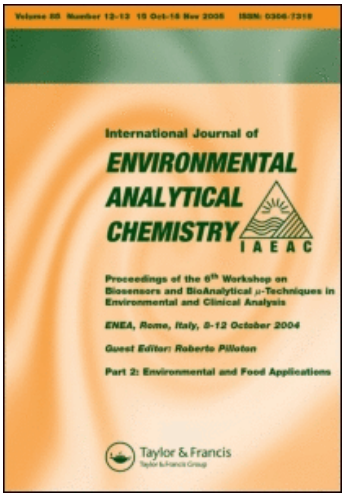

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Quantitative Analysis of Carbon-14 Labelled Polychlorinated Biphenyls and Hexachlorobenzene in Biological Samples Using an Oxidative Combustion Method

A. J. Niimi[a]
[a] Canada Centre for Inland Waters, Great Lakes Biolimnology Laboratory, Burlington, Ontario, Canada

To cite this Article Niimi, A. J.(1979) 'Quantitative Analysis of Carbon-14 Labelled Polychlorinated Biphenyls and Hexachlorobenzene in Biological Samples Using an Oxidative Combustion Method', International Journal of Environmental Analytical Chemistry, 6: 3, 267 — 271
To link to this Article: DOI: 10.1080/03067317908071180
URL: http://dx.doi.org/10.1080/03067317908071180

Intern. J. Environ. Anal. Chem., 1979, Vol. 6, pp. 267–271

Printed in Great Britain

Quantitative Analysis of Carbon-14 Labelled Polychlorinated Biphenyls and Hexachlorobenzene in Biological Samples Using an Oxidative Combustion Method

A. J. NIIMI
Canada Centre for Inland Waters, Great Lakes Biolimnology Laboratory P.O. Box 5050, Burlington, Ontario, Canada L7R 4A6

(*Received October 12, 1978*)

Carbon-14 labelled glucose, polychlorinated biphenyls, and hexachlorobenzene at concentrations of 0.01–1200 nanograms were oxidized in a combustion chamber at 900C. The $^{14}CO_2$ emitted was trapped in an organic base, and its radioactivity measured. Recovery rates of 95–104% were obtained from samples oxidized with mannitol, while recoveries of samples oxidized with dried fish ranged from 93–101%. This method provides an alternate technique of sample preparation for materials that may yield a highly quenched solution following conventional sample preparation procedures for liquid scintillation measurements.

KEY WORDS: Carbon-14 analysis, oxidative combustion, pollutants

INTRODUCTION

Studies on the fate of industrial chemicals in environmental systems often require intensive sampling efforts to monitor residue levels in the nanogram and picogram range. Presently, chromatography is the most common method for analysis. One disadvantage of using this procedure has been the lengthy preparation time required for each sample. This delay may preclude the intensity of sampling that would have been desirable for a specific program. Where applicable, radioisotopic labelled compounds have been used to facilitate studies of this nature by providing a rapid method of quantitative identification. In view of the different types of materials that may be examined, some difficulties in sample preparation

can be anticipated. Chemical digestion has been a common method of preparation, but this procedure may not always yield a product suitable for radioactive measurement. Where carbon-14 labelled materials are used, the oxidative combustion method may provide an alternate procedure for sample preparation. This procedure rapidly oxidizes the sample to carbon dioxide and water. The $^{14}CO_2$ is trapped in a strong organic base, and its radioactivity measured.[1-3] This study evaluates the application of this method by examining the recovery rates of carbon-14 labelled compounds such as polychlorinated biphenyls (PCB) and hexachlorobenzene (HCB) at levels that occur in aquatic biota.

MATERIALS AND METHODS

Carbon-14 labelled compounds were obtained from the following sources. Glucose, with a specific activity of 260 mCi/mmol, was obtained from the Amersham Corporation, Arlington Heights, Illinois. Polychlorinated biphenyls (Arochlor 1242) and hexachlorobenzene, with specific activities of 31.1 mCi/mmol and 35.3 mCi/mmol, were obtained from New England Nuclear, Boston, Massachusetts. Working solutions of these compounds were prepared using distilled water, methanol, and acetone respectively. The 4 concentrations of glucose examined ranged from 0.01–7 nanograms, and the 5 concentrations each of PCB and HCB from 0.01–1200 nanograms.

