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Authors' Response

Thank you for giving us the opportunity to respond to the comments of Warren D. Hendricks and Gerald R. Schultz on our article, "Determination of 1,3-Butadiene Down to Sub-part-per-million Levels in Air by Collection on Charcoal and High-Resolution Gas Chromatography" [Appl. Occup. Environ. Hyg. 5(5):310; 1990].

In stating that OSHA Method 56 specifies analysis by packed column chromatography, we only meant that the method explicitly details use of a packed column. For both NIOSH and OSHA methods, use of the "specified" column is not mandatory. There is, however, a feature of OSHA Method 56 that may inhibit the use of a capillary column to achieve better resolution of interferences. A 10 percent coating of the adsorbent with 4-*tert*-butylcatechol (TBC) results in approximately 9 μg/μL of TBC in desorbed samples. In example chromatograms for the packed column, TBC does not appear to elute, though two small "artifactual" peaks are said to be produced from TBC. An accumulation of TBC may not be tolerable with capillary columns.

In their article, "A sampling and analytical method for monitoring low ppm air concentrations of 1,3-butadiene" [Appl. Ind. Hyg. 1(4):186; 1986], Hendricks and Schultz stated that "Hydroquinone, di-n-butylamine and 4-tert-butylcatechol (TBC), compounds known to inhibit the polymerization of 1,3-butadiene, were each coated on charcoal, and prepared sampling tubes were subjected to sample storage stability tests. The stability of only the samples prepared from TBC-coated charcoal showed dramatic improvement. They also addressed in Table VII and accompanying text the sample stability of 1,3-butadiene on an untreated coconut shell charcoal (SKC Lot 120) as used in NIOSH Method S91. Since we reported results for the same lot of charcoal in our article, we believe that we have not exceeded the scope of their original discussion.

The 34 percent initial recovery that Hendricks and Schultz reported in Table VII for 1,3-butadiene (from SKC Lot 120 charcoal at a loading of approximately 6.6 μg per 100 mg) agrees with the data we show in Figure 1 for desorption with carbon disulfide. They also reported that "... a 'Specially Cleaned' charcoal (coconut-shell base) from Supelco gave acceptable recoveries." After coating the Supelco charcoal with TBC, they observed improved (sample storage) stability as quoted above. Even though the latter results were obtained with a different charcoal, they attribute the poor recovery from the untreated charcoal (SKC Lot 120) to sample instability, i.e., "the reactivity of 1,3-butadiene on uncoated charcoal at low sample loadings." Thus, they seem to be suggesting that 1,3-butadiene is chemically transformed through covalent bond formation, either by reaction with charcoal or by polymerization. Since polymerization would involve a bimolecular reaction, polymerization becomes increasingly unlikely as the concentration is decreased. Moreover, pretreatment with two other polymerization inhibitors apparently had little effect.

Using SKC Lot 120 charcoal, we observed a large increase in recovery (from approximately 30 percent to 80 percent as shown in Figure 1) by desorbing with methylene chloride rather than carbon disulfide. If desorbing with methylene chloride does not regenerate chemically transformed 1,3-butadiene, i.e., undo the formation of covalent bonds, then we have shown that most of the incomplete recovery of 1,3-butadiene from SKC Lot 120 charcoal with carbon disulfide desorption is not due to the reactivity of 1,3-butadiene on charcoal as postulated by Hendricks and Schultz. Recoveries as low as 75 percent are routinely dealt with by applying a desorption efficiency correction, either directly when calibrating with standard solutions, or indirectly by calibrating with media standards.

We also observed losses during sample storage at ambient temperature. Neither NIOSH Method 1024 nor OSHA Method 56 makes any provision for correcting storage losses. Hendricks and Schultz raise an interesting point about forcing the storage study regression line through 100 percent recovery at day zero and dropping the data for day 21. That surely would increase the estimated rate of loss. The same approach also could be applied to the data for the refrigerated samples with the same effect, increasing the estimated rate of loss from essentially none to a statistically significant 6 percent per day. However, the latter estimate is refuted by the data for the blind quality control samples, which showed no significant loss during refrigerated storage for up to 134 days. One of the "special requirements" listed in OSHA Method 56 is "Collected samples should be stored in a freezer." Our analysis of the storage stability data, without the imposition of desorption efficiency constraints, led us to recommend the same for NIOSH Method 1024. It also left us unconvinced that coating charcoal with TBC provides a "dramatic" improvement in sample stability.

In their final comments, which concern the following quotes from our article, Hendricks and Schultz continue to relate the issues of desorption efficiency and sample stability: "Thus, at the lower levels, the accuracy of the total method and/or some of the preparation procedures was in doubt." We followed this statement with a lengthy discussion relating the accuracy question to problems with independent methods used to prepare media standards. These problems resulted in apparent desorption efficiencies as high as 212 percent for the media standards. It is unclear to us how excessive recovery proves the reactivity of 1,3-butadiene on uncoated charcoal.

