American Industrial Hygiene Association Journal

ISSN: 0002-8894 (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/aiha20

Measurement of Multiple Inorganic Arsenic Species

RICHARD J. COSTELLO , PETER M. ELLER & R. DELON HULL

To cite this article: RICHARD J. COSTELLO , PETER M. ELLER & R. DELON HULL (1983) Measurement of Multiple Inorganic Arsenic Species, American Industrial Hygiene Association Journal, 44:1, 21-28, DOI: 10.1080/15298668391404301

To link to this article: https://doi.org/10.1080/15298668391404301

Am. Ind. Hyg. Assoc. J. 44(1):21-28 (1983)

Measurement of Multiple Inorganic Arsenic Species

RICHARD J. COSTELLO, PETER M. ELLER and R. DELON HULL
National Institute for Occupational Safety and Health, Cincinnati, OH 45226

While multiple species of inorganic arsenic can coexist in industrial environments, traditional air sampling methods and analysis by atomic absorption spectrometry quantify only total inorganic arsenic. The National Institute for Occupational Safety and Health (NIOSH) recently conducted laboratory experiments and field studies to develop a technique to separate mixtures of particulate inorganic arsenic compounds and arsine, and to detect and quantify arsenic trioxide vapor. A field study in a lead-acid battery manufacturing plant showed airborne particulate arsenic in Post Burn, Element Battery Repair, and Salvage and Remelt operations; measured widespread low levels of arsine; and suggested that both particulate arsenic and arsine were transported between work areas by in-plant air currents. Arsenic trioxide vapor contributed to the total airborne arsenic collected and was most prevalent in torching or welding areas. This finding suggests that, in the presence of heated arsenic sources, monitoring solely with conventional filters will underestimate arsenic exposure, because arsenic trioxide vapor is not efficiently collected.

Introduction

Arsenic is added as a minor (0.5-0.7 wt %) component of the grids or structural elements of lead-acid batteries to inhibit grid growth in overcharge and to reduce positive grid corrosion.(1) Inorganic arsenic compounds in particulate form, arsenic trioxide vapor, and arsine are possible workplace contaminants during the lead-acid battery manufacturing process and may coexist. Particulate arsenic compounds are found in torching or welding and scrap reclamation operations; arsenic trioxide vapor around hot sources such as welding torches; and arsine in the battery forming and boosting processes, where arsenic is in contact with nascent hydrogen.

Traditional air sampling methods and analysis by atomic absorption spectrometry do not distinguish the inorganic arsenic species collected. Previous investigators have pointed out that traditional filter samplers have low collection efficiencies for arsenic trioxide vapor and that, when this substance is present, quantitative results which neglect filter collection efficiencies are meaningless.(2) In this study, we developed a technique to separate mixtures of particulate inorganic arsenic and arsine, and to detect and quantitate arsenic trioxide vapor. Our findings suggest that, in the presence of heated arsenic sources, monitoring solely with conventional filters will underestimate arsenic exposure, because arsenic trioxide is not efficiently collected.

Background

If particulate inorganic arsenic and arsine coexist in air samples, previously validated NIOSH sampling methods,(3,4) which utilize 37 mm cellulose ester filters for particulate arsenic collection and charcoal tubes for arsine, could produce erroneous results because charcoal tubes can collect small amounts of particulate arsenic which would be interpreted as arsine. A sampling train combining the standard 37 mm cellulose ester filter and the charcoal tube in series would prevent particulate arsenic from reaching the charcoal tube; however, there is no acceptable flow rate for this system. If it is operated at the lower flow rates typically used with charcoal tubes, there is potential bias of particulate samples;(5) and if it is operated at the higher flow rates typical of filter operation, there is potential blow-by and breakthrough in the charcoal tube.

An alternative method for measurement of arsenic in air is the sampling train patterned after the design of Hill and Arnold who developed it for pesticide sampling.(6) This sampling train consists of a 1.2 mm inlet orifice, a 13 mm cellulose ester filter without backup pad, and a standard 150 mg charcoal tube (Figure 1). Air is drawn through the inlet, the filter, and the charcoal tube at 0.2 liter per minute. This flow rate is calculated to give the same cassette inlet velocity and filter face velocity as a 37 mm filter operating at 2 liters per minute. This system was selected for segregation of particulate arsenic and arsine. Experiments were devised to evaluate whether or not the 13 mm filter/charcoal tube system and the standard 37 mm filter were equivalent for particulate arsenic collection and to determine whether arsine was collected on the filters.

The CARB and 37 mm cellulose ester membrane filters were found to be essentially 0% efficient collectors of arsine in this work and quantitative collectors of particulate arsenic.(3,7) The treated filters, referred to as "CARB" filters in this paper, are prepared by adding 0.3 mL of 9:1 1*M* Na_2CO_3: glycerol solution to a conventional cellulose ester filter.(7) The equivalence of the particulate and arsine collection characteristics of 13 mm and 37 mm cellulose ester membrane filters was demonstrated in this work. Charcoal tubes were quantitative collectors of arsine and arsenic trioxide vapor.(4,8)

Arsenic trioxide can exist in both particulate and vapor phases at ordinary room temperatures. The equilibrium

