RI 7999

Bureau of Mines Report of Investigations/1975

Use of Vacutainers for Collection of Mine Atmosphere Samples

UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 7999

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USE OF VACUTAINERS FOR COLLECTION OF MINE ATMOSPHERE SAMPLES

by

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ABSTRACT

As part of a continuing effort to reduce the weight and bulk of equipment that mining personnel must carry underground, the Bureau of Mines and the Mining Enforcement and Safety Administration (MESA) investigated accurate and convenient gas samplers for use by mine inspectors in sampling mine atmospheres. The samplers are septum-stoppered glass vials commonly used for routine blood sampling. These lightweight, compact samplers yield results comparable with those obtained with conventional bottle samplers of 250-ml nominal capacity.

INTRODUCTION

Over the past several years, the amount of equipment mining personnel are required to carry has continued to increase. Mine air samples have been collected for analysis with several types of glass and metal containers, as reported in a previous publication.[3] The Bureau formerly employed vacuum bottles with a nominal capacity of 250 ml for most of the sampling done by inspectors and mining personnel. These are large and cumbersome, and thus limit the sampling capability. Hypodermic syringes satisfy most of the requirements, but their use is limited mainly to research work because storage time after sampling and prior to analysis, if it is more than a few days, presents problems. Gases such as carbon dioxide are lost relatively rapidly from the syringes by permeation. Thus, there was a need to develop more convienent and efficient samplers.

In 1971, the Mount Hope, W. Va., office tested 10-ml Vacutainers[4] made by Becton-Dickenson as sample collectors. These are glass vials stoppered by 0.25-inch-thick butyl rubber septums. Since these units are routinely

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[3] Lang, H. W., and R. W. Freedman. The Use of Disposal Hypodermic Syringes for Collection of Mine Atmosphere Samples. Am. Ind. Hyg. Assoc. J, v. 30, September-October 1969, pp. 523-526.

[4] Reference to a specific trade name does not imply endorsement by the Bureau of Mines.

employed for blood sampling, they are evacuated to only about 250 mm. Nevertheless, the Mount Hope investigators found that consistent results could be obtained for mine air samples if they were compared with gas standards sampled in Vacutainers.[5]

Mine inspectors found samplers of this type to be very convenient, and the results were comparable with those obtained with 250-ml vacuum bottles, even after storage periods of 1 to 2 weeks after sampling. Consequently, they were officially adopted for use by the Bureau in 1972.

However, there are uncertainties inherent in the use of the Vacutainers. In addition to the loss of certain gases mentioned earlier, experience at both the Mount Hope, W. Va., office of MESA and the Pittsburgh Mining and Safety Research Center of the Bureau indicated that storage of either partially or completely evacuated Vacutainers produced levels of carbon monoxide of up to 50 ppm.

Experimental programs were initiated independently by MESA at Mount Hope and the Bureau at Pittsburgh to compare Vacutainers with vacuum bottles. The following objectives were undertaken:

1. Devise a unit that will evacuate several dozen Vacutainers simultaneously to a level lower than that of the commercial Vacutainers.[6]

2. Measure gas leakage from the atmosphere into evacuated vessels as a function of time prior to sampling.[7]

3. Determine safe storage periods (after sampling and prior to analysis) by checking sample stability.[8]

EXPERIMENTAL WORK

Vacutainers were evacuated at Mount Hope, W. Va., to less than 4 mm and were allowed to stand for measured time periods. Some were then filled to atmospheric pressure with pure carrier gas and analyzed to check composition. Others were filled to atmospheric pressure with standard gas mixtures. Several were compared immediately with similar standards collected in 250-ml vacuum bottles to check for sampling error. Others were compared with vacuum-bottle standards, as a function of time comparable with in-use handling requirements.

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[5] Vacutainers of 10-ml nominal capacity actually contain about 13 ml. The 10 ml is sufficient for quantitative flushing and filling of a 1-ml gas chromatograph sample loop.