Ten replicates were oxidized at each concentration. Similarly, 5 replicates of the working solutions were taken for internal standards to provide a suitable reference for recovery rates. Internal standards were prepared by adding 10 μl of each working solution to a 15 ml cocktail of 2:1 solution of PCS, a liquid scintillation counting fluor, and CO_2mMET, an ammonium based CO_2 trapping agent (Amersham Corporation). Each sample consisted of placing a 10 μl aliquot of the working solution on a base of 50 mg mannitol and oxidized. This procedure was repeated for PCB and HCB using finely ground dried fish as the base.

Samples were oxidized with a Biological Material Oxidizer with the Automated Accessory (R. J. Harvey Instrument Corporation, Hillsdale, New Jersey). The material was placed in a quartz combustion chamber heated to 900°C for four minutes. A platinum catalyst was present and an oxygen flow of 300 ml/min was maintained through the chamber. The resulting gases were passed through a silica gel cartridge to remove moisture then bubbled through 15 ml cocktail contained in a scintillation vial. The $^{14}CO_2$ containing solution was then measured following liquid scintillation counting procedures.

RESULTS

Recovery rates of 95–104% were obtained for the carbon-14 labelled glucose, PCB, and HCB oxidized with a mannitol base relative to the recovery of the internal standards (Table I). The values shown for each

TABLE I

Recovery of carbon-14 labelled materials oxidized with mannitol.

Treatment	No. of samples	Nanograms carbon-14 materials			Percent recovery relative to standard
		Mean	SD	Range	
			Glucose		
Standard	5	0.008	0.001	0.007–0.008	100
Oxidized	10	0.008	0.002	0.005–0.012	
Standard	5	0.076	0.001	0.074–0.077	100
Oxidized	10	0.076	0.011	0.062–0.104	
Standard	5	0.74	0.01	0.72–0.75	97.3
Oxidized	10	0.72	0.01	0.70–0.73	
Standard	5	7.42	0.04	7.38–4.47	96.2
Oxidized	10	7.14	0.13	6.83–7.27	
			Polychlorinated biphenyls		
Standard	5	0.093	0.011	0.082–0.108	104.3
Oxidized	10	0.097	0.019	0.063–0.130	
Standard	5	0.96	0.01	0.95–0.98	99.0
Oxidized	10	0.95	0.03	0.91–0.99	
Standard	5	9.53	0.07	9.44–9.60	97.6
Oxidized	10	9.30	0.15	9.04–9.52	
Standard	5	89.9	0.3	89.4–90.4	98.9
Oxidized	10	88.9	1.2	86.6–90.2	
Standard	5	1221.8	12.1	1211.0–1241.0	97.7
Oxidized	10	1193.3	36.6	1095.0–1227.6	
			Hexachlorobenzene		
Standard	5	0.110	0.011	0.094–0.121	100
Oxidized	10	0.110	0.011	0.098–0.129	
Standard	5	1.08	0.03	1.04–1.10	99.1
Oxidized	10	1.07	0.04	0.98–1.13	
Standard	5	10.27	0.08	10.19–10.38	99.3
Oxidized	10	10.20	0.38	9.45–10.69	
Standard	5	96.3	0.9	95.0–97.1	97.2
Oxidized	10	93.6	3.3	90.0–100.5	
Standard	5	1178.5	13.7	1162.6–1197.3	95.4
Oxidized	10	1124.0	76.3	999.2–1220.1	

compound would suggest a decrease in recovery rate with increasing concentrations, however, this effect would be minimal in view of the extended range of concentrations examined. No differences in recovery rates were suggested among the three compounds tested. Recovery rates of labelled PCB and HCB oxidized with dried fish showed greater variability (Table II) although the mean recovery levels were comparable to those measured using a mannitol base.

