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STIBINE/ARSINE MONITORING DURING EV OPERATION

Summary Report on Preliminary Tests
at ANL and at LILCO

by

R. O. Loutfy, D. G. Graczyk, R. Varma,
E. R. Hayes, F. L. Williams,
and N. P. Yao

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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Near-Term EV Battery Project

ANL Office for Electrochemical Project
Management (OEPM)

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February 1981

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ABSTRACT

A series of tests was performed to monitor the evolution and dispersal of stibine and arsine from the lead-acid propulsion batteries in three different Electra-Van Model 600 vehicles operated by Argonne National Laboratory (ANL) and by the Long Island Lighting Company (LILCO). Ambient air was sampled at several locations inside the vehicles and in the garages where testing was done during charge, equalization charge, and on-the-road discharge operations. In addition, direct sampling of cell off-gases was performed with the ANL van. Interpretation of the individual test results was carried out in the context of vehicle characteristics, sampling protocol, and operating conditions.

The test results demonstrated that under the test conditions only small concentrations of stibine and arsine accumulated in occupiable work areas. Measured concentrations in the vehicles and in the garages never exceeded 25% of the Threshold Limit Value-Time Weighted Average (TLV-TWA) standards. Thus, although the potential for hazardous accumulation of the hydrides exists, it can be easily controlled. Isolation of the battery compartment from the vehicle interior and provisions for adequate ventilation are recommended as effective control measures.

A threshold voltage for hydride production, at about 2.45 V per cell, was reflected in the results of the experiments performed during charging of the batteries. Hydride evolution rates were lower during equalization charge than during the overcharge portion of a charge cycle when the on-board charger was used in a normal operating mode. A delayed release of the metal hydrides from the battery cells was observed during on-the-road operation of the vehicles. The implications of these observations for electric vehicle (EV) operation are discussed.

An engineering analysis of the generation and dispersal of the metal hydrides is presented, and equations are derived for estimating minimum ventilation requirements for the EV battery compartment and for garages housing EV operations. Recommendations are made regarding safe handling procedures for battery off-gases, procedures for conducting stibine/arsine monitoring tests, and future work.

SUMMARY

Toxic gases, notably stibine and arsine, may be produced along with hydrogen and oxygen during charging and equalization charging of lead-acid batteries. The accumulation of these gases during operation of electric vehicles (EVs) powered by lead-acid batteries has been recognized as a potential health and safety hazard. In order to assess the magnitude and implications of this problem, a series of tests was performed to monitor the evolution and dispersal of stibine and arsine from the lead-acid propulsion batteries in electric vehicles operated by Argonne National Laboratory (ANL) and by the Long Island Lighting Co. (LILCO). Three different Electra-Van Model 600 vehicles, manufactured by Jet Industries, were tested: one at ANL and two at LILCO. One of the LILCO vans, designated Vehicle 2, had been modified by installing an air-tight cover that replaced the manufacturer's battery compartment cover, and by rewiring the battery compartment exhaust fan to run during on-the-road operation of the vehicle.

Ambient air was sampled at several locations inside the vehicles and in the garages where testing was done during charge, equalization charge, and on-the-road discharge of the vehicles' batteries. In addition, direct sampling of cell off-gases was performed with the ANL van. The results of these tests demonstrated that only small concentrations of stibine and arsine accumulated in occupiable work areas under the test conditions. Measured concentrations in the vehicles and in the garages never exceeded 25% of the Threshold Limit Value-Time Weighted Average (TLV-TWA), a standard that represents a limit on the average exposure level that may be experienced over eight continuous hours of exposure. (The TLV-TWA for SbH_3 is 0.5 mg/min; for AsH_3 , 0.2 mg/ m^3). Because of the variability of the individual test conditions, however, it was necessary to qualify and interpret many of the results. From a detailed analysis of the data, it was concluded that some of the reported concentrations may have been lower than those expected under normal operating conditions. However, tests performed at LILCO under simulated worst-case conditions during equalization charge still did not lead to unacceptable concentrations in the work area. On this basis, it can be stated with confidence that operation of these vehicles under normal conditions will not result in unacceptable exposure levels. This is not to say that the potential for unacceptable accumulation of the hydrides does not exist, but that, for the vehicles tested, control of the evolved gases was adequate.

The results of measurements at the cell outlets and on air inside the battery compartment exhaust indicated that sufficient quantities of the hydrides are evolved to make some form of control mandatory, especially during the overcharge portion of a charge cycle and during equalization charge. Isolation of the battery compartment from the vehicle interior and provisions for adequate ventilation are recommended as effective control measures.

The test results obtained during charging at LILCO were consistent with the existence of a threshold voltage for hydride generation below which no stibine or arsine production occurs. Thus, higher ambient levels of stibine and arsine are likely to occur during the overcharge period of a charge cycle than at the beginning of a cycle before the battery voltage reaches about 2.45 V per cell. The tests during equalization charge at ANL indicated that the rate of hydride evolution is lower during equalization charge than during

the overcharge portion of a charge cycle if the on-board charger is used in the normal mode. However, tests performed at LILCO using an off-board charger with higher current than the finish rate of the on-board charger resulted in higher metal-hydride evolution rates during equalization than during overcharge. This indicates the sensitivity of the hydride evolution rates to the imposed current. It also suggests that restrictions on the use of off-board chargers might be required to ensure the adequacy of design specifications for ventilation.

Measurable amounts of arsine were found inside the vehicle and in the battery compartment during on-the-road discharge with the ANL van. It was postulated that this arsine arose from a delayed release of hydride that was generated during a previous charge or equalization charge cycle and retained inside the battery cells. According to this interpretation, the stibine generated at the same time would have decomposed in the cells during the overnight period before discharge and would not have been detected. This hypothesis was supported by the corresponding tests with Vehicle 1 at LILCO where discharge was carried out immediately after an equalization charge cycle; significant concentrations of both stibine and arsine were measured inside the battery compartment during discharge in this case. Measurements at the cell outlets during discharge indicated that only small quantities of the hydrides are released from the battery cells, but that they can accumulate in the closed volume of the unventilated battery compartment to high concentrations which may seep into the vehicle interior. Isolation of the battery compartment from the interior of the van by an air-tight cover and ventilation of the battery compartment during discharge were found to reduce these accumulations to undetectable levels for the modified Vehicle 2 at LILCO. This result and the lower in-vehicle concentrations found with Vehicle 2 compared to Vehicle 1 during the charging experiments indicate that these modifications represent valuable improvements in vehicle design.

In addition to the stibine/arsine monitoring tests, a few brief experiments were carried out to determine rates of hydrogen evolution during operation of the ANL vehicle and to investigate the possible presence of organic compounds in the ambient air during charging with Vehicle 1 at LILCO. The hydrogen evolution rates during charging and equalization charging were found to agree with theoretical values from calculations based on Faraday's law. In addition, it was found that small amounts of hydrogen gas are also released from the battery cells during on-the-road discharge. It is presumed that this release occurs by a mechanism like that proposed for stibine and arsine. The small quantity of H_2 arising from delayed release during discharge is probably insufficient to pose an explosion hazard.

Only one malodorous organic compound, carbonyl sulfide, was found during the LILCO tests. A number of other species were identified, but these are most probably components of degreasing solvents, lubricants, fuels, etc., which would likely be found in the type of garage where the tests were conducted.

The stibine/arsine monitoring test results were applied, along with data from the literature, in an engineering analysis of the generation and dispersal of the hydrides. In this analysis, equations were derived that describe average rates of stibine and arsine evolution from a lead-acid cell

during charging modes as a function of charging current and cell voltage. Although these equations oversimplify the complex dependence of hydride generation on battery type and operational parameters, they provide a useful basis for establishing ventilation requirements for the battery compartment in an EV and for garages housing EV operations. Preliminary calculations using these equations and tentative acceptability criteria for hydride accumulations recommend minimum air flow rates through the battery compartment that are somewhat higher than those required for safe dispersal of hydrogen. Requirements for garage ventilation are virtually identical to present standards if a small number of vehicles in relation to garage size are charged at one time.

Recommendations are made in several areas related to the problem of stibine/arsine evolution during EV operation. First, a revised version of procedures for safe handling of battery off-gases is presented. Second, procedures for conducting stibine/arsine monitoring tests are outlined, and current methods for stibine measurement are compared and evaluated. Third, suggestions are made concerning research in the near future. This work would include (1) fundamental studies of the mechanisms by which hydrides are generated in lead-acid cells, (2) correlation of evolution rates with battery types and operating parameters under controlled conditions to test the validity of preliminary design equations, and (3) an assessment of the environmental impact of metal-hydride decomposition products and their accumulation. In addition, the production and dispersal of stibine and arsine during regenerative braking should be investigated. The development of sensitive and highly specific instrumentation for continuous monitoring of stibine and arsine should be pursued.

I. INTRODUCTION

Toxic gases, notably stibine (SbH_3) and arsine (AsH_3), may be produced along with hydrogen and oxygen during charging and equalization charging of lead-acid batteries. Standards for occupational exposure to these metal hydrides have been set.¹ A limit on the average exposure level that may be experienced over a period of eight continuous hours is given by the Threshold Limit Value-Time Weighted Average (TLV-TWA). The TLV-TWA for SbH_3 is 0.1 ppm (0.5 mg/m^3); for AsH_3 , it is 0.05 ppm (0.2 mg/m^3). Periods of exposure to concentrations up to three times the TLV-TWA (as given by the TLV-STEL, Short Term Exposure Limit) are acceptable if the average exposure over eight hours does not exceed the TLV-TWA.

Accumulation of arsine and stibine during the operation of electric vehicles (EVs) powered by lead-acid batteries has been recognized as a potential health and safety hazard and procedures have been proposed² to minimize personnel exposure. The calculations and data used to formulate these procedures indicated a need for empirical measurement of actual exposure levels from in-use electric vehicles. Such measurements would serve several purposes:

1. To quantitatively assess the magnitude of the problem. It has been postulated that only exposure to short-term, low-level accumulations of stibine or arsine is possible, but no reliable estimate of the exposure level could be made.

2. To evaluate the premises on which the proposals were based, e.g., to verify that those operations where accumulation is possible were correctly identified.
3. To provide an appropriate data base to be used in revising, modifying, or refining the preliminary safe-handling procedures.
4. To establish testing procedures for use with vehicles or conditions other than those tested.

This report describes a series of tests performed by Argonne National Laboratory (ANL) personnel to monitor the evolution and dispersal of stibine and arsine from lead-acid batteries in electric vehicles operated at ANL and at the Long Island Lighting Co. (LILCO), Hicksville, NY. The results of tests with the ANL vehicle and a preliminary interpretation of the data have been presented in an earlier report.³ They are reexamined here together with results obtained at LILCO in an effort to compare and contrast the individual data sets and thereby assemble a more general picture of hydride behavior during EV operations.

Three different Electra-Van Model 600 vehicles, manufactured by Jet Industries, were tested: one at ANL and two at LILCO. Stibine and arsine were measured at several locations inside the vehicles and in the garage where testing was done during charge, equalization charge, and on-the-road discharge of the batteries. Test conditions were intended to be typical of normal operation since the rate of stibine/arsine generation in lead-acid batteries depends on a number of factors related to operating conditions.²⁻⁴ However, differences in operations between ANL and LILCO, inadvertent changes in sampling protocol, and individual differences among the vehicles all combined to make the test conditions more variable than anticipated. Although these variations make interpretation of the data and comparison of the results difficult, they do provide an added dimension to the data matrix, which, if properly exploited, gives more information than could have been obtained under the uniform conditions initially proposed.

Specific operating conditions for each test can be defined using physical and electrical data describing the performance and condition of the battery during the test. Sampling differences among the tests and individual vehicle characteristics are likewise documented. Using this information, the results of the monitoring tests can be interpreted in terms of operating parameters and test conditions. This interpretation, it is hoped, will provide an insight into stibine/arsine behavior under typical conditions and will allow a valid assessment of the hazards these hydrides present during EV operation.

The stibine/arsine monitoring results have also been applied in an engineering analysis of the generation and dispersal of the hydrides. This analysis must be considered preliminary because of the paucity of available data. Its primary value is that it identifies operational parameters important to controlling hydride accumulation and points out areas where future efforts should be concentrated. Recommendations are made concerning vehicle design, monitoring protocol, operating procedures, and goals for subsequent field and laboratory studies.

II. EXPERIMENTAL

A. Test Sites and Vehicle Descriptions

Tests were conducted in the Building 826 garage at ANL and at the facilities of the Long Island Lighting Company, Hicksville, NY. The garage used for the tests at LILCO was not specifically dedicated to EV operations, but was part of a heavy equipment repair facility. Two separate areas of this facility were used during the tests. One of these, used for Vehicle 1 (see below), was a paint shop.

Three vehicles were tested: one at ANL and two at LILCO. All were Electra-Van Model 600 manufactured by Jet Industries, Austin, TX. (This vehicle model is often called the "Jet-600") The battery pack in the Electra-Van Model 600 comprises seventeen 6-volt propulsion batteries and one 12-volt accessory battery having the following specifications:

Main Power Pack

Manufacturer: SGL Batteries Company

Type: 2HGC-HC, Lead-Acid, 6 V

Weight: 69 lb/Battery

Length: 10-5/16 in.; Width: 7-1/8 in.; Height: 10-1/4 in.

Rating: 20 h Rating: 210 A·h; Reserve Cap., 25 A: 390 min

Minutes at 75 A: 100 min

Accessory Battery

Manufacturer: SGL Batteries Company

Type: 24Ht, Lead-Acid, 12 V

Weight: 55 lb/Battery

Length: 10-7/32 in.; Width: 6-3/4 in.; Height: 9-7/8 in.

Rating: 20 h Rating: 210 A·h; Reserve Cap., 25 A: 100 min

Minutes at 75 A: 15 min

The on-board charger associated with this vehicle model is a Lestronic Model 9458 - Type 12/102LCR25-5ET; it has a normal cooling fan with 2.8 m³/min air-flow capacity.

