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Gas-Sampling Capability of Vacutainers

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GAS-SAMPLING CAPABILITY OF VACUTAINERS

by

Robert W. Freedman,[1] Benjamin I. Ferber,[2]
and Wayne H. Duerr[3]

ABSTRACT

Vacutainers are employed by the Bureau of Mines and the Mining Enforcement and Safety Administration for sampling mine air and other atmospheres containing fixed gases, low-molecular-weight hydrocarbons, and products of combustion. Tests were conducted to study shelf life of evacuated samplers prior to sampling and also to check the stability of sampled gases prior to analysis. An unexplained phenomenon, slow accumulation of carbon monoxide in evacuated samplers, occurred after a few weeks' storage; levels were low but increased with time and could pose a problem for critical applications. Accordingly, attempts to halt CO release by additional means of treatment were made, and storage at low temperature was found to be effective.

INTRODUCTION

Onsite sampling of ambient atmospheres is generally accomplished by gas-tight syringes, evacuated vessels, and plastic bags. Vacutainers,[4] normally employed for blood sampling, are currently in use for sampling mine air, which may contain methane, traces of higher alkanes, and products of combustion such as carbon monoxide and oxygenates. The latter arise from diesel engine operation, from the use of explosives, and from mine fires and explosions. Carbon monoxide also can be present, resulting from the slow ambient oxidation of coal.

Vacutainers are glass, test-tube-shaped vessels capped with butyl rubber septums. These samplers, as supplied commercially in three sizes, are evacuated to only about 250 mm pressure and have the capability of drawing in 10, 20, or 30 ml of fluid. Actual volumes are somewhat larger (13 ml for the 10-ml size).

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

Vacutainers were first used as received. The need for complete evacuation was soon realized, and evacuation chambers were built for this purpose by both the Mining Enforcement and Safety Administration (MESA) and the Bureau of Mines. These chambers are described in the initial Bureau publication on Vacutainers.[5] Since many of the gaseous samples analyzed in Bureau research are products of combustion, the stability of samples of saturated and unsaturated hydrocarbons in the C_1-C_5 range was studied and reported in a second publication.[6]

The shelf life of evacuated Vacutainers was studied to determine the extent of leakage or contamination on standing prior to use for analysis. This was essential since in the field several weeks or even months may elapse before samples are taken. In the previous studies, it was concluded that the shelf life of evacuated Vacutainers should be limited to 1 to 2 months owing to the accumulation of contaminant gases, particularly CO. The mechanism for the appearance of that gas is unknown; it is tentatively explained by absorption-desorption into and from the stoppers.

After collection of samples in Vacutainers, the fixed gases O_2, N_2, CO, and Ar, commonly found in mine air, can be stored indefinitely without loss. Carbon dioxide, however, slowly decreases in concentration and should be analyzed within about 1 week of sampling. Methane and higher hydrocarbons, C_1-C_5, can be stored for weeks with predictable decreases in the concentration.

In the latest Bureau studies, the principal objective was to devise a means of eliminating or limiting the appearance of CO in stored Vacutainers. It was also considered desirable to establish the mechanism for gradual increase in the concentration of contaminants. One area that had not been investigated is the implication of bacteria in the contamination; experiments were devised to explore this possibility.

ACKNOWLEDGMENT

We are indebted to William Stevens of Mercy Hospital, Pittsburgh, Pa., for operation of an autoclave for the thermal sterilization experiments.

EXPERIMENTAL PROCEDURE

Vacutainers of all three sizes were evacuated to 1 mm pressure, or lower, using the evacuation chamber previously described.[7] A simplified diagram of this chamber is shown in figure 1. Samples for the tests described under "Results and Discussion" were added to the evacuated samplers by needle insertion or by removal of stoppers manually in a test atmosphere. The samples were analyzed after transfer to the sample loop of a chromatograph, which was

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[5] Freedman, R. W., W. G. Humphrey, and R. L. Craft. Use of Vacutainers for Collection of Mine Atmosphere Samples. BuMines RI 7999, 1975, 7 pp.

[6] Freedman, R. W., and B. I. Ferber. Sampling Capability of Vacutainers for Fixed Gases and Low-Molecular-Weight Hydrocarbons. BuMines RI 8175, 1976, 9 pp.

[7] Work cited in footnote 6.