"... the desorption efficiency usually fell below 75 percent somewhere between 20 and 110 μg per sample." The storage stability data for blind quality control samples stored in a freezer showed no evidence of sample instability at these levels. NIOSH Method

1024 was designed to cover a wide range of workplace concentrations. Results for the field samples indicated that the recommended sample volume permits monitoring concentrations up to 100 ppm without significant breakthrough and to less than 2 ppm with adequate desorption efficiency. If the adoption of a lower standard makes it necessary to measure lower concentrations, the desorption efficiency at low- and sub-part-per-million levels may be improved by increasing the sample volume.

"Perhaps the most interesting observation concerned the variation in desorption efficiency from one calibration to another." OSHA Method 56 also shows variation in desorption efficiency from one set of samples to another. As with NIOSH Method 1024, such variation may be due to experimental error in determining the desorption efficiency; or, the desorption efficiency may truly vary due to unrecognized changes in experimental conditions. The observed variations seem to be greater than can be explained by storage losses (sample instability) during the time between sample preparation and analysis.

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To the Editor:

The intended changes proposed for hand–arm vibration do not appear to constitute a "threshold" value, since they permit the development of early Raynaud's phenomenon. The documentation does not discuss the control measures which would be necessary to *prevent* such abnormalities. It is my impression that the very concept of "threshold" requires setting exposure levels below that which would cause health abnormalities. Why was there no discussion or serious consideration of controls which would prevent abnormalities above the level they would be expected to occur in a healthy working, but non-vibration exposed, population?

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ACGIH's Response

All letters concerning Notice-of-Intended Change documentations are forwarded to the respective committee for consideration in its regular review procedure.

It would be more useful to the committee if the statements of the author were documented and referenced according to the author's own criteria as set forth in a letter of May 8, 1990.[1] It seems that the author in her July 24, 1990 letter (above) has decided upon a definition of threshold which she is attempting to impose on the committee. The committee has a definition that is clearly stated in the documentation published in *Applied*.[2] There are many thresholds that can be considered, depending upon the agent and the one or more possible effects of that agent. The author's definition may be at odds with the purpose of the Occupational Safety and Health Act as quoted by Dr. Millar of NIOSH.[3] Several groups have developed recommendations in the segmental vibration area. Dr. William Taylor[4] identifies these recommendations as ISO 5349 (1986), BSI 6842 (1987), NASI 5334 (1986) [Ed.—ANSI S3.34 (1986)] and ACGIH (1990). The first Notice of Intent to Establish a Threshold Limit Value (TLV) recommendation goes back to 1984.[5] The Documentation for that Notice of Intent has been available since 1986.[6]

A TLV is intended for use in the practice of industrial hygiene and should be interpreted and applied only by a person trained in this discipline.[7] Certainly the practice of industrial hygiene/occupational medicine is as broad as the components of a full standard under the Occupational Safety and Health Act or a NIOSH Criteria for a Recommended Standard.[3] The author claims that there is "... no discussion or serious consideration of controls which would prevent abnormalities above the level they would be expected to occur in a healthy working, but non-vibration exposed, population." It is difficult to envision a program more comprehensive than that outlined on page 467 in the July issue[2] for "Control of HAVS from the Workplace" and the "Recommended Code of Work Practices." The introductory sentence puts the TLV into perspective.

"It should be recognized that control of HAVS from the workplace cannot occur simply by specifying and adhering to a given TLV. The use of ALL of the following are recommended:

1. Workers should use antivibration tools together with antivibration gloves.
2. Workers should adhere to the work code of practice.
3. Each worksite is advised to have a conscientiously applied medical surveillance program with personnel trained in HAVS detection and practices.
4. TLVs and standards should be used."

The role of the TLV relative to Control Measures was extensively discussed by Wasserman in *Applied Industrial Hygiene* in August 1989[8] in "The Control Aspects of Occupational Hand–Arm Vibration." The abstract says: "Control measures include the use of anti-vibration tools and gloves; recommended work practices; threshold limit values (TLVs) and other standards; medical monitoring and prescreening of workers; education of all concerned; and the use of vibration engineering control techniques of damping and isolation."

A reading of the Foreword of the NIOSH Criteria Document on "Occupational Exposure to Hand–Arm Vibration" gives additional perspective to the appropriateness of the Physical Agents TLV Committee recommendations.[3]

References

1. Ziem, G.: Letter to the Editor of May 8, 1990. Appl. Occup. Environ. Hyg. 5(10):660 (1990).
2. American Conference of Governmental Industrial Hygienists: 1990 Notice of Intended

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appear below.