The ANL vehicle was acquired in October 1979. Prior to these tests, it had been driven 280 km and the battery pack had been subjected to approximately 20 charge/discharge cycles with an average depth-of-discharge of about 60%. No modifications to the ANL vehicle had been made. The first vehicle tested at LILCO was also a standard van, but had a plastic liner installed in the battery box for protection against spilled electrolyte, etc. This vehicle (No. 390330, License No. 57PZK) is referred to as Vehicle 1 in the remainder of this report. Vehicle 2 was modified from the standard van by replacing the manufacturer's battery compartment cover with an air-tight cover. In addition, the battery compartment exhaust fan was rewired to run during on-the-road vehicle operation. Identification numbers for Vehicle 2 were not recorded.

B. Test Procedures and Sampling Protocol

In order to correlate the test results with the condition and performance of the battery at the time of testing, physical and electrical data were

acquired during each monitoring experiment. Battery current and voltage were recorded continuously during each charge or equalization charge cycle. Specific gravity and temperature of the electrolyte in selected cells, and open circuit voltages for selected modules in the battery pack, were usually measured before and after each test. The results of these measurements are listed in chronological order for the tests at ANL in Appendix A of this report; those for the tests at LILCO are in Appendix B.

The ANL Stibine and Arsine Monitoring Field Kit (SAMFK)⁵ was used for collection of AsH₃ and SbH₃ gases. The absorber solutions were analyzed for antimony and arsenic by the Analytical Chemistry Laboratory (ACL) at ANL. Arsenic was converted to AsH₃ and determined by atomic absorption; antimony was measured spectrophotometrically. The details of these methods have been presented elsewhere.⁶ A brief description of the sampling and analytical procedures are also given in Appendix C of the present report where the ANL SAMFK method and the currently recommended NIOSH method⁷ for stibine are compared.

C. Operating Conditions

1. Charge

The EV batteries were charged using the on-board charger associated with each vehicle in a normal operating mode. During the charging cycles, the doors and windows of each van were kept tightly closed, the battery compartment cover was in place, and the battery compartment exhaust fan was always on. Charging at LILCO took much less time than the same operation at ANL because, to save time in the face of tight scheduling, the batteries in the LILCO vehicles were not deeply discharged during on-the-road operation.

2. Equalization Charge

The on-board charger was also used as in normal operation for tests during equalization charge with the ANL vehicle. This charger equalizes the fully charged battery at a voltage corresponding to approximately 2.55 V/cell and a current of about 5 A. Other conditions were identical to those prevailing during the charging tests described above.

In contrast, equalization charging at LILCO was carried out using an off-board charger that was adjusted to maintain a constant current of 10 A through the battery at a voltage of about 2.65 to 2.70 V/cell. These parameters were recommended by representatives of the Aerospace Corporation, Washington, D.C., who wanted to simulate an off-normal situation where loss of control by the charger would lead to a worst-case hydride accumulation.⁸ It was noted that routine equalization charging is not performed at LILCO as part of the EV operation and maintenance regime.

When the off-board charger at LILCO was used, a special wiring arrangement powered the exhaust fan in the battery compartment so that the fan could be kept running during the equalization charge tests. The battery compartment covers were kept in place and the doors and windows were again tightly closed.

3. Discharge

Discharge of the EV batteries was carried out on the road with the battery compartment covers in place and the doors and windows closed. With the ANL vehicle, discharge was accomplished using a cruising speed of 40 km/h which required a current of 100 A. During acceleration, a current of 250 A was required until the cruising speed was regained. The battery compartment exhaust fan does not operate during on-the-road discharge of the standard Jet 600 van.

Discharge at LILCO conformed, insofar as traffic conditions would allow, to the SAE 227 A Schedule C cycle (see Electric Vehicle Test Procedure- SAE J227a, Revised February 1976, Society of Automotive Engineers, Warrendale, Pa). The battery compartment exhaust fan in Vehicle 1 did not operate during discharge. Vehicle 2, however, was modified so that its exhaust fan did operate during discharge.

An additional test was performed with Vehicle 1 in which sampling during discharge was done with the windows open.

D. Test Descriptions

1. In-Vehicle Tests

Ambient air inside the vehicles was sampled continuously during all or part of a charge, equalization charge, and discharge cycle. At the same time, air from inside the battery compartment at the exhaust exit was also sampled. For the ANL vehicle and for Vehicle 1 at LILCO, the specific collection points, shown in Fig. 1, were located (A) in the driver's seat, (B) on top of the battery compartment at the left-center of the van (to simulate the condition of a back-seat passenger), (C) in the right-rear corner of the van and (D) at the exhaust exit where air from inside the battery compartment was collected. Sampling at position (D) was accomplished using an adapter in the exhaust duct which permitted sampling of the air in the duct without dilution by garage air (see Fig. 2).

For Vehicle 2 at LILCO, only one in-vehicle sampling point, centrally located on top of the battery compartment, was used. Sampling at position (D) was also performed with Vehicle 2.

2. In-Garage Tests

Ambient air was monitored inside the garage at three locations during charging and equalization charging of the ANL vehicle and Vehicle 1 at LILCO. These sampling points, also shown in Fig. 1, were located at the exhaust of the on-board charger ventilating fan behind the rear bumper of the van (X), four feet to the left of the van at two feet above the garage floor (Y), and four to six feet to the left of the van at six feet above the garage floor (Z). In addition, a fourth location was sampled in the tests at LILCO on Vehicle 1; it was located at the farthest accessible point in the garage away from the van. This position (T) was approximately ten feet from the front of the van at eight feet above the garage floor and was near the filters

Fig. 1. Ambient-Air Sampling Locations

at the exhaust of the ventilation system for the paint shop that served as the garage for the tests. This ventilation system was turned off during the tests. Garage air was not monitored for Vehicle 2.

3. Measurements at Cell Outlets

In another set of experiments with the ANL vehicle, the gases released in individual cells of the battery were sampled using specially modified cell caps⁵ that allowed air from the battery compartment to be drawn through the cell space above the electrolyte and then into the absorber solution in the SAMFK (see Fig. 2). Several cells were sampled simultaneously during each test.

E. Other Tests

1. Hydrogen Evolution Rates

In a later set of experiments with the ANL vehicle, the rates of hydrogen and oxygen release by individual battery cells were measured during charge, equalization charge, and discharge. The cell off-gases were swept

Fig. 2. Sampling Devices Used with SAMFK

out through a modified cell cap by a flowing stream of high-purity nitrogen. The nitrogen carrier was directed through a SAMFK absorber solution and water trap to remove arsine and stibine, through a soda-lime trap to remove acid mist, and finally through a Pyrex gas-sampling bulb fitted with stopcocks at both ends. The nitrogen was allowed to flush the sample bulb for at least five minutes, during which time its flow rate was carefully measured with a soap-bubble flowmeter. Then, the two stopcocks on the bulb were closed, trapping an aliquot of the eluting gas which was subsequently analyzed for hydrogen and oxygen content by mass spectrometry or gas chromatography. The evolution rate for a specific gas in the eluant is given by the product of its volume fraction in the aliquot and the measured flow rate of the eluting gas. Several samples were taken during each operation to generate evolution-rate profiles over the cycle duration.

2. Hydrocarbon Sampling

In addition to stibine and arsine monitoring during one charge cycle with Vehicle 1 at LILCO, the air inside the van and in the battery compartment was also sampled for organic species. The organics were collected in NIOSH-approved activated charcoal sampling tubes. Samples were taken over a ten-minute period during the overcharge portion of the charge cycle.

The charcoal traps were analyzed by the Organic Analysis Group of ANL's Analytical Chemistry Laboratory. The charcoal adsorbent was leached with carbon disulfide and the leachant was examined by gas chromatography. One sample was found to contain significant quantities of a number of compounds and was submitted for gas chromatographic/mass spectrometric (GS/MS) analysis to Raltech Scientific Services, Madison, WI.

F. Quality of Results

Determination of stibine and arsine using the ANL SAMFK requires measurement of the quantity of arsenic or antimony collected in the absorber solution and the volume of air from which these metals were deposited. Contributions to the error in the measured values from these sources are discussed in Appendix C. For the volume of air generally sampled in the tests at LILCO and at ANL, the standard deviation of the reported arsine concentrations is $\pm 0.005 \text{ mg/m}^3$ or 11% of the reported value, whichever is larger. The limit of detection (LOD) is less than $0.01 \text{ mg AsH}_3/\text{m}^3$ for a sample volume of 50 L of air. For comparison, the TLV-TWA for arsine is $0.2 \text{ mg AsH}_3/\text{m}^3$. Thus, the arsine measurements are adequately sensitive for safety considerations.

The LOD for the stibine determination with a 50-L air sample is 0.02 mg/m^3 compared to a TLV-TWA for stibine of 0.5 mg/m^3 . Error limits (one standard deviation) on the stibine concentrations are generally $\pm 0.02 \text{ mg SbH}_3/\text{m}^3$ or 7% of the reported value, whichever is larger. The stibine measurements also show adequate sensitivity.

The reliability of the SAMFK results was confirmed during the tests at LILCO. An independent testing laboratory, New York Testing Laboratory (NYTL), measured ambient stibine levels using the currently recommended NIOSH method⁷ at the same time ANL performed measurements with the SAMFK. The results obtained by the two laboratories are compared statistically in Appendix D.

Thirty separate measurements were reported by each participant. Of these, twenty-six results were in agreement within the limits set by the statistical model used in the comparison. Of the four discrepant results, one involved substantially different sampling locations between ANL and NYTL; one, though quantitatively discrepant, showed qualitative agreement by being the largest value in each data set; and two results may have involved a sample mix-up at one or the other laboratory. When allowance is made for mitigating circumstances, including the difficulty of comparing ambient samples collected where concentration gradients exist, agreement between all but the two samples which may have been mixed up is judged satisfactory. Because the results on the "mixed-up" samples involved the inside of the battery compartment, they do not affect any conclusions regarding personnel exposure, and therefore are not believed to be a cause for concern.

III. STIBINE/ARSINE MONITORING: RESULTS AND DISCUSSION

In this section, results from the stibine/arsine monitoring tests at ANL and at LILCO are presented and discussed with a view toward comparing the individual test results and, on the basis of this comparison, establishing a general description of hydride behavior during EV operations. The values reported here in terms of concentration, mg/m^3 , represent a time-weighted-average concentration over the duration of the specified test. When interpreting these results or applying them to safety considerations, it should be kept in mind that the actual concentration at any point in time during the test may have been considerably higher or lower than the measured average. The measured average is, however, appropriate for comparison with the TLV-TWA's.

The measurements made at the cell outlets (only for tests at ANL) represent the total stibine or arsine generated within a single cell during the duration of a test. These values provide a valuable source term for assessing potential concentrations in the work area because they give the maximum amount of hydride available for dispersal under the test conditions.

In order to realistically compare and evaluate the test results from the different testing sites, it is important to recognize that the evolution and dispersal of stibine and arsine are sensitive functions of a number of operating parameters.²⁻⁴ Because of differences in experimental conditions, each set of results should be considered in the context of vehicle characteristics, sampling protocol, and operating conditions.

A. Charging the EV Batteries

Typically, a battery is charged at a constant current until the voltage rises to a preset maximum; then the voltage is held constant until either a fixed time has elapsed or a fixed level of current, the finish rate, is reached. The on-board charger on the Electra-Van Model 600 vehicles used in the tests at ANL and LILCO employs a nominally 20-A current to a voltage of about 2.55 V/cell and a finish rate of 5 A. Laboratory studies of stibine and arsine generation in utility load-leveling batteries performed at ANL⁴ have indicated that the rate of hydride evolution is dependent on the pre-set voltage during the overcharge period of the charge cycle, and that a threshold

voltage exists at approximately 2.45 V/cell, below which evolution does not take place. This corresponds to a voltage of about 125 V for the 51-cell battery pack in the Electra-Van 600.

In a typical recharge using the on-board charger on the vehicles tested, then, it may be expected that evolution of stibine and arsine should be restricted to the period during which the voltage exceeds 125 V. Dispersal of the hydrides will depend strongly on the characteristics of the individual vehicles and on the air-flow patterns prevailing in the area where testing is done.

1. Charging the ANL Vehicle

The areas of primary concern with regard to stibine and arsine accumulation during EV operations are those that are likely to be occupied by personnel during the operation. Thus, the results from ambient air sampling in the vehicle and in the garage are of particular interest. Results of the stibine/arsine measurements made during charging of the ANL vehicle are presented in the first column of Table 1. Note that the concentrations in this column are averaged by the sampling method over the entire charging cycle and, therefore, represent the TWA exposure level for personnel in the specified location during the test. Comparison of the reported values with the corresponding TLV-TWAs of 0.5 mg SbH_3/m^3 and 0.2 mg AsH_3/m^3 indicates that, from a safety standpoint, the measured concentrations are quite acceptable. The maximum concentrations, 0.086 mg SbH_3/m^3 and 0.011 mg AsH_3/m^3 found in the garage near the charger, amount to only 17% and 5.5% of the TLV-TWA values, respectively.

The values obtained at the various sampling points indicate that significant concentration gradients existed both inside the vehicle and in the garage during the tests. This observation demonstrates that dispersal of the evolved hydrides is a complex process. The higher stibine concentration on top of the battery compartment relative to other locations inside the van might indicate that leakage around the battery compartment cover contributed to the in-vehicle hydride accumulation.

The samples taken in the garage show a substantially higher stibine/arsine concentration near the charger than at other locations in the garage. This undoubtedly is due to the proximity of the charger and its exhaust system to the battery compartment. The ventilation fan on the charger is specified to circulate 2.8 m^3 air/min. It draws air from the underside of the vehicle and expels it toward the near-charger sampling point. If air from the battery compartment were drawn into this stream, a highly directional dispersal pattern, like that observed, would result.

