

FINAL REPORT -- Grant # NAG-1-2269

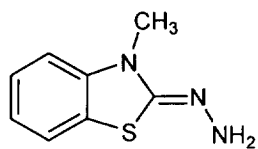
Investigation of Chemically Treated Test-Strips for Ozone Measurement

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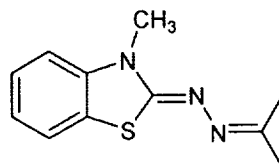
Background:

A colorimetric passive ozone monitoring system is currently in use in the GLOBE project, as well as several other environmental studies, as commercially supplied as Eco-Badge by Vistanomics. This simple, but effective, system consists of papers treated with a chemical preparation, tin(II) diphenylcarbazide¹ that reacts with ozone to change them from white to purple. The intensity of the purple coloration is dependent on the concentration of ozone. Our previous contributions² to that method of analysis involved modest modifications to the chemical substrate employed. The new formulation improved the reproducibility and linearity of the color change of treated papers.

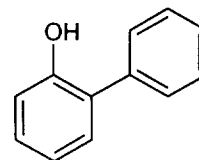
Because of lingering concerns over the reliability of the monitoring papers when used under a great variety of conditions (heat, humidity, presence of other pollutants) we believed that study of an alternate system might be valuable. The literature^{3,4,5} showed that a binary system had shown particular promise in response to ozone and also suffered minimal interference from common competing oxidizing pollutants, such as NO₂, and resistance to changes in humidity and temperature. This system consists of 3-methyl-2-benzothiazoline acetone azine (MBTA) and a phenol compound such as 2-phenylphenol. This mixture is also amenable for treating test papers, and the papers become a purple color in response to ozone exposure. The majority of the work on the grant NAG-1-2269 was therefore focussed on MBTA-based systems.



2-methyl-3-benzothiazolinone
hydrazone
(MBTH)



MBTH acetone azine
(MBTA)



2-phenylphenol

Plan and Progress:

In addition to exploring the efficacy of previously known formulations, we sought to design and develop other azine/phenol systems which would exhibit the desired characteristics of reproducible linear response over a broad range of ozone concentrations, high selectivity to ozone, and stability under various extremes of ambient conditions. Because of the nature of the binary system and its interaction with ozone we concerned ourselves not only with the components of the mixture, but also the ratio of the mixture.

The first portion of our investigation involved confirming that, in our hands, the best phenol component to employ was indeed 2-phenylphenol. We knew from the literature³ that related phenols (2,6-dimethoxyphenol and 2,6-dimethylphenol) were known to show similar responsiveness. We applied a mixture of each of these phenols and MBTA to the test papers and exposed them to varying levels of ozone in our ozone chamber (see Appendix A, page 8, for schematic of our apparatus). Ozone concentrations generally ranged from 50 ppb to 250 ppb. Table 1 summarizes the results of this comparison study.

Table 1. Results of trials involving alternate phenol components in binary formulation with 3-methyl-2-benzothiazoline acetone azine (MBTA).

phenol component	MBTA:phenol ratio	absorbance λ_{\max}	comments
2-phenylphenol	1:4	520 nm	poor linearity <100 ppb O ₃
	1:6	540 nm	better response and linearity
2,6-dimethoxyphenol	1:4	no clear λ_{\max}	red-orange color, but color did not seem stable upon removing treated paper from O ₃ chamber
	1:5	no clear λ_{\max}	
	1:6	no clear λ_{\max}	
2,6-dimethylphenol	1:4	~ 480 nm	response extremely weak

We concluded that the 2-phenylphenol should be retained in further tests. Although the work by Lambert, et al. favored the 1:4 ratio, we found that a higher proportion of the phenol gave slightly better linearity, a slightly steeper slope of response and also provided papers which were more likely to have less initial background color (i.e., they were “whiter” to start with). A steeper slope of response indicates that for each incremental increase in ozone concentration, a greater concomitant change in absorbance is observed. This is desirable because it decreases the margin of error in readings.

