An Application and Modification of the Freeze-out Technique by Quiram and Biller for the Determination of Pollutants in the Atmosphere by Mass Spectrometry

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(Received March 24, 1964)

Many works[1-5] have reported on concentrating air pollutants in a cold trap in order to analyze the concentrates by mass spectrometry. It has long been known that water can be passed through an ordinary in-seal trap at the temperature of liquid air,[6] even though its vapor pressure is almost 10^{-26} mmHg at these temperatures. Extremely small frozen particles are formed at these low temperatures, and these fine crystals are carried into the gas stream through the trap. Contaminants contained in air, other than water, may also pass more or less through a trap in a similar manner. To collect from air sufficient pollutants for subsequent analysis, Shepherd et al.[1] and Quiram and Biller[5] used a cold trap of glass wool or one of silica gel. To compensate the passover of the pollutants, Shepherd et al. took a large amount of the air sample. Quiram's method, on the other hand, requires only 3 l. NTP of air. In his method, by handling glass stop cocks manually, a part of the air sample was introduced into the trap and was then left in contact with the glass wool for about 30 sec. in order to improve the condensation efficiency of the pollutants; then the air sample in the trap was evacuated off.

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1) M. Shepherd, S. M. Rock, R. Howard and J. Stormes, *Anal. Chem.*, **25**, 1431 (1951).

2) P. P. Mader, M. W. Heddon, R. T. Lofberg and R. H. Koehler, ibid., **24**, 1899 (1952).

3) E. R. Quiram, S. J. Metro and J. B. Lewis, ibid., **26**, 352 (1954).

4) K. Suzuki, S. Araki and S. Hirano, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **61**, 26 (1958).

5) E. R. Quiram and W. F. Biller, *Anal. Chem.*, **30**, 1166 (1958).

6) M. Shepherd and A. Martin, *J. Res. Natl. Bur. Standards*, **2**, 1145 (1929).

This procedure was repeated about 50 times until the air in the 3 l. sample bottle was exhausted. By this method they improved the collection efficiency and could collect sufficient hydrocarbons contained in the atmosphere above 10 p.p.m. for subsequent analysis with a mass spectrometer. Though excellent in its capacity of collection, the method of Shepherd et al. is somewhat unhandy to apply in field work, while in that of Quiram and Biller it is very troublesome to handle the stopcocks.

We have employed the method of Quiram and Biller, investigating its usefulness for several pollutants, notably for a trace of mercury vapor in air. Since the results proved to be satisfactory, as will be described below, we have slightly improved the freeze-out technique by automatically circulating the air sample through a glass-wool trap instead of handling the stopcocks manually. Synthetic air samples were analyzed by this procedure, and the results checked.

Experimental

The assembly of the sample-collecting apparatus is shown schematically in Fig. 1. The apparatus is essentially the same as that employed by Quiram and Biller, but it was modified by the addition of a magnetic circulating pump, which is shown in Fig. 1, encircled with a dotted line. The volume of the gas-collecting bottle was about 3 l. Five gas-collecting bottles were assembled in order to prepare synthetic blended samples by a dilution technique using these bottles successively. Blends of appropriate concentrations in the bottles were diluted with air, and could be used immediately to get a calibration curve.

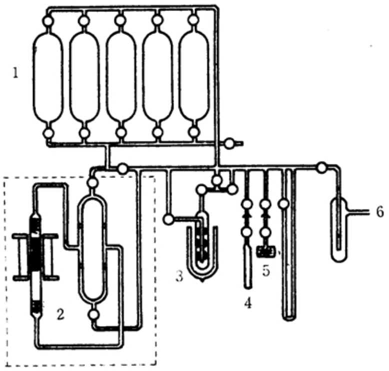

Fig. 1. Sample collecting manifold.

1 Sample bottles
2 Circulation pump
3 Glass-wool trap
4 Contaminant concentration thimble
5 Drying agent
6 To vacuum pump

The magnetic circulation pump was equipped with only one solenoid. The principal features of the pump have been reported by Livingston.7) The 2000-turn coil driving the piston was of enamel wire, 1.5 mm. in diameter. The solenoid was activated by an electronic timer obtained from the Sakashita Factory. When adjusted to an optimum stroke, the pump circulated air at atmospheric pressure at the rate of 3 l./min. with a power consumption of about 50 W. When necessary, the pump can be shunted out from the gas sample manifold by stop cocks. Under these conditions, the method of Quiram and Biller was tested.

The procedure of manual operation for the freezing out of the contaminants from the air sample was the same as that reported by Quiram and Biller. In the mercury analysis, a mercury manometer in the gas-handling manifold of the mass spectrometer was demounted in order to eliminate the mercury background.

