalate) calibration standard.

Statistical analyses of the data were performed using standard techniques (Winer, 1971 and Mendenhall *et al*, 1981).

Results and Discussion

Analytical Results

Measured carbon concentrations for notionally blank samples, and samples containing 25 mg/L TOC are presented in Tables 1 and 2 respectively. The most important conclusion from these results is that none of the treatments resulted in gross contamination of samples with organic carbon, the highest concentration measured in 'blank' treatments being 0.11±0.02 mg/L, for the acidified sample after one week. The quantitation limit (4σ), based on the average standard deviation for all 'blank' treatments was 0.08 mg/L. Therefore, these results imply that carbon contamination from suitably prepared plastic equipment is unlikely to be analytically important.

Table 1 Carbon concentrations (mg/L) in notionally blank samples with different treatments

	Super-Q water/glass 'true blank'	Super-Q water/1 day	Super-Q water/1 week	1% v/v HNO_3/ 1 day	1% v/v HNO_3/ 1 week	1% v/v HNO_3/ membrane filtered	1% v/v HNO_3/ syringe filtered
	0.0103	0.0141	-0.0053	0.0512	0.0960	-0.0053	0.0921
	0.0044	-0.0053	0.0200	0.1077	0.1545	0.0103	0.0960
	0.0103	0.0258	0.0103	0.0804	0.0940	-0.0092	0.0979
	0.0005	0.0180	0.0317	0.0570	0.1233	-0.0092	0.1545
	-0.0034	0.0005	0.1194	0.0570	0.1369	-0.0170	0.0862
	-0.0014	0.0122	0.0200	0.0395	0.0823	-0.0248	0.0999
	-0.0073	0.0005	0.0297	0.0278	0.0960	-0.0092	0.1135
	0.0064	0.0083	0.0297	0.0473	0.1038	0.0005	0.0960
	-0.0092	0.0064	0.0453	0.0356	0.1252	-0.0034	0.1194
	-0.0112	0.0103	0.0609	0.0648	0.1155	-0.0112	0.1311
Mean	**-0.0001**	**0.0091**	**0.0362**	**0.0568**	**0.1128**	**-0.0078**	**0.1087**
Standard Deviation	**0.0078**	**0.0092**	**0.0344**	**0.0234**	**0.0224**	**0.0095**	**0.0212**

Table 2 Carbon concentrations in TOC standard solutions (nominally 25 mg/L) with different treatments

	Glass Container	Super-Q water	1% v/v HNO3/
	23.14	22.83	22.96
	23.35	24.77	24.51
	23.58	23.13	24.65
	23.37	24.64	24.39
	24.27	24.64	24.55
	24.76	23.23	24.86
		24.82	24.35
		24.66	24.69
		23.40	24.78
		24.62	24.41
Mean	**23.75**	**24.08**	**24.42**
Standard Deviation	**0.63**	**0.81**	**0.54**

The samples containing 25 mg/L TOC showed a similar pattern, with the unacidified samples stored for 1 week in HDPE bottles yielding a recovery of about 101%, while the recovery of the acidified samples averaged 103%, both compared with the freshly prepared, glass-stored sample. The following observations can be made from these results.

- The presence of an organic carbon source in samples does not result in markedly enhanced leaching of carbon from the HDPE bottles, compared with a blank solution. Acidification apparently results in slightly increased (though not statistically significant) carbon concentrations, as was found for notionally blank samples.
- Adsorption losses of KHP to the walls of the sample bottles seems to be negligible. This finding would need to be verified for organic carbon sources of different polarity and functional groups.
- The use of HNO_3 to acidify samples (as opposed to HCl or H_2SO_4 recommended in standard methods) does not seem to result in significant oxidation of KHP. Again, this result would need to be verified for other organic compounds.

Statistical Analysis of Results

An initial statistical evaluation was performed on the six notionally blank treatment experiments (ie, excluding the glass-only 'true blank' measurements) using the *F* distribution. This yielded a value for F_{obs} of 53.0, compared with critical values of F(5,54) for α=0.05 and 0.01 of 2.40 and 3.40 respectively. Following the finding that differences among experiment means were highly significant, comparisons were made between various pairs of experiments using the Student's *t* test. Tests that revealed statistically significant differences between means are shown in Table 3.

Table 3 Statistical significance for pairwise comparisons of notionally blank experiments

Comparison#	Common variance	Difference between means	95% confidence interval	99% confidence interval	99.9% confidence interval	Statistical significance
1 vs 2	0.000081	**0.009**	0.008	0.012	0.016	**$p<0.05$**
1 vs 3	0.000338	**0.057**	0.017	0.024	0.032	**$p<0.001$**
1 vs 4	0.000691	**0.036**	0.025	0.034	0.046	**$p<0.01$**
1 vs 6	0.000084	**-0.008**	0.009	0.012	0.016	**$p<0.1$ (ns)**
2 vs 3	0.000351	**0.048**	0.018	0.024	0.033	**$p<0.001$**
2 vs 4	0.000703	**0.027**	0.025	0.034	0.047	**$p<0.05$**
3 vs 5	0.000583	**0.056**	0.023	0.031	0.042	**$p<0.001$**
3 vs 6	0.000354	**-0.065**	0.018	0.024	0.033	**$p<0.001$**
3 vs 7	0.000553	**0.052**	0.022	0.030	0.041	**$p<0.001$**
4 vs 5	0.000936	**0.077**	0.029	0.039	0.054	**$p<0.001$**
6 vs 7	0.000299	**0.117**	0.016	0.022	0.030	**$p<0.001$**

#: **Experiment 1:** 'true blank' using glassware only; **Experiment 2:** unacidified water stored for 1 day; **Experiment 3:** acidified water stored for 1 day; **Experiment 4:** unacidified water stored for 7 days; **Experiment 5:** acidified water stored for 7 days; **Experiment 6:** water filtered using Nuclepore membrane and acidified; **Experiment 7:** water filtered using Alltech syringe cartridge and acidified.