The 1:6 2-phenylphenol formulation was then tested against the improved tin(II) complex². Treated papers were tested simultaneously over a range of <20 ppb to >300 ppb ozone. Coincidentally both systems produce a colored species with an absorbance maximum at 540 nm. The MBTA/2-phenylphenol treated papers showed slightly more uniform color changes, but the tin(II) complex papers gave both a steeper slope of response and slightly better linearity in a standard least squares analysis (see Figure 1). However, it is possible that the MBTA/2-phenylphenol could provide a viable alternative to the tin(II) system should the need arise. Unfortunately, the patent⁴ held by Lambert, Chaing and Paukstelis may limit the application of this system in a broad sense.

Figure 1. Comparison of MBTA/2-phenylphenol system (1:6) and modified tin(II) complex in standard one-hour exposure trials over ~20 to ~250 ppb ozone.

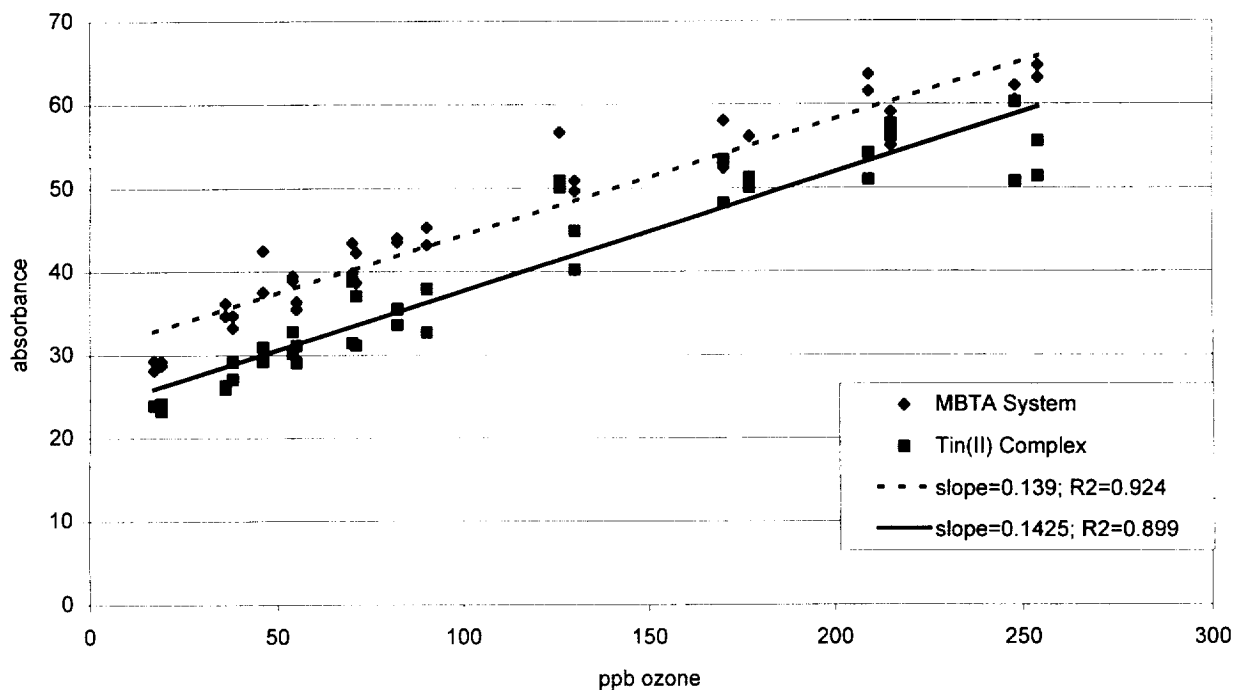
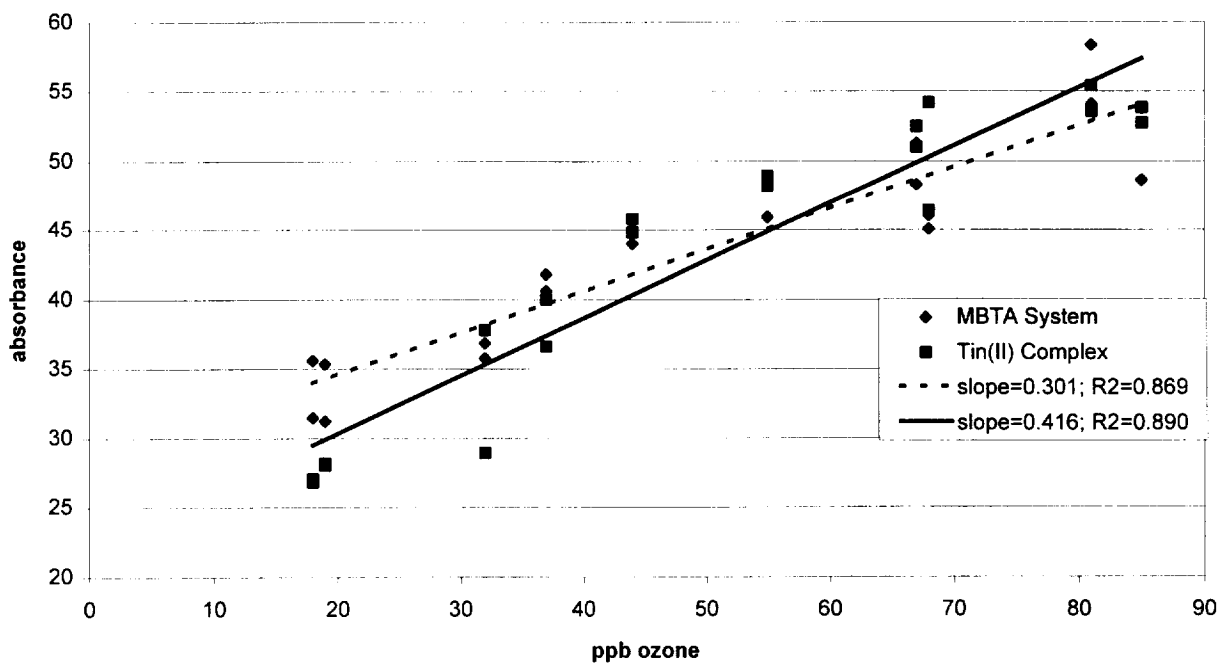


