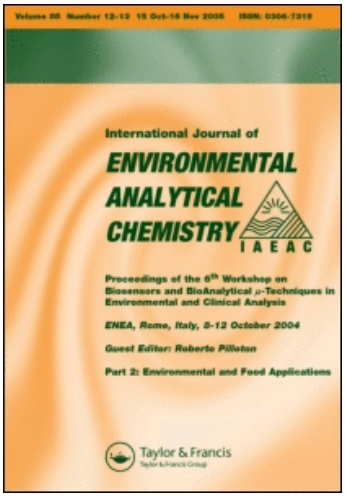

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Odukoya, O. O.(1990) 'Modification of Bethge's Open-System Apparatus for the Determination of Mercury in Biological Materials', International Journal of Environmental Analytical Chemistry, 39: 4, 323 — 327
To link to this Article: DOI: 10.1080/03067319008030505
URL: http://dx.doi.org/10.1080/03067319008030505

Intern. J. Environ. Anal. Chem., Vol. 39, pp. 323–327
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MODIFICATION OF BETHGE'S OPEN-SYSTEM APPARATUS FOR THE DETERMINATION OF MERCURY IN BIOLOGICAL MATERIALS

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(*Received 8 February 1989; in final form 19 August 1989*)

The performance of the open system (Bethge's apparatus) of digestion of biological materials for mercury analysis has been upgraded to compare favourably with the closed systems. Losses at the joints and during refluxing were successfully eliminated by the following modifications: (i) thin PTFE cylinders were used in the joints; (ii) a PTFE two-way stopper was used instead of the glass stopper in the original apparatus; (iii) a double-faced spiral condenser was used to increase the cooling efficiency and minimise losses.

KEY WORDS: Open system, closed system, acid digestion, biological materials, mercury

INTRODUCTION

When determining mercury levels in biological materials, particularly in fish, the destruction of organic matter has always presented a major problem because of the volatility of mercury and its compounds. Dry ashing, no matter how low the temperature, cannot be used and the likelihood of volatilization losses has to be considered when wet digestion procedures are used. The loss of mercury during the wet oxidation of organic materials is widely known and efforts have been made by various workers to overcome this problem. Until recently, most methods use the open-system technique.[1–7]

The use of Bethge's apparatus for digestion of biological materials prior to determination of mercury was pioneered by Gorsuch.[8] Since then, it has been used by other workers.[1,9–11] The apparatus is illustrated in Fig. 1. It consists of a quickfit Kjeldahl flask F of about 150 cm^3 capacity, with a long neck. To this is attached the special digestion (Bethge's) apparatus B, and a condenser C for refluxing. The obvious advantages of this apparatus over loosely stoppered bottles and test tubes are:

- the vapour has a long way to travel to the top of the condenser before it can escape;
- higher temperatures can be used to ensure a more complete and more rapid digestion;
- a refluxing condenser attached to the top of Bethge's apparatus reduces loss of vapour.

Even so, losses of mercury vapour have been encountered by workers using

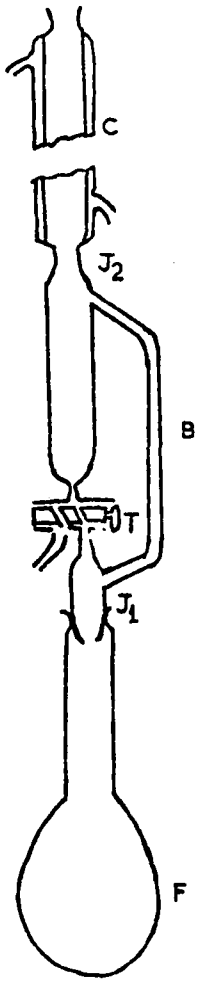

Figure 1 Bethge's apparatus for the digestion of biological material for mercury analysis.

Bethge's apparatus.[8,9] These losses have been suspected to occur via the top of the condenser, if it is not efficient enough. To counteract this, some workers have used traps. These are attached to the top of the condenser and usually contain a potassium permanganate solution through which any escaping vapour has to pass. This introduces problems with regard to completely washing out the trap and over-diluting the final solution. Other suspected sources of losses are the joints, J_1 and J_2, and the space between the stopper T and its socket.

With the invention of the closed-system (bomb) technique of digestion,[12–14] the problem of losses seems to have been eliminated. However, the bomb technique has not been widely embraced and many workers still use Bethge's and other open systems of digestion. The question now is: Can Bethge's system be modified to compare favourably with the closed-system technique, or has it completely outlived its usefulness? Efforts to answer this question led to the present work:

Two closed system techniques, viz. Carius' method,[12] and the most recent Uhrberg method are compared with the modified Bethge's open-system technique.

