METU JOURNAL OF PURE AND APPLIED SCIENCES
Vol. 10, No. 1, pp. 137 – 146 April 1977

COLD-VAPOR MERCURY ANALYSIS - EFFECT OF REDUCTION VESSEL AND ABSORPTION CELL DIMENSIONS ON SENSITIVITY

GERALD J. RAMELOW AND TURGUT İ. BALKAŞ
Department of Marine Sciences, M.E.T.U.

Abstract. Improvements in the cold vapor technique are described which can be easily adopted with available atomic absorption instrumentation. The use of a continuous flow reduction vessel considerably shortens analysis time while the use of long path length absorption cells of small volume greatly increases sensitivity. Detection limits for different sample volumes and absorption cells are given.

I. INTRODUCTION

The cold vapor atomic absorption technique has become widely accepted as the method of choice for the analysis of trace amounts of mercury [1]. Most workers have carried out the reduction process in gas washing bottles or flasks of various kinds, using standard 10-cm absorption cells. However, the work of Gilbert and Hume [2] has demonstrated the advantages of using a reduction vessel with efficient aeration and small dead volume. Hawley and Ingle [3] using a continuous flow reduction vessel and instrumentation of their own design, obtained very high sensitivity by employing extremely long absorption cells of small internal diameter.

It is the aim of the present study to show how significant improvements in the cold vapor technique, with regard to sensitivity and analysis time, can be achieved with available atomic absorption instrumentation by the use of long path length absorption cells and changes in the design of the reduction vessel.

II. EXPERIMENTAL

Apparatus

A Perkin-Elmer Model 305B atomic absorption spectrophotometer equipped with a Model 56 recorder was used in the first phase of the

work. The radiation sourse was a Perkin-Elmer Intensitron hollow cathode lamp operated at the recommended current. The instrument was modified so that the auxiliary air inlet to the burner could be used as an air supply. The flow rates were calibrated with a bubble-type flow meter.

In the latter phase of the work a Varian Model AA-6 atomic absorption spectrophotometer, equipped with a Varian Model A-25 recorder was used. A Varian mercury hollow cathode lamp was the radiation source. The air was controlled by the nitrogen flow meter of a Varian Model 63 carbon rod atomizer. For absorption cells of small I.D. a mask with a small hole cut in it was placed between the hollow cathode and the cell.

The absorption cell was mounted directly on top of the standard air-acetylene burner head. Cells of internal diameter ranging from 1.8 to 0.4 cm and lengths from 10 to 38 cm were evaluated. The dimensions of all cells are given in Table I.

The type of reduction vessel used has been described elsewhere [4]. In the present study, a three-way stopcock was used to connect the reduction vessel to the air supply and to a vacuum flask. Reduction vessels of varying dimensions were evaluated. The dimensions of these vessels are given in Table II.

The bottom of the reduction vessel is connected to a membrane filter holder assembled from the inlet part of a 25-mm syringe filter holder (Gelman no. 4320) and the outlet section of a 25-mm open filter holder (Gelman no. 1107). This combination filter holder is used without an enclosed filter.

Reagents

All reagents used were of reagent grade quality. A 100 mg/liter stock solution of mercury contained 0.0677 gram of $HgCl_2$ and 25 ml of concentrated HNO_3 in a final volume of 500 ml. Dilutions of the stock solution were used to prepare working standards.

Glassware were rinsed first with 2 % $KMnO_4$ then with concentrated HNO_3 to avoid contamination.

The reducing agent was a 1 % solution of $SnCl_2$ in 1 % HNO_3. It was aerated vigorously for at least 30 minutes before use to remove any traces of mercury.

Analysis Procedure

With the three-way stopcock in the aerate position to allow air to continuously pass through the system (0.4 - 1.3 litres/minute depending on the sample volume), a small amount of reducing agent (usually 0.2 ml) is added to the reduction vessel and the recorder zeroed. Sample or standard is added and the peak height recorded. The stopcock is then turned to the flush position to evacuate the system. A couple of water rinses are used between samples. Turning the stopcock to the aerate position readies the system for the next analysis.