In addition to monitoring ambient air in the work area, the tests at ANL also measured the total stibine and arsine released by randomly selected cells during the charging cycle (see Table 2). If it is assumed that the hydrides collected during this experiment were generated solely during the overcharge period (*i.e.* when the battery voltage exceeded 125 V), an average evolution rate for each hydride may be calculated by dividing the amount of hydride collected by the duration of the overcharge period in minutes.

Table 1. Results of Monitoring Stibine/Arsine in Ambient Air during Charging of Jet 600 Vehicles at ANL and LILCO

Type of Test	Sampling Location ^a	Date, Duration	ANL		Vehicle 1 LILCO			Vehicle 2 LILCO		
			SbH ₃ ³ mg/m ³	AsH ₃ ³ mg/m ³	Date, Duration	SbH ₃ ³ mg/m ³	AsH ₃ ³ mg/m ³	Date, Duration	SbH ₃ ³ mg/m ³	AsH ₃ ³ mg/m ³
In-Vehicle	A. Driver's Seat	2/7/80, 626 min ^c	0.008	0.0034	3/26/80, 35 min ^d	ND ^b	0.004	3/27/80	--	--
	B. Left-Center Van		0.041	0.0041		0.06	0.003	68 min ^e	0.02	0.003
	C. Right-Rear Van		0.012	0.0048		0.02	0.003		--	--
In-Garage	X. Near Charger	2/14/80, 438 min ^f	0.086	0.0109	3/26/80, 31 min ^g	ND	0.002		--	--
	Y. 2 ft from Floor		0.015	0.0046		ND	ND		--	--
	Z. 6 ft from Floor		0.010	0.0036		0.04	0.002		--	--
	T. Farthest Point		--	--		ND	ND		--	--

^aSee Fig. 1 and Section II.D for exact locations.

^bND indicates not detectable.

^cIncludes 300 min overcharge, see Fig. 3.

^dIncludes 31 min overcharge, see Fig. 4.

^eIncludes 0 min overcharge, see Fig. 4.

^fIncludes 222 min overcharge, see Fig. 3.

^gIncludes 2 min overcharge, see Fig. 4.

Fig. 3. Current-Voltage Curves during Charging with the ANL Vehicle

Two experiments were performed in which measurements were made at the cell outlets during charging. However, the duration of the overcharge period is known only for one of these because current and voltage curves were not recorded during the other. In the usable experiment, two separate cells were sampled and gave an average of 2.50 mg SbH_3 and 0.22 mg AsH_3 in 180 min of overcharge. The average evolution rates calculated from these data are 0.0139 mg $\text{SbH}_3/(\text{min} \cdot \text{cell})$ and 0.0012 mg $\text{AsH}_3/(\text{min} \cdot \text{cell})$. For the 51-cell battery pack, then, one could expect 0.71 mg SbH_3/min and 0.061 mg AsH_3/min during the overcharge period of a charge cycle at the finish current rate of 5 A.

The exhaust fan in the battery compartment of the ANL vehicle moves 0.212 m^3 air/min through the compartment. Thus, one would expect average concentrations in the battery compartment exhaust of 3.35 mg SbH_3/m^3 and 0.29 mg AsH_3/m^3 during the overcharge period of a charge cycle. The hydride concentrations found in the battery compartment while charging the ANL vehicle

Fig. 4. Current-Voltage Curves during Charging with the LILCO Vehicles

are shown in Table 3. In order to compare the measured values with those calculated above, the measured concentrations must be adjusted to compensate for the fact that sampling was done for a period of time prior to the onset of hydride generation (*i.e.* before the battery voltage reached 125 V). The adjusted concentration is obtained by multiplying the reported value by the ratio of the test duration to the length of the overcharge period. The resulting adjusted battery compartment concentrations for the ANL charging test are 0.044 mg SbH_3/m^3 and 0.015 mg AsH_3/m^3 . Clearly, even after the adjustment, the measured values are significantly lower than those predicted from measurements at the cell outlet. We believe that this is due to additional ventilation of the battery compartment by the fan associated with the on-board charger. If it is assumed that all the air flow ($2.8 \text{ m}^3/\text{min}$) displaced by

Table 2. Results of Stibine/Arsine Measurements at Cell Outlets During Operation of the ANL Vehicle

Operation	Cell ^a	Date	Test Duration ^b	mg SbH ₃	mg AsH ₃
Charge	4b	2/12/80	180 min ^c	1.52	0.11
	8b	2/18/80	304 min ^d	2.39	0.18
	15b	2/18/80	304 min ^d	2.61	0.25
Equalization Charge	4b	2/12/80	290 min	1.76	0.15
	7b	2/12/80	290 min	1.72	0.20
	3c	6/10/80	210 min	1.34	0.21
Discharge	4b ^e	2/13/80	39 min	ND ^f	0.005
	7b ^e	2/13/80	39 min	ND	0.002
	3c ^g	6/18/80	43 min	0.009	0.006

^aSee Appendix A for cell numbering.

^bTotal collection time.

^cCurrent and voltage not recorded.

^dIncludes 180 min overcharge.

^eDischarged the day following previous charge cycle.

^fND indicates not detectable.

^gDischarged same day as previous charge cycle.

the charger fan is drawn through the compartment, then the hydride concentrations in the air expelled by this fan may be calculated by multiplying the previously calculated battery compartment values by the dilution factor $0.212/(2.8 + 0.212) = 0.0704$. The predicted concentrations in the charger exhaust are then 0.235 mg SbH₃/m³ and 0.020 mg AsH₃/m³. These values may be compared to the concentrations found in the charger exhaust during the in-garage test (Table 1). Once again, the measured values must first be adjusted to the overcharge period of the cycle. The adjusted values are 0.170 mg SbH₃/m³ and 0.021 mg AsH₃/m³ and are in good agreement with those calculated above. This agreement lends credibility to the hypothesis that the charger ventilating fan helped to purge the battery compartment of the ANL vehicle. The lower measured stibine value is also reasonable in view of the facile decomposition of stibine which has a half-life in air of only 6 to 12 min.⁹

Table 3. Stibine and Arsine Concentration Inside the Battery Compartment during Operation of the Jet 600 Vehicles at ANL and LILCO

Operation	Date	Test Duration, min	SbH ₃ , mg/m ³	AsH ₃ , mg/m ³
<u>ANL Vehicle:</u>				
Charge	2/7/80	626 ^a	0.021	0.0074
Equalization Charge ^b	2/18/80	126	0.024	0.0048
Discharge	2/8/80	40	ND ^c	0.189
<u>LILCO Vehicle 1:</u>				
Charge	3/26/80	35 ^d	0.15	0.007
Equalization Charge ^e	3/25/80	31	0.30	0.006
Discharge	3/25/80	24	0.96	0.064
Discharge Windows Open	3/26/80	19	ND	ND
<u>LILCO Vehicle 2:</u>				
Charge	3/27/80	68 ^f	0.01	0.002
Equalization Charge ^e	3/27/80	43	1.18	0.034
Discharge	3/27/80	25	0.06	ND

^aIncludes 300 min overcharge.

^bAt 5-A current.

^cND means not detectable.

^dIncludes 31 min overcharge.

^eAt 10-A current.

^fIncludes 0 min overcharge.

From this analysis, it is apparent that the air flow through the battery compartment contributed by the charger ventilating fan has a considerable effect on the dispersal of hydrides evolved during charging of the ANL vehicle. Without this contribution, it is likely that the battery compartment concentrations would be higher than those found during the tests. In addition, the directional character of the in-garage dispersal would probably not be as pronounced. This could result in higher local concentrations in the vicinity of the van. Finally, it should be noted that the adjusted concentrations presented in the foregoing discussion are probably realistic estimates of the levels likely to be encountered during the overcharge period of a charge cycle. Because these values are higher than TWA values over the entire cycle, it may be advisable, in future monitoring tests, to initiate sampling only after the threshold voltage is reached. In this way, a better estimate of the highest exposure levels would be obtained.

2. Charging the Vehicles at LILCO

Results of the stibine/arsine measurements made during charging of the LILCO vehicles are presented in the last two columns of Table 1. All of the reported concentrations are well below the TLV-TWA limits. It will be shown, however, that many of the reported values are not representative of typical conditions, and some are lower than typical values would be.

In-vehicle samples taken during charging of Vehicle 1 were collected primarily during the overcharge portion of the charge cycle when the threshold voltage for hydride production (125 V) had been exceeded (see Fig. 4). Thus, hydride evolution at a rate determined by the design specifications of the charger on Vehicle 1 probably occurred throughout most of the sampling period during the in-vehicle measurements. This set of conditions would, therefore, be typical of the worst case for normal operation of the on-board charger in Vehicle 1. According to this interpretation, the low concentrations of stibine and arsine (less than 0.06 and 0.004 mg/m³, respectively) measured inside the van during charging indicate that isolation of the vehicle interior from the battery compartment was adequate. The higher value for stibine measured on top of the battery compartment suggests, however, that some air might have leaked from the battery compartment.

Concentrations of stibine (0.15 mg/m³) and arsine (0.007 mg/m³) inside the battery compartment during this test verify that the hydrides were evolved. These concentrations may be considered to be steady-state values which are determined by the rate of hydride production and the air flow ventilating the battery compartment. If it is assumed that the battery compartment exhaust fan moves 1.16 m³/min of air (equal to 41 ft³/min, the value measured for the fan in Vehicle 2 by NYTL), then the evolution rates from the battery pack that would result in the measured concentrations are 0.17 mg/min for stibine and 0.008 mg/min for arsine. These rates are considerably lower than those calculated in the preceding section from the cell outlet measurements on the ANL vehicle (0.71 mg SbH₃/min and 0.06 mg AsH₃/min). Given the similarity between the ANL vehicle and LILCO Vehicle 1, it would seem reasonable to suggest that this result reflects additional ventilation of the battery compartment in Vehicle 1 by, for example, the charger ventilating system.

Unfortunately, this possibility cannot be addressed using the results of the in-garage monitoring tests as was done for the ANL vehicle. Although the current and voltage curves of the charging cycle for the in-garage samples were similar to those for the in-vehicle test, sampling was conducted only prior to the overcharge period and was terminated shortly after the threshold voltage for hydride production was exceeded (see Fig. 4). Under these conditions, very little hydride generation is expected to have occurred during the sampling interval. This observation is consistent with the very low, barely detectable, hydride concentrations found in the garage during charging of Vehicle 1 (see Table 1). Thus, these results confirm the existence of the threshold voltage for hydride generation.

This interpretation is further supported by the results of the measurements made during charging of the battery in Vehicle 2. In this test, sampling was also terminated shortly after the threshold voltage was attained. The concentrations of stibine and arsine in the battery compartment (Table 3) were only 0.01 mg/m^3 and 0.002 mg/m^3 , respectively, and were barely above detection limits. These results demonstrate that minimal hydride evolution had occurred.

3. Conclusions from the Charging Tests

Several important conclusions are derived from the results of monitoring stibine/arsine during charging:

1. Both the tests at ANL and those at LILCO showed no evidence of ambient hydride concentrations above acceptable levels in the work areas during the tests. These results do not preclude the potential for accumulation of hydrides to unacceptable levels in certain places. They do indicate, however, that control of the evolved gases was adequate under the specific conditions investigated.
2. The in-garage test with Vehicle 1 and the in-vehicle test with Vehicle 2 at LILCO confirm the existence of a threshold voltage for hydride production.
3. The cell outlet measurements at ANL provided preliminary hydride-evolution rates of $0.014 \text{ mg SbH}_3/(\text{min} \cdot \text{cell})$ and $0.0012 \text{ mg AsH}_3/(\text{min} \cdot \text{cell})$ when the threshold voltage (presumably 2.45 V/cell) is exceeded.
4. Dispersal of the hydrides produced during the charging operation may be complex and is strongly dependent on how well the vehicle interior is isolated from the battery compartment and on the ventilation prevailing in and around the vehicle.

B. Equalization Charging the EV Batteries

Equalization charging with the on-board charger of the Electra-Van Model 600 is accomplished by charging at the finish rate (5 A) for a fixed time or until a predetermined value of electrolyte specific gravity is attained in

all cells. During equalization, the charging current and cell voltage are relatively constant; the voltage will normally exceed the gassing potential throughout the operation (see Fig. 5).

Fig. 5. Current-Voltage Curves during Equalization Charging with the ANL Vehicle

1. Equalization Charging of the ANL Vehicle

Equalization charging with the ANL vehicle was carried out using the on-board charger. Consequently, this operation differed from that of charging the batteries only insofar as the hydride evolution rates may have differed. Dispersal of the evolved gases would be expected to follow a pattern similar to that during charging.

The results of the stibine/arsine monitoring tests during equalization charging at ANL conform to this expectation. A comparison of the values reported in the first column of Table 4 with the corresponding values in

Table 4. Results of Monitoring Stibine/Arsine in Ambient Air during Charging of Jet 600 Vehicles at ANL and LILCO

Type of Test	Sampling ^c Location	Date, Duration	ANL ^a		Date, Duration	Vehicle 1 ^b LILCO		Date, Duration	Vehicle 2 ^b LILCO	
			SbH ₃ , mg/m ³	AsH ₃ , mg/m ³		SbH ₃ , mg/m ³	AsH ₃ , mg/m ³		SbH ₃ , mg/m ³	AsH ₃ , mg/m ³
In-Vehicle	A. Driver's Seat	2/18/80, 125 min	ND ^d	ND	3/25/80, 31 min	ND	ND	3/27/80, 43 min	—	—
	B. Left-Center Van		ND	ND		0.13	0.003		0.03	ND
	C. Right-Rear Van		0.009	0.0031		0.09	ND		—	—
In-Garage	X. Near Charger	2/15/80, 107 min	0.055	0.0031	3/26/80, 41 min	0.03	0.003		—	—
	Y. 2 ft from Floor		0.025	0.0018		0.03	0.003		—	—
	Z. 6 ft from Floor		0.021	0.0018		0.08	0.002		—	—
	T. Farthest Point		—	—		0.12	0.004		—	—

^aUsing on-board charger, 5 A.

