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FURTHER INVESTIGATIONS INTO THE FACTORS AFFECTING SENSITIVITY IN THE COLD-VAPOR ANALYSIS OF MERCURY

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Abstract. Some factors which affect the sensitivity of the cold-vapor atomic absorption method for the analysis of mercury have been investigated. An agitation-aeration system is described which allows the detection of ultra-trace amounts of mercury, such as are commonly found in unpolluted environmental samples. This system is compared with a continuous-aeration system. Detection limits for different cold-vapor systems are presented.

I. INTRODUCTION

The cold-vapor atomic absorption method for the analysis of mercury is routinely used for a wide variety of samples [1]. The advantages of this method are well known and include simplicity and high sensitivity. Where ultra-trace amounts of mercury are to be detected, it has been shown that improvements over the commonly used types of cold-vapor systems, particularly in the use of long path length absorption cells, can lead to considerable improvements in sensitivity [2,3].

During the course of the analysis of mercury in some environmental samples it was observed that the levels of mercury were so low that the cold-vapor systems used in previous work [3 - 5] presented some difficulties with regard to sensitivity. It was discovered that ultra-trace levels of mercury, such as encountered in unpolluted environmental samples, could be detected by making some improvements in agitation efficiency and reduction vessel design. It was thus possible to determine low levels of mercury while at the

same time using only a small volume of sample, a big advantage when several elements are to be determined.

II. EXPERIMENTAL SET UP

A Varian-Techtron Model AA-6 atomic absorption spectrophotometer was used for all analyses. An absorption cell of 235 mm length and 4.5 mm internal diameter, constructed of glass with quartz windows glued in place, mounted directly on top of the standard air-acetylene burner head, was used in all cold-vapor systems evaluated. Several different types of reduction vessel were used; these are illustrated in Fig. 1. Air was supplied to the reduction vessel by a compressor. The reduction vessels were agitated by a Vortex Genie shaker.

A 1000 μg/ml stock solution of mercury contained 0.3385 g mercury (II) chloride in 250 ml of 10% (v/v) HNO_3. Working standards were prepared by dilutions of the stock solution. The reducing agent was a 5% (w/v) solution of $SnCl_2$ in 10% (v/v) HNO_3. It was aerated vigorously before use to remove traces of mercury.

III. RESULTS AND DISCUSSION

(1) Development of Small Volume System. Most of the cold-vapor systems described in the literature for the analysis of mercury in environmental samples involve relatively large sample volumes, ranging from 25 to 150 ml. Samples are usually prepared for analysis by wet digestion of the sample with acid at relatively low temperatures. When bomb-type closed decomposition vessels are used, at most 1 g of wet biological tissue or 0.5 g of wet sediment sample can be digested. Due to the extremely low levels of mercury in unpolluted environmental samples, the dilution of the digested sample solution must be kept to a minimum-usually 25 or 50 ml-to ensure a detectable amount of mercury in the solution.

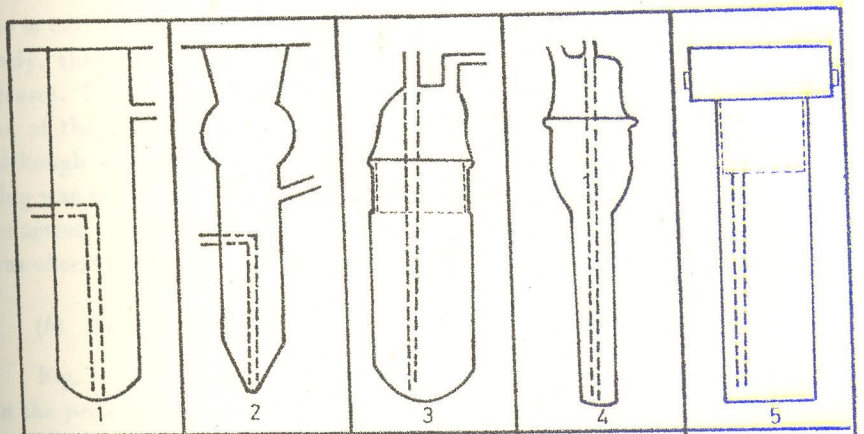
From the preceding discussion it is obvious that a sensitive system with which mercury in a small volume, e.g., 5 ml, could be detected would be very convenient for the replicate analysis of solid samples decomposed in bomb-type vessels. Furthermore, the remaining part of the sample solution after mercury analysis could then be used for the analysis of the other trace metals.

