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# STIBINE/ARSINE EMISSIONS FROM LEAD-ACID BATTERIES

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## INTRODUCTION

Antimonial lead alloys, which also contain some arsenic, have been traditionally used for the fabrication of lead-acid battery electrodes. The addition of antimony and arsenic to the lead is found to improve the metallurgical properties of the grid. Positive grids of lead-acid batteries, currently being developed and evaluated for near term electric vehicle (EV), utility load-leveling, and solar electric applications are expected to be fabricated from antimonial-lead (1.5 to 4.5% Sb plus about 0.0 to 0.3% As) alloys. Negative grids, on the other hand, may well be fabricated from antimony free calcium alloys. However, during cycling of the lead-acid batteries, some of the antimony is solubilized and thereby transfered to the negative electrode.

The lead anode potential may attain levels, more negative, than -0.6V (vs. a Normal Hydrogen Electrode) during charging of lead-acid cells when cell voltages exceed 2.40V. In a theoretical analysis[1], it was reported that lead anode potentials more negative than -.6V vs. NHE may promote stibine generation at the negative electrode of lead-acid cells in which the positive electrode grids are fabricated from antimonial-lead alloys. Thus, stibine and arsine must be considered as possible cell-effluents during charge and equalization of such batteries. This anticipation is confirmed by previous studies by Varma[2] and Yao, and Holland[3]. It was shown that, during charging, stibine and arsine gases can be produced in significant amounts from industrial lead-acid cells having both positive and negative electrode grids of antimonial-lead alloy.

Arsine and stibine are colorless gases with garlic-like odours. Unlike arsine[4], stibine[5] is thermally unstable, reported to decompose[6] in air to the extent of about 50% in 6 to 12 minutes. Despite this thermal instability of stibine, both hydrides may accumulate in atmosphere of poorly ventilated enclosed working areas where the emission rates are high.

Stibine and arsine are toxic gases. Possible poisoning of humans from inhalation is a concern which must be assessed for a variety of work situations and scenerios. Fatalities reported[7] on board a British submarine in 1919 were attributed to poisoning by exposure to stibine in the work-space air. No other injuries from use of lead-acid batteries have been documented in the literture.

Standards have been set for occupational exposure to both stibine and arsine. The Threshold Limit Values - Time Weighted Average (TLV-TWA) represents a limit for average exposure levels experienced by humans in their work places over a period of 8 continuous hours. The National Institute of Occupational Safety and Health (NIOSH) has set these TLV-TWA limits[8] at 0.1 ppmv (or 0.5 mg/m$^3$) for $SbH_3$ and 0.05 ppmv (or 0.2 mg/m$^3$) for $AsH_3$. The American Conference of Government Industrial Hygienists recommends[9] that Short Term Exposure Limits (STEL) be greater than TLV-TWA by a factor of three, for 15 minute exposures, for $AsH_3$.

## STIBINE/ARSINE GENERATION

The study reported by Holland[3] on the generation of stibine and arsine involved experiments on cells of several thousand ampere-hour capacity. The cell-grids were fabricated from alloy compositions containing 8 and 3 percent antimony. Stibine generation was monitored over a 30 month period. A number of conclusions may be drawn from this study: (1) Stibine generation took place at cell voltage greater than 2.45 V, most of the emissions were limited to the overcharge period, (2) Stibine generation rates were observed to be higher with the grids having the higher antimony content and, (3) Stibine generation rates remained substantially unchanged during the entire 2.5 years of testing.

Argonne National Laboratory (ANL) has an on-going program of research on lead-acid batteries. A study[2] was completed on the generation of stibine and arsine from a large 4.2 kWh industrial lead-acid cell (2250 A-h capacity at 5-h rate) for a utility load-leveling duty cycle. Both positive and negative grids contained antimony and arsenic. The stibine and arsine generated during charging were absorbed in tubes containing 3N $H_2SO_4$ with kI and $I_2$ dissolved in it. The antimony and arsenic contents of the absorbate solution were determined by colorimetry and atomic absorption spectrophotometry (AAS) respectively. The total emission of stibine and arsine as well as their generation rate profiles were determined for experiments in which the cell would, each week, undergo, four normal charge-discharge cycles followed by an equalization-type of cycle. A number of conclusions may be drawn from results obtained in the study. The rates of stibine and arsine generation from the lead-acid cell, could be reduced to insignificant amounts if the voltage during charge and equalization charge-cycles were kept below 2.40 V. Generation rates of stibine and arsine were found to be most significant during the overcharge period of the charge cycle and even higher during equalization charging, which was conducted at 2.55 and 2.65 V, no emissions were observed from the lead-acid cell during stand or discharge, (the study by Holland[3] supports this finding). A typical stibine/arsine generation profile during a typical charge cycle is shown in Figure 1. A brief summary of hydride emission data obtained on a lead acid cell is given in Table 1.