^bUsing off-board charger, 10 A.

^cSee Fig. 1 and Section II.D for exact locations.

^dND means not detectable.

Table 1 indicates similar concentrations and gradient directions for the two sets of data. Again, the highest concentrations found in the work area were near the exhaust of the charger ventilating system.

The measurements made at the cell outlets during equalization charge suggest a lower rate of stibine/arsine evolution during equalization charging than during the overcharge period of a charging cycle. Two separate measurements at the cell outlets were made (see Table 2). In the first an average of 1.74 mg SbH_3 and 0.17 mg AsH_3 were collected in 290 min of equalization charging for average rates of 0.0060 mg $\text{SbH}_3/(\text{min} \cdot \text{cell})$ and 0.00060 mg $\text{AsH}_3/(\text{min} \cdot \text{cell})$. In the second, 1.34 mg SbH_3 and 0.21 mg AsH_3 were collected in 210 min for rates of 0.0064 mg $\text{SbH}_3/(\text{min} \cdot \text{cell})$ and 0.0010 mg $\text{AsH}_3/(\text{min} \cdot \text{cell})$. From these values, an average rate of stibine evolution from the 51-cell battery pack is 0.32 mg/min and of arsine evolution is 0.041 mg/min.

2. Equalization Charging of the Vehicles at LILCO

In the equalization charging tests at LILCO, an off-board charger was used to maintain a constant current of 10 A through the battery pack. This high current and the concomitant high voltage (see Fig. 6) suggest a higher rate of hydride production relative to the tests at ANL. The experimental results given in Tables 3 and 4 confirm this expectation. In particular, the stibine and arsine concentrations inside the battery compartments of both vehicles were quite high during these equalization charging tests. It is noteworthy, however, that none of the ambient concentrations measured either in the vehicles or in the garage (Table 4) exceeded the TLV-TWA limits. This observation demonstrates that, even under the conditions of simulated worst-case hydride generation established in these experiments, control of the evolved hydrides was adequate.

The hydride concentrations found in Vehicle 1 show a significant gradient within the closed van, with the highest values (0.13 mg SbH_3/m^3 and 0.003 mg AsH_3/m^3) found on top of the battery compartment cover. This suggests that leakage of air from the battery compartment to the interior of Vehicle 1 may contribute to the in-vehicle hydride accumulation. In contrast, hydride concentrations inside Vehicle 2 were barely detectable (0.03 mg SbH_3/m^3 and no detectable arsine). This comparison demonstrates the value of the air-tight replacement cover installed in Vehicle 2.

Air flow characteristics during equalization charging of Vehicle 1 are not available, and, therefore, no estimate can be made for the rates of hydride evolution during the tests with it. For Vehicle 2, however, an air flow through the sealed battery compartment was reported by NYTL as 41 ft^3/min (1.16 m^3/min). It is possible to estimate the rates of stibine and arsine generation by taking the product of this volume air flow and the battery compartment concentration for each hydride. The resulting rates are 1.37 mg SbH_3/min and 0.039 mg AsH_3/min .

In order to compare these evolution rates with those obtained during equalization charging with the ANL vehicle, the data must be normalized to a common reference point. It will be shown in a later section of this report that the hydride-evolution rate can be taken as roughly proportional to the

Fig. 6. Current-Voltage Curves during Equalization Charging with the LILCO Vehicles

current if battery type, history, etc. are constant. On this basis, one would expect the LILCO tests, where a 10-A current was used, to show twice the evolution rates found in the ANL tests where the current was about 5 A. The evolution rates predicted for the LILCO tests from the ANL results are thus 0.64 mg/min for stibine and 0.081 mg/min for arsine.

The rates found with Vehicle 2 at LILCO are not in agreement with this prediction: stibine evolution with Vehicle 2 is too high and arsine evolution is too low. These differences may reflect a dependence of the hydride generation rates on any of a number of variables which may have differed between the two sites. These include battery manufacturing characteristics, operating history, and experimental procedure. The good agreement between duplicate measurements at the cell outlets of the ANL vehicle shows

that, for a given vehicle and controlled conditions, the rates determined by the ANL method are reproducible. This makes measurement error an improbable source of this discrepancy between the ANL and LILCO results.

With regard to the possible influence of experimental procedure on the evolution rate data, it may be noted that the stibine evolution rate calculated above for Vehicle 2, 1.37 mg/min, is essentially twice that obtained with the ANL vehicle during the overcharge period of a charge cycle (0.71 mg/min; see section III.A.1) at the 5-A rate. This observation might suggest that the operation carried out at LILCO as an equalization charge may have more closely approximated the overcharge portion of the charge cycle. In fact, if the current and voltage curves recorded at LILCO during this test and during the preceding charge cycle are examined (see Figs. 4 and 6), it is found that the charging cycle was terminated just prior to the overcharge period shortly after the voltage reached 125 V. On this basis the similarity of the rates given above for stibine evolution seems reasonable.

Unfortunately, the arsine evolution rate cannot be rationalized in this manner. Obviously, stibine and arsine generation in lead-acid batteries cannot be fully characterized on the basis of the small number of experiments carried out in this study. Without additional research under controlled conditions, it is not possible to identify all of the important variables, particularly in the case of atypical situations like the equalization charge tests performed at LILCO.

3. Conclusions from the Equalization Charging Tests

The conclusions drawn from the foregoing discussion may be summarized as follows:

1. When air flow patterns are the same, dispersal of stibine and arsine evolved during equalization charge follows a similar pattern to that during charging.
2. Since acceptable hydride concentrations were measured both in the vehicles and in the garage during the tests at LILCO using 10-A currents, operations there under normal conditions (5 A) should also be safe.
3. The air-tight replacement cover in Vehicle 2 proved advantageous in reducing hydride accumulation in the vehicle during the tests at LILCO.
4. The cell outlet measurements at ANL provided preliminary values of 0.0062 mg $\text{SbH}_3/(\text{min}\cdot\text{cell})$ and 0.0008 mg/(min·cell) for the hydride-evolution rates during a normal equalization charging cycle at 5 A. These rates are smaller than those found during the overcharge period of a charge cycle under normal conditions.
5. The rates of stibine evolution determined from the equalization charge test data obtained at LILCO is consistent with the ANL values if the LILCO equalization charge is considered to

be representative of an overcharge condition, but the arsine rate could not be explained in this way. This result emphasizes the preliminary nature of the work described here, and should serve to caution against indiscriminate application of such rate data to vehicles and conditions not actually tested.

C. Vehicle Discharge

1. Discharge with the ANL Vehicle

In the absence of regenerative braking or cell reversal, electrolytic generation of arsine or stibine during on-the-road discharge of EV batteries should not occur.² However, as shown in Tables 3 and 5, measurable arsine concentrations were found in ambient air samples taken in-vehicle and in the exhaust exit of the battery compartment during discharge of the ANL vehicle. Stibine in the same samples was below detection limits in all cases.

Table 5. Results of Monitoring Stibine/Arsine in Ambient Air during Discharge of Jet 600 Vehicles at ANL and LILCO

Vehicle Tested	Sampling Location	Date, Duration	SbH ₃ , mg/m ³	AsH ₃ , mg/m ³
ANL	A. Driver's Seat	2/8/80, 40 min	ND ^a	ND
	B. Left-Center Van		ND	ND
	C. Right-Rear Van		ND	0.012
Vehicle 1, LILCO (Windows Closed)	A. Driver's Seat	3/25/80, 24 min	0.06	0.009
	B. Left-Center Van		0.03	ND
	C. Right-Rear Van		0.05	0.012
Vehicle 1, LILCO	A. Driver's Seat	3/26/80, 19 min	ND	ND
	B. Left-Center Van		ND	ND
	C. Right-Rear Van		ND	0.008
Vehicle 2, LILCO	B. Left-Center Van	3/27/80, 25 min	ND	ND

^aND means not detectable.

One possible explanation of these observations is that, although no stibine/arsine is generated in the EV battery during discharge, a delayed release of gases generated during a previous charge or equalization charge cycle does occur. It is probable that, during a charge cycle or equalization charge cycle with the battery cells capped and no air flow through the cells, some residual arsine and stibine will be retained in the cell electrolyte, trapped in the air space above the electrolyte, or trapped between plates. During discharge, the electrolyte temperature increases (see Appendix A) and the solubility of dissolved gases decreases. This phenomenon, together with agitation of the electrolyte caused by vehicle movement, could allow the gases to escape from the cell. Because the battery compartment exhaust fan does not operate during discharge of the ANL vehicle, the small amounts of gas released in this manner may accumulate in the battery compartment to give high concentrations of the gases in the compartment air.

The results of the arsine monitoring tests during discharge of the ANL van are consistent with this hypothesis. The amount of arsine collected from the cell outlets during discharge (Table 2) was only a few micrograms per cell, yet the concentration of arsine in the battery compartment (Table 3) averaged 0.19 mg/m^3 during the test. In fact, this value is considerably smaller than that calculated assuming only three micrograms of retained arsine is released by each cell. The calculated value under these conditions is around $15 \text{ mg AsH}_3/\text{m}^3$. The smaller measured value could indicate that not all of the available arsine escapes the cells, or that some ventilation of the battery compartment was provided by ram ventilation due to vehicle motion.

The absence of measurable stibine during the discharge tests also supports the delayed-release hypothesis. The discharge tests were performed on the day following the previous charge cycle. Owing to the instability and rapid decomposition of stibine compared to arsine, it is unlikely that the SbH_3 retained in the cells could survive the overnight period before discharge. If this interpretation is valid, discharging the vehicle shortly after completion of a charge cycle would produce much higher concentrations of this hydride. Evidence supporting this conclusion is available from the last cell outlet measurement during discharge in Table 2. In this experiment, the batteries in the ANL vehicle were discharged on the same day as the previous equalization charge cycle. A larger amount of stibine ($9 \text{ }\mu\text{g}$) than arsine ($6 \text{ }\mu\text{g}$) was collected.

2. Discharge with the Vehicles at LILCO

The results of the stibine and arsine monitoring tests performed at LILCO during discharge with Vehicle 1 (Tables 3 and 5) support the delayed-release hypothesis that was postulated to explain the data obtained at ANL. At LILCO, discharge was carried out immediately following equalization charge, and measurable amounts of both stibine and arsine were found inside Vehicle 1 during discharge with the windows closed. In addition, the battery compartment contained higher concentrations during this test than were found for the charging cycles.

It should be emphasized that the high battery-compartment concentrations do not indicate the delayed release of large amounts of the hydrides,

but rather reflect the lack of ventilation in the battery compartment during discharge of the standard Jet 600 van under normal conditions. Considering the small quantities of the hydrides involved, a modest air flow through the battery compartment would probably be sufficient to lower the concentrations to insignificant levels. This prediction is borne out by the data obtained for discharge of Vehicle 1 with the windows open. Not only did the air flow from the windows reduce the in-vehicle hydride concentrations, but it also apparently swept out the battery compartment as well, leaving undetectable amounts of the hydrides behind. A further indication that the hydrides found during discharge originated prior to the discharge cycle is that the stibine-to-arsine ratio for samples taken during discharge is substantially lower than that obtained during equalization charge. This decrease results because of the high rate of decomposition of stibine relative to arsine.

From the foregoing discussion, it would be anticipated that discharge with Vehicle 2 should produce no accumulation of hydrides in the battery compartment or in the vehicle, because the battery compartment was ventilated as part of the modifications made to this vehicle. Indeed, this was the case (see Tables 3 and 5).

3. Conclusions from Tests Made During Discharge

1. Stibine and arsine may accumulate during vehicle discharge by delayed release of gases trapped within the battery cells.
2. The quantities of hydrides released in this manner are quite small, on the order of a few micrograms per cell, and become significant only when allowed to accumulate in a small closed volume such as the battery compartment.
3. Results from the tests at LILCO suggest that ventilation of the battery compartment during discharge is very effective in preventing accumulation by delayed release.

D. Summary of Conclusions and Implications for EV Operation

The results of the stibine/arsine monitoring experiments at ANL and LILCO demonstrated that operation of the Jet 600 vehicles under normal conditions does not result in accumulation of these hydrides to unacceptable levels. At both sites, measured concentrations in the vehicles and in the garages never exceeded 25% of the TLV-TWA limits. Because of the variability of the individual test conditions, however, it was necessary to qualify and interpret many of the results. From this analysis of the data, it was concluded that some of the reported concentrations may have been lower than those expected under normal conditions. However, the equalization charging tests at LILCO, which should have resulted in higher hydride concentrations owing to the use of higher currents, still did not lead to unacceptable concentrations in the work area. On this basis, it may be stated with confidence that operation of the vehicles under normal conditions will not result in unacceptable exposure levels. It must be recognized, however, that the potential for accumulation of the hydrides to unacceptable levels does exist. The results of measurements at the cell outlets and on air inside the battery-compartment exhaust indicate that evolution of the hydrides is severe enough to make some form of

control imperative, especially during the overcharge portion of a charge cycle and during equalization charge. A detailed examination of the quantitative aspects of this requirement is deferred to Section VI where a model describing hydride evolution is developed for use in engineering applications, and to Section VII.A where recommendations are presented for the safe handling of battery off-gases during EV operation.

The test results obtained during charging at LILCO are consistent with the existence of a threshold voltage for hydride generation. Thus, higher ambient levels of stibine and arsine are likely during the overcharge period of a charge cycle than at the beginning of a cycle before the battery reaches about 2.45 V per cell. The tests during equalization charge at ANL indicated that the rate of hydride evolution is lower during equalization charging than during charging if the on-board charger is used in the normal mode. However, the corresponding LILCO tests suggest that equalization charging will result in higher evolution rates if the current imposed on the battery exceeds the finish rate of the on-board charger. On this basis, the use of high currents during equalization charge should be avoided. This recommendation should not hinder EV operations because equalization is not thought to be significantly faster at high currents than at low currents, and, in fact, the excessive gassing which occurs with high currents may shorten battery life.