EXPERIMENTAL

Modifications

As was mentioned above, the suspected sources of loss of mercury vapour in Bethge's apparatus are the joints, J_1 and J_2, the space between the stopper T and its socket as well as from the top of the condenser. To eliminate losses from these sources, three modifications were made:

- thin cylindrical PTFE sealings were used in the joints J_1 and J_2;
- a PTFE stopper was used instead of the glass stopper at T;
- a double-faced spiral condenser was used to increase cooling efficiency.

After these modifications had been introduced, Bethge's apparatus was compared with the closed systems. The details of the procedure are given below.

Bethge's Method—Experimental Procedure

The entire apparatus (Fig. 1) was cleaned with boiling concentrated nitric acid and rinsed with Milli-Q water (made by passing distilled water through two mixed-bed resins and a third tube of very pure activated carbon). Blank digestions were performed using a mixture of 2 ml sulphuric acid and 3 ml nitric acid. Thereafter, about 150 mg of the sample were digested with an identical acid mixture. The solutions were each made up to 25 ml.

Carius' Method 12—Experimental Procedure

The apparatus consists of thick-walled glass tubes, 2 mm thick with an external diameter of 9–10 mm. Each glass tube fits into a metal jacket. The metal jackets are housed in a metal block, in which they are heated. The tubes were cleaned with boiling concentrated nitric acid and dried. Small thin-walled glass cups were similarly cleaned, dried and about 20 mg of the sample were weighed into each one. The cups were introduced into the tubes, 0.5 ml of concentrated nitric acid was added and each tube was sealed with a flame. The tubes were heated in the metal block at 250 °C for 8 h. The digest was then made up to 25 ml with Milli-Q water. Blank digestions were similarly prepared.

Uhrberg's Method 14—Experimental Procedure

The apparatus consists of quartz tubes, 28 mm thick with about 2.6 cm external

Table 1 Comparison of Bethge's, Carius' and Uhrberg's methods

Sample	*Bethge*	*Carius*	*Uhrberg*
Blank	0.00	0.00	0.00
Fish Sample 1	0.57	0.61	0.60
Fish Sample 2	0.61	0.59	0.63
Fish Sample 3	0.58	0.59	0.64
Fish Sample 4	0.57	0.58	0.63
MEAN	0.58 ± 0.02	0.59 ± 0.01	0.63 ± 0.02

Table 2 Comparison of Bethge, Carius and Uhrberg methods[a]

	Bethge				*Carius*				*Uhrberg*			
Blank	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mercury in fish sample	260	255	257	252	52	43	43	34	218	233	235	245
Amount of standard added	50	50	50	50	25	25	25	25	50	50	50	50
Mercury in fish sample + standard	300	309	306	300	78	67	67	59	269	280	282	296
Recovery (%)	80	108	98	96	104	96	96	100	102	94	94	102

[a]Results for samples 1–4 (see Table 1); all mercury data expressed in ng.

diameter. Each tube fits into a metal jacket with a PTFE disc below the tube and a PTFE stopper to cover it. The metal jacket has a screw cap which can be screwed to a pre-determined torque. The metal jacket is heated in a metal block.

The tubes were cleaned with boiling nitric acid and dried; about 100 mg of sample were weighed into each one and 3 ml of concentrated nitric acid were added. They were heated in the metal block at 200 °C for 1 h, and the digest was made up to 10 ml. Blank digestions were similarly prepared.

RESULTS AND DISCUSSION

A fish sample of *Hydrocynus forskali*, a fresh-water fish, was chosen to compare the methods of digestion. The fish muscle was freeze-dried and ground into powder. Following the procedure described earlier, four reagent blanks, four replicates of the fish sample and four replicates of the same sample spiked with 50 ng of mercury (50 μl of solution) were digested by the modified Bethge method. The digestions were similarly carried out using the Carius method and the Uhrberg method. Mercury in the digests was determined by the cold vapour AAS technique. The results are shown in Table 1. Obviously, with careful handling to avoid loss of mercury, identical results can be obtained with all three techniques.

Table 2 shows the results of the recovery test. As expected, the closed systems show excellent recoveries. Bethge's method shows similarly good results except in one case. Careful manipulation of Bethge's apparatus by a competent analyst is required to give results comparable to those of the closed systems. In our hands, the co-efficient of variation for replicate analysis for all three methods was found

to be about 3%. In other words, the modified Bethge method can confidently be used for the determination of mercury where facilities for the closed-system technique are not available.

Acknowledgement

I wish to express my gratitude to Prof. B. Nygard, Depart. Analytical Chemistry, University of Uppsala, Sweden for provision of facilities; to the International Seminar, Sweden for award of a fellowship; to R. Uhrberg and the staff of the Water Laboratory, Swedish Environmental Protection Board, Institute of Limnology, Uppsala, for providing the facilities of their laboratory for the Uhrberg closed-system digestion method and for the use of the AAS and cold vapour kit; to Knuutila, Lassez, Eric and Ingwar, Dept. Analytical Chemistry, University of Uppsala, for the necessary technical support.

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