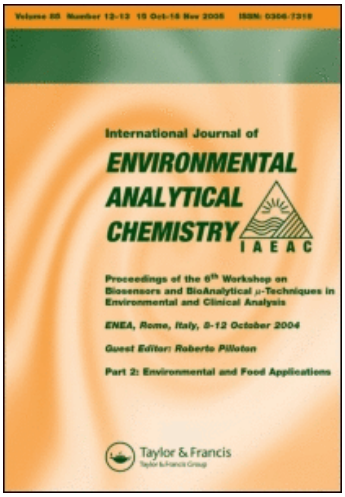

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Investigation of a Method for Routine use of General-Purpose Teflon Bombs for the Digestion of Samples for Trace Metal Analysis

Carola H. Kirchner[a]; G. A. Eagle[a]; H. F. K. O. Hennig[a]
[a] National Research institute for Oceanology, Council for Scientific and Industrial Research, slenbosch, South Africa

To cite this Article Kirchner, Carola H. , Eagle, G. A. and Hennig, H. F. K. O.(1988) 'Investigation of a Method for Routine use of General-Purpose Teflon Bombs for the Digestion of Samples for Trace Metal Analysis', International Journal of Environmental Analytical Chemistry, 32: 1, 9 — 21
To link to this Article: DOI: 10.1080/03067318808079073
URL: http://dx.doi.org/10.1080/03067318808079073

Intern. J. Environ. Anal. Chem., Vol. 32, pp. 9–21
Photocopying permitted by license only

Printed in Great Britain

Investigation of a Method for Routine use of General-Purpose Teflon Bombs for the Digestion of Samples for Trace Metal Analysis

CAROLA H. KIRCHNER, G. A. EAGLE and
H. F.-K. O. HENNIG*

National Research Institute for Oceanology, Council for Scientific and Industrial Research, Stellenbosch, South Africa

(*Received 15 December 1986; in final form 1 June 1987*)

The merits of teflon bomb and open system digestion of marine biological material and sediments have been investigated. Marine tissue and sediments with known metal concentration were digested at different temperatures (90 °C, 100 °C and 110 °C) and different acids (HCl, H_3PO_4, aqua regia and HNO_3). It was found that aqua regia digestion was more suitable for carbon furnace metal analysis. Nitric acid is recommended for flame metal analysis. The final conclusion was that teflon bomb digestion is preferred over open system digestion with samples up to a maximum mass of 0.1 g dry weight at a temperature of 110 °C.

KEY WORDS: Metal, teflon bomb, acid, temperature, biological tissue, sediment.

INTRODUCTION

Analysis by atomic absorption spectroscopy requires that all materials must be in solution. One of the problems of analysis of biological materials for trace elements is that they must first be decomposed so that the metals are dissolved without loss or

contamination. Acid-digestion bombs have been extensively used, although most methods described use hydrofluoric acid and/or perchloric acid.

The teflon decomposition vessels have been used successfully in the past for a variety of samples.[1] Rapid decomposition of silicates by hydrofluoric acid at 110 °C is achieved in a specially designed vessel made of teflon (Du Pont) without volatilization losses.[2] A fluoroboric-boric acid system was found to provide a favourable decomposition medium and a suitable saltfree single matrix system.

The decomposition of bovine liver (NBS-SRM 1577) with small amounts of nitric and perchloric acids in a sealed teflon vessel at elevated temperature has been described.[3] The method was satisfactorily applied to the decomposition of various biological samples.

Uchida *et al.*[4] described the decomposition of bovine liver in sealed teflon vessels. Samples of 250 mg and 25 mg of NBS-SRM 1577 were decomposed in two steps, at 90 °C for 3 h and then at 120 °C for 3 h; 1–2 mg samples were decomposed at 130 °C for 3 h. Reproducibility and accuracy were satisfactory and the results obtained for 1 and 2 mg samples also showed reasonable precision and accuracy.

In a short communication Van Eenbergen *et al.*[5] studied the losses of elements during sample decomposition in Parr[6] acid digestion bombs. This was done by means of radioactive nuclides of the elements.

Okamoto and Fuwa[7] used a teflon double vessel for digestion of biological materials. For the digestion acid they used distilled nitric acid at 90 °C for 2 h and then increased the temperature to 140 °C for 4 h. Hydrofluoric acid was used to dissolve siliceous materials contained in mussel and oyster samples. The disadvantage of this system, however, is that the PFA vial has to be replaced after four to five uses under pressure. This makes the method very costly.

The aim of this study was to find a routine laboratory method in which the teflon bombs could be employed to dissolve samples without the use of either perchloric acid or hydrofluoric acid. Our decomposition vessels are made of teflon.