Delayed release of the metal hydrides was observed during discharge both at ANL and at LILCO. Although only small quantities of arsine and stibine are released in this manner, they can accumulate in the closed volume of the battery compartment to high concentrations which may seep into the vehicle interior. Isolation of the battery compartment from the interior of the van by an air-tight cover and ventilation of the battery compartment during discharge were found to reduce these accumulations to undetectable levels for the modified Vehicle 2 at LILCO. This result and the lower in-vehicle concentrations found with Vehicle 2 compared to Vehicle 1 during equalization charging indicate that these modifications represent valuable improvements in vehicle design.

The evidence of a delayed release of stibine and arsine from the battery cells during discharge requires that concern over personnel exposure not be limited to only those operations where actual generation of the gases takes place. It is important to provide adequate ventilation to disperse local hydride accumulations whenever the batteries are not isolated from the work area. For example, it would be inadvisable to remove the battery compartment cover and measure specific gravity of the electrolyte, etc., close to the battery without ensuring adequate air flow over the battery pack. Again, because the quantities of hydride are small, a modest air flow, such as provided by prevailing garage ventilation, should be sufficient.

IV. HYDROGEN EVOLUTION DURING EV OPERATION

During the overcharge portion of a charge cycle and during equalization charge, gaseous hydrogen and oxygen are produced in a lead-acid battery by electrolysis of water in the strongly acid electrolyte. The control of ambient-air hydrogen concentrations is essential in order to lessen the risk of explosion, since the lower limit of flammability for H_2 is 4 vol % at standard temperature and pressure conditions. Design features such as the

battery compartment ventilation system, incorporated into electric vehicles to control accumulation of evolved H_2 , significantly affect the dispersal of the metal hydrides, stibine and arsine, which are concurrently generated within the battery. In addition, the evolved H_2 and O_2 serve as carrier gases to sparge the hydrides from the electrolyte, flushing them from the cells where they are generated. Consequently, discussion of the generation and dispersal of stibine and arsine during electric vehicle operation must also consider the hydrogen produced.

In the present study, a few brief experiments were performed wherein the rates of evolution of hydrogen and oxygen were measured during charge, equalization charge, and discharge of the ANL vehicle. The electrolysis of water during the charging and equalization charge cycles is well characterized, and the generation of H_2 and O_2 can be simply and accurately calculated. The measurements described here were made primarily to verify that the calculated rates are applicable under the conditions of normal vehicle operation. The measurements during discharge were made as a result of the observation that stibine and arsine could accumulate in an unventilated battery compartment during discharge by delayed release from the battery cells. It was of interest to determine whether a delayed release of hydrogen gas also takes place, and if so, whether accumulation to hazardous levels is possible.

The generation of hydrogen and oxygen during equalization charge is the simplest of the cases to be considered. During this operation, the current through a cell is essentially constant and the voltage is normally greater than the gassing potential (2.45 V per cell). Under these conditions, it may be assumed that all of the current passing through a cell electrolyzes water and evolves hydrogen and oxygen.¹⁰ Faraday's law predicts an evolution rate at standard temperature and pressure (STP) of 6.97 mL H_2 per cell per ampere and an oxygen evolution equal to one-half this value. Figure 7 shows a graphical presentation of the hydrogen-evolution rates measured during equalization charge with the ANL vehicle. For the charging current of 6.0 A, Faraday's law predicts rates of 41.8 mL/min for H_2 and 20.9 mL/min for O_2 . The average of the measured rates plotted in Fig. 7 is 41.5 mL H_2 /min. The corresponding oxygen rates averaged 20.8 mL/min. These values are in excellent agreement with the calculated rates and certainly verify the applicability of the calculations. This agreement also demonstrates the reliability of the method used to measure the evolution rates.

The evolution rate profile during the overcharge period of a charge cycle is shown in Fig. 8. As the battery voltage increases, so does the rate of hydrogen evolution. It would be expected that when the voltage becomes sufficiently high, the evolution rate would again be given by Faraday's law. For the charge cycle shown in Fig. 8, the experiment was terminated before this point was reached.

The evolution of hydrogen and oxygen during discharge of the ANL vehicle is profiled in Fig. 9. These results indicate that a small amount of these off-gases is indeed evolved by the cells during discharge, and the rate of release increases with time. This profile is consistent with the delayed-release mechanism postulated from the arsine/stibine results discussed in Section III. The hydrogen-evolution rate during this discharge cycle appears to level off after about 20 min at a value of 0.42 mL H_2 /min per cell or

Fig. 7. Hydrogen Evolution Rate as a Function of Time During Equalization Charge with the ANL Vehicle

Fig. 8. Hydrogen Evolution-Rate Profile during Charging with the ANL Vehicle

Fig. 9. Hydrogen Evolution-Rate Profile during Discharge with the ANL Vehicle

21 mL/min for the 51-cell battery pack. If this amount of hydrogen were allowed to accumulate in the unventilated battery compartment, it might be possible during a discharge cycle of long duration to build up a concentration approaching the lower explosion limit of 4 vol %. By analogy with the behavior of the stibine and arsine released during discharge, it seems probable that all of the gases available for release from the cells would not actually escape and, if they did, that ram ventilation due to vehicle motion would prevent accumulation in the battery compartment. Thus, it appears unlikely that an explosion hazard due to delayed release of hydrogen during discharge exists. Nevertheless, this phenomenon should be more fully investigated. It is important to note that, like the situation for stibine and arsine, the delayed release of hydrogen during discharge could be easily handled by providing minimal ventilation to the battery compartment during on-the-road vehicle operation.

V. HYDROCARBON SAMPLING

A secondary purpose of the stibine/arsine monitoring tests performed at LILCO was to address the problem of a disagreeable odor sometimes detected during operations with Vehicle 1. This odor might be attributed to the strong, garlic-like odor of arsine, but could as well be due to other chemical species generated in or around the battery pack. Testing for the presence of potentially offensive compounds could help to elucidate the source of the odor. Toward this end, organic compounds present in the air inside the battery compartment and in the interior of Vehicle 1 were collected during the overcharge portion of a charge cycle. Gas chromatographic (GC)

analysis of the in-vehicle sample gave no peaks above blank levels, indicating undetectable levels of organic compounds in the sampled air. The chromatogram from the battery compartment, on the other hand, showed the presence of at least four compounds at levels above detection limits.

Estimated concentrations of the compounds detected by GC analysis ranged from 0.2 to 3 mg/m³. These values represent fairly high concentrations in the ventilated battery compartment and, if the compounds are odorous, could be related to the odor detected during operation of Vehicle 1. This sample was, therefore, submitted for GC/MS identification of the compounds. The results are presented in Table 6. Fifteen components of the sample were identified. Of these, only one, carbonyl sulfide (COS), is likely to have been generated within the battery compartment. The other compounds are more likely to come from a source outside the vehicle, possibly from the air displaced by the exhaust fan prior to its passage through the vehicle. This possibility is enhanced by the nature of the workspace in which testing at LILCO was done; a repair-facility garage and paint shop is likely to contain a variety of oils, solvents, lubricants, fuels, etc. The chlorinated hydrocarbons listed in Table 6 are common components of degreasing solvents; the aliphatic and aromatic hydrocarbons are common in paint thinners, fuels, and numerous other products.

The COS detected in the battery compartment is the only potentially malodorous organic compound recovered. In addition, its concentration, about 3 mg/m³, was higher than any other component of the sample. Carbonyl sulfide is a colorless, flammable gas with an unpleasant odor similar to rotten eggs. It is only slightly irritating to the lungs.

Experience with exposure of humans has not been recorded. The effects are probably due to the action of hydrogen sulfide resulting from partial decomposition of COS in the lungs.¹¹ Thus, the permissible limit should be somewhat higher than that for H₂S which has a TLV of 10 ppm. The measured concentration in the battery compartment corresponds to only 1.2 ppm and is thus within a safe range.

Of course, the results of this single hydrocarbon-sampling test do not necessarily implicate COS as a cause of the EV odor problem. However, they do suggest that the source of this compound is worthy of investigation.

VI. ENGINEERING ANALYSIS AND ASSESSMENT

A. Overview

The preliminary stibine/arsine monitoring tests described in this report indicate that sufficient quantities of these hydrides are generated during EV operation to require that some control of the dispersal of cell off-gases be incorporated into the design of these vehicles. Isolation of the battery compartment from the vehicle interior and ventilation to dilute and carry away the evolved gases would be two particularly simple and effective means for this control. The quality of isolation provided by the battery compartment cover was shown, in the tests with the LILCO vans, to directly affect

Table 6. Organic Compounds Identified in Battery Compartment
Air of Vehicle 1 during a Charging Cycle

Sulfide Compounds	Aliphatic Hydrocarbons	Aromatic Hydrocarbons	Alcohols	Chlorinated Hydrocarbons
Carbonyl Sulfide	2-Methylbutene	Benzene	Methanol	1,1,1-Trichloroethane
	Heptene	Toluene		Dichloromethane
		Xylene (two isomers)		Trichloroethylene
		C ₃ -Alkylbenzene		Chloroform
		Styrene		Tetrachloroethylene

in-vehicle hydride accumulations. The battery compartment cover should, therefore, provide as airtight a seal between the battery compartment and vehicle interior as is practical within the constraints of manufacturing considerations and operating convenience.

Ventilation of the battery compartment and work area has long been recognized as an important criterion for design specifications because of the potential explosion hazard of H₂ evolved during EV operation. Ventilation requirements for hydrogen management have been established using a design equation that relates the air flow necessary to maintain a safe level of H₂ in the ambient air to an easily measured operating parameter such as the charging current during overcharge or equalization charge. The objective of the following discussion is to derive an analogous equation describing the requirements for controlling accumulation of the metal hydrides arsine and stibine. It will be seen that not all of the information necessary for accurate assessment of a design criterion is available at this time. Consequently, the treatment presented here must be regarded as tentative, and should be applied cautiously until those areas where details are lacking are better defined. The primary value of this derivation is that it presents a straightforward approach to the problem and identifies specific shortfalls in available data which should be addressed by research in the near future.

B. Hydrogen Management

Since our approach to a design equation for control of stibine and arsine is analogous to that employed for hydrogen management, it is useful to briefly describe the derivation of that formula. In addition, later in the development we will compare the requirements for hydrogen control to those for control of the hydrides to determine whether precautions exceeding presently recommended standards should be proposed.

In establishing a criterion for the design equation, we will address the situation of maximum gas evolution so that other conditions, where smaller accumulations are encountered, will also be safely provided for. Maximum hydrogen evolution from lead-acid batteries arises during the overcharge period of a charge cycle and during equalization charge; this is a simple case to deal with from a computational standpoint. As showed in Section IV, the rate of hydrogen evolution during these operations is, according to Faraday's law, directly proportional to the charging current. Thus, for a battery pack containing n cells,

$$\frac{dH_2}{dt} = n \cdot k \cdot I \quad (1)$$

where k is the proportionality constant from Faraday's law [$7 \text{ mL } H_2/(\text{min} \cdot \text{cell} \cdot \text{A})$], and I is the charging current. An air flow of at least twenty-five times the hydrogen evolution rate is required in order to maintain the hydrogen concentration in the battery compartment below the lower limit of flammability, 4 vol %. A safety factor, F , must also be introduced into the expression because the minimum air flow may not be sufficient to ensure safe operation. The design equation appropriate to hydrogen management is then:

$$\text{Air Flow} = 25 \cdot F \cdot n \cdot k \cdot I \quad (2)$$

The value of I to be used in this equation is the finish rate specified for the charger associated with the vehicle under consideration. The safety factor, F , should be large enough to accommodate the maximum current that the charger is capable of delivering in the event of a controller malfunction. The Association of German Electrical Engineers in the Federal Republic of Germany recommends a factor of five.¹² If this value is adopted, Eq. 2 may be rewritten:

$$\text{Air Flow} = 25 \cdot 5 \cdot n \cdot k \cdot I = (8.75 \times 10^{-4} \cdot n \cdot I) \text{m}^3/\text{min} \quad (3)$$

For the Jet 600 van, which has 51 cells in the battery pack and a nominal finish current rate of 5 A, Eq. 3 recommends an air flow through the battery compartment of $0.223 \text{ m}^3/\text{min}$ for safe dispersal of evolved hydrogen. This value is similar to that found in the ANL vehicle ($0.212 \text{ m}^3/\text{min}$) and considerably lower than that measured with Vehicle 2 at LILCO ($1.16 \text{ m}^3/\text{min}$). Both of these vans may be considered safe, therefore, from hydrogen detonation.

C. Control of Stibine/Arsine

The steps leading to the derivation of Eq. 2 may be outlined as follows:

1. Establish a model describing evolution of the gas as a function of some easily measured operating parameter.
2. Establish a maximum acceptable concentration of the gas in the battery compartment using a suitable criterion of acceptability.

3. Calculate the air flow required to maintain this maximum concentration.
4. Multiply by a safety factor.

These same steps may be followed in deriving an analogous equation for stibine/arsine control. Because the situation is more complex and less understood for the metal hydrides, the first few steps will be presented in detail below.

1. Model Describing Hydride Evolution

The generation of stibine and arsine in a lead-acid cell has been shown in a number of studies^{4,13,14} to be much more complicated than the generation of hydrogen. The stibine generation rate depends on the relative rates of a variety of competing processes including the rate of leaching of antimony from the grids into the electrolyte by anodic corrosion, transport of antimony species towards the negative plate, and electrodeposition of antimony on the negative plate. As a result, it may be anticipated that the evolution rates of the metal hydrides could vary substantially from one type of battery to another, depending on the alloy used in manufacturing the positive grid and on the battery construction. Thus, it should be clear from the outset that no single expression and set of parameters describing stibine/arsine evolution will be applicable to all available EV batteries. It is possible, however, to assemble a qualitative picture of hydride evolution from a lead-acid cell that is general enough to accommodate the differences among battery types and serve as a framework for evaluating hydride evolution rates on an empirical basis.

