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EVALUATION OF THE USE OF COMMERCIALLY AVAILABLE DETECTORS FOR HYDRAZINE AND NITROGEN DIOXIDE AS COLORIMETRIC DOSIMETERS

ROBERT F. RAKOWSKI, CAPTAIN, USAF, BSC

Foreword

This research was performed in the Chemical Hazards Branch, Toxic Hazards Division of the Aerospace Medical Research Laboratory, Wright-Patterson Air Force Base, Ohio 45433. The work was performed in support of Project 6302, "Toxic Hazards of Propellants and Materials," Task 630203, "Identification of Toxic Materials." The report covers work conducted in May and June 1968.

The detectors compared in this report were commercial items that were not developed or manufactured to meet Government specifications, to withstand the tests to which they were subjected, or to operate as applied during this study. Any failure to meet the objectives of this study is of no reflection on any of the commercial items discussed herein or on any manufacturer.

This technical report has been reviewed and is approved.

C. H. KRATOCHVIL, Colonel, USAF, MC
Commander
Aerospace Medical Research Laboratory

Abstract

The color response of several commercially available detector papers for hydrazine and nitrogen dioxide was determined in order to evaluate their usefulness as personal dosimeters which could give an estimate of the concentration-time product (CT) of an exposure. The Bug-it H25B Hydrazine Detector gave satisfactory results in the CT range of toxicological interest. Appropriate color standards should be prepared and a reusable holder for the detector strips manufactured. The Bug-it H30A Nitrogen Dioxide Detector was satisfactory as a detector for low concentrations of nitrogen dioxide but did not give colors which darkened enough to permit a quantitative estimate of the CT product to which the strips were exposed. Melpar Nitrogen Dioxide Detector Tapes were also satisfactory as a detector for low concentrations of nitrogen dioxide; but since the color developed did not darken at all with increasing exposure time, it was not possible to estimate the CT product of an exposure with this detector.

Section I.
INTRODUCTION

A colorimetric dosimeter for hydrazine fuels has been developed by the Mine Safety Appliances Company under contract to the Air Force (Plantz, 1967). An evaluation of the performance of the detector strips has been completed recently (Arnold and Rakowski, 1968). The device was shown to be generally satisfactory, but several difficulties were noted. The detecting reagent, an acid-base indicator, is subject to a wide range of interferences. Also, the sensitivity of different lots of dosimeter strips varies considerably.

A dosimeter for nitrogen dioxide has also been developed (Rakowski, 1968). This device appears to be promising as a dosimeter in the range of concentration-time products (CT) of toxicological interest but has not been field tested or evaluated by an independent laboratory.

Several detector papers for nitrogen dioxide and for hydrazine fuels are commercially available. These detector papers might be suitable as dosimeters if a set of color standards and a clip-on holder for the detector strips were manufactured. This report covers efforts to determine the color response of several commercially available detector papers to various concentration-time products of nitrogen dioxide or monomethylhydrazine and to determine if the detector paper could be used as a personal dosimeter.

Section II.

RESPONSE OF BUG-IT H25B DETECTOR BADGE TO MONOMETHYLHYDRAZINE

A detector paper for hydrazine fuels is manufactored by American Gas and Chemicals, Inc., 511 East 72nd Street, New York, N. Y. 10021. The paper is available with an adhesive backing (Bug-it H25), as a plain 4- by 8-inch sheet of sensitive paper (Bug-it H25A), and as a laminated plastic badge which may be clipped to a person's lapel (Bug-it H25B). Detector paper with a reduced sensitivity is also available.

The detecting reagent is sensitive to ammonia and amine vapors as well as the hydrazine fuels. Tobacco smoke can give a false positive indication. The response of the H25B hydrazine detector badge to monomethylhydrazine (MMH) is shown in table I. The apparatus and method of determining the concentration of MMH are given in a previous report (Arnold and Rakowski, 1968). The color response is quite good. The badge has adequate sensitivity in the range of interest although color development is somewhat slow. The color continues to develop after the badges are removed from the test chamber. The colors listed were read 1 minute after exposure. A slightly greater sensitivity might be desirable. Satisfactory color response was obtained in the range of CT values from about 10 to 500 ppm-minutes. A set of color standards should be selected for each of the three commonly used hydrazine fuels. Appropriate values as color standards for MMH might be 50, 200 and 500 ppm-minutes. These values include the CT range of the emergency exposure limits for short duration exposures set by the National Academy of Sciences.

TABLE I.