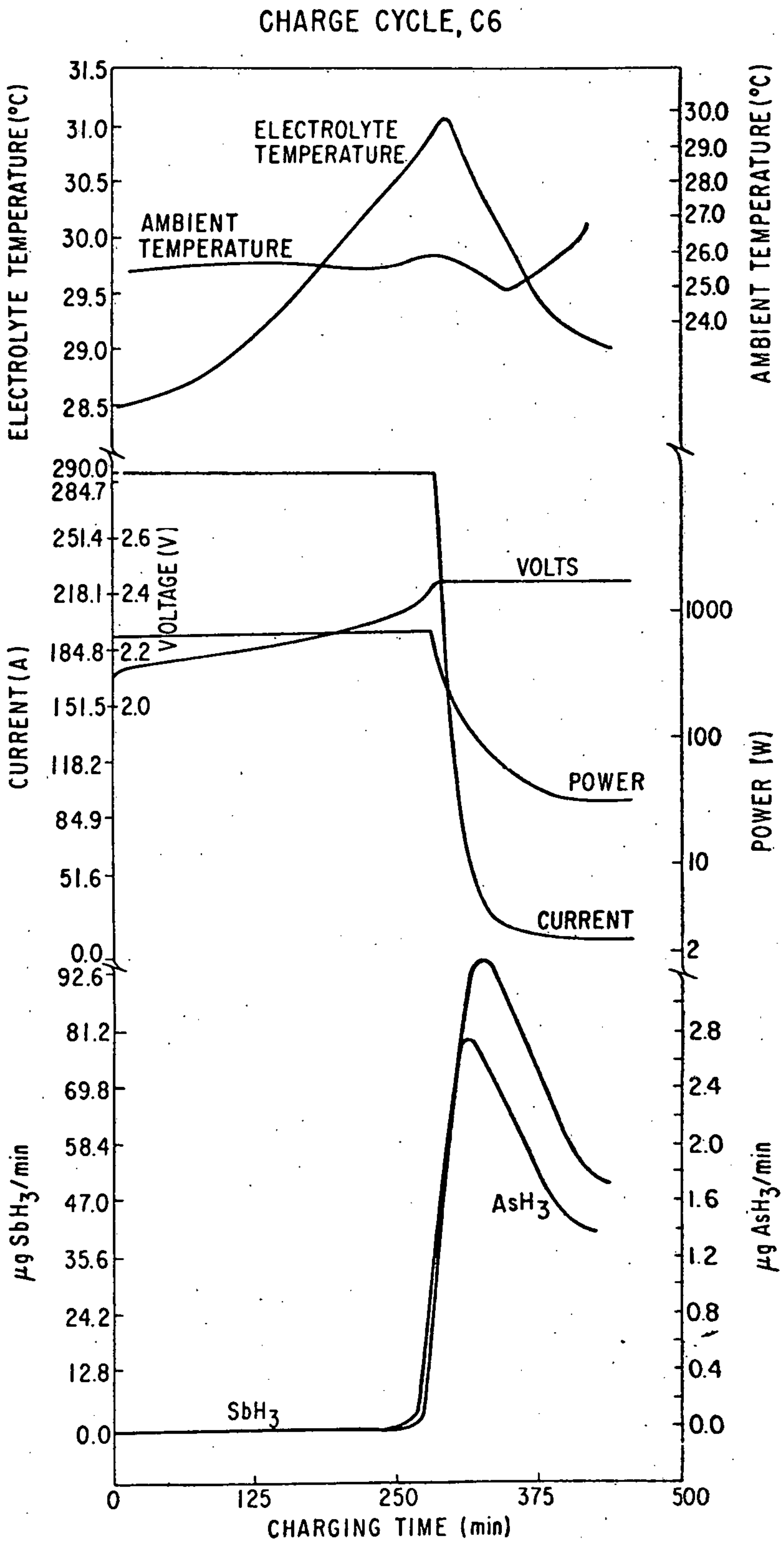

Figure 1. Stibine/Arsine Generation From a Lead-Acid Cell During a Charge Cycle

## PUBLISHED ANALYTICAL PROCEDURES FOR DETERMINATIONS OF STIBINE AND ARSINE

The few methods that have been described for the direct determination of stibine and arsine in air are based upon the use of impregnated paper, indicator tubes and absorption in chemically reacting solutions followed by colorimetric or AAS determination of the hydrides.