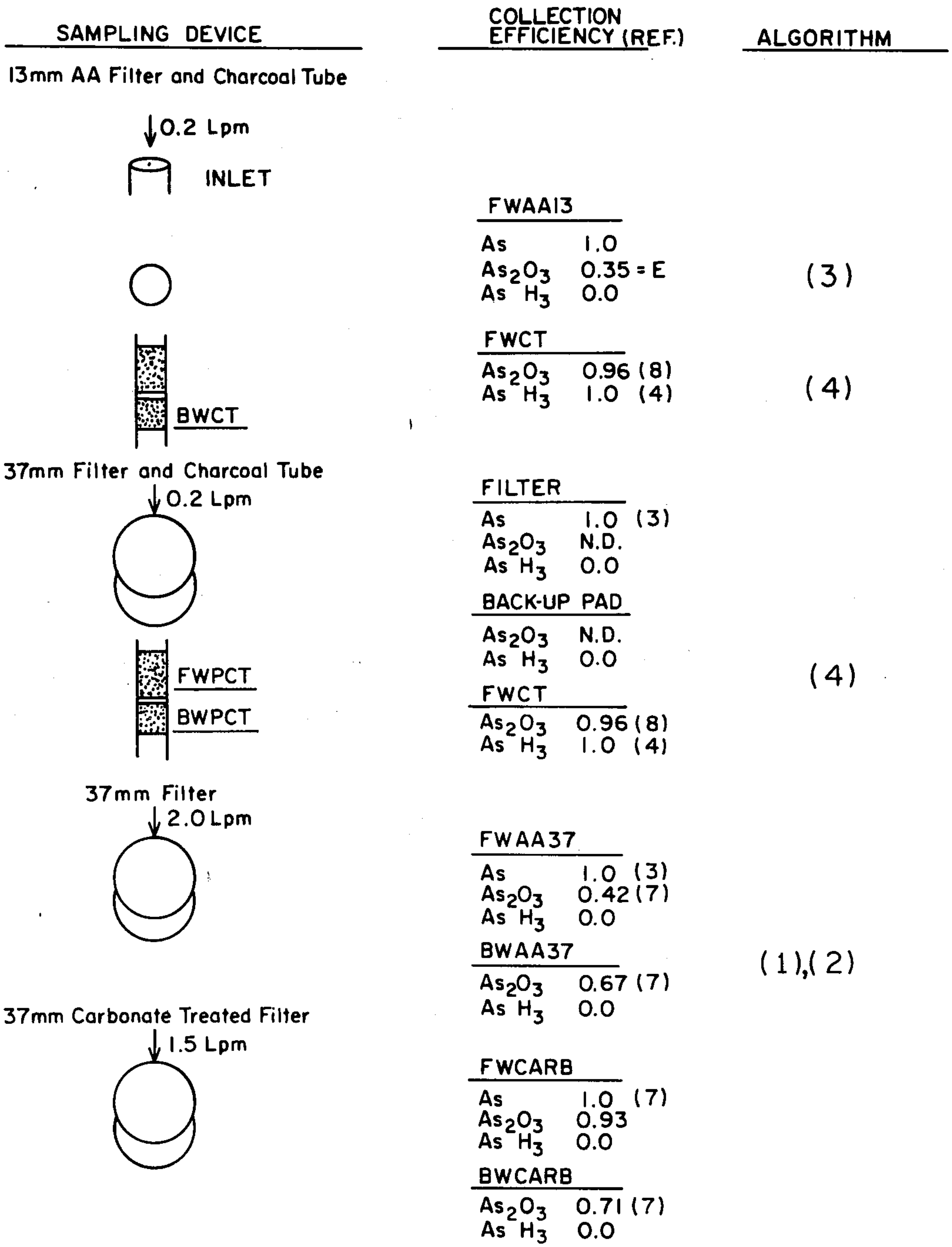

Figure 1 — Field study: devices, nomenclature, collection efficiencies, and algorithms. N.D. means not determined. The collection efficiencies assume that 1.0 units of a species enter the sampling device. For the AA37 filter, 0.42 units are collected on the filter, 0.39 on the backup pad, and 0.19 units escape. The collection efficiency of the backup pad is equal to 0.39 divided by 0.58, (the sum of 0.39 and 0.19), or 0.67. The corresponding fractions for the CARB filter are 0.93, 0.05, and 0.02. If no reference is given, the collection efficiency was determined in this work. "As_2O_3" means arsenic trioxide vapor (V); "As" means particulate arsenic (P); and "AsH_3" means arsine (A).

vapor pressure of arsenic trioxide is strongly influenced by temperature. It can exist in significant concentrations at the melting point of lead, 327.5 °C. Arsenic trioxide vapor would be an anticipated contaminant in workroom air during torching or welding operations (Table I). Table I presents calculated equilibrium arsenic concentrations due to arsenic trioxide vapor.[2,9]

Arsenic trioxide in vapor phase can be collected on a 0.8 μm cellulose ester filter with 42% efficiency,[7] on a conventional cellulose filter back up with 67% efficiency,[7] or a charcoal tube with 100% efficiency.[8] Previous investigators have shown that pretreatment of cellulose ester filters with sodium carbonate and glycerol allowed 98% collection of arsenic trioxide vapor, 93% on the filter, and 71% of the

TABLE I
Properties of Arsenic Trioxide

Temperature °C	Equilibrium Arsenic Concentration in Vapor Phase $\mu g/m^3$	Reference
25	4.5×10^{-1}	(2)
30	9.5×10^{-1}	(2)
35	2.0	(2)
40	4.0	(2)
50	1.56×10^{1}	(2)
100	1.4×10^{3}	(9)
200	2.8×10^{6}	(9)
300	1.3×10^{8}	(9)
350	4.9×10^{8}	(9)

In the battery plant, the assumed source of arsenic trioxide vapor was torching or welding operations. Some of this vapor could condense forming a fume which then coexists with the vapor phase. When it is collected on a filter in a battery plant environment, arsenic trioxide fume would ordinarily be interpreted as particulate arsenic; when collected on the backup pad, arsenic trioxide vapor would not be analyzed in routine samples; and when collected on charbalance on the backup pad.(7) The preparation of the treated filters, referred to as "CARB" filters in this paper, is described in Volume 7 of the NIOSH Manual of Analytical Methods.(10)

coal tubes, arsenic trioxide vapor would be interpreted as arsine.