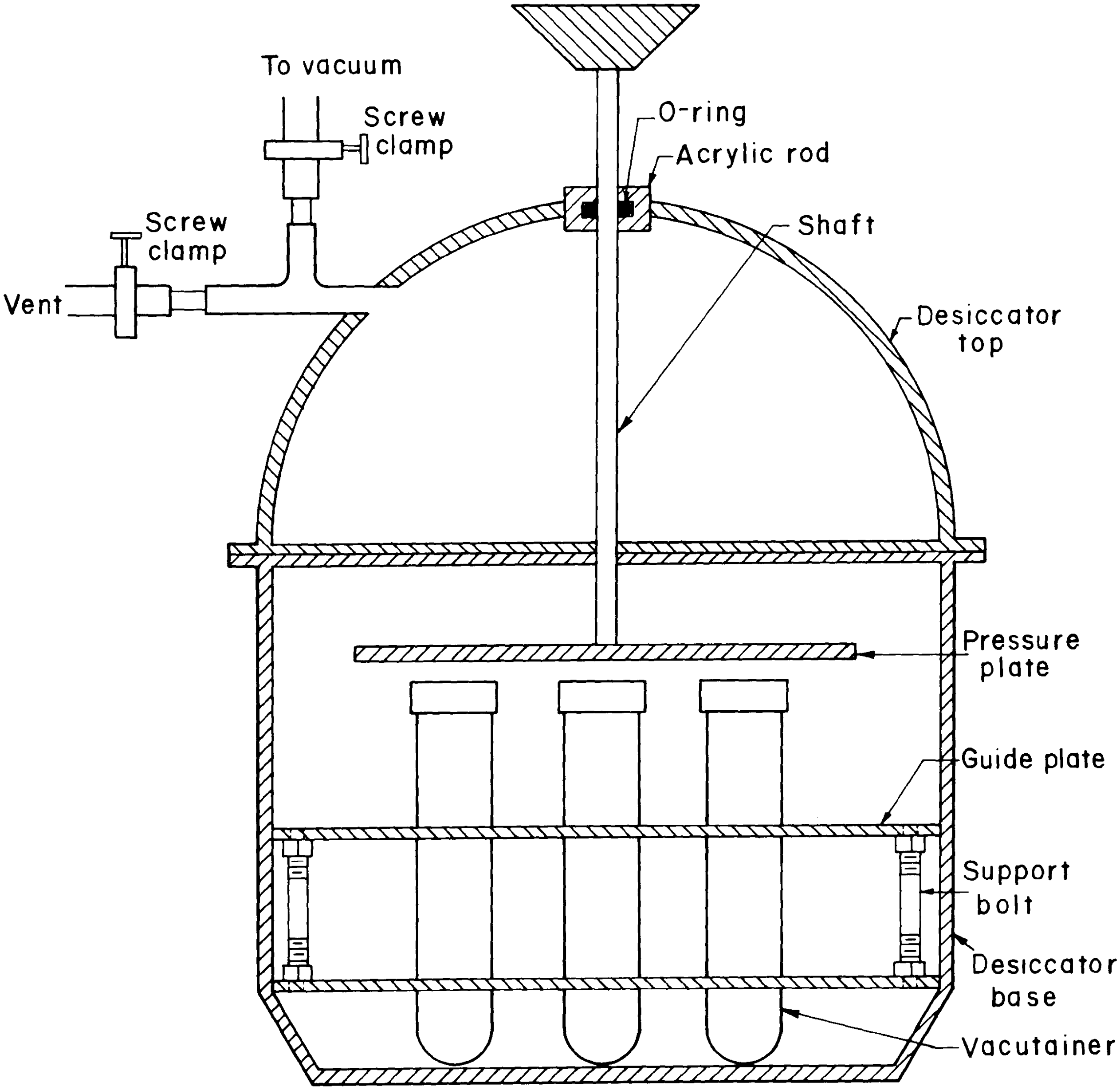

FIGURE 1. - Evacuation chamber.

accomplished by inserting mercury through the septum to pressurize the contents, followed by transfer using a gastight syringe. Alternatively, mercury displacement from the Vacutainer into the loop can be employed.

The 20-ml Vacutainers were used to study the effects on CO and CO_2 of destroying or inhibiting bacteria by thermal sterilization, treatment with antiseptics, and prolonged storage at low temperature.

Except for some samplers kept in an untreated state, the 20-ml Vacutainers were steam-sterilized in an autoclave for 30 minutes at 133° C. Some were then exposed to an atmosphere of ethylene oxide at 25° C for 1 hour, while others were prewashed with a quaternary mixture (Q-San) containing dimethylbenzylammonium chloride and ethylbenzylammonium chloride or with an iodine containing mixture (1-Dene) before exposure to the C_2H_4O. The Vacutainers to be prewashed were filled with either mixture at a dilution of 20 g/l of water, allowed to steep for 1 hour, drained, and dried under vacuum. All the sterilized Vacutainers were evacuated, sealed, and allowed to stand either at room temperature (25° C) or at -15° C in the freezing compartment of a refrigerator for 7 weeks.