III. RESULTS AND DISCUSSION

Effect of Absorption Cell Dimensions

It is obvious that for maximum sensitivity, the absorption cell should contain the highest effective concentration of mercury vapor. Nevertheless, it was not generally realized until the work of Hawley and Ingle [3] that the sensitivity of the cold vapor technique could be improved substantially by increasing the path length of the absorption cell while at the same time reducing the internal diameter. In Table III the relative peak heights obtained with 50 ng mercury in a 1-ml sample volume are given for all cells evaluated in this study. For comparison purposes the peak height of the standard 10-cm cell is arbitrarily assigned a value of 1.

In Fig. 1 the peak height obtained with 50 ng of mercury is plotted against cell volume for absorption cells of various I.D.'s. As expected the combination of long path length and small volume results in maximum sensitivity. It is interesting that the peak height increases up to a maximum and then decreases. Thus there is no advantage to be gained by increasing the path length beyond a certain value for each cell of a particular I.D. However, the maximum will be shifted to longer path lengths with decreasing I.D. The effect of cell volume is also seen in Fig. 2 where the peak height and volume are plotted against the internal diameter for cells of approximately the same length.

Although long path length absorption cells of small I.D. give the highest sensitivity, the maximum length of cell which can be used is determined by the dimensions of the sampling compartment of the instrument being used. For example, the maximum length of cell which

can be used with the Perkin-Elmer Model 305B is about 25.5 cm while the Varian AA-6 can incorporate a cell up to about 38 cm.

Effect of Reduction Vessel

The type of reduction vessel described in this work which operates with a continuous air flow considerably shortens the time required for each measurement since the contents of the vessel are removed rapidly by the vacuum between analyses. Depending on the flow rate and sample volume, analysis times as short as one minute can be achieved. In addition, very small sample volumes can be measured.

The size of the vessel is also of importance because the dead volume of the system should be kept to a minimum. The choice of reduction vessel will be mainly determined by sample volume. Close attention should be paid to matching the sample volume to the volume of the reduction vessel otherwise dilution of the mercury vapor will result. Small variations in the vessel volume will cause little change in the sensitivity because the volume of the mercury plug will be much larger than the volume of the cell. This is evident from Fig. 1 where 1-ml sample volumes were used throughout. In the present work for a 1-ml sample volume, reduction vessel 2 was found to be best.

Effect of Flow Rate

In figure 3 the peak height and half-width are plotted versus flow rate. The volume of the mercury plug can be estimated from twice the half-width in ml at the optimum flow rate. With absorption cell number 10 and reduction vessel 3, the volume of the plug was found to be 108 ml. As pointed out by Hawley and Ingle [3], if the volume of the plug is much greater than the volume of the absorption cell, the volume of the cell should have little effect on the half-width of the absorption peak. This was observed in the present study.

Detection Limit

Detection limits calculated for different sample volumes using absorption cells 10 and 17 are given in Table IV. Thsese are not the best obtainable values since a rather high flow rate was used to reduce the analysis time. It is apparent that the minimal concentration which can be detected decreases with increasing sample volume, the improvement from 1 to 5 ml being particularly striking. Secondly, the consider-

able improvement resulting from the use of longer cells of small volume is obvious. It should be noted, however, that the noise level increases as the I.D. decreases. Thus, the usefulness of scale expansion is reduced. Other workers [3] have pointed out the advantages of a more intense source of radiation such as the mercury pen lamp when working with very small I.D. cells.