Organic material and sediments can be digested successfully by using an open system with mineral acids like nitric, perchloric, sulphuric and hydrofluoric acid, or a mixture of these. The advantages of a closed system are;

1) less risk of contamination
2) no losses of volatile elements
3) less reagent needed, and
4) much faster digestion.

In this study various samples (fish meal, sediments) were digested in open and closed systems to compare the efficiency of the two methods.

The concentration of metals in organic materials are in the $\mu g/g$ range, which meant that graphite furnace atomic absorption had to be used. This gave rise to a further problem. In order to be able to run an appreciable number of samples on a graphite tube, acid concentrations should not exceed about 1%. This meant that digested samples normally had to be diluted about 100 times, further aggravating the problem of detection limits. An alternative solution would be to use a different acid in the bombs, which does not attack the graphite tube to the same extent. An effort was therefore made to ascertain if any acid (or mixture of acids) other than nitric acid could be used for the digestion. Because biological samples, like whole mussels, are often much larger than specified by the manufacturers as the maximum which should be digested in the bombs, the sample size was also examined.

METHODS AND RESULTS

The decomposition vessels used in this study were made by Berghof GmbH, Labortechnik, Tübingen, and consisted of pure, isostatically pressed PTFE (Model 504120). The bombs are thick-walled (outer dimensions ∅ 51 mm, inner ∅ 25 mm) with screw lid (outer dimensions ∅ 70) of 81 mm total height with a 20 ml total volume and may be used only when low pressures are applied (maximum pressure 15 bar (100 °C) and maximum temperature 150 °C (10 bar)). The 150 °C temperature limit for these bombs does not place undue restrictions on their normal application but, for safety reasons, this limit must be carefully observed.[8]

Standard stock solutions for spectroscopy (1000 ppm in 1 M nitric acid) from BDH Chemicals, whose given concentration were assumed to be correct, were used to prepare the standards. Standard

BDH stock was also used for the standard additions. The mineral acids used for digestion were of super special grade (BDH Chemicals Analar). All the glassware and bombs used, were soaked overnight in 50% nitric acid and then rinsed twice with Milli-Q-Water.

Operating conditions for the atomic absorption analysis are given in Table 1.

Table 1 Operating conditions for atomic absorption spectroscopy

Element	*Lamp current mA*	*Wave length nm*	*Slit width nm*	*Maximum Ash °C*	*Atomize °C*
Cu	4	324.8	0.5	900	2300
Fe	5	248.3	0.2	800	2300
Mn	5	279.5	0.2	800	2400
Zn	5	213.9	1.0	400	1900

The standards were made up in the same concentration of nitric acid as the samples, and a blank was neccessary for the standards as well as for the bombs. Both the flame and furnace (Varian AA, 1475 Series, Atomic Absorption Spectrometer with a Varian GTA-95 graphite tube atomizer) were used to read the trace metals in the sample. For the flame the highest acid concentration used was 50%, although flame AAS is not usually done with such high acid concentration. In this case the trace metal concentration was too low to dilute the sample any further. By aspirating the sample for a short time only and allowing the burner to rinse thoroughly with distilled water between each sample, the effect of the strong acid was minimized.

Two interlaboratory calibration samples were tested. The first was a sample of dried marine tissue which was circulated by the Council for Scientific and Industrial Research to all participants in the Marine Pollution Programme, while the second was a sediment sample (no. SD-N-1/2) issued by the International Atomic Energy Agency (IAEA) in Monaco. For both samples the results of the intercalibration were available. In addition, it was known that the results obtained by this laboratory for the IAEA sample, when the sediment was digested in boiling tubes on an air bath using 4:1 nitric/perchloric acid, were consistently 75–80% of the mean value.

The marine tissue sample was dried overnight in an oven at 90 °C, and cooled in a desiccator. Ten replicates ranging between 0.1 and 1.0 g were accurately weighed into the bombs. Different acids, hydrochloric acid (BDH Chemicals Analar), orthophosphoric acid (M + B Pronalys), nitric acid (M + B Pronalys redistilled) and aqua regia were used to examine the best digestion. The digesting mineral acid (5 ml) was added to the sample (marine tissue and sediment) in the bomb. The acid mixture in the bombs was then placed open in a fume cupboard for about 5 hours until any frothing or violent reactions had ceased. At room temperature bombs were closed tightly and heated in an oven at different temperatures 90 °C (Table 2), 100 °C (Table 3) and 110 °C (Table 4) for at least 12 hours. Bombs were allowed to cool thoroughly before opening.