Algorithms based on the known capture efficiencies of the sampling train components can resolve the weight of arsenic collected into weights of particulate arsenic, arsine, and arsenic trioxide vapor. In the field, 4 different sampling trains were used (Figure 1). Arsenic was measured with atomic absorption spectrometry. Algorthims were used to resolve the arsenic species.

Experimental

Exposure chamber experiments were conducted to compare the particulate arsenic collection characteristics of the standard device, a 37 mm Millipore AAWP filter (AA37) with the 13 mm filter/charcoal tube system. In the particulate aerosol generator, a stream of filtered air was split and used to operate a nebulizer (Retec, Portland, OR) and to act as the diluent. Aqueous solutions of sodium arsenite were used to generate the aerosol in the nebulizer. The aerosol was passed from the nebulizer through a charge neutralizer (TSI Inc., St. Paul, MN) and into the exposure chamber. The aerosol was forced to mix with the dilution air and was passed through a flow straightener before being sampled. The air flow rates through the sampling tubes were controlled by critical orifices. Particulates were also continuously monitored with an optical particle counter (Climet

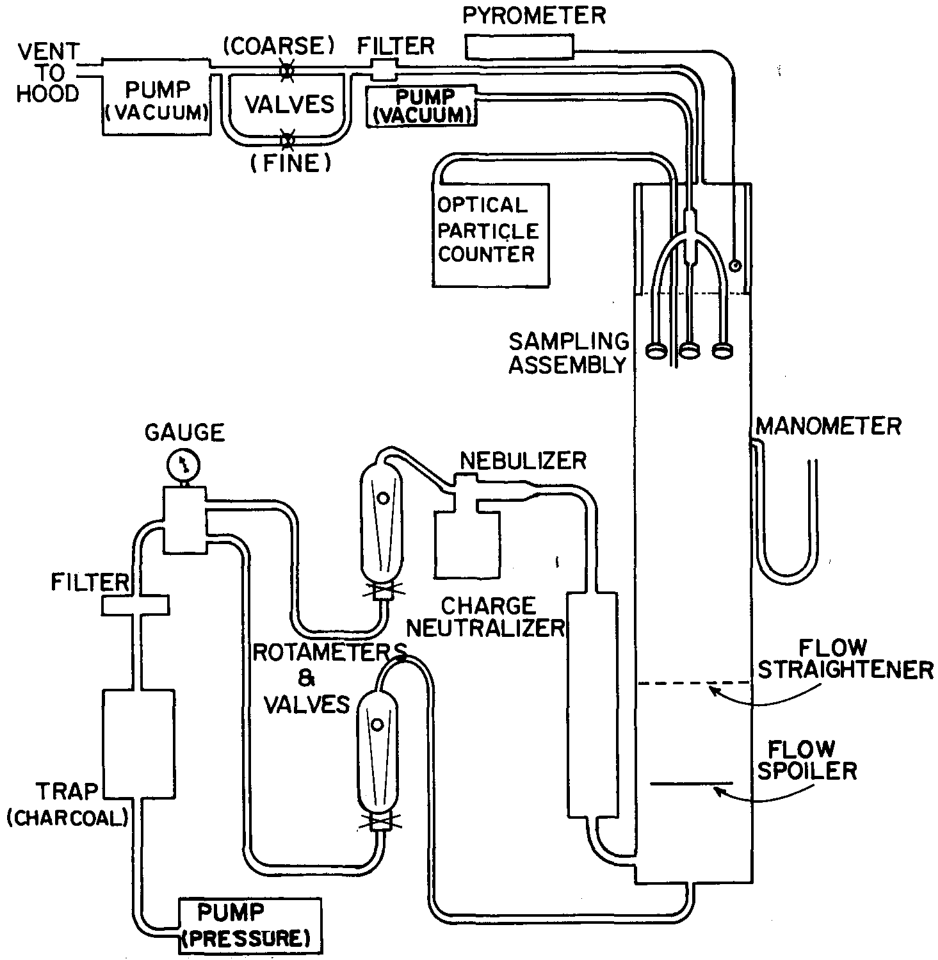

Figure 2 — Laboratory particulate arsenic generation and sampling equipment.

TABLE II
Comparison of Filter Digestion Methods

Method	Number of Analyses	% Recovery		% Relative Standard Deviation
		Mean	Standard Deviation	
Wet Ashing with 0.1% HNO_3/H_2O_2	6	101.8	28.5	28.0
Wet Ashing with 0.1% HNO_3/H_2O_2 and Ultrasonic Dissolution	6	90.6	7.8	8.6
NIOSH Method S309 Wet Ashing with ($HNO_3/HClO_4$)	6	55.7	10.4	18.6

Instruments, Redbud, CA) to give a size estimate and particle count for each size. Because of the nebulizer used, essentially all particles were smaller than 3 μm. A thermocouple was used to monitor the temperature in the system (Figure 2). Four samplers of each type were simultaneously exposed to sodium arsenite ($NaAsO_2$) aerosol. A Perkin-Elmer Model 603 atomic absorption spectrophotometer with AS-1 autosampler and HGA-2100 graphite furnace was used for arsenic analyses.(3)