The production of colored stains is the principle behind commercially available arsine detector tube-kits. The Kitagawa* and Draeger+ detector kits, claims a detection sensitivity for $AsH_3$ over levels .05 to 160 ppm in air and the arsine/phosphene electronic monitor*, claims a detection sensitivity of 0.005 to 0.2 ppmv $AsH_3$ during sampling of 10L of air.

Table 1. Stibine and Arsine Generation From a 4.2 kWh (2250 A-h at 5-hr Rate to 1.75V) Lead-Acid Cell

| | Total Generation[c] mg | |
|---|---|---|
| Experiment | $SbH_3$ | $AsH_3$ |
| Charge Cycle[a] | 12.1 ± 1.4 | 0.33 ± 0.06 |
| Equalization[b] | | |
| 2.55 V | 25.5 ± 0.7 | 0.23 ± .01 |
| 2.65 V | 63.1 ± .05 | 0.33 ± .01 |

a. The 4.2 kWh (2250 A-hr at 5-hr rate) cell was discharged for 5 hr at constant current to 80% DOD and charged at constant (290A) current for 5-6 hrs to 2.45 V, followed by a current limited constant-voltage (tapering) charge at 2.45 V for 3 hr.

b. The fully charged cell was given an additional 4-hr charge at constant voltage.

c. The values given are the average for several cycles.

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*Distributed by Matheson Gas Products Co., East Rutherford, N.J.

+Distributed by National Draeger Company

Both use the reaction of mercuric halides $HgX_2$ (X = Br, CL) with $AsH_3$ in the presence of moisture, which leads to the formation of colored stains. The reaction products are yellow or brown. This reaction is far less sensitive to stibine than arsine, therefore, it would be more expensive to develop solid-state colorimetric procedures for monitoring stibine based on the reaction.

Stibine in air can be absorbed in a solution of methylfluorone in an aqueous silver sulfate solution to form a colored solution. Short and Wheatly[10] developed instrumentation based on this analytical procedure for monitoring $SbH_3$ in ambient air on board British Admiralty ships in the 1960's. The disadvantages of the procedure are the chemical instability and carcinogenic property of methylfluorone.

A solution of $NaI_3$ ($NaI + I_2$) in $HClO_4$ solution was successfully used by Gann[11] to collect stibine and arsine from the charge gas of lead-acid batteries. However, the use of $HClO_4$ requires special handling procedures because of the potential fire and explosion hazard.

## SAMFK DESIGNS, FUNCTIONS AND TESTING

A Stibine/Arsine Monitoring Field Kit (SAMFK) was developed at ANL for the field collection and evaluation of the extent of $SbH_3$ and $AsH_3$ release. It has been used for monitoring these gases from cells under charge and in the ambient air near lead acid batteries.

The kit (See Figure 2) consists of a $SbH_3/AsH_3$ collection train, a Bendix Model BDX-56 Air Sampler Metering Pump, universal battery cap connectors and a hand held Bausch and Lomb Spectronic mini-20 spectrophotometer. The SAMFK was designed for collection of $SbH_3$ and $AsH_3$ gases directly from battery charge gas or ambient air and to permit on-site spectrophotometric determination of antimony in the absorber solution. The absorber solution is 3N $H_2SO_4$ containing 8% KI and 1% $I_2$.

In the Battery Charge Gas Sampling Mode (See Figure 3) an appropriate battery cap connector is affixed to the watering hole of the lead-acid cell with the outlet tube of the cap connected to the gas inlet port of the kit. Air, under the action of the pump, is sucked through the cell-space above the moss plate, carrying with it the charge gases, the contaminated air is then bubbled through a 50 or 100 mL aliquot of absorber solution in the bottle labeled B001.

Ambient air can be sampled by the SAMFK (See Figure 3) at rates of 1 - 2 L per minute. The collecting of $SbH_3$ and $AsH_3$ is by a similar operation except that the battery cap is not used and air is admitted directly at the kit inlet port.