It is evident from the analyses in Table 3 that storage of Super-Q water in HDPE bottles for periods of 1 and 7 days results in small but statistically significant increases in the concentration of organic carbon. This is accentuated when the water is acidified. The effect of filtration, followed by acidification, is not consistent. We infer that water progressively leaches low molecular mass compounds (monomers, oligomers, and/or additives) from the containers, and that the effect is enhanced by acid.

Filtration through a <0.45 µm polycarbonate membrane before acidification results in a TOC concentration significantly lower ($p<0.001$) than for equivalent (acidified) unfiltered samples. In fact, the measured concentration is less than in the 'true blank', though not significantly so. A suggested mechanism for the apparent removal of carbon by filtration is given below.

With the equipment used to determine TOC, there is no direct observation of the carbon concentration in a sample (such as a chart recorder trace), so zero is defined by a blank presumed to contain no carbon. This presumption may not be justified for Super-Q water. The Super-Q system used employs a reverse-osmosis membrane, followed sequentially by a carbon cartridge, two resin-based mixed-bed ion exchange cartridges and a millitube <0.22 µm filtration cartridge.

In previous work concerned with measuring ultratrace zinc concentrations (leGras and Noller 1989), Super-Q water stored in acid-soaked HDPE bottles reported occasional, random zinc contamination in the range 500-800 ng/L on acidification. Careful examination of recorder traces for graphite furnace AAS determination of zinc in the water before acidification showed that, for those bottles shown to be contaminated after acidification, [Zn] was consistently near 20 ng/L, compared with about 8 ng/L for those bottles subsequently shown to be uncontaminated. These results were interpreted then as implying the passage of Zn-contaminated, colloidal resin particles through the Millitube filter. These particles then mainly adhered to the walls of the bottles, releasing their zinc on acidification. This interpretation was supported by laboratory records which showed that the ion exchange cartridges had been replaced immediately before the contamination problem emerged, suggesting a initial flush-out of fines.

We believe that, for the present experiment, resin colloids adhered to the membrane, and/or apparatus during filtration, because the <0.45 μm membrane would not be expected to remove particulates that had previously passed through a <0.22 μm filter. Acid soaking of apparatus may activate surfaces, and make adsorption of some colloids more favourable. If this interpretation is correct, then unfiltered Super-Q water may contain approximately 0.06 mg/L of TOC. As this concentration is below the generally accepted detection limit (and near the limit found in this study), this degree of contamination should not present a serious quality control problem. In the case of the syringe filter cartridge, the significantly greater ($p<0.001$ for both comparisons) carbon concentration (0.11 mg/L) is probably an artefact of less-rigorous cartridge preparation. However, this concentration would be negligible for most applications.

To test whether rigorous cleaning of glass autosampler vials is required between uses, vials were filled with a 25 mg/L standard solution, emptied, rinsed three times with Super-Q water, then refilled with Super-Q water. The [TOC] concentration in these vials ($n=10$) was -0.005± 0.02 mg/L, suggesting that contamination of samples by insufficiently cleaned autosampler vials is unlikely to occur if normal precautions are used.

Conclusions

The results of this limited study support the idea that there is no compelling reason to avoid the use of polymer containers and apparatus to store and process samples acquired for total organic carbon analysis. This statement assumes that plasticware has been prepared in accordance with proper standards of laboratory cleanliness. The present experiments used containers and filtration apparatus prepared by the protocol used for heavy-metal samples. The main findings of the study were as follows.

- The leaching of TOC from HDPE bottles was greater after one week than for one day, for both acidified and unacidified samples. For acidified samples the effect was greater, though in no case was the final [TOC] greater than about 0.1 mg/L.

- The effects of filtration on [TOC] were also minimal, with minor contamination apparently ensuing from syringe cartridges not rigorously prepared, and acid-soaked membrane filters seemingly removing some TOC from Super-Q water; possibly by adsorption of resin colloids from the high-purity water system.

- There was no evidence for analytically meaningful adsorption of TOC to the walls of HDPE containers from 25 mg/L standard solutions (hydrogen phthalate). In addition, the acidification of standard solutions (1% v/v HNO_3) did not result in any measurable degradation.

We stress that these experiments do not provide a comprehensive endorsement of the use of plastic apparatus in TOC analysis. In particular:

- no claims can be made for the behaviour of solutions stored for more than a week. However, as it is recommended (APHA) that analyses be completed within this time, and this is good laboratory practice, we did not see a need to continue the study over a longer period,

- some plastics may not be suitable for use with TOC analyses, particularly those that contain significant concentrations of residual monomers and/or plasticisers. We did not test any polymers based on cellulose esters; commonly used for filter membranes. Nor can the small degree of contamination evidently contributed during the short contact time with the nylon 66/polypropylene syringe cartridges conclusively be attributed to insufficient preparation alone, and

- the effects of adsorption and oxidative degradation (by HNO_3) were studied for one compound only, and for seven days only. Longer storage periods with different classes of compounds may yield different results.

We nevertheless believe that, for the protocols, equipment and reagents used in this laboratory, substitution of HDPE for glass containers can be effected without seriously compromising sample integrity. In addition, where filtration is required, normal laboratory equipment can be used without detriment.

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