A modification of the sample treatment described in NIOSH Method S309(3) was developed because Method S309 was found to give low recoveries at 0.25 μg of arsenic per sample. This modified procedure, which included wet ashing of the filter or backup pad with concentrated nitric acid (5 mL per filter and 10 mL per backup pad) and 30% hydrogen peroxide (2 mL per filter and 4 mL per backup pad) on a hot plate, ultrasonic dissolution of the ash in the presence of 1000 μg per milliliter of nickel as $NiNO_3$, precautionary rinsing of the inside surfaces of the filter cassettes, and analysis of the rinse for arsenic, gave quantitative arsenic recoveries (Table 2). There was no significant difference between the particulate collection characteristics of the 13 mm filter/charcoal tube system and the AA37 filter (i.e., collection efficiency was 1.0; Figure 1).

Experiments were conducted to determine whether arsine (AsH_3) was collected on the cellulose ester filters. Atmospheres of 0.1 to 0.2 mg of arsine per cubic meter were generated by preparing a stock gas mixture of 10 ppm arsine in hydrogen by sodium borohydride reduction of a sodium arsenite solution in a carrier stream of hydrogen. The stock mixture was diluted with air, metered into the sampling chamber, and concurrently sampled through 12 critical orifice-controlled ports. In each run, there were six charcoal tube controls for the six 13 mm Millipore AAWP (AA13)

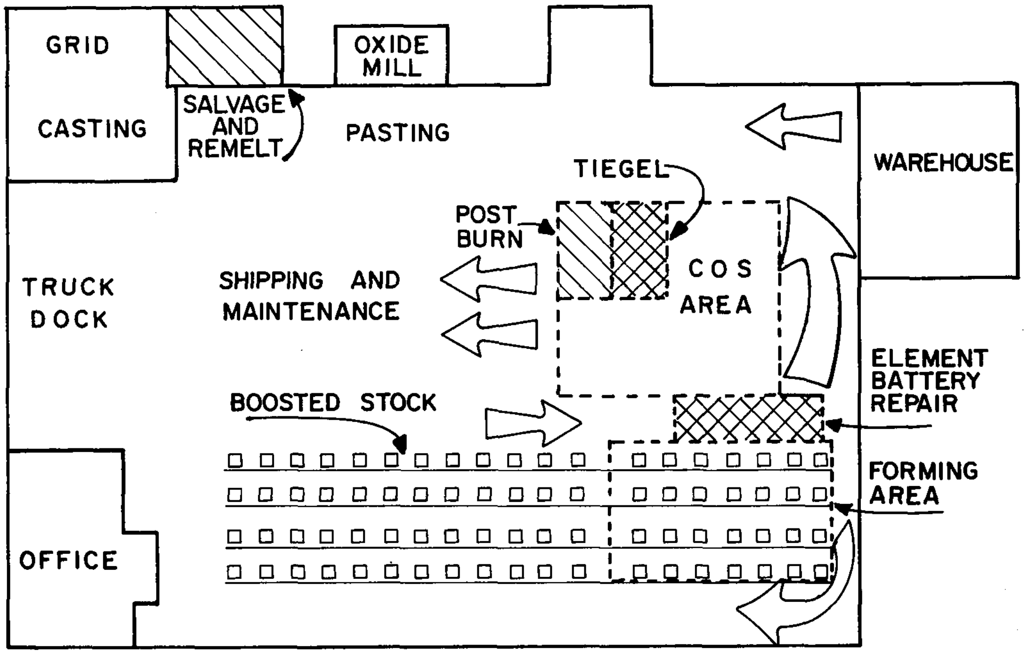

Figure 3 — Floor plan. Diagonal striping indicates sources of particulate arsenic. Cross hatching indicates sources of particulate arsenic and a suspected source of arsenic trioxide. Small squares indicate sources of arsine. The heavy arrows show the direction of air movement demonstrated by smoke candles.