In the circulation method, the air sample was repeatedly circulated from a sample bottle through a cold trap for an appropriate period. The other operations were the same as in Quiram and Biller's method. Carbon dioxide was not removed from the collected contaminants in the present experiment, however. Rather, the amount of carbon dioxide in the room air itself was determined beforehand using argon as the internal standard, and in the subsequent analysis of the various components in the collected pollutants, carbon dioxide, collected simultaneously, was used as the internal standard, since one of the main components of the substance frozen-out from the air itself of the room was carbon dioxide, and the same air was introduced into the sample bottle containing an appropriate amount of blended materials in order to prepare the air sample.

In order to determine the appropriate circulating time, the carbon dioxide in the room air was collected under various circulating times, ranging from 5 to 60 min. The amount of carbon dioxide collected was then determined, using argon as the internal standard. Table I shows the result. Since a 10-min. circulation was found to be sufficient to attain a maximum, an almost constant collection efficiency in the case of carbon dioxide, all the samples were circulated for 10 min. in the following determinations.

The gases used to prepare the samples were standard gases obtained from the Takachiho Chemicals Co. Anhydrous magnesium perchlorate, the

TABLE I. CIRCULATION TIME VERSUS FREEZED-OUT AMOUNT OF CARBON DIOXIDE FROM ROOM AIR

Circulation time min.	Argon added as internal standard mmHg×ml.	(CO_2/Ar) ratio determined by mass spectra	Carbon dioxide collected* mmHg×ml.
5	55.77	16.08	896.8
10	57.53	16.59	954.0
20	54.02	17.59	932.8
30	63.57	15.20	966.7
60	59.67	18.01	994.5

* Corrected for volume of sample bottle.

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7) R. Livingston, *J. Phys. Chem.*, 33, 956 (1929).

drying agent, was a guaranteed reagent obtained from the Toyama Kagaku Co. A Consolidated Electrodynamics Corp. mass spectrometer, type 21-103C, was used.

Results and Discussion

Mercury Determination. — Table II shows the mean deviation of the determination of the mercury vapor in the air by Quiram and Biller's method. The samples were prepared as follows. An evacuated 3 l. sample bottle containing a drop of mercury was immersed in water, which was kept at a constant temperature. The atmosphere in the bottle was found to come to an equilibrium with liquid mercury in about an hour. After 3 hr. of immersion, the mercury drop was removed from the bottle containing the mercury vapor corresponding to the temperature of the water; then, by opening a cock, the bottle was filled with room air. The pressure of mercury in the sample bottle was estimated from the Table recording vapor pressure versus temperature.[8] The samples in Table II and Table III were obtained by successively diluting the air prepared by the procedure. The data in Table III indicate the known content of mercury and the ratio of the mercury found to the known content. The rather low value of the ratio is probably due to poor collection efficiency, since little memory effect was observed in the mass spectrometer. For analysis we used a working curve. Figure 2 indicates such a working curve. A synthetic air sample containing 1.7×10^{-2} p.p.m. of mercury vapor was analyzed by the method. The result was 2.0×10^{-2} p.p.m., which is 20% over the blended value. As much mercury vapor contained in atmosphere as the maximum allowable tolerance, i. e., about 1/100 p.p.m., may be determined by this method, with a mean deviation of about 20% (Table II), whereas, according to our experiment, with hydrocarbons contained in the air, the detection limit of the present technique was 1 p.p.m.*

TABLE II

Concn. of mercury in air p.p.m.	Peak height of m/e 202 of concd. material arbitrary unit	Deviation	Standard deviation
1.4	43.1	5.0	
1.4	33.1	5.0	
1.4	38.0	0.1	
1.4	38.1	0.0	
mean	38.1	2.6	3.6

Electron current, 9 μamp. Sample is air in equilibrium with mercury at 18.5±0.3°C.

Concn. of mercury in air p.p.m.	Peak height of m/e 202 of conced. material arbitrary unit	Deviation	Standard deviation
0.015	1.4	0.0	
0.015	1.2	0.2	
0.015	1.7	0.3	
mean	1.4	0.2	0.2

Electron current, 30 μamp.

Volume of air sample, ca. 3 l. Electron voltage, 70 eV.

All freezed-out mercury was introduced into the reservoir of MS.

TABLE III. MERCURY CONTENT AND COLLECTION EFFICIENCY

Dilution ratio	1*	1/2	1/4	1/8	1/32	1/96
Collection efficiency, %	84	63	50	35	28	15

* 1.03 μHg of mercury is contained. Other samples were prepared from the same one by successive dilution.

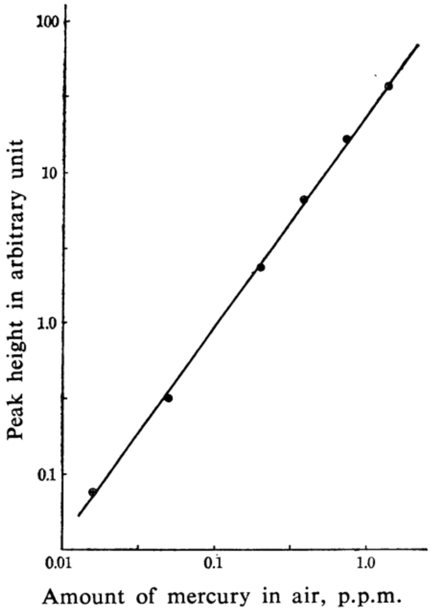

Fig. 2. Working curve of mercury in air.