Laboratory studies of hydride evolution from utility cells⁴ have shown that the evolution rate during a charge or equalization charge cycle goes through a maximum and then levels off, as illustrated in Figs. 10 and 11. It has been suggested that the maxima in the rate profiles are due to the depletion and inadequate replenishment of freshly deposited antimony or arsenic on the negative plate. Despite the complexity of the evolution profiles, the quantities of arsine and stibine emitted during similar cycles were found to be quite reproducible. This observation suggests that an average evolution rate determined over a fixed interval during the charge or equalization charge cycle could be used to characterize the generation of the hydrides.

Average evolution rates for stibine and arsine calculated from the data of Varma and Yao⁴ for a lead-acid cell under a utility load-leveling duty cycle are given in Table 7. These rates were obtained by dividing the total amount of stibine or arsine recovered during a specific cycle by the duration of the overcharge portion of the charge cycle or the total time of the equalization charge. Several important inferences can be drawn by examining the rate data in Table 7 in relation to the experimental conditions. First, when similar voltage and current are imposed on the cell, higher rates of evolution for both hydrides are found during the overcharge portion of a charge cycle than during equalization charge. Second, the rate of stibine formation during equalization charge increases in direct proportion to the charging current. In contrast, the arsine rate appears to vary linearly, not with the current, but with the preset voltage during equalization charge. This observation may reflect different mechanisms for generation of the hydrides. If

Fig. 10. Rate Profiles for Stibine and Arsine Generation in a Utility Load-Leveling Cell during a Charge Cycle

Table 7. Rates of Stibine and Arsine Evolution from a Lead-Acid Cell during Charging Modes under a Utility Load-Leveling Duty Cycle^a

Experiment	Current, A	Voltage, V	Evolution Rates	
			Stibine, mg/min	Arsine, mg/min
Charge Cycle ^b	12.3	2.45	0.067	18.3×10^{-4}
Equalization ^c	9.5	2.45	0.030	4.6×10^{-4}
	29.8	2.55	0.106	9.6×10^{-4}
	77.5	2.65	0.262	13.8×10^{-4}

^aData from Ref. 4.

^b23 cycles, 8-h cycle includes 3 h of overcharge.

^c4 cycles, 2.45 V, 4 h each; 2 cycles, 2.55 V, 4 h each; 2 cycles, 2.65 V, 4 h each.

Fig. 11. Rate Profiles for Stibine and Arsine Generation in a Utility Load-Leveling Cell during an Equalization Charge Cycle.

these relationships between hydride evolution rates and operating conditions are valid for lead-acid batteries of the EV propulsion type, then simple expressions describing the generation rates as a function of operating conditions could be written.

$$R_{\text{SbH}_3} = k_{\text{SbH}_3} \cdot I \quad (4)$$

$$R_{\text{AsH}_3} = k_{\text{AsH}_3} \cdot (V_{\text{cell}} - 2.35) \quad (5)$$

In these formulas, R is the rate of evolution of the subscripted hydride, and k is a corresponding proportionality factor. Because k is anticipated to vary in an unpredictable way with materials, geometry, and other parameters related to battery construction, it must be evaluated empirically for each hydride for different battery types under the different charging modes. For a given battery type, a larger value for k is likely for the overcharge portion of a charge cycle than for equalization charge.

Equations 4 and 5 describe the data in Table 7, from which they were derived, very well. It would be desirable, however, to test how well the formulas predict evolution rates under other conditions with a variety of battery types. Unfortunately, few data are available which provide all the information needed to apply the formulas. Two additional studies reported in the literature^{15,16} support the linear dependence of the stibine evolution rate on the charging current. In addition, the results of the preliminary EV

monitoring tests with the ANL van and Vehicle 2 at LILCO might be interpreted as consistent with Eq. 4 (see Section III.B.2). Arsine data appropriate for use in Eq. 5 have not been found in the literature. The EV monitoring test data for arsine are not consistent with the formula, but because the experimental conditions during the LILCO overcharge experiments were not well defined, these data (as well as the stibine results mentioned above) may not provide a valid test of the formula.

Table 8 shows the order of magnitude of more or less typical k-values and their variation among different battery types.

Table 8. Proportionality Factors (k-values) for Stibine and Arsine Evolution Rates in Lead-Acid Batteries

Battery Type	Charging Mode ^a	$k_{\text{SbH}_3}^b$, mg/(min·cell·A)	$k_{\text{AsH}_3}^c$, mg/(min·cell·V)
Utility Load-Leveling ^d	C	0.0054	0.0182
	EC	0.0034	0.0047
EV Propulsion ^e	C	0.0028	0.0061
	EC	0.0012	0.0029
Unknown ^f	C	0.0023	
Unknown ^g	C	0.0058	

^aC = Charge; EC = Equalization Charge

^bDefined by Eq. 4.

^cDefined by Eq. 5.

^dC and D Batteries, Type C-160-31; Ref. 4.

^eSGA Batteries, Type 2HGC-HC; This study; based on cell-outlet measurements with ANL vehicle.

^fReference 15.

^gReference 17.

2. Criteria for Acceptability of Hydride Accumulations

Because the nature of the stibine/arsine hazard is different from that imposed by hydrogen, the definition of acceptability criteria must be approached differently. In the case of hydrogen, the lower limit of flammability must not be exceeded, even momentarily, or detonation could occur. In contrast, stibine and arsine accumulation must be controlled only to the extent that would limit personnel exposure to safe levels. Thus, attention should be focused on hydride concentrations in occupiable areas inside the vehicle and in the garage. This places the primary burden for control (1)

on the garage ventilation, which must adequately dilute and carry away the gases expelled from the battery compartment, and (2) on isolation of the battery compartment from the vehicle interior in order to maintain low in-vehicle accumulations. Ventilation of the battery compartment is important only insofar as it influences the effectiveness of these other precautions.

The maximum tolerable concentrations for the work areas, as set by the TLV-TWAs, are $0.5 \text{ mg SbH}_3/\text{m}^3$ and $0.2 \text{ mg AsH}_3/\text{m}^3$. In addition, it would be prudent to limit the battery compartment concentrations (by ventilation) to a low level so that localized in-garage concentrations would never exceed acceptable limits if the garage ventilation should fail. Rather than using a completely arbitrary value for this level, a value equal to the short-term exposure limit (STEL) will be used. The STEL is three times the TLV for stibine and arsine or $1.5 \text{ mg SbH}_3/\text{m}^3$ and $0.6 \text{ mg AsH}_3/\text{m}^3$.

3. Design Equation for Stibine/Arsine Management

In the previous section we established two separate criteria for acceptable stibine and arsine levels during charging of the batteries in an electric vehicle. One of these recommends concentration limits for the battery compartment exhaust and relates directly to vehicle design. In particular, this criterion may be used to specify a minimum airflow for the battery compartment exhaust fan comparable to that given by Eq. 3. The other criterion establishes maximum allowable concentrations in the occupiable work areas. It relates to requirements for the garage ventilation system, and is the more important of the two. Because the first of these criteria is easier to address, it will be considered first.

If the k -values in Table 8 for stibine and arsine are substituted into Eqs. 4 and 5, it is found that the rate of stibine evolution is much higher than that for arsine under similar conditions. Furthermore, because the current, to which the stibine rate is proportional, increases faster than the voltage, to which the arsine rate is related, the ratio of stibine to arsine in the battery off-gases may be expected to become even larger as the charging current increases. It is clear, then, that design specifications established to control evolved stibine will also suffice to prevent hazardous arsine accumulation. On this basis, ventilation requirements for stibine/arsine management should be established using the model describing stibine evolution, Eq. 4. The minimum air flow required to maintain the stibine concentration at $1.5 \text{ mg}/\text{m}^3$ in the battery compartment exhaust is then given by:

$$\text{Air Flow} = (n \cdot k_{\text{SbH}_3} \cdot I) / 1.5 \quad (6)$$

For conditions of maximum evolution, the appropriate values of k_{SbH_3} and I are those for the overcharge period of a charge cycle. For the SGA batteries in the Jet 600 vehicle used in the present study (see Table 8 for k_{SbH_3}), Eq. 6 recommends an air flow of $0.48 \text{ m}^3/\text{min}$. This air flow is more than twice that required for safe dispersal of the hydrogen evolved under identical conditions ($0.22 \text{ m}^3/\text{min}$; see Section VI.B). This result suggests that the minimum requirements for hydrogen control are probably inadequate for stibine management, and is especially noteworthy because no safety factor has been incorporated into Eq. 6. Because the consequences of

an increased stibine evolution rate are more dependent upon the capacity of the garage ventilation system than on the battery-compartment exhaust system, it may not be necessary to overdesign the latter to provide for sporadic, short-term excursions due to equipment malfunctions. Because exposure to acute levels of stibine or arsine gas as a result of battery charging or operation of available electric vehicles is virtually impossible, occasional concentrations exceeding the STEL may be tolerated inside the battery compartment (however, not in the garage).

Comparison of the requirement for battery compartment ventilation set by Eq. 6 with the air flows measured in the vans used in these preliminary monitoring tests shows that Vehicle 2 at LILCO (air flow - 1.16 m³/min) would easily meet the requirement while the ANL van (air flow - 0.212 m³/min) would not. However, if the additional ventilation provided by the battery-charger exhaust system (see Section III.A.1) is taken into account, the ANL van does meet the requirement. This situation obviously is undesirable because it suggests that safe operation of this van depends on a feature not specifically intended for this purpose. If, for example, an experiment like that performed during equalization charge with the LILCO vans, using an off-board charger, were done using the ANL vehicle, the stibine concentration in the air expelled from the battery compartment would be more than 6 mg/m³. Under these conditions, ambient concentrations in the garage near the battery compartment exhaust exit could easily exceed the TLV limits.

Whether or not these limits would be exceeded depends heavily upon the quality of mixing and displacement provided by the garage ventilation system. Under normal operating conditions with a vehicle whose ventilation fan meets the requirement set by Eq. 6, the garage ventilation must be adequate to dilute the battery compartment exhaust by a factor of three. In addition, a safety factor of at least five should be incorporated into the design to accommodate equipment malfunctions and compensate for concentration gradients resulting from stratification of the expelled gases. To meet these demands, the garage ventilation should input or remove at least fifteen times the volume of air displaced by the battery-compartment exhaust fan. Thus, a minimum air flow through the garage could be established, for each vehicle, according to Eq. 7.

$$\begin{aligned} \text{Air Flow (garage)} &= 15 \cdot n \cdot k_{\text{SbH}_3} \cdot I/1.5 \\ &= 10 \cdot n \cdot k_{\text{SbH}_3} \cdot I \end{aligned} \quad (7)$$

For the example of a single Jet 600 van charged in the garage, an air flow of 7.1 m³/min (200 cfm) is recommended by this equation. It should be emphasized that the value of k_{SbH_3} is not a fundamental constant but will vary unpredictably with the type of battery employed. From the limited data available in Table 8, it appears that k -values twice as large as that found for the SGA batteries could occur. Because it is not possible to restrict the use of a garage to one type of EV battery, it would be advisable to establish design requirements for the maximum k_{SbH_3} observed for available EV batteries. Until evaluation of a number of available battery types is carried out, using a value for k_{SbH_3} of 0.006 mg/(min·cell·A) should provide a safe margin for error.

D. Summary and Generalization of Design Requirements

The design equations derived in the preceding section can be used in two ways: (1) to assess the adequacy of ventilation systems in existing vehicles and garages, and (2) to establish design specifications for new or proposed vehicles and facilities. For this first application, Eqs. 6 and 7 may be used if k_{SbH_3} is measured during the overcharge period of a charge cycle for the battery type employed. In the second application, however, the battery type is uncertain and the design should be based on the value for k_{SbH_3} given above. Substituting this value into the design equations gives:

$$\text{Air Flow (Battery Compartment)} = 0.004 \cdot n \cdot I(\text{m}^3/\text{min}) \quad (8)$$

and

$$\text{Air Flow (Garage)} = 0.06 \cdot n \cdot I(\text{m}^3/\text{min}) \quad (9)$$

It was noted already that the air flow recommended by Eq. 8 is greater than the minimum required for safe dispersal of hydrogen and should be regarded as a better minimum standard for EV design specifications. It is also of interest to compare the garage ventilation recommended by Eq. 9 with existing standards. One such standard² specifies a minimum of three air changes per hour in the garage. For a typical garage with a volume of 350 m³, an air flow of 17.5 m³/min is needed to meet this requirement. If a single vehicle containing 51 cells and using a finish rate of 5 A is charged there, Eq. 9 recommends a flow of 15.3 m³/min. Thus, for this situation, the two recommendations are virtually equivalent. However, in a garage of this size, it would be possible to recharge two vehicles simultaneously. If this usage were proposed, Eq. 9 would double the required ventilation while the other standard would not. In this respect, the design equation presented by Eq. 9 provides the better margin of safety.

VII. RECOMMENDATIONS

A. Procedures for Safe-Handling of Off-Gases from Electric Vehicle Lead-Acid Batteries

One of the primary goals of the preliminary stibine/arsine monitoring tests described in this report was to provide an appropriate data base for evaluating previously proposed safeguards and procedures² in order to allow safe testing, charging and operation of EVs. In general, the results and data analysis of the monitoring experiments have not identified any major shortcomings in the preliminary safe-handling procedures. However, since a better understanding of hydride behavior has been derived from these tests, we can suggest some modifications and revisions that should be made. An updated version of these procedures is presented below.

During Recharge

1. Maintain a minimum air flow through the garage of 0.06 m³/min (1.7 cfm) for each cell in the vehicles being charged and each ampere of current imposed on the battery during the overcharge portion of a charge cycle. This air flow should be sufficient to

maintain safe levels of stibine even if the charger should malfunction and the current increase during the overcharge portion of the charging cycle. Note that this air flow is essentially equivalent to the one recommended previously (i.e., three air changes per hour) if a small number of vehicles in proportion to the garage size are charged simultaneously. However, if several vehicles are charged in a small garage, the new recommendation indicates the need for additional ventilation. If the garage ventilation system fails, stop charging as soon as possible and open doors and windows to establish increased natural ventilation. Do not stay in the garage while it is being aired out.