RESULTS AND DISCUSSION

The concentration of gases accumulating in evacuated 10- and 30-ml Vacutainers over a 17-week period is shown in table 1. If the concentrations found in the 10- and 30-ml samplers are averaged, levels found after 17 weeks are 0.37 pct O_2, 0.91 pct N_2, 271 ppm CO_2, 0.75 ppm CH_4, and 20 ppm CO.

TABLE 1. - Concentrations[1] of gases[2] accumulating in 10- and 30-ml Vacutainers at 25° C

Time,	O_2, pct		N_2, pct		CO_2, ppm		CH_4, ppm		CO, ppm	
weeks	10 ml	30 ml	10 ml	30 ml	10 ml	30 ml	10 ml	30 ml	10 ml	30 ml
1	0.13	0.05	0.16	0.10	59	68	1.0	-	1.0	1.4
2	.15	.03	.19	.09	72	101	1.0	-	1.6	3.0
4	.26	.10	.44	.23	97	122	1.2	0.5	3.4	4.0
8	.42	.08	.68	.28	152	175	1.0	.4	8.6	7.0
16.6	.59	.14	1.18	.63	271	270	1.0	.5	19.0	21.0

[1] All concentrations shown are averages of 5 measurements.
[2] Percent standard deviations are predominantly about ±25 pct.

Removal of glycerine lubricant from stoppers by detergent wash produced no change in gas accumulation. Heating the stoppers at 70° C for 3 weeks under vacuum followed by storage of the evacuated Vacutainers for 3 weeks at 25° C removed most of the CO_2 (average residual concentration = 33 ppm) but produced no change in CO level.

External exposure of evacuated samplers to pure CO and CO_2 did not significantly increase the concentrations of these gases within the Vacutainers, indicating lack of penetration.

A set of samplers filled with a mixture of gases and stored for 41 days prior to analysis displayed minor changes in all gas concentrations except CO_2, as shown in table 2.

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

	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

Several aliphatic hydrocarbons, C_2-C_5, stored in Vacutainers for 4 weeks, displayed decreases in concentration as shown in figure 2. In unknown samples, it should be possible to make a rough estimate of initial concentrations for several of the compounds after storage for a few weeks.

Vacutainers exposed to ethylene oxide and evacuated yielded results shown in figure 3. The curves for untreated samples were obtained from previous data. The effect on CO is minimal, but CO_2 evolution is strongly suppressed initially. It is difficult to speculate on the cause of this behavior.

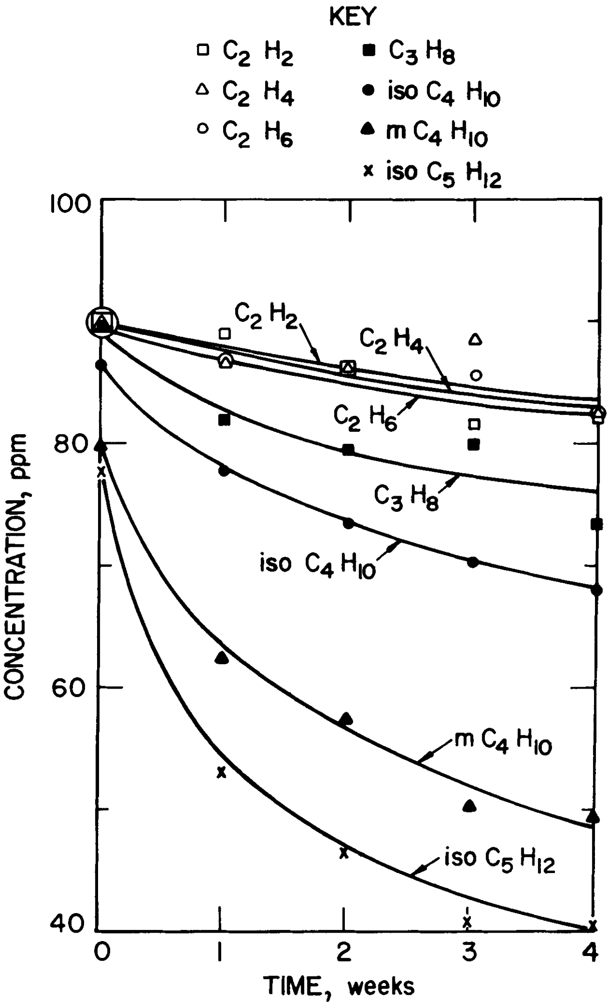

FIGURE 2. - Concentration change of hydrocarbons during storage.