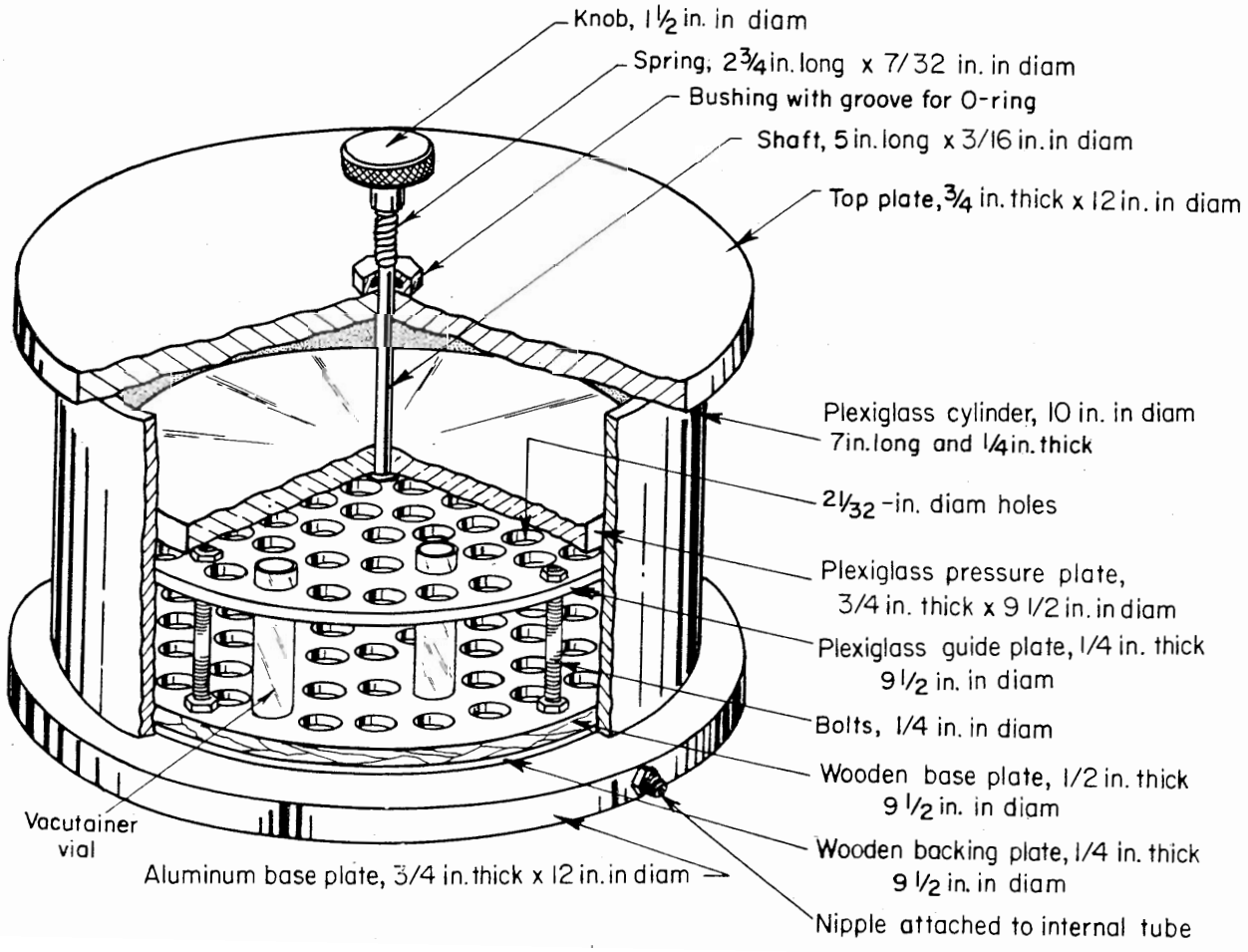
[6] Completely evacuated vessels were unavailable from Becton-Dickinson, the manufacturer. Also, time of evacuation can be documented by using an in-house system.

[7] In the Mount Hope mine inspection program, storage of evacuated Vacutainers for weeks or even months was difficult to avoid.

[8] In routine mine sampling, delays of 1 to 2 weeks prior to analysis at a distant laboratory are common.

Apparatus

A device was constructed for evacuating up to 56 Vacutainers to a few millimeters of pressure (fig. 1). It consists of a plexiglass cylinder 1/4 inch thick, 10 inches in diameter, and 7 inches high, sealed to a 3/4-inch-thick plexiglass plate. A shaft,3/4 inch in diameter and 5 inches long, extends vertically through a bushing mounted within the plate. The bushing contains an O-ring seal to render it vacuum-tight. The end of the shaft extending into the evacuation chamber is attached to a plexiglass, axially mounted pressure disk, 9-1/2 inches in diameter and 3/4 inch thick. The latter can be moved downward by exerting a force on the knob attached to the shaft. A spring placed on the shaft between the knob and the vacuum-tight bushing prevents the pressure disk from moving downward as the chamber is evacuated. The tube support rack consists of a base plate and backing plate of wood, and a plexiglass guide plate spaced 2-1/2 inches above the base units with four bolts. Holes 21/32 inch in diameter are drilled as shown in figure 1. The rack rests on a rubber gasket placed on an aluminum base plate. The aluminum plate is equipped with a horizontal internal tube connected to a central hole drilled partially through the base plate. An external nipple attached to this tube can be seen extending horizontally from the base plate.