For comparison the same samples were digested in an open system using nitric/perchloric acids (4:1) according to the usual method used in this laboratory.[9] The marine tissue sample was dried overnight at a temperature of 90 °C. Twenty replicates ranging between 0.1 and 1.0 g were weighed and transferred to vials. Nitric acid (5 ml) was added to the organic material and the mixture was left standing at room temperature for 24 hours. After this time the samples were evaporated to dryness on a hotplate at 120 °C. This step was repeated until the residue started turning white. When dried, 5 ml of a 4:1 mixture of nitric and perchloric acids were added. The mixture was evaporated to near dryness and if the supernatant solution was either clear or slightly yellow, the sample was fumed to dryness. If the supernatant liquid was orange, a further aliquot of nitric/perchloric acid was added and the sample was fumed to dryness.

The dry residue was allowed to cool and 5 ml of 10% nitric acid were added. This mixture was allowed to stand for two hours with occasional shaking to bring the residue into suspension. These samples were then analysed by flame AAS.

Sediment sample sizes were between 0.1–1 g, only nitric acid and aqua regia were used for digestion (Table 5). The method was essentially the same as that for the marine tissue. Because the concentrations of the metals in the sediments were much higher than in the organic samples, the flame AAS could be used more easily for the sediments.

Initially it was assumed that the bombs sealed tightly and that no

Table 2 Digestion of marine tissue at 90 °C

Mass of marine tissue	*Cu (μg/g)*
Acid: Aqua regia	
0.24	1.87
0.29	2.77
0.44	1.90
0.53	1.95
0.71	1.68
0.74	1.90
0.77	1.87
1.15	1.24
Mean:	1.82 (0.28)
Acid: Nitric acid	
0.14	4.04
0.39	2.37
0.40	2.60
0.42	2.10
0.49	2.51
0.88	3.38
Mean:	2.83 (0.73)
Intercalibration values:	
UPE	1.5 (0.06)
SFRI	1.7 (0.00)
NIWR	1.44 (0.07)

Figures in brackets are standard deviations.
Background on.
Blanks substracted.
Furnace AAS.
UPE, SFRI, NIWR are three different laboratories participating in the intercalibration exercise.

sample was lost during digestion. From Tables 3 and 4, it was clear that the bombs did loose acid, so that the final solution was less than 5 ml. Thus, total samples were taken from the bomb by means of pasteur pipettes, and then made up to the mark in 10 ml flasks.

It was soon found that digestion did not proceed with the hydrochloric and phosphoric acids and their use was therefore abandoned.

Table 3 Digestion of marine tissue at 100 °C

Mass of marine tissue	*Cu (μg/g)*	*Mass of material lost*
Acid: Aqua regia		
0.26	1.82	0.83
0.27	1.70	0.84
0.41	1.41	1.04
0.43	1.88	1.14
0.61	1.92	1.16
0.68	1.39	1.08
0.89	1.46	
1.01	1.31	0.95
Mean:	1.61 (0.25)	
Acid: Nitric acid		
0.39	2.77	1.58
0.47	2.30	1.55
0.63	2.08	2.41
Mean:	2.38 (0.35)	
Intercalibration values:		
UPE	1.5 (0.06)	
SFRI	1.7 (0.00)	
NIWR	1.44 (0.07)	

Figures in brackets are standard deviations.
Background on.
Blanks subtracted.
Determination: Furnace AAS.
UPE, SFRI, NIWR as in Table 2.

DISCUSSION

Choice of acid

The first objective was to determine which acid or mixture of acids was most useful for bomb digestions.

Hydrochloric acid is known to digest proteins, but there was a decrease in the organic material reactivity. There are two processes connected to this decrease: (a) the solubility of the oxides varies according to the temperatures to which the analysed substances were exposed and according to the rate of backhydration; (b) the specific