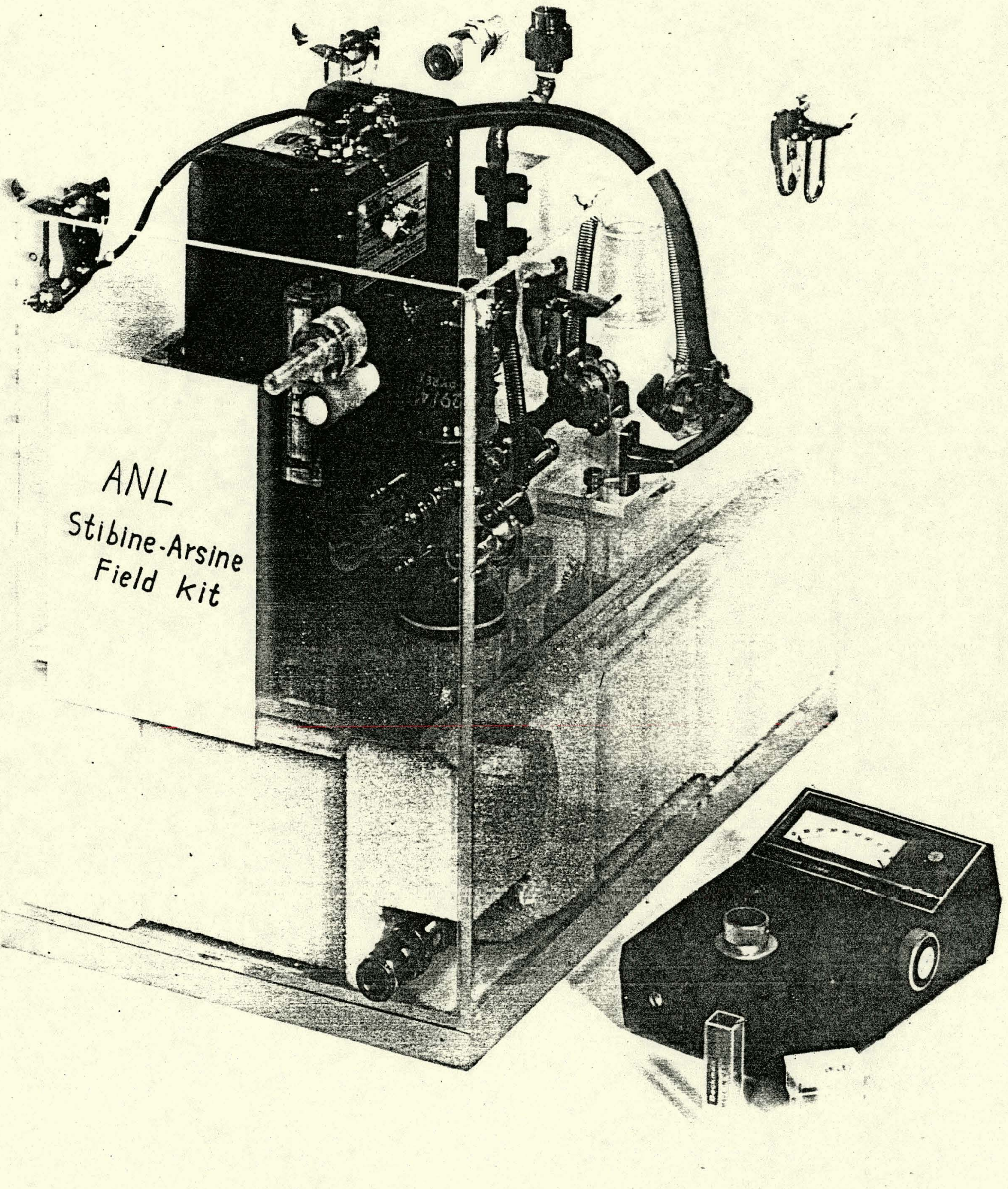

Figure 2. Stibine/Arsine Monitoring Field Kit (SAMFK).

