

are easily evaluated numerically using either of two standard series representations (6) depending on the value of  $\xi^*$ . The curves in Figure 1 were obtained by fixing  $a$ , varying  $\delta$  over the desired range, and solving Equations 38 and 29 for  $\xi^*$  and  $R$ . The solution to these nonlinear equations was obtained numerically by using the least squares program mentioned earlier (8) to minimize

$$F = \left(\frac{d\eta}{d\xi}\right)^2 + (A_R - (1 + a)A_2)^2$$

with respect to  $R$  and  $\xi$ .

### APPENDIX III

This appendix presents the set of nonlinear equations which define the error curves for triangulation appearing in Figure 1. The following equations define areas indicated in Figure 3.

$$A_R = \int_{\xi_{M_2}}^{\infty} \eta d\xi \quad (39)$$

$$A_M = \int_{\xi_{M_1}}^{\xi_{M_2}} \eta d\xi = \int_{\xi_{M_1}}^{\infty} \eta d\xi - A_R \quad (40)$$

where  $\xi_{M_1}$  and  $\xi_{M_2}$  are the value of  $\xi$  at the maximum of Peaks 1 and 2, respectively.

The area estimate for Peak 2 by triangulation is

$$A_E = \left(\frac{\Delta_2}{\Delta_1 + \Delta_2}\right) A_M + A_R \quad (41)$$

whereas its true area is given by Equation 36. If  $\xi_1$  and  $\xi_2$

are the values of  $\xi$  at the right inflection point of Peak 1 and the left inflection point of Peak 2, respectively, one can show that the areas  $\Delta_1$  and  $\Delta_2$  are given by:

$$\Delta_1 = \frac{-1}{2\eta'(\xi_1)} (\eta'(\xi_1) (\xi_{M_1} - \xi_1) + \eta(\xi_1))^2 \quad (42)$$

$$\Delta_2 = \frac{1}{2\eta'(\xi_2)} (\eta'(\xi_2) (\xi_{M_2} - \xi_2) + \eta(\xi_2))^2 \quad (43)$$

where  $\eta'(\xi_i)$  is  $\frac{d\eta}{d\xi}$  evaluated at  $\xi_i$ .

Equation 30 must be satisfied at both  $\xi_1$  and  $\xi_2$  and Equation 29 at  $\xi_{M_1}$  and  $\xi_{M_2}$  supplying four added equations. The final equation is

$$A_E - A_2 = aA_2. \quad (44)$$

Equations 39, 40, 41, 42, 43, 30 twice, 29 twice, and 44 relate the variables  $\xi_{M_1}$ ,  $\xi_{M_2}$ ,  $\xi_1$ ,  $\xi_2$ ,  $R$ ,  $\delta$ ,  $A_R$ ,  $A_M$ ,  $A_E$ ,  $\Delta_1$ ,  $\Delta_2$ , and  $a$  giving 10 equations in 12 variables. By fixing  $a$  and varying  $\delta$  over the desired range, values of  $R$  were obtained for Figure 1. The least squares program mentioned earlier was used to solve numerically this set of nonlinear equations on the computer.

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## Gas Chromatography of Oxidants Using a Flowing Liquid Colorimetric Detector

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**A flowing liquid colorimetric detector was used for the gas chromatographic determination of hydroperoxides and nitrogen dioxide for possible application in air pollution studies. Half the effluent from the column went to a flame ionization detector, and half to a bubbler, in which the hydroperoxides reacted with a flowing ferrous thiocyanate liquid reagent. The liquid passed through a colorimeter, and the transmittance was recorded automatically. Several stationary phases were studied; the best was polyethylene glycol 400 on Chromosorb G, treated with hydrogen peroxide. The detection limit with the apparatus used was about nine micrograms of hydroperoxide. Nitrogen dioxide eluted from the same stationary phases; but, on most of them the colorimetric detector indicated that only about 1% of the eluted sample gave the NO<sub>2</sub> colorimetric reaction.**

ONE OF THE PROBLEMS in the study of air pollution has been the difficulty in obtaining quantitative data on the individual oxidants to be found in polluted air. These include ozone, nitrogen oxides, various peroxides, and peroxyacetyl nitrates.

While colorimetric methods for the analysis of ozone (1) and hydrogen peroxide (2) are specific for these compounds, iodometry (3) has been used much of the time for analysis of oxidants. Iodometry cannot differentiate among different oxidants except in model systems (4). The total oxidant level, and sometimes ozone, are usually reported.

Gas chromatography affords a suitable method to overcome these difficulties, but uncertainty existed in the literature as to whether oxidants, such as hydroperoxides, could be successfully chromatographed. Altshuller (5) indicated that ethyl hydroperoxide largely decomposed to ethyl alcohol and acetaldehyde, while others reported successful separation and elution of lower hydroperoxides (6, 7).

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