(2) Factors Affecting Sensitivity. Some important factors which affect the sensitivity of the cold-vapor technique are : (*i*) absorption cell dimensions, (*ii*) flow rate of carrier gas, (*iii*) geometry of reduction vessel, (*iv*) sample volume, (*v*) shaking efficiency, and (*vi*) heating of the system. In this study no work was done on the absorption cell dimensions because this parameter has been thoroughly studied in a previous work [3]. Also, no investigation of the effect of heating was made because the system used was not convenient for heating.

(*a*) *Flow Rate and Reduction Vessel Geometry* :

The effect of air flow rate on the shape and height of the absorption peak has been studied by many workers and is thus well known. However, workers have usually confined their investigations to the particular type of reduction vessel used. Gas washing bottles and small glass-stoppered flasks equipped with bubblers have been the preferred type of reduction vessel. In the present study the effect of air flow rate was investigated for several different types of vessel to better understand the importance of reduction vessel geometry.

The reduction vessels illustrated in Fig. 1 can be grouped into two main types. One type is a gas washing bottle with outlet at the top (vessels 3,



	1	2	3	4	5
Total V.	17ml	15ml	34ml	52ml	150ml
Sample V.	5ml	3ml	10ml	12ml	30ml

Figure 1. Types of reduction vessels used.

4, and 5); the other type can be considered as a modified gas washing bottle whose outlet is on the side rather than at the top (vessels 1 and 2).

It was observed that the effect of air flow rate was much more pronounced for vessels 1 and 2 than for vessels 3, 4, and 5. The latter vessels with outlets at the top contain only minimum dead volume. The reduced mercury is contained in the air space above the solution as a plug. This plug is carried to the absorption cell with essentially the same volume of air regardless of the air flow rate; in other words, the volume of the mercury plug is not dependent on the air flow rate. The flow rate only affects the rate at which the plug passes through the absorption cell, with the result that the peak height remains essentially the same with increasing flow rate. Thus, no change in absorbance was observed at flow rates higher than 450 ml/min.

In reduction vessels 1 and 2 the volume above the solution can be separated into two parts, as shown in Fig. 2. The mercury in the effective volume (part 1) is passed to the absorption cell as with vessels 3,4, and 5 and is responsible for the major part of the peak; the mercury in the dead volume (part 2) is carried very slowly to the absorption cell, causing tailing in the peak. An increase in the flow rate increases the rate with which the mercury in the dead volume is carried to the absorption cell. Consequently, the peak sharpens, and the height increases. This is shown in Fig. 3 where the volume of the plug is plotted against flow rate. Although a rapid decrease in the volume of the plug was observed with increasing flow rate for reduction vessels 1 and 2, no essential change was observed for the other vessels studied.

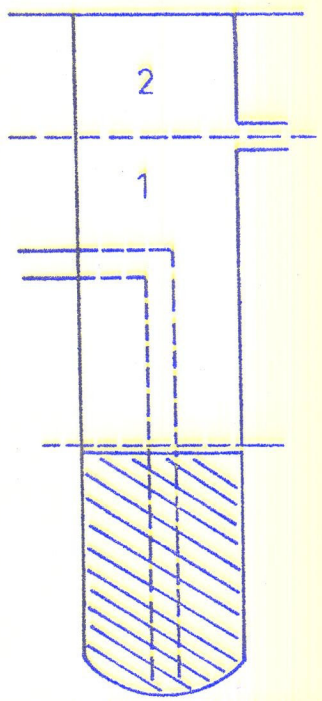


Figure 2. Diagram of reduction vessel showing effective (1) and dead (2) volumes.