Table 4 Digestion of marine tissue at 110 °C

Mass of marine tissue	*Mass of material lost*	*Acid*			
		Aqua regia		*Nitric acid*	
		Cu (μg/g)	*Mn* (μg/g)	*Fe* (μg/g)	*Zn* (μg/g)
Determination: Furnace AAS					
0.12	0.60	1.78	1.22	23.31	23.80
0.23	0.77	1.70	1.13	24.80	23.36
0.28	1.05	1.48	1.11	25.64	22.10
0.43	1.22	1.39	1.20	23.00	22.29
0.53	1.15	1.28	1.20	27.85	21.80
0.64	1.11	1.79	1.30	25.37	21.20
0.65	1.07	—	1.39[a]	29.14	23.16
0.80	1.18	1.93[a]	1.31	28.28	22.56
0.99	0.91	1.77	1.22	28.28	23.94
Mean:		1.57	1.36	26.19	22.69
		(0.21)	(0.23)	(2.28)	(0.94)
R.S.D.		13.38	16.91	8.71	4.14
Determination: Flame AAS					
0.13	0.16	—	1.28	25.25[a]	25.32
0.23	1.05	1.44	1.95	34.26	26.67
0.26	1.07	1.74	2.05	30.30	25.45
0.29	0.96	1.37	1.45	28.19	24.93
0.37	1.44	1.67	1.15	32.02	25.96
0.43	1.44	1.57	1.64	28.41	24.78
0.52	1.63	2.16[a]	1.56	28.90	25.24
0.60	2.16	1.47	1.40	28.03	25.07
0.75	3.27	0.49[a]	1.68	33.06	23.44
Mean:		1.54	1.57	30.40	25.21
		(0.14)	(0.29)	(2.43)	(0.88)
R.S.D.		9.09	18.47	7.99	3.49
Intercalibration values:					
UPE		1.5	1.72	39	19
		(0.06)	(0.08)	(7)	(1)
SFRI		1.7	2.2	35.1	19.5
		(0.00)	(0.1)	(0.7)	(0.4)
NIWR		1.44	2.00	36.6	21.6
		(0.07)	(0.06)	(1.4)	(0.6)

[a]Excluded from the calculation of the mean.
Figures in brackets are standard deviations.
Blanks subtracted.
Background on: Cu, Mn.
Background off: Fe, Zn.
UPE, SFRI, NIWR as in Table 2.

Table 5 Digestion of sediments at 110 °C

Mass of sediment	*Aqua regia*			
	Cu (μg/g)	*Fe (%)*	*Mn (μg/g)*	*Zn (μg/g)*
0.12	67.39	2.9	826	402
0.28	64.21	3.5	660	379
0.35	53.66	3.2	959	370
0.42	49.70	3.1	686	382
0.48	50.60	2.2	704	367
0.58	58.08	2.5	629	350
0.90	52.08	—	718	315[a]
Mean:	56.53	2.9	740	366
Standard deviation:	6.94	0.48	115	28
R.S.D.	12.28	16.55	15.54	7.65
	Nitric acid			
0.15	64.61	3.4	661	392
0.30	56.59	—	503	402
0.34	44.03	3.3	735	395
0.45	57.48	2.6	716	395
0.72	54.44	—	—	310[a]
0.77	56.36	—	655	323[a]
Mean:	55.58	3.1	654	396
Standard deviation:	6.08	0.44	91	4
R.S.D.	10.94	14.19	13.91	1.01
NRIO value:	53.40	2.82	607.77	358.98
Standard deviation:	5.41	0.29	36.84	32.72
Intercalibration value:	72.17	3.64	777.10	439.00

[a]Excluded from the calculation of the mean.
Blanks subtracted.
Background on: Cu.
Background off: Fe, Mn, Zn.
Determination: Furnace AAS: Cu
Flame AAS: Fe, Mn, Zn.
Confidence limits of the intercalibration value at the 0.05 significant level:
Cu 68.10– 75.20
Fe 3.53– 3.78
Mn 728.00–800.50
Zn 423.06–451.77.

surface of solid phases is decreased by high temperatures and the organic lattice is often reorganized.[10]

Orthophosphoric acid did not digest much of the biological samples either. Although H_3PO_4 has no oxidizing properties, even at temperatures near 300 °C, it was investigated because it strongly affects redox equilibria by formation of variously stable complexes with the individual members of redox couples (for example, Fe(III)/Fe(II).[10]

Therefore, nitric acid and aqua regia (3:1, HCl:HNO_3) were the only acids to be discussed further. The problem with strong nitric acid and carbon rod analysis has been discussed above.

The means of results obtained from nitric acid and aqua regia digestions were compared statistically to see whether the acid used caused any differences in the results (Table 6). It can be seen that only two means did not compare, while all others showed no significant difference. The choice of acid, therefore, depends on practical considerations only. Aqua regia is better if the carbon furnace is required because the dilution factor can be smaller. For flame work it is recommended that nitric acid be used.