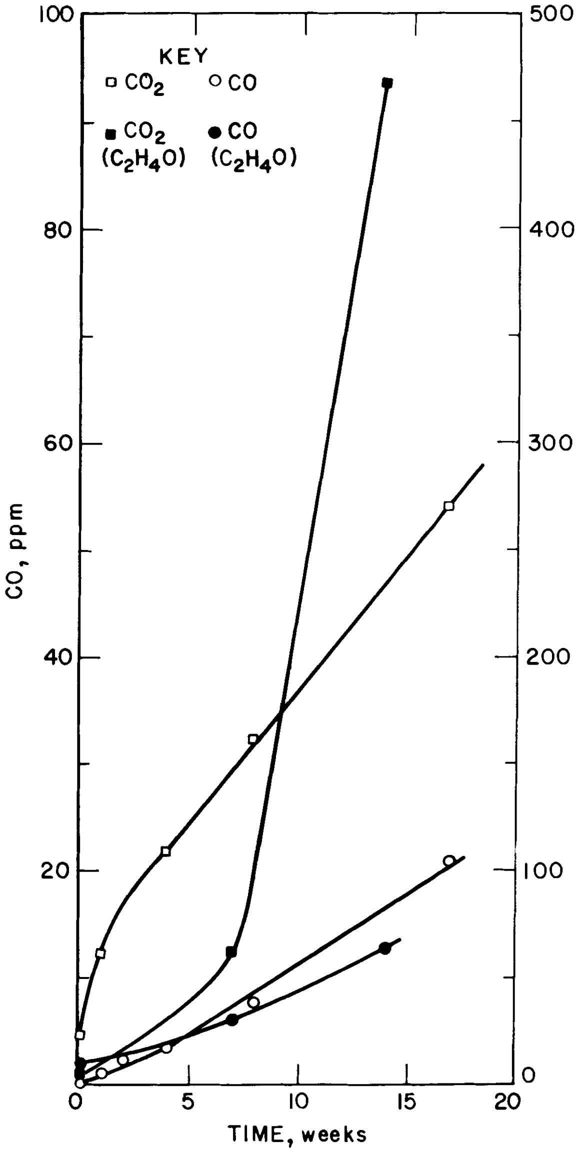

FIGURE 3. - Effect of ethylene oxide treatment prior to storage of evacuated Vacutainers.

In the experiments designed to inhibit bacteria, with room-temperature storage the CO values with Q-San or 1-Dene pretreatment were similar to those obtained with C_2H_4O alone and also to those for untreated Vacutainers (fig. 3). The CO_2 values with Q-San or 1-Dene were likewise similar to those obtained with C_2H_4O alone, ranging from 4 to 12 ppm, but differed from those for untreated Vacutainers, which average 32 ppm CO_2. In the Vacutainers stored at low temperatures, CO levels were zero in all cases, and CO_2 levels were low and comparable to those obtained with ethylene oxide alone.

At this point it was suspected that low-temperature treatment alone without added antiseptics would be effective. Accordingly, a set of untreated Vacutainers was stored in the freezing compartment for 7 weeks and again yielded no measurable CO; CO_2 levels ranged from 12 to 20 ppm. When the same batch of Vacutainers was allowed to stand at 25° C for an additional 7 weeks after the refrigeration treatment, carbon monoxide reappeared; levels of 5 to 6 ppm CO were measured.

From the behavior of CO and CO_2 in evacuated Vacutainers, it is difficult to establish the presence of related microrganisms. CO_2 appearance at room temperature could conceivably be inhibited by the use of germicides. However, definite conclusions cannot be made based upon these experiments.

No mechanism for gradual appearance of contaminants has been firmly established. However, it has been definitely shown that refrigerated storage can block the formation of CO, the most significant contaminant. This provides a simple and convenient means of maintaining extended shelf life for evacuated Vacutainers. Chemical treatment appears to be unnecessary.

CONCLUSIONS

1. Vacutainer storage of inert low-molecular-weight gases, such as O_2, N_2, CH_4, CO, and Ar, is feasible for extended periods. Low concentrations of CO may show a slow increase in evacuated samplers and also in collected gases.

2. Gases such as CO_2, which are relatively soluble in rubber, slowly decrease in concentration and should be analyzed within 1 to 2 weeks.

3. Aliphatic hydrocarbons in the C_2-C_5 range also slowly decrease in concentration over several weeks' time. Analysis should be conducted promptly, but some extrapolation to zero time is possible.

4. The use of germicides and heat treatment has some effect upon the inhibition of CO_2 appearance in evacuated Vacutainers. However, CO generation could not be suppressed by such means.

5. A mechanism for contaminant appearance could not be established.

6. Extended storage in a freezer at -15° C completely suppressed the appearance of CO in evacuated Vacutainers over a 7-week period.

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