(*b*) *Sample Volume :*

Fig. 4 shows the effect of sample volume on the peak height using vessel 1. An increase in peak height with increasing sample volume might be expected since with increasing sample volume, the volume of the air space above the sample decreases, thereby effectively concentrating the mercury in the air. A continuous

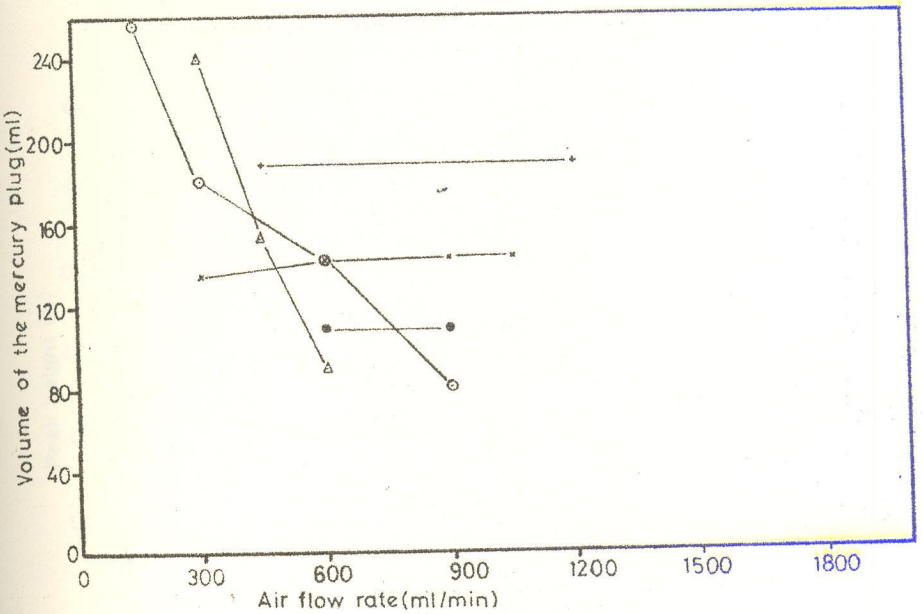


Figure 3. Effect of air flow rate on mercury plug volume.
⊙ : reduction vessel 1; △ : reduction vessel 2;
● : reduction vessel 3; × : reduction vessel 4;
+ : reduction vessel 5.

increase in peak height was not observed because an additional factor is important; viz., as the sample volume increases, the efficiency of mixing and the removal of mercury from the solution decreases. When the volume of the air space above the solution (reduction vessel volume minus sample volume) is plotted against volume of mercury plug, a plot very similiar to that in Fig. 4 is obtained, again demonstrating the inverse relationship between peak height and plug volume.

(c) *Shaking Efficiency* :

In the literature little attention has been paid to shaking (agitation) efficiency. In most studies establishment of an equilibrium between mercury in the vapor phase and in solution upon shaking for 10-20 seconds has been reported [6]. An investigation of shaking times up to 4 minutes was reported to show no increase in peak height [7]. In these studies the samples were agitated either by hand or with a magnetic stirrer. In the first phase of the

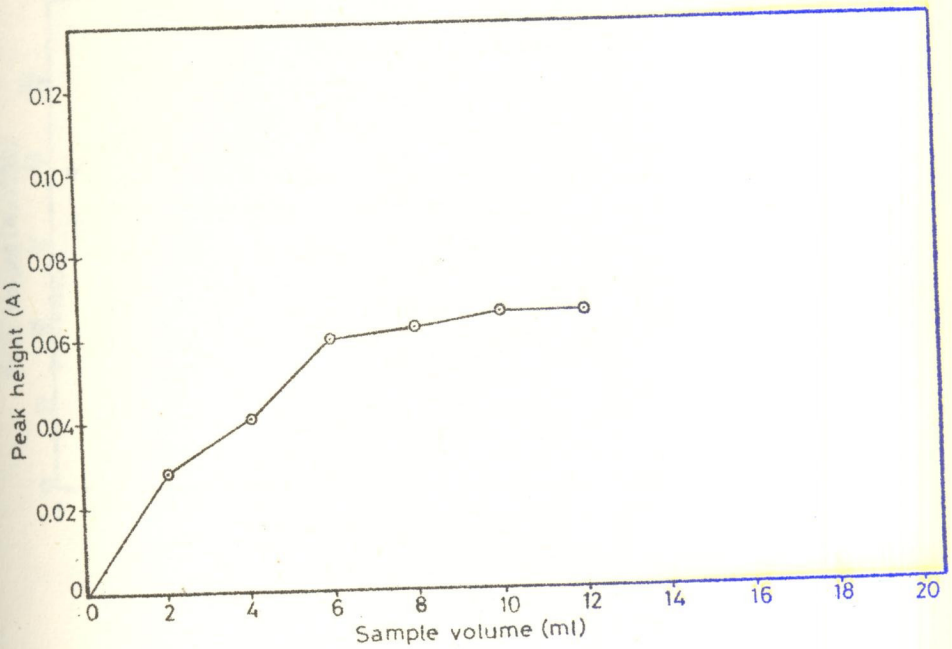


Figure 4. Effect of sample volume on peak height.

present study, samples were agitated by hand; later a vortex mixer was used, either with or without a table top with clamps for holding test tubes. A magnetic stirrer was also used with reduction vessel 5. The speed of the vortex mixer without table was at least twice as fast as with the table in place.