Figure 2. Comparison of MBTA/2-phenylphenol system (1:6) and modified tin(II) complex in two-hour exposure trials over ~20 to ~85 ppb ozone.



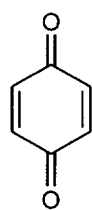
Irrespective of the patent, we sought to address the issues of sensitivity and reduction of error in response and readings at low ozone concentrations, i.e. less than 100 ppb. To this end,

we tested both the improved tin(II) complex and the 1:6 MBTH:2-phenylphenol system in a series of two-hour exposures. It was our hypothesis that bringing the degree of response (development of the reagent system's coloration) into a more advanced range might level out discrepancies we had previously observed. Figures 1 and 2 show the results of both the one-hour and two-hour trials. Thus, based on our studies to this point, we sought to explore modifications which were outside the scope of Lambert's patent, and which might show better response and reliability. Modifications to the azine component were permissible and seemed the logical next step.

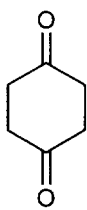
Our understanding of the system offered two avenues of inquiry with the intent of increasing linearity, sensitivity and reproducibility. These were (1) to extend the conjugation in the system in a way that would red-shift the absorbance and increase the molar absorptivity, and (2) to moderate the azine component concentration by linking two benzothiazolinone units through a bifunctional azine linker. We hoped to accomplish both of these with one compound. Unfortunately our efforts in this regard were largely unsuccessful.