The Vacutainers used have a nominal capacity (draw) of 10 ml. The Vacutainers are glass vials 16 mm ID by 10 cm long, stoppered by a butyl rubber septum, and are obtainable from most laboratory supply houses. Luer needles, numbers 21-25, are employed for injecting samples into Vacutainers. This operation is carried out safely by employing a Vacutainer needle holder, which is also available from supply houses. The gas chromatographic equipment used was similar to that used in previous work for rapid mine air analysis.[9]

Evacuation and Sampling

Vacutainers are inserted into the holes in the rack with the stoppers positioned gently on top of them (without inserting them in place).[10] The top compression unit is then positioned in contact with the rubber gasket and vacuum applied for 3 to 4 minutes. Stoppers are then inserted by forcing the pressure plate downward.

Samples are introduced into the evacuated samplers by needle injection or by removing the stopper manually in the atmosphere being tested. For laboratory evaluation with standard gases, the sample is injected into the Vacutainer with a needle. Sample pressure is measured with a manometer attached to a second needle inserted through the stopper.

Samples are introduced into the chromatograph by mercury displacement into a sample loop. At the Mount Hope laboratories, two parallel needles mounted to a rack-and-pinion device were simultaneously inserted through the Vacutainer stopper. Mercury was introduced by a reservoir and leveling bulb through one needle; the other needle, extending slightly through the stopper, was connected to the sample loop inlet. At Pittsburgh, the same system was employed using manual insertion of the needles, but samples were withdrawn from Vacutainers with a 50-ml gas-tight syringe containing a shut-off valve between the needle and syringe body. After withdrawal of the needle, the syringe plunger moves inward of itself to yield an atmospheric pressure sample of about 9 ml. This is sufficient for filling a 1-ml chromatograph sample loop.

RESULTS AND DISCUSSION

A standard mixture at Mount Hope containing 0.25% CH_4 and 0.25% CO_2 in air was stored in 250-ml vacuum bottles and 10-ml Vacutainers for 7 days at 1-atm internal pressure. Precision expressed in percent standard deviation of integrator counts[11] for the bottles was O_2, 0.34%; N_2, 0.25%; CH_4, 1.28%; and CO_2, 2.17%. The corresponding values for Vacutainers were O_2, 0.45%; N_2, 0.32%; CH_4, 1.68%, and CO_2, 2.27%. Thus, sampling and storage errors were

[9] Lang, H. W., and R. W. Freedman. Three-Minute Gas Chromatographic Analysis of the Main Constituents of Mine Atmospheres. BuMines RI 7696, 1972, 7 pp.

[10] The stoppers supplied by Becton-Dickinson are notched at the bottom. This permits air to be withdrawn from the vials prior to inserting the stoppers fully in place.

[11] Statistical comparison based upon counts (peak integrands) is more accurate than comparison using the percentage values calculated from counts.

small. Percentages of CH_4 and CO_2 were calculated from each set of counts (table 1). The mean values for the two types of samplers were very close for each gas. If the individual percentages are calculated to three decimal places, and the t-test applied for the difference in means,[12] values of t are 0.75 and 0.44 for CO_2 and CH_4, respectively. This is well within the two-tailed critical value $t_{0.975,26} = 2.06$, and indicates insignificant difference due to sampling or storage.

TABLE 1. - Comparison of vacuum bottles with Vacutainers at Mount Hope, W. Va.

Sample	Methane, %			Carbon dioxide, %		
	10-ml Vacutainer	250-ml bottle	Difference	10-ml Vacutainer	250-ml bottle	Difference
1	0.25	0.24	-0.01	0.26	0.26	0.00
2	.25	.24	-.01	.25	.26	+.01
3	.24	.24	.00	.24	.25	+.01
4	.24	.24	.00	.24	.25	+.01
5	.24	.24	.00	.25	.25	.00
6	.24	.24	.00	.25	.25	.00
7	.24	.24	.00	.25	.25	.00
8	.24	.24	.00	.24	.25	+.01
9	.24	.24	.00	.24	.25	+.01
10	.24	.24	.00	.26	.26	.00
11	.24	.24	.00	.24	.25	+.01
12	.23	.24	+.01	.25	.25	.00
13	.24	.24	.00	.26	.25	-.01
14	.24	.23	-.01	.26	.25	-.01
15	.24	.24	.00	.25	.24	-.01
16	.24	.24	.00	.25	.25	.00
17	.24	.24	.00	.24	.25	+.01
18	.24	.24	.00	.24	.24	.00
19	.24	.24	.00	.25	.24	-.01
20	.25	.24	-.01	.26	.23	-.03
21	.23	.24	+.01	.25	.25	.00
22	.24	.24	.00	.25	.25	.00
23	.24	.24	.00	.25	.25	.00
24	.24	.24	.00	.25	.25	.00
25	.24	.24	.00	.26	.25	-.01
26	.24	.24	.00	.26	.25	-.01
27	.24	.25	+.01	.26	.25	-.01
Mean	.250	.249	-	.250	.249	-

To examine the effect of longer storage, 20 samples of a gas mixture were allowed to stand for 41 days at the Pittsburgh laboratory. Results are given in table 2. Precision is only fair (up to ±4% standard deviation) for CH_4, CO. and CO_2. In addition, CO_2 shows substantial change in concentration over the 41-day period. The loss of 16.1% of the initial level in the standard is

[12] Spiegel, M. R. Theory and Problems of Statistics. Schaum Publishing Co., New York, 1961, 359 pp.