When hand shaking was employed or when the vortex was used with table or the magnetic stirrer used, the results were similiar to those in the literature. Fig. 5 shows the peak height as a function of shaking time when the vortex was used with its table in place. As can be seen from this figure, an equilibrium was reached within 90 seconds, after which no increase in peak height was observed. The decreases observed after long shaking periods were probably due to diffusion from the vessel.

The same trend was not observed when the vortex mixer was used without table and at maximum speed. From the results shown in Fig. 5 it appears that with efficient shaking it is possible to shift the equilibrium and thus to remove more mercury from the solution.

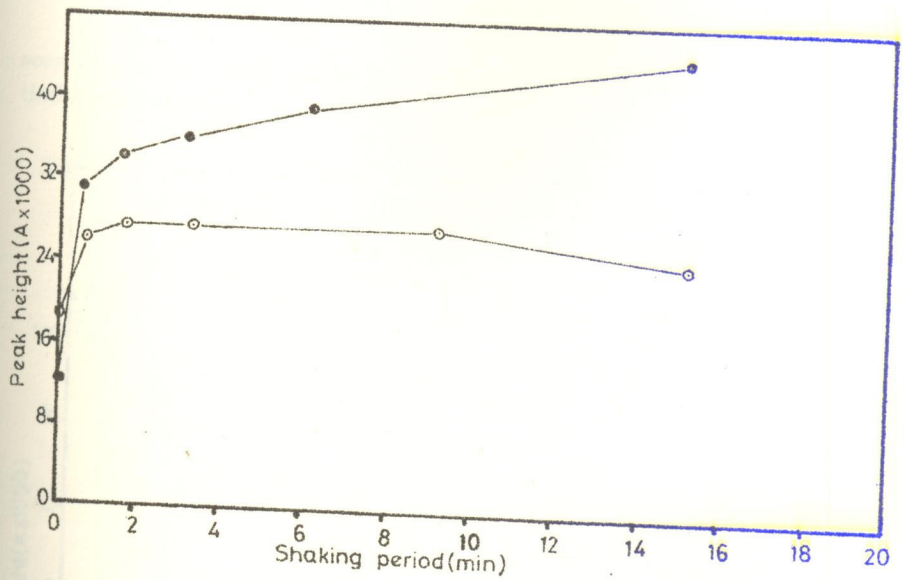


Figure 5. Effect of shaking time on peak height.
⊙ : with vortex table; ● : without table.

In order to see the effect of shaking on peak height and removal of mercury from the sample, reduction vessel 1 with vortex shaking was compared with vessel 5 with magnetic stirring. For this purpose a mercury standard containing 50 ng Hg in 25 ml was placed in vessel 5. After adding reducing agent the system was agitated with a magnetic stirrer at maximum speed for 90 seconds. The absorption peak was recorded by passing the reduced mercury with air through the absorption cell. Without any further additions (including reducing agent) the system was agitated for another 90 seconds, and the absorption peak recorded as before. This procedure was repeated until the peak height returned to the blank level. The same procedure was applied to vessel 1 with a 5-ml volume first with 12 ng and then with 50 ng Hg. The results are shown in Fig. 6.

Due to inefficient mixing with the magnetic stirrer, an equilibrium was reached in 90 seconds, but much of the mercury was still in solution. Only after seven successive agitations was it possible. to remove all the mercury from the sample. With the efficient mixing of the vortex, almost all the mercury in the sample was passed to the air phase with a single agitation. As

seen in Fig. 6, this behaviour is independent of the amount of mercury initially present.