TABLE I

Dimensions of Absorption Cells

Cell no.	Length (cm)	I. D. (cm)	Volume (cm^3)
1	10.0	1.80	25.5
2	10.0	1.34	14.1
3	17.2	"	24.3
4	21.4	"	30.2
5	23.6	"	33.3
6	25.3	"	35.7
7	9.9	0.98	7.5
8	17.0	"	12.8
9	22.1	"	16.7
10	24.1	"	18.2
11	24.8	"	18.8
12	23.6	0.83	12.8
13	23.3	0.72	9.5
14	23.6	0.58	6.2
15	23.6	0.47	4.1
16	28.0	"	4.9
17	32.2	"	5.6
18	37.0	"	6.4
19	37.9	0.40	4.8

TABLE II

Dimensions of Reduction Vessels

Vessel no.	Length (cm)	I. D. (cm)	Volume (cm^3)
1	10.0	1.0	7.9
2	10.3	1.4	15.9
3	11.0	1.6	20.8
4	12.2	2.0	36.4
5	16.0	2.4	72.4
6	20.0	2.7	114.5
7	31.0	4.1	409.3

TABLE III

Relative Sensitivity of Absorption Cells

Cell no.	Relative peak height (50 ng Hg)
1	1.00 (arbitrary)
2	1.08
3	1.86
4	2.15
5	2.64
6	2.38
7	1.29
8	1.68
9	2.90
10	3.03
11	2.92
12	3.41
13	3.86
14	—
15	4.01
16	4.40
17	5.64
18	6.30
19	> 6.50

TABLE IV

Detection Limits[a]

Sample volume (ml)	Cell 10[b]		Cell 17[c]	
	ng	μg/l	*ng*	μg/l
1	0.09	0.09	0.03	0.03
5	0.16	0.03	—	—
11	0.25	0.02	—	—
26	0.48	0.02	—	—

[a] Defined as the amount or concentration which gives a signal equal to twice the standard deviation of a series of ten determinations near the blank level.

[b] 3x recorder expansion used.

[c] No expansion used.