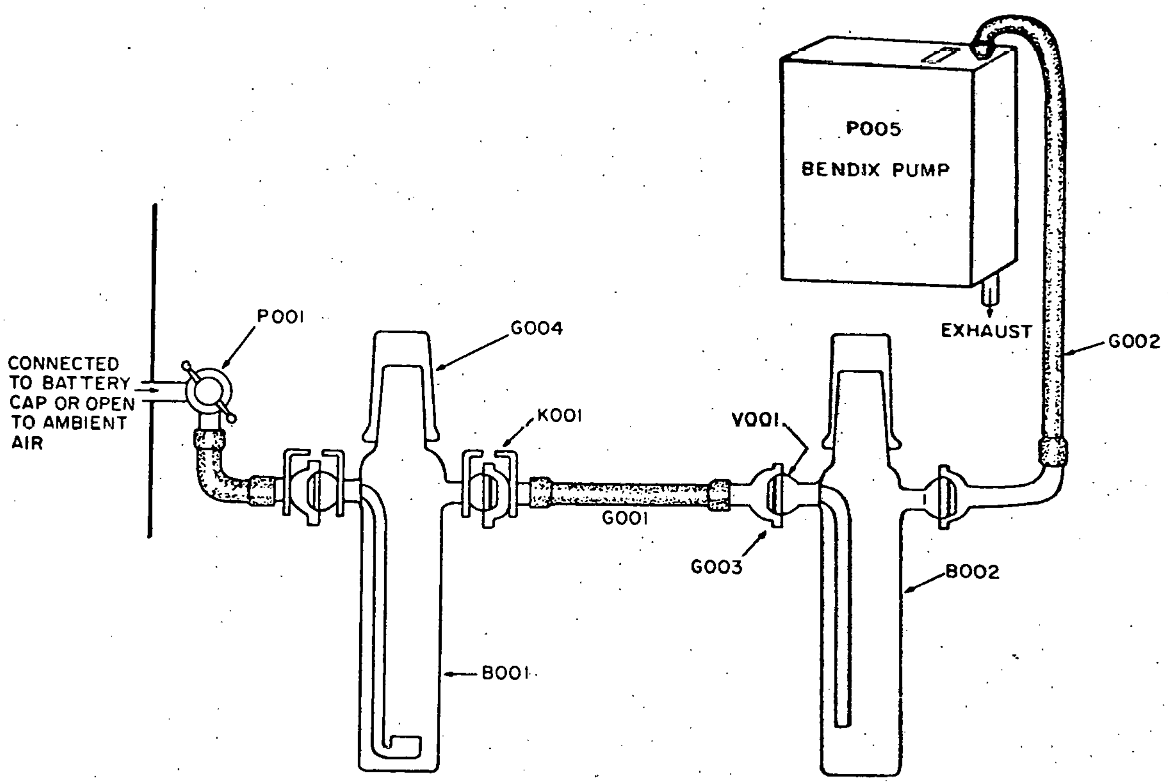

Figure 3. Ambient Air and Battery Charge Gas Sampling Modes of the SAMFK.

For on-site determination of antimony in the absorber solution, an aliquot of the solution is treated with $H_3PO_3$ and $H_2SO_4$. The absorbance of the resulting solution is determined at 425 nm with the hand held spectrophotometer. Precalibration curves are used for converting the observed absorbance values into ppmv of $SbH_3$. The arsenic content of the absorber solution is measured by an AAS procedure at an Analytical Chemistry Laboratory.

Two experiments were performed to assess the reliability of the mini-20 spectrophotometer for field measurements. In the first experiment, the absorbances of three absorber solutions containing known amounts of antimony were measured with the mini-20. The calibration curve was used to redetermine the antimony contents of the three solutions. The known and calculated values are shown in Table 2. In the second experiment ten solutions (total antimony of 7.6 to 18.6 $\mu$g/ml) were analyzed by both the mini-20 and a laboratory Cary-16 spectrophotometer. The ratio of the two determinations was .953 ± .047, with one set of measurements responsible for about 90% of the error.

Table 2. Antimony Content of Three Known Solutions

|  | Antimony Content, $\mu$g/mL |  |  |
|---|---|---|---|
| Sample Number | Known Value | Determined using mini-20 Spectrophotometer | % Difference |
| 1 | 10.6 | 10.0 | 6.4 |
| 2 | 13.5 | 13.6 | 1 |
| 3 | 22.8 | 24.1 | 5.8 |

## CONTROLLING EMISSIONS: USE OF HYDROGEN-OXYGEN RECOMBINATION DEVICE (HORD)

Design features for Hydrogen-Oxygen Recombination Devices (HORD), for use in conjunction with load leveling lead-acid cells, have been developed by VARTA A.G. under a subcontract with ANL. Further, a 435 W HORD (See Figure 4) has been fabricated and tested. Functionally the HORD can recombine stoichiometric $H_2$-$O_2$ with about 97% efficiency while scavenging the charge gas of much of the $SbH_3$ and $AsH_3$ content. The activated charcoal cartridge, the scavenging component of the HORD has been tested for its efficiency in removing $SbH_3$ and $AsH_3$ from battery off-gases.