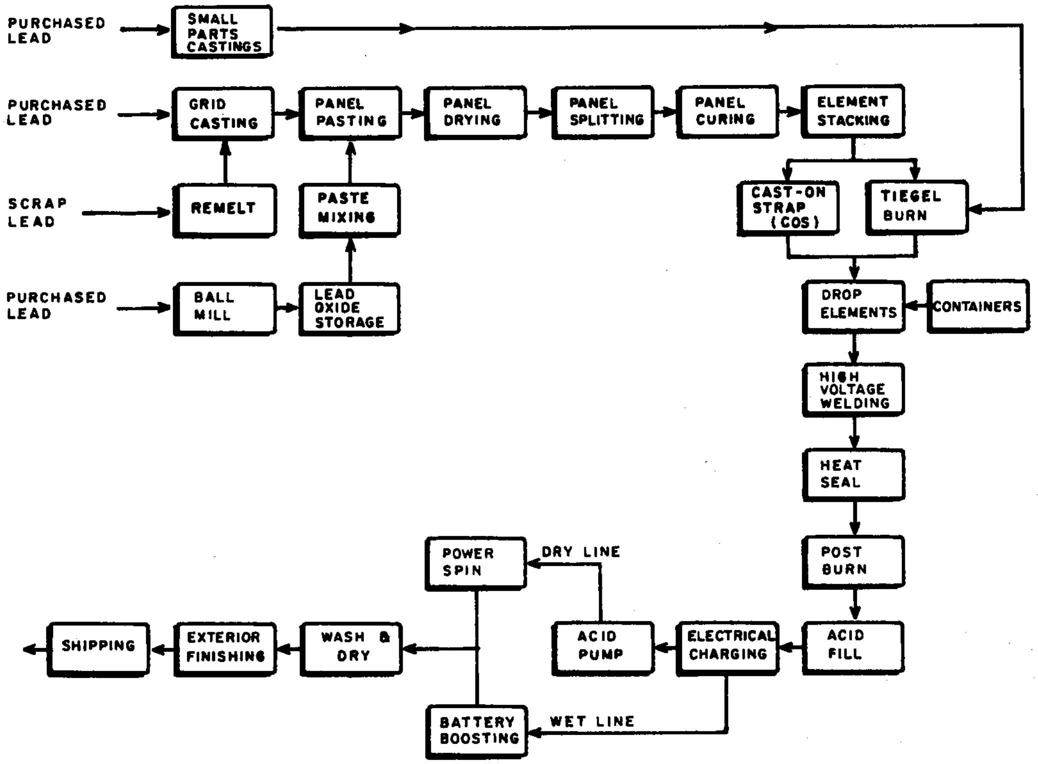

Figure 4 — Process description. In Salvage and Remelt, scrap lead is fed into a melt furnace. Melted lead is poured into pigs. The furnace is drossed to remove impurities. In Tiegel, cured plates are blocked on a tamping box, interleaved with separators, and assembled into groups. The operator forms elements by burning (torching) on small parts. In Post Burning, those batteries which do not have side-mounted connections have molds placed in the top and molten lead poured to form posts. In Formation, batteries are connected to a source of electric current for 18 to 24 hours and the initial electrochemical reactions, which convert inert pastes into active plates, are induced. In Boosted Stock, those batteries which are to be shipped wet (filled with electrolyte) are electrically charged. In Element Battery Repair, batteries with correctable defects are refurbished. Oxygen/acetylene torching is frequently used.

filters or six 37 mm AA37 filters. All samples were analyzed according to method S229.[4] No measurable arsine was collected on any of the filters.

Field Study

The battery manufacturing plant studied has been in operation since 1965 and occupies 140,000 square feet (Figure 3). Two hundred workers were employed on three shifts. The unit processes included casting structural elements (grids), coating the grids with pastes to form plates, interleaving the positive and negative plates to form cells, connecting the cells electrically, sinking the cells into the battery case, filling the case with electrolyte, inducing electrochemical reactions to convert the inert pastes into active plates (forming), and packaging and shipping the product (Figure 4).

Flow rate-controlled personal sampling pumps drew air through four sampling trains (Figure 1) positioned side-by-side at six fixed locations: Boosted Stock, Element Battery Repair, Forming, Post Burning, Salvage and Remelt, and Tiegel. Nuclepore filter samples were collected at the same sites for microscopic analysis. Particulate arsenic had been demonstrated in Element Battery Repair, Post Burning, Salvage and Remelt, and Tiegel areas in an earlier study.[11] Torching operations in the Element Battery Repair and Tiegel areas were suspected sources of arsenic trioxide vapor. The forming process generated arsine[11] and the Boosted Stock area was a suspected arsine source. Element Battery Repair was located immediately adjacent to the Forming Area and Boosted Stock (Figure 3).

Full-shift samples were collected during 4 consecutive days. The front and back-sections of each charcoal tube and the filter and backup pad of each cassette were analyzed separately. There were 49 sample sets. Filters and backup pads were analyzed by NIOSH Method S309 with modified sample treatment as described above.

Individual particles collected on Nuclepore filters were examined by scanning electron microscopy to determine their size. Many were spherical and their median circular area equivalent diameter was less than 1 μm (Figure 5). The spherical shape of the particles is indicative of a fume. Single particle X-ray fluorescence showed that the major elements in the particles were, in order of decreasing frequency of occurrence, lead, silicon, sodium, iron, and antimony.[12] Arsenic was not detectable. This indicates that the arsenic concentration in the particles analyzed was less than 1% of the total mass. Lead and antimony are constituents of battery grids.[11] Iron is frequently detected in the air near moving machinery. Silicon may be due to abrasion of the con-

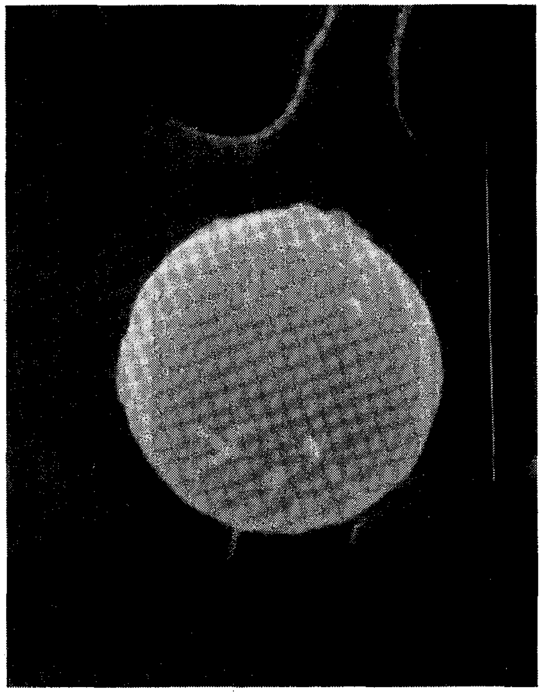

Figure 5 — Scanning electron photomicrograph, 35,000X. Fume collected in Boosted Stock area on a 0.6 μm Nuclepore filter. The marker line equals 1.5 μm.

crete floor in the plant. Sodium compounds are ubiquitous, but may be due to the use of Na_2CO_3 to neutralize acid spills or NaCl for ice control in winter.