2. The EV ventilation system for control of the hydrogen concentration must be fully operational during all recharging. If the EV has a ventilating fan for this purpose, charging should cease if the fan is not operating. Electrical interlocks should be used to prevent the charger from functioning if the fan is not operating. Try to minimize time spent in or near the air stream leaving the battery-compartment exhaust exit. The stibine concentration in this stream will probably be somewhat higher than that in the rest of the garage.
3. Do not open the battery compartment while the charger is on. This action would not only result in exposure to unacceptable levels of stibine, but would also impair the effectiveness of the hydrogen-control system and present a serious electrical hazard. When the battery compartment is opened, to measure electrolyte specific gravity, for example, allow a few minutes for the garage ventilation to disperse the small amounts of stibine and arsine that may have accumulated in the compartment. If the only access to the battery compartment is inside the vehicle, the vehicle doors and windows should be opened to facilitate removal of these gases. (The time limits for personnel in the garage during and after equalization charge that were recommended previously appear to be unnecessary.)
4. If the passenger compartment is fully separated from the battery compartment, positioning of the EV windows during recharge is unimportant. If there is any uncertainty regarding the effectiveness of that seal, leave the EV windows open so that the garage ventilation will prevail.
5. Real-time monitoring of stibine levels can be done with colorimetric techniques. The ANL Field Kit or a NIOSH-approved method for stibine will verify if the level of SbH_3 is below the TLV.

During Operation

6. During battery discharge and stand, small amounts of off-gases trapped inside the battery cells may be released. If the battery compartment is located inside the vehicle, the compartment cover should be in place during vehicle operation. If possible, the exhaust fan provided for removing off-gases during recharge should

be rewired to operate during discharge as well. It should be noted that exposure levels during vehicle driving as a result of release of these trapped gases probably will not approach the TLV. However, any unnecessary exposure should be considered unacceptable.

7. During regenerative braking, the ventilation system in place for hydrogen dispersion must be operating. Ram air, from EV motion, will act to disperse any gases generated. Again, if there is any doubt about the effectiveness of the seal around the battery compartment, open the windows during regenerative braking.

B. Procedures for Conducting Stibine/Arsine Monitoring Tests

The proposed guidelines for stibine/arsine control provide a basis for evaluating the precautions employed at specific EV demonstration sites. However, many uncertainties exist in the data base, its interpretation and extrapolation, and in actual operating conditions. Because of these uncertainties, monitoring of the hydride concentrations during actual operation or test situations is still the best way to verify that specific precautions are effective. The following recommendations are based upon the experience and understanding gained during the preliminary monitoring tests described in this report.

1. Sampling Protocol

In testing the effectiveness of the overall hydride management at a specific testing site, it is advantageous to carry out the monitoring experiment when hydride evolution is at its maximum. Under normal operating conditions, this occurs during the overcharge period of a charge cycle (Section VI.C). Thus, if only one set of tests is to be performed, it should be done during this period. For a valid assessment of ambient hydride accumulation during the overcharge portion of the charge cycle, sampling should not be initiated until the battery voltage reaches an average value of 2.45 V/cell. Alternatively, sampling could be initiated earlier and the assumption made that all of the stibine/arsine collected was generated after the voltage reached this value (Section III.A). In either case, some means for monitoring the battery voltage as charging progresses is required.

Sampling locations inside the vehicle and in the garage should be chosen to represent areas likely to be occupied by personnel during normal operations. In addition, samples should be taken near the battery compartment exhaust exit and in areas where strong, directional air currents occur, such as in the exhaust of the charger cooling fan; these areas are likely to exhibit higher hydride concentrations than other areas in the garage.

2. Choice of Method

Field measurements of ambient stibine concentrations may be obtained by either of two presently available methods. These are (1) absorption in Holland's solution followed by spectrophotometric determination of antimony as SbI_4 and (2) absorption on mercuric chloride-coated silica gel followed by spectrophotometric determination of antimony as the Rhodamine B complex. The first of these forms the basis of the ANL SAMFK,⁵ while the

second is used in the method currently recommended by NIOSH.⁷ These two methods are compared in Appendix C. From this comparison, it was concluded that the ANL SAMFK method has significant advantages over the NIOSH method and should be preferred when establishing a monitoring program. The primary advantages of the ANL method arise from its ability to provide immediate, in-the-field stibine analysis results and from its ability to provide stibine and arsine concentration data from a single sample. From the standpoint of reliability, the ANL and NIOSH methods are virtually identical.

Because the ANL method has not been evaluated by NIOSH, and therefore is not validated or approved for commercial testing situations, it may be advantageous to employ the NIOSH method when the delay between sampling and reporting of results can be tolerated.

C. Future Work

The preliminary stibine/arsine monitoring test results obtained at ANL and at LILCO have contributed substantially to an understanding of the behavior of these metal hydrides during electric vehicle operations. Analysis of these data suggests that the generation and dispersal of battery off-gases could be predictable in the general case under well-defined operating conditions. However, basic information required for modeling the system is lacking at the present time. The release of stibine and arsine gases from lead-acid cells needs to be more fully characterized with regard to such parameters as composition of the grid alloy in the battery, battery construction, and charging current and potential. Such fundamental questions as whether the equations proposed for describing stibine and arsine evolution rates are generally applicable must be addressed before a final form for a design equation can be established. Laboratory studies of stibine/arsine evolution from a variety of commercially available EV propulsion batteries would be an efficient means of achieving this characterization. In addition to providing the empirical data base needed to model hydride evolution and to set design specifications, these studies could provide a deeper insight into the detailed mechanism of hydride generation in lead-acid cells. Better understanding of this phenomenon might lead to technology for controlling the generation of stibine and arsine at its source.

The rates and mechanisms of stibine and arsine decomposition under conditions that prevail in EV applications also need to be studied. Furthermore, the environmental impact of the decomposition products of these compounds and their accumulation needs to be investigated.

The production and dispersal of stibine and arsine during regenerative braking should be evaluated with respect to possible accumulations and safety considerations.

Finally, it would be of interest to study more fully the presence of organic compounds in the EV battery compartment and their possible role in the odor problem encountered with some vehicles at LILCO. Because this odor problem is apparently alleviated by providing an air-tight cover and ventilation for the battery compartment during discharge, in-depth understanding of its cause may not be necessary. However, it might be possible

to completely eliminate the problem by identifying its source. For example, if the odor is caused by deterioration of materials used in manufacturing the batteries or the vehicle, better suited alternative materials could be chosen.

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APPENDIX A

CHRONOLOGICAL SEQUENCE AND BATTERY PERFORMANCE DATA
FROM ANL PRELIMINARY STIBINE/ARSINE MONITORING TESTSFebruary 5, 1980

Test: None

Data: (Modules in battery numbered as in Figure A-1 for reference in all tests)

Open Circuit Voltage (O.C.V.)

Module #	O.C.V.	Module #	O.C.V.	Module #	O.C.V.
1	6.34	7	6.39	13	6.36
2	6.35	8	6.37	14	6.33
3	6.37	9	6.33	15	6.36
4	6.35	10	6.35	16	6.37
5	6.34	11	6.31	17	6.40
6	6.39	12	6.36

Modules numbered according to diagram; Cells are designated with letters: Positive Side of Battery = a (as in anode), Center of Battery = b, Negative Side of Battery = c (as in cathode)

Fig. A-1. Numbering System for Modules and Cells in EV Battery

February 7, 1980

Test 1.1: In-Vehicle, Charge (110 V A/C Power)
 Duration: 626 min
 Ambient Temperature: 18°C

Data:

Module	O.C.V.	<u>Specific Gravity</u>			Cell Temperature, °C
		a	b	c	
1	6.63	1.225	1.240	1.280	
2	6.60	1.206	1.226	1.241	
3	6.61	1.221	1.226	1.221	
4	6.64	1.201	1.195	1.215	
5	6.60	1.236	1.240	1.221	
6	6.55	1.232	1.248	1.262	25.5
7	6.62	1.247	1.257	1.243	
8	6.57	1.247	1.222	1.227	
9	6.62	1.196	1.171	1.216	
10	6.59	1.220	1.226	1.221	
11	6.58	1.221	1.253	1.225	23.0
12	6.61	1.256	1.246	1.226	
13	6.68	1.215	1.208	1.261	
14	6.61	1.181	1.238	1.211	
15	6.56	1.201	1.206	1.221	
16	6.61	1.190	1.245	1.240	
17	6.61	1.269	1.284	1.280	

February 8, 1980

Test 2.1: In-Vehicle, Discharge
 Duration: 40 min, 27 km

Data:

Cell #	Specific Gravity	Temperature, °C
7b	1.223	30.3
11b	1.218	29.2

EV charged over weekend, but used for demonstration on 2/11/80.

February 12, 1980

Test 1.2: Cell Outlets, Charge (220 V. A/C Power)

Duration: 180 min

Ambient Temperature: 19°C

Data:

Cell #	Specific Gravity	Temperature, °C
7b	1.296	24.5
4b	1.270	20.0

Test 1.4: Cell Outlets, Overcharge

Duration: 293 min

Data:

Module #	O.C.V.	Cell	Specific Gravity	Temperature, °C
1	-	b	-	22
3	-	b	-	-
4	-	b	1.292	23
7	-	b	1.294	26
9	6.66	b	-	-
10	-	b	-	23.5
11	-	b	-	24
13	6.65	b	-	-
14	6.69	b	-	26

February 13, 1980

Test 2.2: Cell Outlets, Discharge

Duration: 39 min, 21 km

Data:

Cell #	Specific Gravity	Temperature, °C
4b	1.246	27
7b	1.258	30

February 14, 1980

Test 3.1: In-Garage, Charge
Duration: 438 min

Dry-ice traps connected to cells 4b and 7b.

Data:

Cell #	Specific Gravity	Temperature, °C
4b	1.292	-
5b	1.277	23.5
7b	(Low on water)	-
8a	1.292	26
8c	1.293	25
10b	1.293	23
11b	1.292	24.5
16b	1.297	25

February 15, 1980

Test 3.2: In-Garage, Overcharge
Duration: 107 min

Dry-ice and charcoal adsorbent traps on cells 4b, 5b, and 7b.

Data:

Cell #	Specific Gravity	Temperature, °C
4b	1.293	-
5b	1.293	-
6b	-	20
7b	1.193	20

February 18, 1980

Test 1.3: In-Vehicle, Overcharge
Duration: 126 min

EV Discharge, 30 min

Cell #	Specific Gravity	Temperature, °C
5b	1.242	20
7b	(Low on water)	-
8b	1.256	22
10b	1.249	21
15b	1.256	20

Test 1.2: Repeat (220 V Power): Cell Outlets, Charge
Duration: 304 min

Data: O.C.V. between 6.48 and 6.53 V for cells tested.

Cell #	Specific Gravity	Temperature, °C
5b	(Low on water)	20
8b	1.283	22
10b	1.287	19
15b	1.272	20

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APPENDIX B

CHRONOLOGICAL SEQUENCE AND BATTERY PERFORMANCE DATA FROM
STIBINE/ARSINE MONITORING TESTS AT LILCOMarch 25, 1980

Test: None

Data: Initial Conditions

Module No.	Electrolyte Temperature, °C	Specific Gravity
1	19	1.269
4	19	1.244
7	19	1.269
8	19	1.269
11	19	1.259
16	19	1.279

Open-Circuit Battery Voltage: 106 V

Test: In-Vehicle, Equalization Charge (Vehicle 1)
Duration: 31 min; Off-Board Charger

Data: After test (Open-Circuit Voltage = O.C.V.)

Module No.	Temperature, °C	Specific Gravity	O.C.V.
1	22	1.285	7.40
7	23	1.294	7.38
16	21	1.295	7.30

Open-Circuit Battery Voltage: 132.7 V

Test: In-Vehicle, Discharge (Vehicle 1)
Duration: 24 minData: Before Test, Battery O.C.V.: 115.3 V
After Test:

Module No.	Temperature, °C	Specific Gravity
1	30	1.248
7	31	1.250
16	30	1.234

Battery O.C.V.: 99.6 V

March 26, 1980

Test: In-Vehicle, Charge (Vehicle 1)
Duration: 35 min; Hydrocarbon Samples Taken, 10 min

Data: After Test:

Module No.	Temperature, °C	Specific Gravity
1	28	1.272
7	32	1.275
16	30	1.273

Test: In-Garage, Charge (Vehicle 1)
Duration: 31 min

Data: None Taken

Test: In-Garage, Equalization Charge (Vehicle 1)
Duration: 41 min; Off-Board Charger

Data: After Test:

Module No.	Temperature, °C	Specific Gravity
1	30	1.290
7	32	1.295
16	29	1.295

Test: In-Vehicle, Discharge (Vehicle 1; Windows Open)
Duration: 19 min

Data: After Test:

Module No.	Temperature, °C	Specific Gravity
1	38	1.225
7	42	1.230
16	39	1.225

March 27, 1980

Test: Charge (Vehicle 2)
Duration: 68 min

Data: Before Test

Battery O.C.V.: 107.6 V; Temperature: 20°C; Specific Gravity:
1.25 to 1.26

Data: After Test
Temperature: 24 to 25°C; Specific Gravity: 1.264 to 1.275

Test: Equalization Charge (Vehicle 2)
Duration: 43 min

Data: After Test:
Temperature: 29°C; Specific Gravity: 1.284 to 1.295

Test: Discharge, (Vehicle 2)
Duration: 25 min

Data: After Test
Specific Gravity: 1.260 to 1.265

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APPENDIX C

COMPARISON OF THE ANL SAMFK AND NIOSH METHODS
FOR DETERMINATION OF STIBINE

Stibine and arsine in ambient air are collected in the ANL SAMFK method by drawing an air sample through 50 mL of Holland's solution (8% KI, 1% I₂, 3N H₂SO₄) at a flow rate of approximately 1.5 L/min. The volume of air sampled during a measurement is determined as the product of the sampling time and the air flow rate appropriate to the pump-bottle combination used in sampling. This flow rate is established by calibration of the combination and is estimated to be reliable to about ±5%.