Circulation Method.—Air samples containing about 10 p.p.m. to 100 p.p.m. each of acetylene, ethane, propylene, n-butane and freon-12 were blended for analysis. Table IV shows the results of a run. In analysis we used a working curve, since a part of the blended pollutant

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[8] International Critical Tables, Vol. III, McGraw-Hill, New York (1928).

* Quiram determined pollutants below 10 p. p. m. by another freeze-out technique.

TABLE IV. ANALYSIS OF SYNTHETIC BLEND

Component	Pressure in gas reservoir of MS μHg	Content*	
		Collected	Synthesized
Acetylene	0.16	7.83	8.44
Ethane	0.19	8.99	7.98
Propylene	0.18	9.25	10.19
n-Butane	0.19	9.44	10.71
Freon-12	0.19	9.74	11.02
Carbon dioxide	26.57		
Total	27.48**		

Pressure of carbon dioxide (internal standard) in air determined beforehand was 0.4471 mmHg.

Electron current: 9 μamp., ionizing voltage: 70 eV.

* (mmHg·ml.) in 3 l. of air.

** Measured with micromanometer, introduced pressure was 25.02 μ.

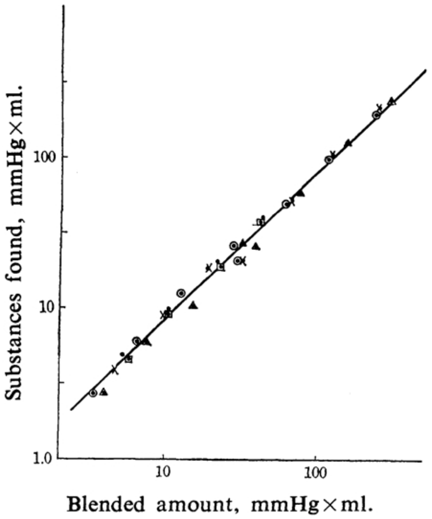

Fig. 3. Found amount versus synthetic values of various substances in air (1 atm.).

⊙ C_2H_2 △ C_2H_6 • C_3H_6
× C_4H_{10} ▣ F 12

is not recovered. Figure 3 shows the relation between the amount of blended compounds and the amount collected. As may be seen in the figure, the working curves of various compounds coincide remarkably in this range of concentration. This is not surprising, however, as these pollutants are physically, rather than chemically, adsorbed on glass-wool. When samples of the same composition were analyzed several times, the reproducibility of the analysis was found to be about ±10%. Blended samples of various compositions were analyzed, but no interference effect among components was observed.

In the range of 10~100 p.p.m., about 90% of each of the pollutants was recovered. With the object of seeing the whereabouts of the uncollected pollutants, the remaining air of the once-freezed-out sample containing *n*-butane was treated afresh. By this treatment, about 10% of the original amount of *n*-butane was collected. From this result it seems that the uncollected portion of the pollutants is not lost in the process, but remains in the gas phase.

The compounds in the lowest concentration blend tested, which contained about 10 p.p.m. of each of the compounds, gave peak heights of 20~80 divisions of the recorder chart of mass spectrometer, according to their sensitivities. Since a difference of one division has significance under favorable circumstances, a one- or two-fold decrease in concentration, depending on the compounds, may be tolerated in analyzing a sample of air of this size. The time necessary for the sample manipulation, including mass spectrometric recording, is about 3 hr. per sample.

The merit of the present procedure is that it requires only mechanical operations, no mental concentration. The method has, however, a few limitations. One of these concerns the fact that some contaminants which are often encountered, such as carbon monoxide, methane and hydrogen, cannot be collected by this technique. Those substances which dissolve or attack vacuum grease, such as benzene or boronfluoride, also do not give reliable results when one uses ordinary greased stopcocks. For a similar reason, a drying agent may also limit the usefulness of the method.

Summary

Quiram and Biller's freeze-out method, originally devised to determine hydrocarbons contained in air above 10 p.p.m. and using a mass spectrometer, was tried on a trace (down to 1/100 p.p.m.) of mercury vapor in atmosphere; it was proved to give satisfactory results. The freeze-out procedure was then slightly modified. To collect the pollutants, the air sample was circulated automatically for ten minutes through the freezing-out trap instead of repeatedly handling the stopcocks. By this procedure, a blended air sample containing various pollutants above 10 p.p.m. have been analyzed. The precision is about ±10%.

The authors would like to express their thanks to Dr. Shun Araki for his advice and to Mr. Ryuzo Shiota for his valuable discussions and survey of the manuscript.

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