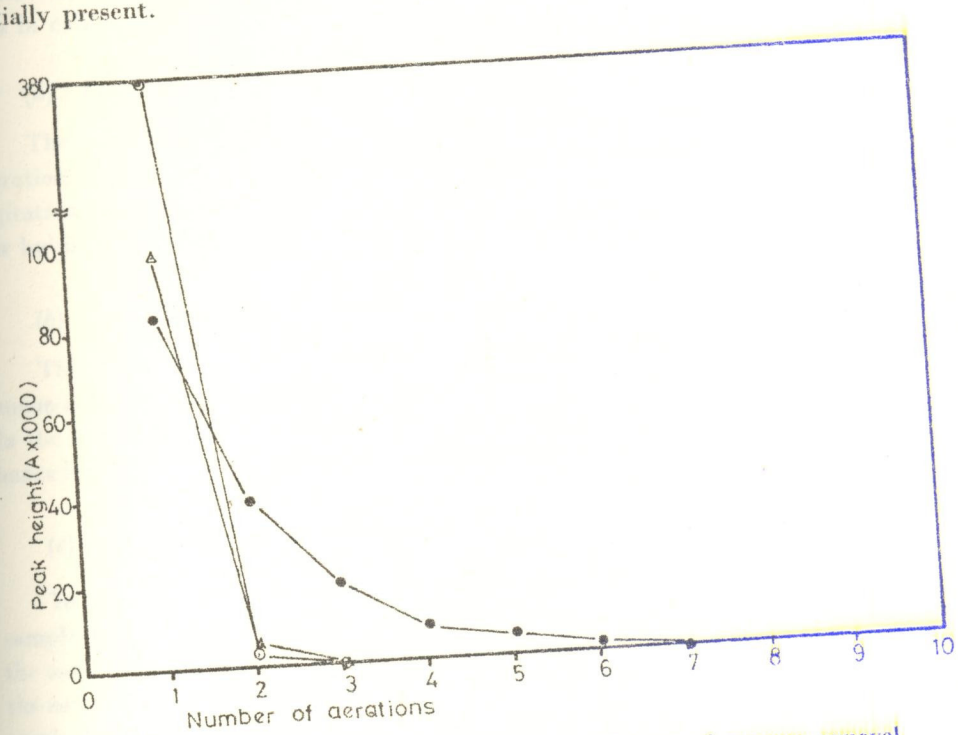


Figure 6. Effect of reduction vessel design on efficiency of mercury removal. ⊙ : 50 ng Hg in reduction vessel 1; △ : 12 ng Hg in reduction vessel 1; ● : 50 ng Hg in reduction vessel 5.

(3) Comparison with Continuous Aeration. Most cold-vapor systems described in the literature are based on the agitation-aeration principle in which the sample is reduced while agitated and then the reduced mercury vapor passed into the absorption cell with a stream of air or other gas. Hawley and Ingle [2] designed a continuous-aeration system which was simple to operate and extremely sensitive. Ramelow and Balkaş [4] developed a similar system and investigated the parameters affecting the sensitivity. In the present work an agitation-aeration system was used mainly, but for some determinations a continuous-aeration system was used. The reduction vessel used in the continuous-aeration system was the same as described by Ramelow and Balkaş [4].

Three main disadvantages of the continuous-aeration system have been observed; these are (*i*) low peak height, (*ii*) low precision, and (*iii*) difficulties in calibration.

(*a*) *Low Peak Height :*

The peak heights observed by injecting 50 ng Hg into the continuous-aeration system were found to be 34.5% less than those obtained with the agitation-aeration system. The reason for this is inefficient mixing by the air bubbles in the continuous-aeration system.

(*b*) *Low Precision :*

The precision of the absorption peak heights obtained with the continuous-aeration system was not as good as with the agitation-aeration system. In the latter the ralative standard deviation of eight peaks at the 0.1 absorbance level was 1.36%, while with the continuous system it was 9.6%.

(*c*) *Difficulties in Calibration :*

In the agitation-aeration system the analysis of some environmental samples with calibration-curve and standard-addition methods always gave the same results, indicating that the reduction and removal of mercury from the sample was independent of matrix. In the continuous-aeration system the results with the calibration-curve method were less than those found with the method of standard additions for each sample. The reason is that reduction and subsequent removal of mercury from simple aqueous solutions is much more rapid than in complex sample matrices. Thus, the standard-addition method of calibration must be employed when using a continuous-aeration technique. This is a serious drawback since it eliminates one of the main advantages of the technique, viz., speed of analysis.