2.6% per week on a linear basis. These findings indicate that storage periods of longer than 1 week should be avoided if accurate CO_2 levels are important. It can be presumed that CO_2 is lost by permeation[13] rather than by diffusion through small orifices. The difference between the two types of flow are described in a previous publication.[14]

TABLE 2. - Effect of storage of gas for 41 days (20 samples)

	O_2	N_2	CH_4	CO	CO_2
Percent in standard gas mixture.....	9.80	83.75	1.05	0.45	5.00
Sample mean.....	10.135	84.26	1.0105	.446	4.195
Standard deviation.....	.2345	.3234	.0481	.0193	.2038
Percent of standard deviation.	2.31	.384	4.76	4.33	4.86
Change, sample mean minus percent in standard gas mixture.....	.335	.510	-.040	-.004	-.805
Percentage of change (based on standard gas mixture).....	3.31	.61	-3.96	-.90	-16.1

A problem noted at Mount Hope was the gradual concentration of carbon monoxide when evacuated units (either factory-supplied or completely evacuated) were stored for extended periods in the laboratory. Levels as high as 50 ppm were measured when the Vacutainers were filled with CO-free air or helium. This fact was verified at Pittsburgh (table 3).

It is postulated that change in relative concentrations of the gases is due in part to external permeation from the atmosphere through the septum. However, the high CO levels attained are as yet unexplained, since ambient levels generally do not exceed 5 ppm. The results in table 3 indicate that, for a 1-week storage period, gaseous inflow is insignificant. After 6 months (25 weeks), average values for all the gases tended to reach a plateau, indicating attainment of equilibrium. The ambient conditions in the Pittsburgh laboratory were not controlled. Although the N_2:O_2 ratio of 4:1 in air did not vary, there probably was some variation in CH_4 and CO_2 levels. In addition, permeation rates increase significantly with temperature, and the laboratory temperature ranged from 20° to 30° C. Permeation rates also depend linearly upon pressure differences (inside and outside the container). However, these are small on a relative scale, and would not be expected to produce significantly large variations in permeation rates. The effects of variations in septum geometry and composition did not appear significant over the short periods recommended for storage of Vacutainers.

[13] Scaringelli, F. P., S. A. Frey, and B. E. Saltzman. Evaluation of Teflon Permeation Tubes for Use With Sulfur Dioxide. Am. Ind. Hyg. Assoc. J., v. 28, May-June 1967, pp. 260-266.

[14] Work cited in footnote 3.

TABLE 3. - Effect of storage time on gas concentration for evacuated Vacutainers stored in the laboratory at Pittsburgh

Sample	Storage period, weeks	O_2, %	N_2, %	CO_2, %	CH_4, ppm	CO, ppm
1	1	0.07	0.12	0.0172	<1	0.6
2	1	.06	.09	.0116	<1	.1
3	1	.07	.10	.0085	<1	.6
4	1	.05	.10	.0212	<1	.1
5	1	.06	.09	.0200	<1	.1
6	25	.37	1.07	.04	7	13
7	25	1.36	2.87	.07	10	29
8	25	.53	1.77	.09	6	39
9	25	.65	2.01	.10	7	36
10	52	-	-	-	-	28
11	52	-	-	-	-	35
12	52	-	-	-	-	40
13	78	-	-	.06	5	41
14	78	.79	.92	.03	5	21
15	78	.84	.93	.03	5	19
16	78	.55	.85	.06	5	31
17	78	.65	1.11	.07	5	44

CONCLUSIONS

Based upon this experimental work, it can be concluded that samples of mine gases can be collected rapidly and conveniently in 10-ml Vacutainers for subsequent gas chromatographic analysis. Storage of evacuated Vacutainers prior to analysis should not exceed 1 to 2 months if they are used for analysis of low levels of carbon monoxide. Better control over storage time can be accomplished by in-house evacuation. In-house evacuation also removes more of the air within the Vacutainer, thus eliminating a possible source of variation in results.

Analysis of samples taken in Vacutainers provides results comparable with those obtained with 250-ml vacuum bottles. However, if precise values for CO_2 are required, this analysis should be accomplished within 1 week after taking samples because some CO_2 may be lost by permeation.

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