The azine reagent is easily prepared by reacting 3-methyl-2-benzothiazoline hydrazone (MBTH) with an aldehyde or ketone under acidic conditions⁶. The product of this condensation reaction is then dissolved in some low-boiling solvent to produce a solution into which the paper disks are dipped. Disks are treated with the solution for 20-30 seconds and then removed to a clean glass plate to air dry. The use of some less volatile solvents required application of a stream of warm air to complete the drying process. All treated papers were stored in a dark dessicator until use. Treated papers were not usually stored more than one week, although we have no reason to believe longer storage would have any impact on our results.

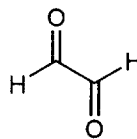
Six different carbonyl compounds were tried in place of acetone as the aldehyde or ketone component of the azine. Four of these were bifunctional, that is, they contained two carbonyl sites where azine formation was anticipated. These were: quinone, 1,4-cyclohexanedione, glyoxal and 2,4-pentanedione. Of these, two produced a tractable product. The other two carbonyl compounds tried were acetophenone and urea.



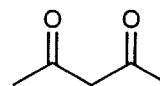
quinone



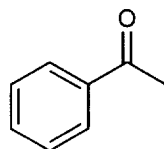
1,4-cyclohexanedione



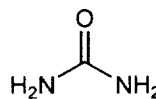
glyoxal



2,4-pentanedione



acetophenone



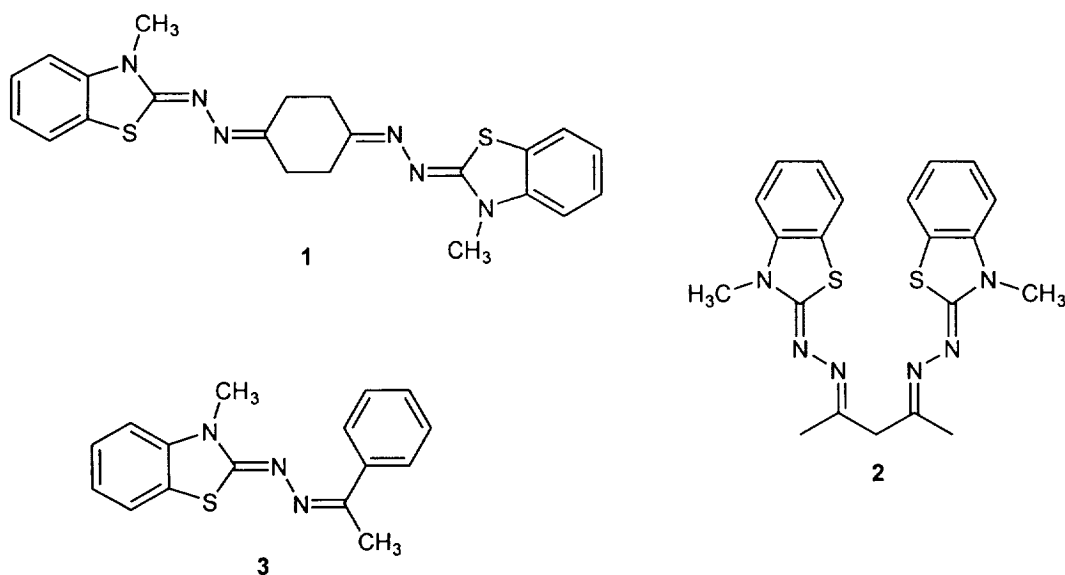
urea

Only the acetophenone gave a useful product. The condensation with urea looked successful, but isolation of the product proved unmanageable. Thus, we were able to obtain and study only three new azine compounds (in mixture with 2-phenylphenol) as passive ozone monitoring systems.