In-plant airflow patterns were observed by noting the movement of artificial clouds generated by smoke candles. Air moved from Boosted Stock through the Element Battery Repair and Formation Areas from west to east (Figure 3). The air stream divided at the eastern plant wall: one branch moved north for a short distance and then turned westward, and the other turned south and then westward. The air flow patterns were consistent with the widespread low levels of arsine and also suggest that particulate arsenic is transported from Element Battery Repair to the Forming area, where there is no known source of particulate arsenic (Figure 3).

Algorithm Development

The results of this study and previously reported collection efficiencies studies were used to develop equations, using the nomenclature defined in Figure 1, to estimate the true concentrations of particulate arsenic (P), arsenic trioxide vapor (V), and arsine (A), in units of micrograms of arsenic per cubic meter. The equations were used to calculate the concentration of each species in six areas of the battery plant from field data (Table 3).

In deriving estimates of arsenic trioxide vapor concentrations for each area sampled, it was known that AA37 filters were 100% efficient collectors of particulate arsenic and 0% efficient collectors of arsine (Figure 1). An AA37 filter collects about 42% of the arsenic trioxide vapor in the airstream, and its backup pad collects about 39%.(7) Any arsenic found on the AA37 backup pads (BWAA37, as μg of arsenic) was assumed to have been collected as arsenic trioxide vapor. These relationships can be expressed as:

$$V = \frac{\text{BWAA37}}{(0.39)\ (\text{AA37VOL})} \tag{1}$$

where AA37VOL is the volume, in cubic meters, of the AA37 air sample.

Arsenic trioxide vapor is collected on the front of the CARB filter (FWCARB, as μg of arsenic) and on the front of the AA37 filter (FWAA37, as μg of arsenic) with efficiencies of 93% and 42%, respectively. The particulate arsenic concentration was calculated by averaging the total concentration of arsenic collected on FWAA37 and FWCARB and

TABLE III
Arsenic Species by Plant Area

Parameter	Determined By	Boosted Stock	Element Battery Repair	Forming	Post Burn	Salvage and Remelt	Tiegel
	All Values, Except Ratios, are in μg/m³ of Arsenic. Standard Deviations are in Parentheses.						
		N = 10	N = 3	N = 11	N = 7	N = 11	N = 7
Arsenic Trioxide Vapor							
V	Calculation	<0.02	0.36 (0.06)	0.11 (0.07)	0.18 (0.14)	0.07 (0.12)	0.06 (0.07)
V/CARB	*Ratio*	---	0.52 (0.07)	0.76 (0.40)	0.33 (0.40)	0.25 (0.29)	0.91 (0.88)
Particulate Arsenic							
AA37	Measurement	0.02 (0.02)	0.57 (0.13)	0.13 (0.16)	0.57 (0.46)	0.39 (0.35)	0.06 (0.06)
AA13	Measurement	<0.08	0.42 (0.10)	0.06 (0.08)	0.47 (0.32)	0.15 (0.19)	<0.08
CARB	Measurement	0.03 (0.03)	0.69 (0.06)	0.14 (0.08)	1.25 (1.32)	0.48 (0.64)	0.07 (0.07)
P	Calculation	0.03 (0.02)	0.30 (0.07)	0.07 (0.10)	0.60 (0.52)	0.37 (0.32)	0.04 (0.06)
AA37CORR	Calculation	0.01 (0.02)	0.28 (0.13)	0.06 (0.15)	0.37 (0.44)	0.28 (0.30)	0.02 (0.04)
AA13CORR	Calculation	<0.04	0.29 (0.10)	0.04 (0.07)	0.41 (0.30)	0.14 (0.19)	<0.04
CARBCORR	Calculation	0.02 (0.02)	0.32 (0.09)	0.05 (0.06)	1.07 (1.32)	0.41 (0.63)	0.04 (0.05)
FWAA37/(FW+BW) AA37	Ratio	1.0 (0.0)	0.75 (0.04)	0.70 (0.19)	0.84 (0.11)	0.97 (0.05)	0.76 (0.28)
FWCARB/(FW+BW) CARB	Ratio	1.0 (0.0)	0.93 (0.02)	1.0 (0.0)	0.95 (0.05)	0.99 (0.02)	1.0 (0.0)
Arsine							
CT	Measurement	6.3 (3.4)	40 (4)	41 (33)	2.1 (1.1)	0.33 (0.62)	0.69 (0.52)
A	Calculation	6.3 (3.4)	40 (4)	41 (33)	2.0 (1.0)	0.32 (0.62)	0.58 (0.57)