Despite all of the discussion about medical examinations for people who will use respirators, Rajhans and Blackwell and most everyone else seems to miss the essential point. There is no doubt that wearing respiratory protection results in an additional physiological burden. The burden may be minimal or considerable. There are no valid data to show that medical examinations or any tests of whatever nature predict whether a respirator can be worn without harm to the individual or without undue discomfort to the individual. Careful reading of the references cited, including those by Rajhans and Blackwell, will confirm the validity of what has just been stated. Because OSHA requires attestation by a physician of the individual's ability to wear a respirator and the physician really does not know what else to recommend, much time, money, and effort goes into a series of studies that mean nothing as far as our ability to say whether someone can wear a respirator. Put the respirator on the individual and have him/her exercise at the level he/she will be working. The worker will tell you soon enough whether he/she can tolerate the respirator. The only exception might be someone with significant heart disease who might already be on limited duty.

Unfortunately, many of my fellow physicians have long disallowed people to work at certain jobs because of vague ideas about the difficulty of the job. We should not discriminate against certain workers because of unvalidated ideas about their ability or inability to wear a respirator. Let those who exclude workers from a good paying job because of arbitrary, unvalidated criteria be aware that they might well be the target of a discrimination suit.

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To the Editor:

We would like to correct misinterpretations of our work [A Sampling and Analytical Method for Monitoring Low ppm Air Concentrations of 1,3-Butadiene. Appl. Ind. Hyg. 1(4):186; 1986] which were made by the authors of a recently published paper [R. Alan Lunsford *et al:* Determination of 1,3-Butadiene Down to Sub-part-per-million Levels in Air by Collection on Charcoal and High-Resolution Gas Chromatography. Appl. Occup. Environ. Hyg. 5(5):310; 1990]. We also feel compelled to comment on the interpretation of their storage data and point out some of their observations which are probably due to the reactivity of 1,3-butadiene on uncoated charcoal.

The authors state that "Other recently developed methods for the determination of 1,3-butadiene in the air are OSHA Method 56 ... these methods specify analysis by packed column gas chromatography." Although we used a packed column in our evaluation and list conditions for its use in our paper, we specifically stated that "a column capable of resolving 1,3-butadiene from the solvent front and other interferences" is required. We also make a similar statement in OSHA Method 56. Gas chromatography presents a variety of parameters (including column selection) that can be altered and fine tuned; it is our policy not to deny that latitude to the analyst.

The authors state that "A dramatic improvement in sample stability has been reported for samples collected on a specially treated coconut shell charcoal coated with 4-tert-butylcatechol (TBC). It was also concluded that collection on uncoated charcoal would be inadequate at low ppm levels because of poor sample stability. Our results do not support these conclusions." We stated that "... it was necessary to determine if the method used by OSHA to monitor 1,3-butadiene air concentrations would be adequate at low ppm levels. It was found that this method, NIOSH Method S91, would be inadequate because of poor sample stability." We confined our conclusion only to the scope of Method S91. We feel that the authors' data do suggest sample instability may be the underlying cause of their method's questionable usefulness at low ppm levels (< 2 ppm).

Because media standards are used in their storage tests, the calibration amounts to comparing aged samples to fresh samples. If samples and media standards could have been analyzed on day zero, they would have been indistinguishable. Thus the regression lines should be forced through 100 percent at day zero, which is a valid data point defined by the method of calibration. If this is done for the ambient data, the last point (Figure 2) is conceivably an outlier and the rate of sample loss is greater than suggested. Therefore, the authors' regression line for the ambient data does not appear to be a good estimate of true behavior. The rate of loss is probably much worse than that presented in the paper and considerably worse than that found with TBC-coated charcoal.

Also, one must be vigilant in the use of media standards, which have a way of "cooking" the data by masking biases. The authors' use of media standards masks the fact that the initial recoveries from uncoated charcoal are close to 80 percent, which is the approximate amount that can be recovered from TBC-coated charcoal after 17 days of ambient storage. Thus the comparison of 1,3-butadiene loss rates on coated and uncoated charcoal is superfluous.

By using a known inhibitor (TBC) of 1,3-butadiene polymerization, we showed that the unacceptable sample loss found with Method S91 at the 1 ppm level was almost certainly due to the reactivity of 1,3-butadiene on uncoated charcoal. We feel this reactivity of 1,3-butadiene on uncoated charcoal at low sample loadings does restrict the usefulness of uncoated charcoal in making determinations down to sub-part-per-million levels and is the likely root cause of the authors' following observations:

> "Thus at the lower levels, the accuracy of the total method and/or some of the preparation procedures was in doubt."
>
> "... the desorption efficiency usually fell below 75 percent somewhere between 20 and 110 μg per sample." (0.4–2 ppm in 25 L samples)
>
> "Perhaps the most interesting observation concerned the variation in desorption efficiency from one calibration to another."

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