RESPONSE OF THE BUG-IT H25B HYDRAZINE DETECTOR BADGE

*Conc. MMH (ppm)**	*Time (min)*	*CT (ppm-min)*	*Color Standard***
1	5	5	9F4
1	5	5	9G3
5	1	5	9G2
5	2	10	9G3
5	5	25	9J6
25	1	25	9G5
25	2	50	9J7
25	4	100	9J9
100	1	100	9F7
100	5	500	9F10

*Monomethylhydrazine in dry nitrogen.
**See Maerz and Paul, 1950.

A reuseable detector strip holder such as the one used for NO_2 (Rakowski, 1968) should be fabricated to hold disposable paper detector strips.

Section III.

RESPONSE OF BUG-IT H30A NITROGEN DIOXIDE DETECTOR PAPER

Detector materials similar to the previously described hydrazine detector paper and badge are available for the detection of nitrogen dioxide. American Gas and Chemicals, Inc. manufactures these detectors as 4 by 8 paper sheets backed with adhesive (Bug-it H30), plain paper sheets (H30A), or detector paper laminated in a plastic badge (H30B).

Nitrogen dioxide gives a light-yellow color on the detector paper. Since the detecting reagent is a nonspecific oxidation-reduction indicator, other oxidizing substances may interfere. The response of the Bug-it H30A detector paper is given in table II. The apparatus and method of determining the NO_2 concentration is given in a previous report (Rakowski, 1968).

The sensitivity of the strips is somewhat lower than is desirable and the range of the color intensity is very small, making it difficult to match color standards accurately. However, the sensitivity of the strips might be increased by using a greater concentration of detecting reagent or by using a silica gel supporting material such as Eastman Chromagram Sheet (K301R2). It may be advisable to use a more sensitive oxidation indicator reagent such as diphenylamine or diphenylbenzidine. In any case, the detector strips are not suitable for use as a dosimeter in their present form. They are not satisfactory for quantitative estimation of concentration-time products, but are satisfactory as a detector for low concentrations of NO_2.

TABLE II.

RESPONSE OF BUG-IT H30A NITROGEN DIOXIDE TEST PAPER TO 40 ppm NO_2

Concentration-Time Product (ppm-mins)	*Color Standard**
0	9A1 (White)
40	9A1
100	9B1 (vy lt yellow)
200	9C1
300	9C2 (light peach)
400	9D2
500	9D2
600	9D2
1000	9E2
3000	10E5 (yellow orange)

*See Maerz and Paul, 1950.

Section IV.

RESPONSE OF MELPAR NO_2 DETECTOR TAPES

Detector tapes for nitrogen dioxide are manufactured by Melpar, Inc., Falls Church, Virginia. Both high and low sensitivity tapes are available. The detecting reagent is an acid-base indicator which gives a bright purple-red color when the tapes are exposed to NO_2. Samples of both the high- and low-sensitivity tapes were tested at 40 ppm of NO_2 in the same apparatus used for the Bug-it H30A tests. The results are given in table III.

TABLE III.

RESPONSE OF MELPAR NITROGEN DIOXIDE DETECTOR TAPE TO 40 ppm NO_2

Sensitivity	*Concentration-Time Product (ppm-min)*	*Color Standard**
High	0	3B1 rose-gray
High	20	51A7 purple-red
High	40	52A9 purple-red
High	100	52A9 purple-red
High	800	52A9 purple-red
Low	0	2B1 rose-gray
Low	40	51A2 rose-gray
Low	100	51A2 rose-gray
Low	200	51A2 rose-gray
Low	400	51A2 rose-gray
Low	800	51A2 rose-gray

*See Maerz and Paul, 1950.

The color change which takes place on the high-sensitivity strips after exposure to NO_2 is rapid, and the color very bright and vivid. The sensitivity of the strips is within the concentration range of toxicological interest; however, the color which is developed does not gradually darken, but rather shows an all or none response. This is to be expected since the detector reagent is a pH indicator. The high-sensitivity strips are excellent as detectors for low level NO_2 concentrations; but since the color response is not gradual, the tapes cannot be used as a dosimeter to estimate the concentration-time product of an exposure.

This same result was seen with the low-sensitivity strips. A faint rose color which was only slightly different from the color of an unexposed strip develops at concentration-time product values as low as 40 ppm-minutes. However, the color does not darken with increasing time of exposure. The Melpar NO_2 detector tapes are excellent for their intended purpose as leak detectors, but cannot be used as a dosimeter.

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Robert F. Rakowski, Captain, USAF, BSC

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13. ABSTRACT

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