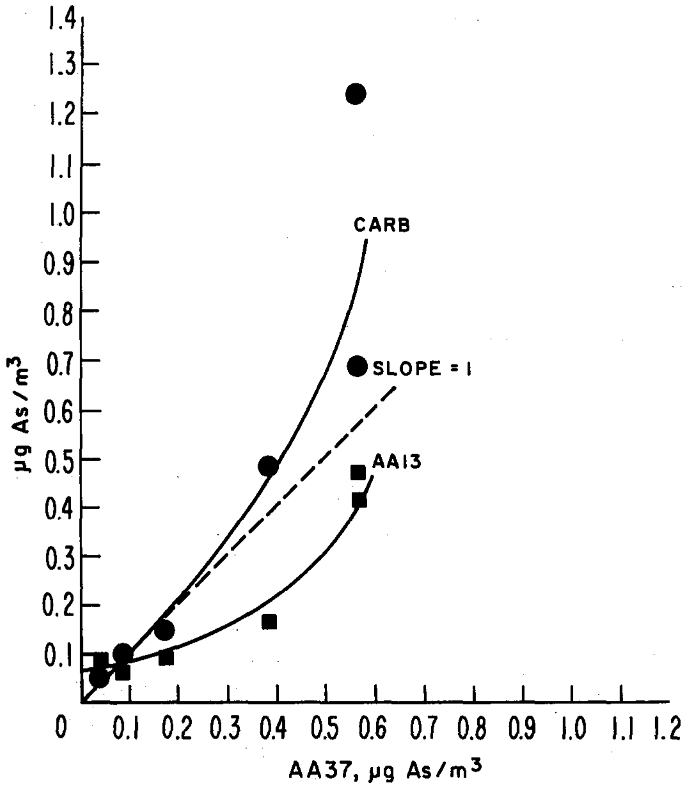

Figure 6 — AA13 and CARB results vs AA37. Squares depict AA13 filter results. Circles depict CARB filter results.

correcting for the arsenic trioxide vapor collected on the same filters:

$$P = 1/2 \left[\left(\frac{FWAA37}{AA37VOL} - 0.42V \right) + \left(\frac{FWCARB}{CARBVOL} - 0.93V \right) \right] \quad (2)$$

For the 13 mm filter/charcoal tube sampling train, the arsenic trioxide vapor collection efficiency, E, of the 13 mm filter was equal to the total weight of arsenic collected (FWAA13, as µg of arsenic), less the calculated particulate arsenic for the area sampled, divided by the calculated concentration of arsenic trioxide in the area. This is expressed by the equation:

$$E = \left(\frac{FWAA13}{(AA13VOL)} - P \right) / V \quad (3)$$

where AA13VOL is the volume, in cubic meters, of the AA13 air sample. The 13 mm filter did not utilize a backup pad.

Arsenic trioxide vapor which penetrated the 13 mm filter was collected with 96% efficiency by the charcoal tube.(8) The true arsine concentration, A, was set equal to the difference between the total weight of arsenic on the charcoal tube (FWCT + BWCT) and the weight of arsenic trioxide vapor which penetrated the filter.

$$A = \left(\frac{FWCT + BWCT}{CTVOL} \right) - 0.96\,V\,(1-E) \quad (4)$$

where CTVOL is the volume, in cubic meters, of the 13 mm filter/charcoal tube sample.

Results and Discussion

The field study demonstrated the presence of airborne fumes and particles with elemental compositions similar to the metals being welded which contained arsenic. Arsenic trioxide has a significant equilibrium vapor pressure at torching and welding temperatures. There were three characteristics of the air sample data attributable to arsenic trioxide vapor: the AA37 results were higher than the calculated values for particulate arsenic (P) (Table 3); significant amounts of arsenic were found on the AA37 backup pads in the Element Battery Repair, Forming, Post Burn, and Tiegel areas; and only small quantities of arsenic were found on the CARB backup pads. The calculated values of V by plant area were shown in Table 3. The ratio of V to CARB is also shown. This ratio is an estimate of the contribution of arsenic trioxide to total non-arsine arsenic and suggests that the proportion of arsenic trioxide vapor ranges from about 25% in Salvage and Remelt to more than 50% in Element Battery Repair, Forming, and Tiegel. This is reasonable because there are torching operations in Tiegel and Element Battery Repair and because the Forming Area is close to Element Battery Repair. The highest concentration of arsenic trioxide vapor found, 0.36 $\mu g/m^3$, was in Element Battery Repair. This concentration is close to the equilibrium vapor concentration of arsenic trioxide (Table I).

The filter samplers performed as anticipated. The particulate collection efficiencies of the three are identical (Figure 1). However, the AA13 filter collected less total arsenic than the corresponding AA37 filter, which in turn collected less arsenic than the corresponding CARB filter (Figure 6). These relationships may be seen in the data tabulated in Table 3.

This result is not surprising when the effect of arsenic trioxide vapor is considered. The CARB filter has the highest arsenic trioxide vapor collection efficiency (98% for FWCARB + BWCARB). The AA37 filter has a backup pad and the weight of arsenic it collects is the sum of the weight of arsenic and arsenic trioxide particulate on the filter plus the weight of arsenic trioxide vapor that passes through the filter and is collected on the backup pad. There is no backup pad for the AA13 filter and its collection efficiency for arsenic trioxide vapor is less than the AA37 filter-backup pad combination. When the weight of arsenic trioxide vapor was subtracted from the total weight of arsenic collected on the filters using equations 5, 6, and 7,

$$AA37CORR = AA37 - 0.81\,V \quad (5)$$

$$AA13CORR = AA13 - 0.35\,V \quad (6)$$

$$CARBCORR = CARB - 0.98\,V \quad (7)$$

better agreement was seen among the corrected filter results (Table 3). The lone unexplained outlier remains the high CARB results from Post Burn.

Additional evidence of the presence of arsenic trioxide vapor is seen in the ratio of mass of arsenic collected on the filter to the total mass collected on filter plus backup pad. Since the AA37 and CARB filters are 100% efficient collectors of particulate arsenic, any arsenic found on the backup pad is assumed to have been present as arsenic trioxide vapor. The ratios were calculated for both filters and appear in Table 3. In each case where a ratio of less than 1.0 is observed, arsenic trioxide vapor is judged to be present. The CARB filters, as expected by their higher collection efficiency for arsenic trioxide vapor of FWCARB, appear to give a ratio closer to 1.0.