After sampling, the absorber solution is transferred to a sample bottle after the volume of the absorber, including rinses, is measured and recorded. The concentration of antimony in the absorber solution is determined by diluting an aliquot to a standard volume with Holland's solution while decolorizing with hypophosphite (either as H₃PO₂ or NaH₂PO₂ solution) and spectrophotometrically measuring the stable SbI₄⁻ complex which results. If necessary, the aliquot size may be varied to give an antimony concentration within the range of calibration standards. This spectrophotometric antimony assay has a precision of ±1 µg Sb or ±5%, whichever is larger, based on the total antimony in the absorber solution. The limit of detection (LOD) is such that 1 µg Sb in 50 mL of absorber solution can be determined.

The stibine concentration in the ambient air sample, C_{SbH₃}, is computed according to Eq. C-1.

$$C_{\text{SbH}_3} = \text{mg SbH}_3/\text{m}^3 = \frac{C_{\text{abs}} \cdot V_{\text{abs}} \cdot 1.025}{V_{\text{air}}} \quad (\text{C-1})$$

where C_{abs} is the concentration of Sb in the absorber solution, V_{abs} is the volume of absorber in mL, including rinses, recorded at the time of transfer to the sample bottle, V_{air} is the volume of air (in m³) drawn through the absorber during sampling, and 1.025 is a conversion factor from µg Sb to µg SbH₃. The error associated with the stibine determination is given (approximately) by

$$\sigma_{C_{\text{SbH}_3}} = \left[\left(\frac{\sigma_{C_{\text{abs}}}}{C_{\text{abs}}} \right)^2 + \left(\frac{\sigma_{V_{\text{air}}}}{V_{\text{air}}} \right)^2 \right]^{1/2} \cdot C_{\text{SbH}_3} \quad (\text{C-2})$$

For samples where 20 µg Sb or more are collected in the absorber solution, each of the terms in the brackets equals 5%, and

$$\text{Sb} \geq 20 \text{ } \mu\text{g}: \sigma_{\text{SbH}_3} = \left[(0.05)^2 + (0.05)^2 \right]^{1/2} \cdot C_{\text{SbH}_3} = 0.07 \cdot C_{\text{SbH}_3} \quad (\text{C-3})$$

Thus, a relative standard deviation of 7% is anticipated for these samples. When less than 20 μg Sb is collected, the error limits increase in accord with Eq. C-2 to a maximum of 100% of the measured concentration at the detection limit.

The concentration of arsenic in the absorber solution may also be determined by direct analysis of an aliquot using an atomic absorption spectrophotometer equipped with a hydride generation system that converts the As to arsine by reaction with sodium borohydride. This method allows the determination of arsenic as arsine to a precision of $\pm 10\%$. Using expressions and assumptions analogous to those presented above for stibine, error limits of $\pm 11\%$ are estimated for samples containing more than 2.5 μg As in the absorber solution. The LOD for the As determination is 0.25 μg As in the 50-mL absorber solution.

In the currently recommended NIOSH method for the determination of stibine in ambient air (NIOSH Manual of Analytical Methods, Method S243), the stibine is absorbed on silica gel coated with mercuric chloride. Following collection, the absorbed antimony is leached with concentrated HCl and determined colorimetrically as the Rhodamine B complex. Flow diagrams illustrating the steps in measuring stibine in ambient air by the two methods are presented in Fig. C-1. The relative simplicity of the ANL method is evident from this figure.

Fig. C-1. Flow Diagrams for ANL and NIOSH Methods of Stibine Measurement

A more detailed comparison of the ANL and NIOSH methods is summarized in Table C-1. The qualities associated with the NIOSH method were taken from the evaluation presented in the NIOSH manual. On the basis of the information in this table, several noteworthy conclusions can be made regarding the relative merits of the ANL and NIOSH methods.

1. The reliability of the two methods is very similar; precision and accuracy at the TLV are not significantly different. However, the ANL method shows somewhat better sensitivity for a given sample size and is capable of efficient collection at considerably higher concentrations. Thus, the ANL method has a larger useful range than the NIOSH method.

Table C-1. Relative Merits of ANL and NIOSH Procedures for Measuring Ambient Stibine

Quality	ANL Method	NIOSH Method (S 243)
Precision (at OSHA Standard Limit)	7%	9%
Accuracy (at OSHA Standard Limit)	7%	9%
Limit of Detection (20-L Air Sample)	0.02 mg SbH ₃ /m ³	0.1 mg SbH ₃ /m ³
Maximum Concentration (90-min Sample)	> 50 mg SbH ₃ /m ³	3.9 mg SbH ₃ /m ³
Collection Medium	Holland's Solution (KI, I ₂ , 3N H ₂ SO ₄)	Mercuric-Chloride on Silica-Gel
Effectiveness under Specified Use	Complete	Complete
Convenience	Messy	Neat
Method of Measurement	Spectrophotometric	Colorimetric
Ease of Sample Preparation	Simple	Moderately Complex
Steps in Preparation	1	3
Relative Analysis Time	1	2
Interferences	Bi, (Hg, Pb)	(Fe, others)
Other Information Available	AsH ₃	None
Field Measurement Possible?	Yes	No

2. The ANL analysis procedure is much simpler and faster than the NIOSH procedure. It is this simplicity of sample workup that allows convenient in-the-field measurement of stibine with the SAMFK. In addition, the ANL method provides more information by allowing arsine to be determined from an aliquot of the same absorber solution used for the stibine measurement.
3. Bismuth collected in the absorber solution of the SAMFK could result in erroneous values for the stibine measurement by the ANL method. Other metals (notably Pb and Hg) could also interfere if present at high concentrations. The NIOSH method is not susceptible to interferences except at high concentrations of Fe and other, less common, elements. Because the presence of airborne Bi during EV monitoring tests is highly unlikely, the sensitivity of the ANL method to this element is not considered a serious drawback.
4. The primary advantage of the NIOSH method lies in the convenient sampling provided by the silica-gel tubes employed. The liquid absorber in the SAMFK is corrosive and messy. However, the price paid in sample preparation, complexity, and analysis time do not seem to justify the use of the NIOSH method.
5. The information in the table indicates that the ANL procedure offers significant advantages over the NIOSH method. Therefore, the ANL method should be recommended as the preferred technique. Of course, NIOSH method can also be used if the individual preference or policy of a particular testing laboratory so dictates.

APPENDIX D

STATISTICAL COMPARISON OF STIBINE MONITORING RESULTS
OBTAINED BY ANL AND BY NYTL AT LILCO

While ANL conducted the stibine/arsine monitoring tests at LILCO, simultaneous measurement of ambient stibine concentrations was carried out by New York Testing Laboratories (NYTL) using the NIOSH method for stibine determination. The results of these stibine measurements by the two laboratories are presented in Tables D-1 and D-2. The NYTL values, originally reported in ppm, were converted to units of mg/m^3 to simplify comparisons with the ANL data. The error limits given for the ANL data are $\pm$ one standard deviation, σ_{ANL} , calculated on the basis of the error analysis given in Appendix C. Because similar precision and accuracy are expected for the SAMFK and NIOSH methods (Table C-1), the approximation is made in the following treatment that identical error limits can be expected for the NYTL results.

The model used for statistical comparison of the two data sets is as follows: The ANL and NYTL values for each sampling point were averaged, giving the entries shown in the third column of the tables. Then the difference between the ANL value and this average value was compared with the error associated with the ANL value by taking the ratio of the difference to σ_{ANL} . Assuming a normal distribution of the measured values around the "true" value, and further assuming that the average value is a good approximation to the true value, then the ANL value should lie within $2\sigma_{\text{ANL}}$ of the average 95% of the time, within $3\sigma_{\text{ANL}}$ 99% of the time, etc. Thus, a ratio in the last column of less than 2 is indicative of statistical agreement between the ANL and NYTL values at the 95% confidence level. This criterion is met by 26 of the 30 entries in the tables. Of the four values for which the ANL-NYTL average is greater than $2\sigma_{\text{ANL}}$ from the ANL value, one corresponds to a sample for which the NYTL and ANL sampling locations were different (last entry in Table D-1). The comparison in this case is obviously not valid.

Examination of the other two discrepant entries in Table D-1 suggests that a sample mix-up might have occurred at one or the other of the laboratories. If the results from either laboratory are interchanged between samples, the deviation of the ANL value from the average falls to less than $2\sigma_{\text{ANL}}$ for one of the two samples and to slightly over $2\sigma_{\text{ANL}}$ for the other. Data checks by ANL and NYTL did not show evidence of such a mix-up, and therefore the discrepancy between the results must stand. However, the possibility of a sample mix-up mitigates the impact of this discrepancy.

The final case in which the ANL and NYTL results differ significantly involves samples taken inside the battery compartment in Vehicle 2 during equalization charge (Table D-2). It is noteworthy that, although the ANL and NYTL values differ quantitatively, the values reported for this sampling location are the largest members of the data set from each laboratory. Thus, a correlation between stibine concentration and sampling point does exist.

In comparing results like these, it must be realized, that the nature of the sampling and the difficulty of obtaining comparable, independent samples under real-world conditions may introduce additional error. Based on the ANL

Table D-1. Comparison of ANL and NYTL Stibine Results from Tests at LILCO with Vehicle 1.

Operation	Sampling Location	ANL ^b mg SbH ₃ /m ³	NYTL mg SbH ₃ /m ³	Average NYTL + ANL	ANL-Avg. σ_{ANL}
Charge	Driver's Seat	<0.02 ± 0.02	<0.01	<0.02	0
	Top of B.C. ^a	0.06 ± 0.02	<0.01	<0.04	1.0
	Right Rear of EV	0.02 ± 0.02	0.07	0.05	1.5
	Inside of B.C. ^{a,d}	0.15 ± 0.02	0.74	0.45	15. ^d
Equalization Charge	Driver's Seat	<0.02 ± 0.02	<0.01	<0.02	0
	Top of B.C. ^a	0.13 ± 0.02	0.08	0.11	1.
	Right Rear of EV	0.09 ± 0.02	0.06	0.08	0.5
	Inside B.C.	0.30 ± 0.03	0.32	0.31	0.3
Discharge	Driver's Seat	0.06 ± 0.03	0.02	0.04	0.7
	Top of B.C. ^a	0.03 ± 0.03	0.02	0.03	0
	Right Rear of EV	0.05 ± 0.03	0.07	0.06	0.3
	Inside B.C. ^{a,d}	0.96 ± 0.08	0.06	0.51	5.6 ^d
Discharge (Windows Open)	Driver's Seat	<0.03 ± 0.03	<0.01	<0.02	0.3
	Top of B.C. ^a	<0.05 ± 0.05	<0.01	<0.03	0.4
	Right Rear of EV	<0.09 ± 0.09	<0.01	<0.05	0.8
	Inside B.C. ^a	<0.04 ± 0.04	<0.01	<0.03	0.3
Charge ^c	Behind Rear Bumper (2 ft up, 4 ft out); 2 ft up, 2 ft out	<0.02 ± 0.02 <0.02 ± 0.02	0.05 0.02	<0.04 <0.02	1.0 0
	(6 ft up, 6 ft out); 5 ft 6" up, 2 ft out	0.04 ± 0.02	0.01	0.03	0.5
	(8 ft up, 10 ft out); 8 ft up, 2 ft out	<0.02 ± 0.02	0.01	<0.02	0
Equalization Charge ^c	Behind Rear Bumper (2 ft up, 4 ft out); 2 ft up, 2 ft out	0.03 ± 0.02 0.03 ± 0.02	0.04 0.01	0.04 0.02	0.5 0.5
	(6 ft up, 6 ft out); 5 ft 6" up, 2 ft out	0.08 ± 0.02	0.03	0.05	1.5
	(8 ft up, 10 ft out); 8 ft up, 2 ft out	0.12 ± 0.02	0.01	0.06	3.0

^aB.C. refers to the Battery Compartment.

^bError limits ± one standard deviation.

^cNote that sampling positions were not the same during these tests for ANL and NYTL measurements.

^dThe discrepancy between ANL and NYTL values for these samples might be due to a sample mix-up. If the data are transposed, the last column would read 2.3 and 1.4 for the Charge and Discharge samples, respectively.

Table D-2. Comparison of ANL and NYTL Stibine Results from Tests at LILCO with Vehicle²

Operation	Sampling Location	ANL ^a mg SbH ₃ /m ³	NYTL mg SbH ₃ /m ³	Average ANL + NYTL	ANL-Avg. σ_{ANL}
Charge	In-Vehicle	0.02 $\pm$ 0.01	<0.01	<0.02	0
	In B.C. ^b	0.01 $\pm$ 0.01	<0.01	<0.01	0
Equalization Charge	In-Vehicle	0.03 $\pm$ 0.02	<0.01	<0.02	0.5
	In B.C. ^b	1.18 $\pm$ 0.08	1.94	1.56	4.8
Discharge	In-Vehicle	<0.02 $\pm$ 0.02	<0.01	<0.02	0
	In B.C. ^b	0.06 $\pm$ 0.06	0.01	0.04	0.3

^aError limits are $\pm$ one standard deviation.

^bB.C. refers to Battery Compartment.

monitoring data we concluded that significant concentration gradients existed within the areas where sampling was done. Thus we have reason to suspect that the statistical criterion, which considers only the measurement errors associated with each method, may be too stringent in some cases. If the criterion is relaxed somewhat to allow for inherent sampling difficulties, the agreement between all but the two samples that may have been mixed up is judged satisfactory.

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