The condensation of 1,4-cyclohexanedione and two equivalents of MBTH gave a good yield of bis-azine product (**1**) as a yellow solid. The color was not surprising and we believed it might hint at that the desired red-shift of the chromophore. We encountered a slight solubility problem in preparation of the dipping solution, but after switching to a non-polar (and less volatile) solvent, we were able to treat papers with a 1:4 mixture of the bis-azine and 2-phenylphenol. However, the intensity of response, even at 250 ppb ozone, was slight in comparison to the known systems. Furthermore, the absorbance maximum (λ_{\max}) was 520-540 nm, thus exhibiting none of the expected red-shift.

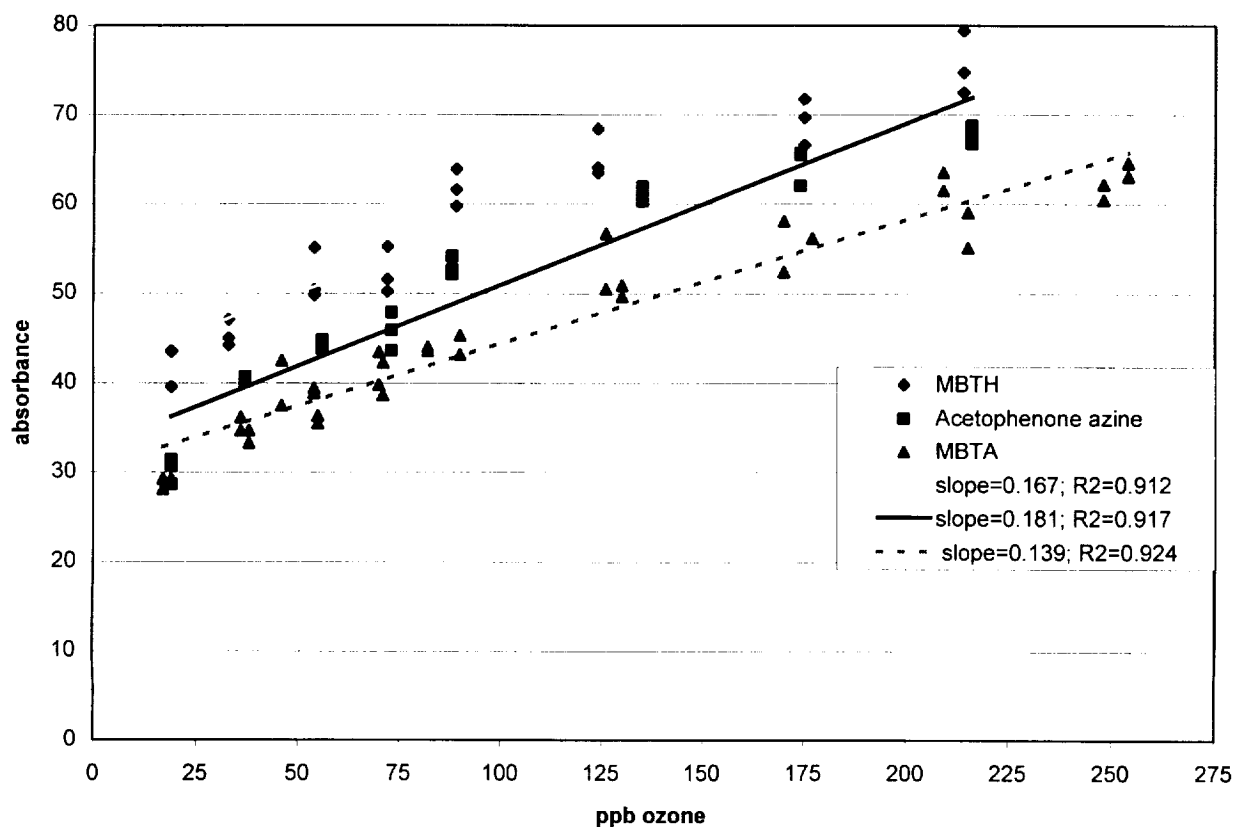
The other bis-azine (**2**) we prepared via condensation of 2,4-pentanedione and two equivalents of MBTH. This also gave a yellowish solid. When papers were treated with a mixture of this bis-azine and the phenol compound, the response to ozone was quite intense but with no distinct absorbance maximum in a useful region. While we were heartened by the increase in sensitivity, as seemed to be evidenced by the intensity, the lack of a λ_{\max} led us to discontinue this bis-azine as a fruitful system to study.