# Principle of 435W-Recombination Device

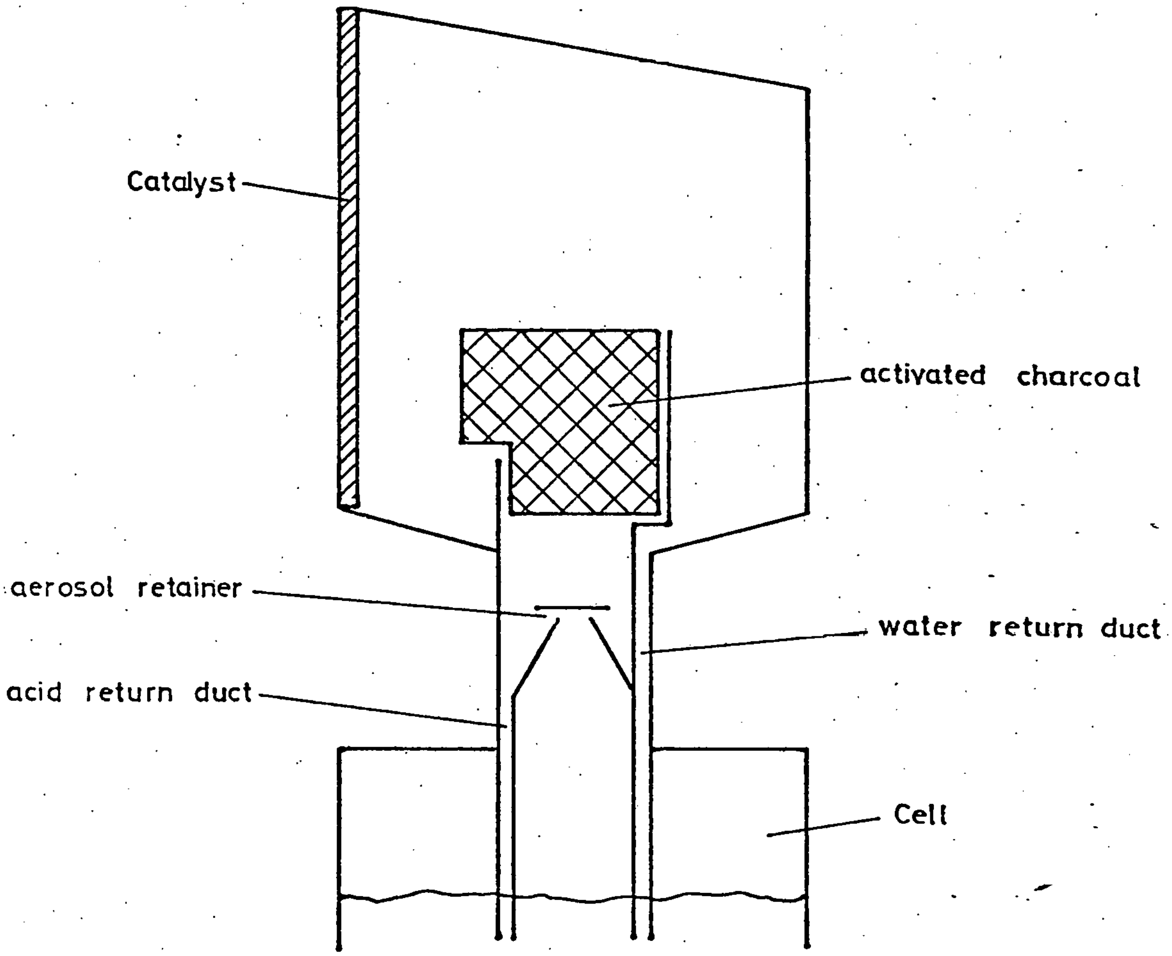

Figure 4.

## ON-GOING TESTS FOR ELECTRIC VEHICLE DEMONSTRATION PROGRAM OF THE DEPARTMENT OF ENERGY

The SAMFK developed at ANL is being used for collecting $SbH_3$ and $AsH_3$ from EV battery-off gases and from ambient-air during the charging of lead-acid batteries. Analytical procedures detailed previously[2] will be used for determination of antimony and arsenic in the absorber solution.

The experiments[12], currently under way, are designed to estimate the driver and maintenance personnel exposures to be expected from batteries used in electric vehicles. Data for in-vehicle, in-garage, and on-the road conditions are being collected. The information is expected to assure the continued safe use of lead-acid batteries in electric vehicles.

## ACKNOWLEDGEMENT

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