TABLE II

Recovery of carbon-14 labelled polychlorinated biphenyls and hexachlorobenzene oxidized with fish.

Treatment	No. of samples	Nanograms carbon-14 materials			Percent recovery relative to standard
		Mean	SD	Range	
			Polychlorinated biphenyls		
Standard	5	0.134	0.019	0.116–0.157	
Oxidized	10	0.127	0.011	0.104–0.138	94.8
Standard	5	1.04	0.03	1.01–1.07	
Oxidized	10	1.02	0.03	0.99–1.07	98.1
Standard	5	11.58	0.09	11.45–11.65	
Oxidized	10	11.06	0.18	10.78–11.37	95.5
Standard	5	115.8	0.4	115.4–116.3	
Oxidized	10	113.6	3.4	106.8–119.5	98.1
Standard	5	1227.8	29.4	1176.6–1248.7	
Oxidized	10	1163.3	12.8	1137.4–1184.2	94.7
			Hexachlorobenzene		
Standard	5	0.121	0.008	0.113–0.132	
Oxidized	10	0.113	0.019	0.087–0.147	93.4
Standard	5	1.36	0.02	1.34–1.39	
Oxidized	10	1.33	0.06	1.24–1.41	97.8
Standard	5	14.22	0.38	13.59–14.60	
Oxidized	10	14.39	0.72	13.27–15.46	101.2
Standard	5	121.8	0.9	120.4–122.6	
Oxidized	10	121.3	5.1	110.9–129.3	99.6
Standard	5	990.6	21.6	966.6–1022.1	
Oxidized	10	919.6	34.1	781.3–983.6	92.8

DISCUSSION

Early applications of the oxidiative combustion method were limited to examining the distribution of carbon-14 labelled biological materials in

animal tissues.[4] Presumably, both labelled material and substrate were oxidized well below the operating temperatures of 600–750°C.[1,4] This study examined the feasibility of using this procedure to quantitatively monitor carbon-14 labelled industrial chemicals, notably the more persistent contaminants such as PCB. Its application would be highly relevant in environmental trophodynamic studies where analytical restrictions often includes the amount of working materials available, concentrations in the nanogram and picogram range, and the processing of materials of differing compositions. The use of radioisotopic labelled materials have been well documented to be particularly advantageous in circumstances where both limited sample weight and low working concentrations are encountered. Recovery rates and detection levels that were observed in this study would support this view. The specific activity of each compound would determine the lowest level of detection, and the amount of material oxidized would determine its relative concentration.

There should be no limitations on using this oxidation method for materials of differing composition provided the combustion of the chemical under investigation is complete. The oxidation procedure used in this study which included a chamber temperature of 900°C, and a catalyst in an oxygen atmosphere with a transit time of 4 minutes, was sufficient to oxidize the PCB and HCB. These conditions would be equivalent to the temperatures of 675–1000°C required for the combustion of PCB and HCB with a transit time of several seconds.[5]

Current liquid scintillation counting procedures use agents such as tissue solubilizers to render biological materials into a state suitable for counting. The resulting product may acquire a coloured or opaque medium with high quenching properties or yield a product that may not be entirely suitable for liquid scintillation analysis. The oxidative combustion method would provide an alternate procedure for sample preparation.

References

1. J. I. Peterson, F. Wagner, S. Siegel and W. Nixon, *Anal. Biochem.* **31,** 189 (1969).
2. J. I. Peterson, *Anal. Biochem.* **31,** 204 (1969).
3. S. Mlinko, E. Dobis, K. Payer, J. Ottinger, D. Banfi, T. Palagyi and A. Turi, *Anal. Biochem.* **83,** 7 (1977).
4. M. H. Griffiths and A. Mallinson, *Anal. Biochem.* **22,** 465 (1968).
5. B. Ahling and A. Lindskog, *Sci. Total Environ.* **10,** 51 (1978).