Flame or furnace

It can be seen that the relative standard deviations when using the flame (Table 4), were lower than those obtained when using the furnace. Therefore, when metal concentrations are sufficiently high

Table 6 Comparison of mean values obtained using different acids

Sample	*Element*	*Nitric*	*Aqua regia*	*DF*	*t-value*	*Sig. diff.*	*Confidence*
Marine tissue	Cu	1.54	1.57	10	0.5669	no	
	Fe	1.57	1.36	15	1.6624	no	
	Mn	22.69	25.21	16	5.8710	yes	>99.95%
	Zn	26.19	30.40	14	3.6703	yes	>99.50%
Sediment	Cu	55.6	56.5	11	0.2631	no	
	Fe	3.1	2.9	4	0.6234	no	
	Mn	692	740	10	0.08061	no	
	Zn	396	366	5	2.5852	no	

the flame method is preferable. The furnace is also timeconsuming and samples need to be diluted if nitric acid is used.

Closed or open system

When using the open system the results are comparable with the intercalibration values (Table 7). The standard deviations for the open system were higher than those obtained with bombs, but this is probably due to contamination while the samples stood open for a few days. Open system digestion is very timeconsuming and is therefore not recommended over a closed system.

Loss of material

From Tables 3 and 4 it can be seen that as the mass of the marine tissue sample increased, there was a definite decrease of material from the bomb during digestion. The results (Tables 2 to 7) obtained were of the same order of magnitude as the intercalibration values, although some were too high and others too low. Our standard deviations were reasonably low and therefore the error seems to be systematic. Although a considerable part of the acid (Tables 3 and 4) had vanished from the decomposition vessels, comparisons with the intercalibration values and our standard deviation show that no metals had been lost. Still, such bomb decomposition procedures are undesirable and show that the loading limits had been exceeded. This has been realized by most decomposition vessel manufacturers, and the latest recommended loading limits for a 20 ml bomb stress that the sample must not contain more than 0.1 g of dry organic matter with 2.5 ml to 3.0 ml acid. This makes the acid digestion bomb system suitable only for sediment and tiny biological samples. For routine biological pollution monitoring it was found to be unsuitable.

Table 7 Results of digestion of marine tissue in an open system using nitric:perchloric acids

Mass of tissue	*Fe* (μg/g)	*Mn* (μg/g)	*Zn* (μg/g)
0.21	34.24	9.10[a]	25.90
0.22	29.71	3.92[a]	25.30
0.31	31.63	3.38	26.17
0.33	37.63	3.55	24.97
0.35	36.45	3.35	24.98
0.39	31.00	2.21	25.48
0.40	30.23	2.46	25.86
0.41	—	2.11	7.98[a]
0.45	33.41	5.75[a]	24.81
0.50	30.72	2.46	24.72
0.50	30.07	2.22	25.09
0.52	35.19	2.61	24.61
0.62	33.21	2.39	23.58
0.66	33.15	2.52	54.98[a]
0.66	45.55[a]	1.68	22.92
0.77	31.83	2.88	22.99
0.80	35.95	3.24	22.37
0.81	32.28	2.89	22.52
0.86	32.68	2.08	22.31
0.92	35.16	2.28	21.57
0.92	28.42	5.70[a]	20.00
0.92	31.97	2.01	21.16
Mean:	32.75	2.58	23.87
	(2.45)	(0.55)	(1.70)
Intercalibration value:			
UPE	39	1.27	19
	(7)	(0.08)	(1)
SFRI	35.1	2.2	19.5
	(0.7)	(0.1)	(0.4)
NIWR	36.6	2.00	21.6
	(1.4)	(0.06)	(0.06)

[a]Excluded from the calculation of the mean.
Blanks subtracted.
Background off
Determination: Flame AAS.
UPE, SFRI, NIWR as in Table 2.

Acknowledgements

This work was carried out by one of us (CHK) as an Honours project in the Department of Analytical Science at the University of Cape Town.

References

1. R. Uhrberg, *Anal. Chem.* **54,** 1906 (1982).
2. B. Bernas, *Anal. Chem.* **40,** 1682 (1968).
3. C. Iida, T. Uchida and I. Kojima, *Anal. Chim. Acta* **113,** 361 (1980).
4. T. Uchida, I. Kojima and C. Iida, *Anal. Chim. Acta* **116,** 205 (1980).
5. E. Van Eenbergen and E. Brunnix, *Anal. Chim. Acta* **98,** 405 (1978).
6. Parr digestion bombs, *Parr Bulletin 4745.*
7. K. Okamoto and K. Fuma, *Anal. Chem.* **56,** 1758 (1984).
8. Berghof GmbH Labortechnik, bulletin.
9. R. J. Watling, South African National Scientific Programmes, *Reports* **44,** 13 (1981).
10. Z. Sulcek, P. Povondra and Z. Dolezal, *CRC Critical. Rev. Analyt. Chem.* **7,** 255 (1977).