(4) Optimum Conditions and Detection Limits for Various Reduction Vessels. The conditions found to be optimum for each reduction vessel evaluated are given in Table I along with the detection limits. The detection limits were calculated from the calibration plots shown in Fig. 7. From this work it was concluded that reduction vessel 1 provided the greatest sensitivity of all vessels studied, as well as being simple to use. In all subsequent work on environmental samples this vessel was used, in the agitation-aeration mode.

TABLE I

Optimum Operating Conditions and Detection Limits for Different Reduction Vessels and Cold-Vapor Systems

Reduction vessel	Reduction vessel volume (ml)	Sample volume (ml)	Detection limit (ng)
1	17	5	0.12
2	15	3	0.14
3	34	10	0.23
4	52	12	0.27
5	150	30	0.74
6	15	2	0.20*

*Continuous-aeration system: detection limit determined by Ramelow and Balkaş [3].

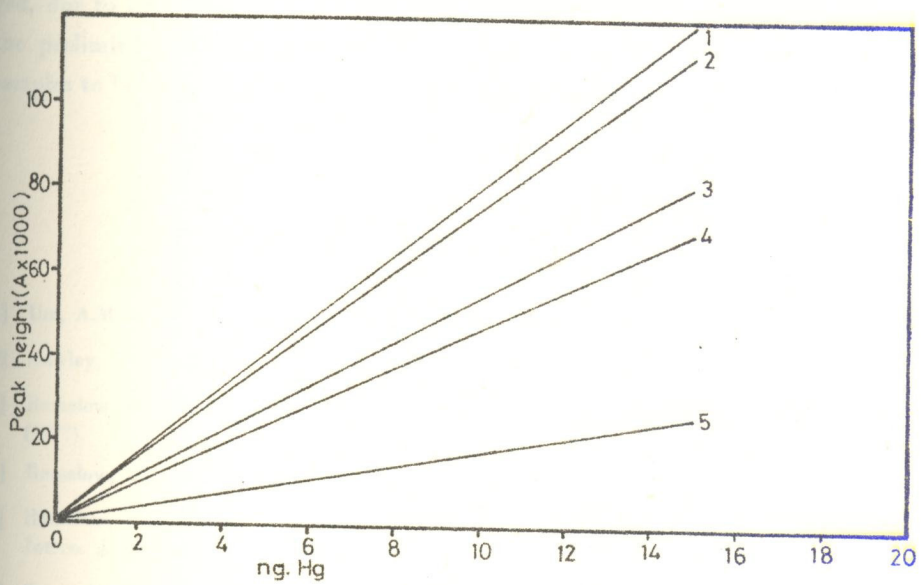


Figure 7. Calibration plots obtained with reduction vessels 1 to 5.

(5) Analysis of Marine Environmental Samples. The investigations of the factors affecting sensitivity in the cold-vapor analysis of mercury described in this work were made preliminary to the measurement of mercury

levels in marine environmental samples. The system employing reduction vessel 1 was used for the analysis of several types of marine samples, including water, biological material and sediments. The analytical results, as well as the specific procedures employed, will be presented in another communication elsewhere, but it can be stated here that the system developed proved quite useful for the determination of mercury in widely ranging concentrations.

The accuracy of the system was checked by the use of NBS standard reference material #1571 (orchard leaves) and two marine samples, copepod and sea plant, supplied by the International Laboratory of Marine Radioactivity as part of an intercalibration program. The mercury concentration found in the orchard leaves was within 4% of the certified value. The actual concentrations of mercury in the marine samples have not been divulged, due to the continuing nature of the intercalibration program; however the preliminary results [8] indicate our mercury concentrations for these samples to be close to those reported by the majority of the laboratories.

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Ö Z E T

SOĞUK BUHAR ATOMİK ABSORPSİYON TEKNİĞİ İLE CİVA ANALİZ YÖNTEMLERİNDE DUYARLILIĞI ETKİLEYEN ETKENLERİN GENİŞ OLARAK İNCELENMESİ

Bu çalışmada soğuk buhar atomik absorbsiyon tekniği ile civa analiz yöntemlerinde duyarlılığı etkileyen bazı etkenler incelendi ve tayin sınırı civarının çevredeki doğal düzeylerinin analize yetecek kadar düşük olan bir kesintili akım sistemi geliştirildi. Bu sistem daha önceki çalışmalarda kullanılmış olan sürekli akım sistemi ile karşılaştırıldı ve kullanılan değişik soğuk buhar sistemleri için tayin sınırları saptandı.

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