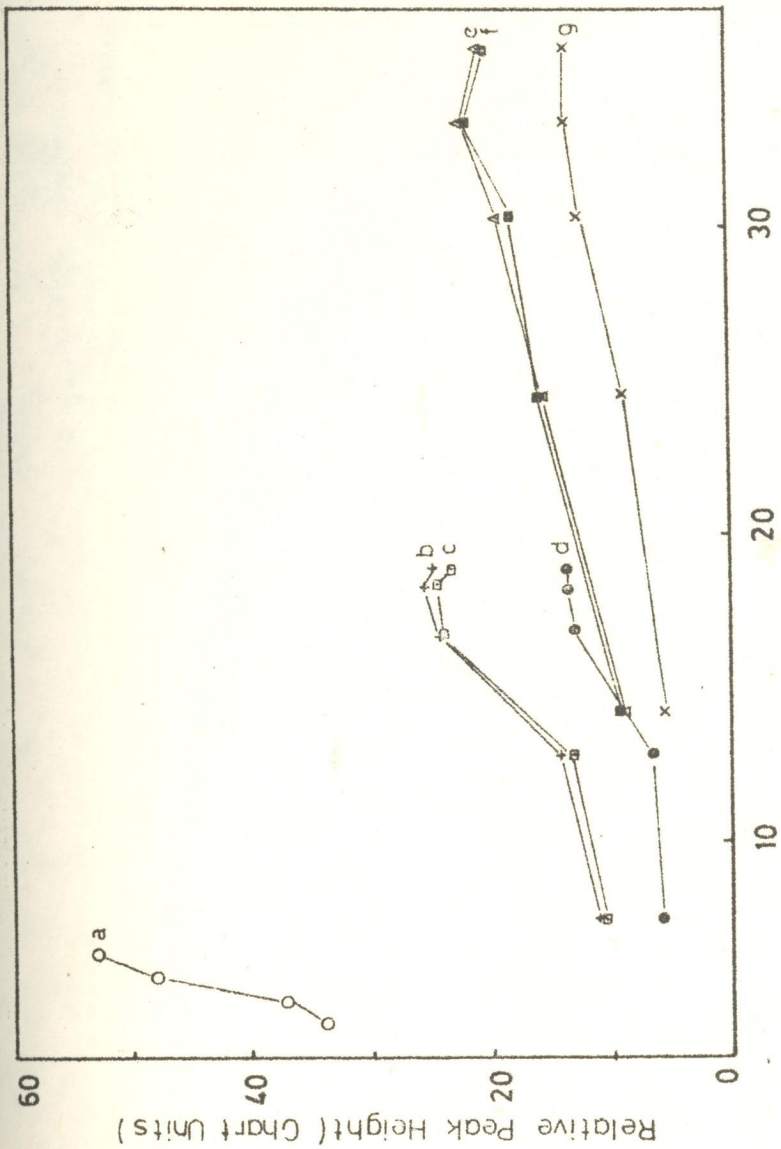

Fig. 1 Effect of cell dimensions on peak height.
0.47-cm cell : (a) vessel 2;
0.98-cm cell : (b) vessel 3, (c) vessel 4, (d) vessel 6;
1.34-cm cell : (e) vessel 4, (f) vessel 3, (g) vessel 6.

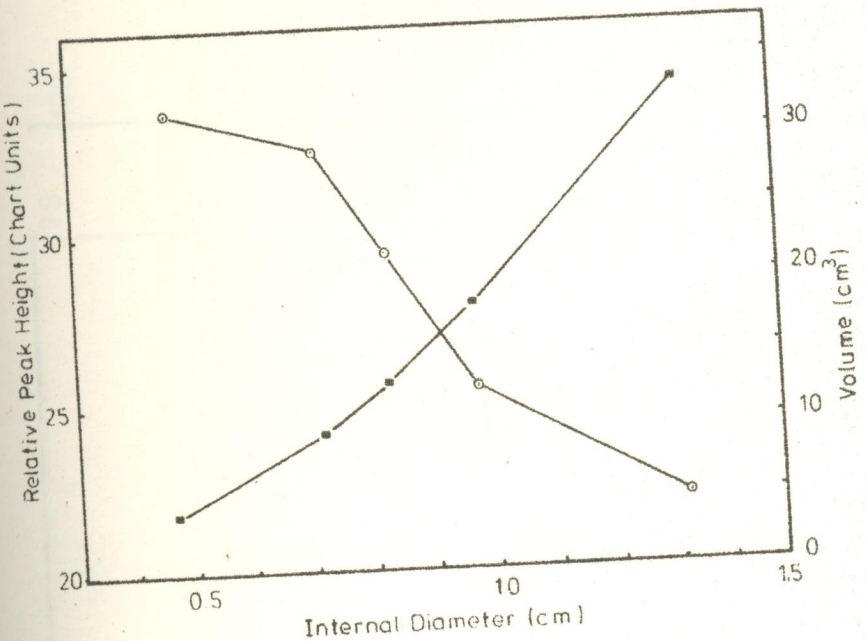

Fig. 2 Relationship between cell volume and peak height.
(⊙) peak height; (■) cell volume.

Fig. 3 Effect of flow rate on peak parameters.
Peak height : (+) cell 1; (●) cell 10. Half-width (sec) : (○) cell 1; (▽) cell 10. Half-width (ml) : (▽) cell 1; (□) cell 10.

REFERENCES

[1] A. M. Ure, Anal. Chim. Acta, 76, p. 1, (1975).
[2] T. R. Gilbert and D. N. Hume, Anal, Chim. Acta 65, p. 561, (1973).
[3] J. E. Hawley and J. D. Ingle, Jr., Anal. Chem., 47 p. 719, (1975).
[4] G. J. Ramelow and T. İ. Balkaş, Atomic Absorption Newsletter, 15, p. 55, (1976).

ÖZET

SOĞUK BUHAR TEKNİĞİNDE BAZI GELİŞMELER

Soğuk buhar tekniğinde, laboratuvarlarımızdaki mevcut atomik absorpsiyon cihazını kullanmak sureti ile yapılan bazı gelişmeler tarif edilmiştir. Sürekli hava akımı geçen bir indirgenme küveti kullanılması analiz zamanını önemli derecede kısaltmış; uzun boylu, küçük hacimli absorpsiyon küveti kullanılması ise duyarlığı büyük ölçüde arttırmıştır. Bu çalışmada kullanılan değişik numune hacimleri ve absorpsiyon küvetleri için tayin sınırları verilmiştir.

Middle East Technical University, Ankara, Turkey

Received August 26, 1976