The arsenic trioxide collection efficiency of the AA13 filter (E) was not measured in the laboratory. It is 0.42 for AA37 filters;(7) and should be similar for AA13 filters, since the filter face velocity and composition are identical. E was calculated from field study results using equation (3) and a value of 0.35 ± 0.07 was obtained in Element Battery Repair where the highest levels of arsenic trioxide vapor were found. In three areas, Boosted Stock, Forming, and Tiegel, the filter loadings were too low to estimate E. Negative E values were calculated using data from the Post Burn and Salvage and Remelt, where relatively little arsenic trioxide vapor and high particulate arsenic concentrations were found.

The value E = 0.35 was used in calculating the effect of arsenic trioxide penetration of the charcoal tube (CT) which was in series with the AA13 filter. This was greatest, about 10%, in the Salvage and Remelt area (Table 3).

Good agreement was seen, as expected, between results of the two charcoal tubes, CT and PCT, which were in series behind the 13 mm and 37 mm filters ($r = 0.76, p < 0.00001$). The calculated true values of arsine, after correction of charcoal tube results for the arsenic trioxide vapor contribution (Equation 4), are quite close to the measured values because of the relatively high concentrations of arsine (Table 3).

Conclusions

Used by itself, the CARB filter(7,10) is a more efficient collector of arsenic trioxide vapor than the classical filter method(3) and is an equivalent collector of particulate arsenic. This suggests that when heated sources of arsenic were present, previously reported arsenic values, derived solely from filter samples, have underestimated arsenic exposure.

When concurrent CARB and untreated 37 mm filter samples are collected, and the backup pad of the 37 mm filter is analyzed, particulate arsenic and arsenic trioxide can be distinguished and quantified using equations (1) and (2). This method is applicable to personal exposure monitoring in the presence of heated arsenic sources in the copper smelting and primary metals refining industries, as well near welding operations. Where there is no arsenic trioxide vapor, the NIOSH Method S309(3) gives reliable results.

The Hill/Arnold 13 mm filter/charcoal tube sampling train effectively separates particulate arsenic from arsine and has been used to collect personal exposure data. If, in addition, arsenic trioxide vapor is present, an estimate of its contribution to the weight of arsenic collected on the filter and charcoal tube can be made using equations (3) and (4). This requires three concurrent samples and is not suitable for personnel exposure monitoring.

The field study points to the presence of arsenic trioxide vapor near welding or torching operations as well as widespread low levels of arsine in lead-acid battery manufacture. These potential exposures are not generally recognized.

Acknowledgements

The authors thank Mr. Harry Donaldson, CIH, for his suggestion that they collaborate; Charles Geraci, Ph.D., CIH, for suggesting use of the Hill/Arnold device; James Perkins, Ph.D., Utah Biomedical Test Laboratory, for supervision of the field study analyses; and Mr. Bill Stringer for data automation and statistical analyses.

References

1. **John Wiley and Sons:** *Kirk-Othmer Encyclopedia of Science and Technology,* Vol. 3, 3rd Ed., p. 652. New York (1978).
2. **Lao, R.C., R.S. Thomas, T. Teichman and L. Dubois:** Efficiency of Collection of Arsenic Trioxide in High Volume Sampling. *The Science of the Total Environment 2:*373-379 (1974).
3. **U.S. Department of Health, Education, and Welfare:** NIOSH Manual of Analytical Methods, Volume 3, Method S309. NIOSH, Division of Physical Sciences and Engineering, Cincinnati, OH (1977).
4. **U.S. Department of Health, Education, and Welfare:** NIOSH Manual of Analytical Methods, Volume 3, Method S229, NIOSH, Division of Physical Sciences and Engineering, Cincinnati, OH (1977).
5. **Bowman, J. and J. Smith:** Performance Expectations for Dust Samplers. Presented at the ACGIH Symposium, Dosimetry for Chemical and Physical Agents, Cincinnati, OH (1980).
6. **Hill, R.H. Jr., and J.E. Arnold:** A Personal Air Sampler for Pesticides. *Archives of Environmental Contamination and Toxicology, 8:*621-628. (1979).
7. **Lynn, C., G. Colovos, D. Garland, M.E. Jamin, M. Klenck and T. Long:** Analytical Methods Evaluation and Validation, Rockwell International Corporation, Final Report, NIOSH Contract 210-79-0060. NIOSH, Division of Physical Sciences and Engineering, Cincinnati, OH (1981).
8. **Crecelius, E.A. and R.W. Sanders:** Development of an Arsenic Trioxide Vapor and Arsine Sampling Train. *Analytical Chemistry 52:*1310-1312 (1980).
9. **The Chemical Rubber Company:** *Handbook of Chemistry and Physics,* 51st Ed. p. D166. Cleveland (1970).
10. **U.S. Department of Health and Human Services:** NIOSH Manual of Analytical Methods, Volume 7, Method P&CAM 346 (Revised). NIOSH, Division of Physical Sciences and Engineering, Cincinnati, OH (1982).
11. **Costello, R.J. and P.J. Landrigan:** Health Hazard Evaluation Project HE 78-98-710. NIOSH, Division of Surveillance, Hazard Evaluations, and Field Studies, Cincinnati, OH (1980).
12. **Stettler, L.E.:** Report of Particle Analysis. NIOSH, Division of Biomedical and Behavioral Science, Cincinnati, OH (1981).

29 January, 1982; Revised 24 June, 1982