Finally, the acetophenone azine of MBTH (**3**) gave useful results. This azine, when used in mixture with 2-phenylphenol, gave a more intense response than the standard formulation and had a λ_{\max} of 540 nm. The higher absorbance of the chromophore in this case, however, proved to be misleading. As shown in Figure 3, this system also showed a greater background absorbance and a negligible increase in slope (sensitivity) relative to the standard MBTA. Since acetone is far more widely available than acetophenone it would seem imprudent to advocate the widespread use of the acetophenone azine instead of MBTA.



A serendipitous error in this work, however, led us to test the free hydrazone as well. The results were interesting and are included in Figure 3. Our experiments show that an azine moiety is not required for the binary system to respond to ozone. It might seem superfluous then to worry about formation of an azine at all, but we believe the overall reactivity of a bare hydrazone could complicate the system outside the laboratory setting. Hydrazones, and even their hydrochlorides, are known for sensitivity to moisture and oxidation, thus reliability and selectivity are likely to be quickly sacrificed. This could also be the explanation for the higher background absorbance observed in these samples. Therefore, while this result is theoretically interesting, it is not likely to be useful to us in practice.

Figure 3. Comparison of response of papers treated with 2-phenylphenol and MBTA, MBTH, or acetophenone azine of MBTH at standard one-hour exposures.



Conclusions:

While this work did not directly bring about any improvements to the passive ozone monitoring system currently available (Eco-Badge) from Vistanomics and used in NASA's GLOBE program, it did allow us, quite unarguably, to assure participants and evaluators of that program that the reagents and formulation currently in use are the most sensitive and reliable to date. Anyone searching for an alternative reagent system would first choose the MBTA system because it has been reported to have better selectivity for ozone and insensitivity to heat and humidity. While this may still be the case, it is not more sensitive overall. Additionally, recent testing of reformulated tin(II) complex treated papers in a smog chamber has shown that the interference by other adventitious oxidizers is minimal under most conceivable circumstances⁷. Our acetophenone modification of the azine component was the most encouraging, but gains would not likely outweigh costs.

Finally, the experiments involving relatively low ozone concentrations showed that error can be reduced by extending the exposure time to two hours, especially with the current formulation of tin(II) complex reagent. Perhaps an alternate correlation chart or algorithm for the Zikua reader⁸ could be devised for cases where a two-hour exposure was warranted.

Acknowledgements:

Laboratory work and all data collection was carried out by Robert Cable, an undergraduate chemistry major at Knox College. We also thank Jack Fishman (NASA-LRC) and Gary Short (Vistanomics, Inc.) for their assistance and informative discussions.

References:

1. Lambert, J. L.; Beyad, M. H.; Paukstelis, J. V.; Chejlava, M. J.; Chiang, Y. C. *Anal. Chem.* **1982**, *54*, 1227-1229.
2. Work done by L.C.B. 1998-1999 at Salisbury State University, Salisbury, MD.
3. Lambert, J. L.; Paukstelis, J. V.; Chaing, Y. C. *Environ. Sci. Technol.*, **1989**, *23*, 241-243.
4. Lambert, J. L.; Chiang, Y. C.; Paukstelis, J. V. U.S. Patent 4,859,607, January 17, 1989.
5. Zhou, J.; Smith, S. *J. Air & Waste Manage. Assoc.*, **1997**, *47*, 697-703.
6. Following the procedure of Lambert et al. in ref. 3.
7. Personal communication from Jack Fishman, NASA-Langley Research Center.
8. Available from Vistanomics, Inc., P.O. Box 847, Montrose, CA 91021-0847.

Appendix A

Diagram of ozone generation, exposure and measurement apparatus used in this work:

