CHEMISTRY

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The subject of this paper essentially involves the problem of relating oxidant air quality to emissions. And because, unlike carbon monoxide, oxidant is a secondary pollutant, the problem is doubly complex. It has all the complexities of the dispersion process plus the complexities of the chemical process in which the reactant pollutants are converted into oxidants. This paper examines the various methods now available to relate ambient oxidant to emissions, but first discusses briefly the chemical and physical mechanisms by which emissions are dispersed in the atmosphere, get transported, and react to form urban, suburban, and nonurban oxidant.

CHEMICAL MECHANISM

Figure 1 shows the chemical process that occurs when hydrocarbon (HC) and nitrogen oxides (NO_x) in air are irradiated by sunlight. The overall process consists of 2 stages. In the first stage, NO is converted into NO₂; when all NO has reacted, O₃ begins to form and accumulate until either the irradiation ceases or the system runs out of reactants. This process was studied intensively in the laboratory (smog chambers), and the findings are as follows (1):

1. Increasing HC reactant concentration increases the rate of NO oxidation and in most cases increases resultant O_3 levels also (Figure 2);

2. Increasing NO concentration has a nonmonotonic effect, first increasing O_3 yield and then causing a decrease (Figure 3);

3. The nature of the HC reactant is also a factor; and

4. All these factors, HC, NO, irradiation time, and HC nature, interact to create further complications.

Subsequent mechanistic studies explained all these effects, at least for some hydrocarbons, e.g., propylene, n-butane. Thus, in a condensed form such a mechanism is approximately as follows:

 $NO_2 \xrightarrow{h\nu} NO + O$

(1)

 $O + O_2 \stackrel{M}{\rightarrow} O_3 \tag{2}$

$$O_3 + NO \rightarrow NO_2 + O_2 \tag{3}$$

 $O, O_3 + HC \rightarrow products + R (e.g., R, RO_2, RCO_3, HO)$ (4)

Figure 1. Illustration of atmospheric HC and NO_x reaction systems.



3.0

1.0

0

NMHC, ppm C

3.0

2.0

1.0

0

2.0

Figure 2. Maximum 1-hour oxidant as a function of NMHC at various NO_x levels.



Figure 3. Maximum 1-hour oxidant as a function of NO_x at various NMHC levels ("rational" extrapolation to zero).

Figure 4. Maximum daily 1-hour-average oxidants as a function of averages of NMHC from 6 to 9 a.m. in several large cities, June through September, 1966 through 1968, and in Los Angeles, May through October 1967.



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NO + NO₂ + H₂O \rightarrow HONO $\stackrel{h\nu}{\rightarrow}$ HO

$$RO_2 + NO \xrightarrow{O_2} NO_2 + R'$$

 $R + R' \rightarrow RR'$ (e.g., PAN)

In the absence of HC, O_3 reacts rapidly with NO to regenerate the photolyzed NO₂ so that O_3 accumulation is not permitted. Therefore, in clean air, ambient NO₂ will give little O_3 . In the presence of HC, radicals are formed that through chain reactions convert the NO back to NO₂; therefore, O_3 accumulation is now possible. This explains the enhancive effect of HC concentration and HC reactivity.

The NO effect is twofold. First, a relatively simple effect is caused by the fact that O_3 buildup does not start until all NO has been oxidized into NO_2 . Therefore, for given irradiation time, higher NO concentration will delay the O_3 formation process and will cause lower O_3 levels. Second, a more complex purely mechanistic effect occurs as follows: The higher the concentration of NO_2 is, the higher the rate of O_3 formation is because there is more NO_2 to photolyze and to form O-atoms and O_3 . However, when NO_2 is in large excess (relative to HC), then the $RO_2 + NO \rightarrow NO_2$ step does not remove NO sufficiently fast and NO is left to prevent O_3 from accumulating. This explains the HC/NO effect.

This is an extremely simplified explanation. The process includes perhaps 300 or more reaction steps. However, such detail is not needed for the purposes of this discussion.

PHYSICAL MECHANISM

Physical mechanism is the overall process that starts with the discharge of emissions into the atmosphere above the source areas and terminates with the development of an oxidant problem in the receptor areas. Alternatively, the physical mechanism can be understood as the mechanism that describes the relation between source area and receptor area.

The first mechanism adopted for use was the one that appeared to occur in the Los Angeles basin. By this relatively simple mechanism, referred to here as the local oxidant plume mechanism, the oxidant problem in a locality is caused entirely by the emissions discharged in that same locality. Thus, by this mechanism source area and receptor area coincide. Furthermore, occurrence of such a mechanism means that control of the local emissions is necessary and sufficient for reduction of oxidant in a given locality. This local oxidant plume mechanism is the mechanism adopted by EPA in the development of the oxidant control strategy now in use.

Today it is known that, although this mechanism may be approximated in some localities, it certainly does not have universal validity. Recent studies have revealed that in some localities the oxidant problem is caused by an area oxidant plume, meaning that a significant part of the problem is caused by emissions emitted outside the locality in upwind areas (2). Such an area plume mechanism has been observed to occur in the central and northeast part of the United States; the local plume mechanism appears to be the predominant one in the Los Angeles basin.

METHODS FOR RELATING AMBIENT OXIDANT TO PRECURSOR EMISSIONS

It should be stressed at the outset that all methods now available for relating emissions to oxidant air quality and calculating control requirements are meant to apply to urban

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(5)

(6)

(7)

air quality only; in fact, they apply only to oxidant formed by the local oxidant plume mechanism. This, of course, is because the oxidant pollution control strategies now in effect are for urban oxidant only.

To relate emission rates to oxidant air quality, we need to quantitate 2 processes: (a) the precursor emission dispersion process and (b) the photochemical reaction process. This has been done—however well or poorly—and the method that resulted is the well-known Appendix J method. This method was derived as follows.

The dispersion process was quantified by assuming a simple rollback model: C = b + ke. This led to the well-known simple rollback equation (3):

 $R = \frac{(gf)Cmax - Std}{(gf)Cmax - b} \times 100$

where Cmax and Std denote present and desired air quality (standard) respectively in terms of pollutant concentration, and gf is the growth factor.

For a primary pollutant, R is the percentage of control of emission needed. For oxidation, however, we need to express Cmax and Std in terms of precursor concentrations because it is the precursor emissions that can be controlled, not the oxidant. Here, the quantification of the photochemical process is needed, that is, a quantitative relation between ambient oxidant concentration and ambient precursor concentration. This relation was obtained from aerometric data in the form of the well-known upper limit curve or envelope curve (Figure 4). This curve was constructed by plotting daily maximum 1-hour oxidant concentration against nonmethane hydrocarbons (NMHC) from 6 to 9 a.m.; both the oxidant and NMHC were measured in the downtown areas of several large cities. From Figure 4 (discussed in the EPA criteria documents for NO_{\star} and HC), one can read off the NMHC values corresponding to Cmax, that is, to the maximum 1-hour oxidant observed in a location, as well as the NMHC value corresponding to Std, that is, to 0.08 ppm O₃. This NMHC value was determined to be 0.24 ppm C, and it is the U.S. air quality standard for HC, which is to be used as a guide only and not as a true air quality standard. By using these NMHC values and the rollback formula, and by assuming b = 0 (i.e., no background oxidant or NMHC), the control requirement for the percentage of NMHC was calculated as a function of oxidant concentration, and results (Figure 5) were published by EPA in the form of the Appendix J curve (4).

Appendix \overline{J} has several limitations arising from the assumptions used in the quantification of both the dispersion process and the photochemical process. But before these limitations are discussed, 4 alternative methods for relating air quality to emissions are presented briefly.

1. Use rollback formula (with b = 0) in conjunction with a simple proportionality relation between ambient oxidant concentration and ambient NMHC (or reactive HC) concentration, the latter relation to be used in lieu of the upper limit curve;

2. Use rollback formula in conjunction with oxidant-precursor relations derived from smog chamber data, the latter relations to be used in lieu of the upper limit curve;

3. Use more detailed mathematical expressions for the dispersion process in conjunction with theoretically derived mathematical expressions for the photochemical process (mathematical models); and

4. Use statistically supported empirical relations either between early-in-themorning precursor levels and oxidant or between emission rates and oxidant within a given area.

Two of these alternative methods, the proportional rollback method and the smog chamber method, are discussed here in more detail.

The proportional rollback method is currently a fairly popular alternative to Appendix J, mainly because it is not based on the highly objectionable upper limit curve and

Figure 5. Required hydrocarbon emission control as a function of photochemical oxidant concentration.



Figure 6. Equal response lines representing combinations of NMHC and NO_x corresponding to oxidant and NO_2 yields equal to the federal air quality standards.



because, relative to Appendix J, it leads to lower control requirements. The key part of the proportional rollback method is the assumption that ambient oxidant is proportional to the reactive hydrocarbon emission rate. The only justification for this assumption is offered by the smog chamber data. Such data show that the oxidant-to-HC dependence is not far from a linear relation (Figure 2). Relative to Appendix J, the proportional rollback method leads to lower control requirements, especially for locations with high oxidant levels.

The smog chamber method is also a popular alternative to Appendix J for the time being, mainly because it considers the role of NO_x quantitatively, a feature that lately has been shown to be an important one, as will be discussed later. The key part of the

smog chamber method is the oxidant isopleth diagrams that relate oxidant to both the NMHC and NO_x precursors (Figures 6 and 7). These diagrams were constructed by using data obtained from smog chamber irradiations of HC-NO_x mixtures at varied initial HC and NO_x concentrations. The shaded areas designate the HC-NO_x reactant combinations corresponding to 0.08 ppm O₃ or less. These diagrams reveal one important fact: The higher the ambient NO concentration is, the lower is the requirement for HC control to achieve the oxidant standard. Again, all this pertains only to oxidant formed by the local oxidant plume mechanism.

Specific procedures by which the oxidant isopleths of Figure 8 can be used to calculate numerical control requirements are several, varying in complexity and, presumably, in accuracy also. By the simplest method, it is assumed that the initial reactant concentrations in the smog chamber can be identified with the 6 to 9 a.m. ambient concentrations of HC and NO_x in an urban locality, and the maximum 1-hour O₃ concentration observed in the chamber can be identified with the day's maximum 1-hour O₃ concentration observed in the same urban monitoring site. The accuracy of this method, obviously, depends on how closely the real atmosphere conditions were simulated in the smog chamber. For example, if the chamber light intensity is lower than the sunlight intensity, then the smog chamber data will lead to a degree of control greater than needed. Even if the real atmosphere conditions are closely simulated in the chamber, it is still questionable that the assumption used in this method is valid. This is simply because the reactant (HC, NO_x) and product (O₃) concentrations in the smog chamber obey a cause-effect relation, but the ambient 6 to 9 a.m. HC, NO_x, and later-in-theday O₃ concentrations do not.

To circumvent the shortcomings of this simple method, LACAPCD investigators (Hamming) offered a technique by which the smog-chamber-predicted O_3 values are mathematically related to the ambient O_3 concentration values (in Los Angeles). This mathematical relation (Hamming transform) is then used to apply smog chamber deductions upon the real atmosphere in Los Angeles. The weaknesses of this LACAPCD method are two: First, the smog chamber data proposed for use are of poor quality; second, the mathematical relation between smog chamber O_3 values and ambient (Los Angeles) O_3 values is unproved. Extensive discussions and critiques of this technique have been presented at technical meetings and published (5, 6). A new method, proposed by this author (7), has the following key steps.

1. The smog chamber data proposed for use are data that have been shown to obey a cause-effect relation reasonably close to the one manifested in a real (urban) atmosphere.

2. The smog chamber counterparts of the ambient HC and NO_x concentrations responsible for observed ambient oxidant are determined from the ambient oxidant value (Cmax, that is, maximum concentration of O₃ observed in reference year) and the ambient 6 to 9 a.m. HC-to-NO_x ratio. Thus, the chamber concentrations of HC and NO_x are obtained from the intersect of the Cmax isopleth and the straight line of the slope equal to the ambient HC-to-NO_x ratio (Figure 7).

3. The so-derived chamber concentration value for NO_x is then reduced as dictated by the NO_2 problem in the locality under consideration.

4. Hydrocarbon control is calculated by taking into consideration that ambient NO_{\star} may vary downward from its maximum value.

Unlike the previous, simpler method, this method does not assume that the 6 to 9 a.m. ambient precursor concentrations are the ones that caused the oxidant concentration observed later in the day; instead, it assumes that the NMHC-to-NO_x ratio in the precursor mixture that caused the observed oxidant has the same value as the ratio in the 6 to 9 a.m. precursor mixture. This latter assumption certainly is a much more valid one, for atmospheric dispersion occurring during the day-long reaction affects the absolute levels of the precursors but not their ratio.

One final point of interest here pertains to the air quality standard for NMHC, that is, the NMHC concentration value corresponding to 0.08 ppm O_3 . Based on these chamber data (Figure 7), and considering the unavoidable downward variation of NO_x from



Figure 7. Oxidant isopleths corresponding to various maximum 1-hour oxidant values.

Figure 8. Maximum 1-hour oxidant as a function of NO_x at various NMHC-to- NO_x ratios (smog chamber data).



the maximum NO_x value (dictated by the NO₂ standard), it can be shown that the NMHC concentration corresponding to 0.08 ppm O₃ is about 0.15 ppm C—a value not far off the EPA value of 0.24 ppm C derived from the (upper limit) aerometric data curve (7). Interestingly, using the same smog chamber data, the National Academy of Sciences (NAS) derived an air quality standard for NMHC equal to 0.75 ppm C, that is, 5 times larger in value than the standard derived here (8). However, the NAS derivation ignored the unavoidable daily variation of the NMHC-to-NO_x ratio, an oversight that accounts for the disagreement.

CRITICAL EXAMINATION OF THE METHODS FOR RELATING OXIDANT AIR QUALITY TO EMISSIONS

By far the most important basis for assessing the value of a method is the ability of the method to predict air quality changes from emission changes. Since obtaining pertinent and complete data on emission changes and resultant air quality changes is not possible at present, it follows that direct validation by anyone of the methods available is not possible. This is a problem that is especially serious in the cases of the empirical methods in which the air quality -emission relation does not have a cause-effect nature. It was hoped that this problem could be solved by developing air quality-emission relations based on theory, as in the mathematical modeling methods, and validating such models by using data on absolute (present) air quality. But these hopes have not been justified yet, as will be discussed shortly. For the time being, it appears that the only assessment that can be made of the relative accuracies of the various methods is the one based on qualitative critiques such as the ones presented next.

Critique of the Appendix J Method

The key elements of this method are the upper limit curve depicting the oxidant-to-NMHC dependence, the simple rollback model, and the assumption that there is no background oxidant or NMHC. All 3 elements suffer from inadequacies or uncertainties. The limitations of the upper limit curve are as follows:

1. The curve may depict the dependence of oxidant on the dispersion factor rather than the dependence on the HC reactant factor;

2. The curve depicts a purely empirical relation, not a cause-effect one, and it, therefore, cannot automatically be assumed to have predictive value (it would have a more cause-effect nature if oxidant was measured within the same air mass in which the HC and NO_x measurements were made);

3. The curve disregards the NO_x factor;

4. Experimental error makes the low end of the curve (air quality standard for NMHC) highly uncertain;

5. Scarcity of data points makes the upper part of the curve highly uncertain;

6. The curve is not necessarily valid in locations other than those from which it was derived; and

7. The curve disregards oxidant transport phenomena.

Justification of the upper limit curve relation is mainly based on the following:

1. It is derived from real atmosphere data, a more realistic alternative to smog chamber data;

2. It is in qualitative agreement with the smog chamber data, at least insofar as the oxidant-to-HC dependence is concerned; and

3. It can be improved with the acquisition of additional data.

The simple rollback model also has limitations, the main ones being that it cannot be validated experimentally and that it assumes that all sources behave identically. A more extensive critique has been published (3). The main justification of the model is in its simplicity and in its relatively small demands for input data. The assumption that there is no background oxidant or NMHC is also incorrect, but has been adopted in the interest of simplicity.

Critique of the Smog Chamber Method

The key elements of the smog chamber method are again the rollback model and background oxidant assumption (as in the case of the Appendix J method), and the oxidant- $HC-NO_x$ relations derived from smog chamber data. The limitations of the rollback model and associated assumptions have already been discussed. The limitations of the chamber-derived oxidant-precursor relations are as follows:

1. Chamber atmospheres are only crude simulations of real atmospheres, and chamber data and associated relations, therefore, cannot automatically be assumed to be applicable to real atmospheres; and

2. Chamber data can define oxidant yield as a function of the precursors, but they tell us nothing about the frequency of oxidant occurrence (this inadequacy is significant since the NAQS for oxidant is defined in terms of an oxidant level as well as in terms of a frequency of oxidant occurrence).

Justification of the chamber-derived relations is based on the following:

1. The chamber-derived relations are truly cause-effect relations;

2. The chamber-derived relations are complete in that they involve all controllable oxidant precursors (HC, NO, NO₂);

3. For certain applications, the chamber-derived relations constitute the only option now available, e.g., in development of oxidant control strategies using the approach of coordinated control of HC and NO_x emissions; and

4. Chamber data and associated relations are amenable to improvement.

Critique of the Mathematical Modeling Method

Main input requirements of the mathematical modeling method are emission inventory data, atmospheric reaction mechanism for the emission mixture, and meteorological data. The main limitations of the modeling method arise from the fact that neither the emission inventories nor the reaction mechanism is sufficiently well know, at least now. Another limitation, this one of conceptual nature, arises from the fact that mathematical models cannot be validated directly, i.e., by using real atmosphere data, the main reason being that inhomogeneity makes real atmosphere undefinable, especially at the lower layers. Justification of the mathematical modeling methods is based on the following:

- 1. They are inherently more valid than the empirical methods, and
- 2. They are more useful than the other methods.

Discussion of Methods of Relating Emissions to Oxidant Air Quality

All of the existing methods of relating air quality to emissions suffer from uncertainties because of several problems. One problem is that the methods cannot be validated directly since it is not possible to obtain—within a reasonable period of time—pertinent and complete data on emission modification and resultant air quality changes. Validation of a method using data on absolute levels of emissions and air quality (as, e.g., the mathematical model method is to be validated) is also problematic because of the difficulty to uniquely define and quantitate oxidant air quality. Definition and quantitation of such air quality in terms of monitoring data of the usual type are unsatisfactory in that such air quality is not a function of emission rate only; it depends also on the position of the monitoring station relative to the position of emission sources, and on mixing factors—dependencies that are not quantifiable. In the face of this problem, it would perhaps be advisable to abandon the practice of using the customary monitoring data to define and express absolute levels of air quality (such data should be used only to define and express air quality trends). Validation of the various methods would then have to be done somehow else, e.g., against smog chamber data, primarily, and against real atmosphere data secondarily; and predictions by the so validated methods would be used to define and express absolute levels of air quality.

Another problem in the development of useful air quality-emission relations arises from our incomplete understanding of the physical process—by which emissions disperse, react (to form oxidant), and cause oxidant problems in a given area. Most of the existing methods of relating emissions to air quality are based on a simplistic scenario referred to here as the local oxidant plume concept. By this concept, as already discussed, emissions are discharged and dispersed in the air above the source area, react while being continuously diluted and mixed with fresh emissions, and finally cause oxidant pollution that afflicts the very same source area. Recent evidence, however, suggested that the oxidant problem in a locality may be caused by an area oxidant plume. In such localities, it is obvious that certain methods, e.g., the Appendix J method, will have much less validity. Also, monitoring data taken in such localities would be even more inappropriate for validation of mathematical models.

Notwithstanding these imperfections of the existing methods for relating air quality to emissions, a decision has to be made as to which of these methods is the least imperfect one, at the present time, for universal application. Based strictly on technical soundness, my recommendations are as follows.

1. The mathematical model methods are not ready and cannot be used yet—at least not for applications for which other usable methods are available.

2. The statistical emission-versus-oxidant methods are usable only in the localities for which they were developed and validated, and these methods are, therefore, conceptually inappropriate for universal application.

3. The Appendix J, the smog chamber method, and the statistical precursor concentration-versus-oxidant method are the least objectionable ones at present.

4. Of these 3 methods, the Appendix J and the statistical method have the same conceptual and accuracy limitations, already mentioned in the Appendix J critique. The chamber method, therefore, may have a slight advantage over all methods now available. The existing chamber data do not cover the entire range of HC and NO_x combinations of interest. Specifically, data are needed for HC-to-NO_x ratios up to 30:1 and for HC and NO_x concentrations closer to zero. I think that such data could be obtained through the use of a photochemical model developed and validated by using the existing chamber data.

Such an appraisal of the relative merits or drawbacks of the various methods is necessarily a qualitative one. A quantitative comparison, for example, a comparison of the confidence intervals associated with the predictions by the various methods, would be highly desirable, but does not seem to be possible at present or at any time in the future. My recommendations toward an improved method for relating oxidant air quality to emissions are as follows:

1. Conduct field studies, where necessary, to establish the various physical mechanisms by which emissions cause oxidant problems (information from such studies will serve to design appropriate smog chamber studies and to provide the input needed by the mathematical models) and also conduct special field studies to obtain data for validation of mathematical and smog chamber models;

2. Conduct comprehensive smog chamber studies of the O_x -HC-NO_x relations in which properly designed outdoor smog chambers are used and operated under widely diverse static and dynamic conditions, including those that maximize oxidant yield

from given $HC-NO_x$ mixture and those suggested by the field studies on physical mechanism;

3. Use such smog chamber data to develop and validate a mathematical model (use of such diverse data to validate the model might lessen the errors caused by the mechanism uncertainties) and further validate mathematical models with data from special field studies; and

4. Use the validated models to define and express air quality levels in localities or areas and to design control strategies.

ROLE OF NO, AND OF NATURAL EMISSIONS IN URBAN AND NONURBAN OXIDANT PROBLEMS

The preceding discussion was concerned entirely with the urban oxidant problem. Furthermore, most-but not all-of the methods discussed for relating oxidant to emissions were based on the premise that urban oxidant is an increasing monotonic function of the NMHC reactant; the NO_x role was ignored. Recent findings from field and laboratory studies raised some important implications regarding the relative roles of the NO_x and NMHC reactants, but clearly did not invalidate the premise regarding the NMHC role. Therefore, the control approach now in use-i.e., unilateral control of NMHC-continues to be justified. Some of the specific implications raised by the more recent studies are as follows.

The most important recent finding is the one (from the oxidant transport studies) that led to the distinction between the urban oxidant plume mechanism and the area oxidant plume mechanism by which emissions cause oxidant problems. In areas in which the urban oxidant plume mechanism is the predominant one, the role of NO_x is well understood, thanks to the smog chamber data available. Thus, in such areas emissions should be controlled so as to reduce the HC-to-NO_x ratio in air. In fact, if the ambient HC-to-NO_x ratio is maintained at a low level, e.g., 2.0 or less, it is reasonably certain that the oxidant standard will be achieved (Figure 8). In areas in which the area oxidant plume mechanism is the predominant one, the role of NO_x may be much more complex, as illustrated in the following examples.

1. A suburban or nonurban area has an oxidant problem that is caused almost entirely by man-made emissions transported from upwind areas. The NO_x , in this case, acts as an inhibitor, and control of upwind emissions so as to reduce the HC-to- NO_x ratio will probably be beneficial.

2. A nonurban area has no oxidant problem or has a small problem caused by reactions of local natural HC mixed with man-made (transported or local) NO_x. This is a hypothetical—but not improbable—example of an area in which the natural (local) HC and NO_x emissions alone have an extremely high HC-to-NO_x ratio such that oxidant buildup is not possible or is small. With the injection of additional NO_x, however, such mixtures will develop oxidant producing potential. Therefore, unlike in the previous example, in this example control of upwind NO_x emissions is beneficial. In fact, control of HC alone may be detrimental in that it will cause more NO_x to survive the photochemical process in the upwind areas and to be transported into the nonurban area of this case.

Because of the possibility that the problem in example 2 may be a real one, a sound emission control strategy for oxidant reduction should be designed to ensure that the NO_x levels in air, at least, will not increase as a result of the HC control. Such increase could occur for 2 reasons: first, some methods of controlling HC emission from combustion processes cause an inadvertent increase in NO_x emissions. Second, control of HC to reduce oxidant to 0.08 ppm will cause more NO_x to survive the photochemical process.

In summary, this paper attempts to present a concise picture of the oxidant problem; attention is focused on the aspects thought to be most relevant to the quantitative dependence of ambient oxidant on precursor emissions. Opinions are expressed with the

understanding that they should not be taken as representing established or all-accepted viewpoints. Rather they should be taken as a challenge to other viewpoints or a departure point to a review process.

REFERENCES

- 1. B. Dimitriades. On the Function of Hydrocarbon and Nitrogen Oxides in Photochemical Smog Formation. U.S. Bureau of Mines, Report of Investigations, R17433, Sept. 1970.
- Investigation of Rural Oxidant Levels as Related to Urban Hydrocarbon Control Strategies. U.S. Environmental Protection Agency, Research Triangle Park, N.C., Rept. EPA-450/3-75-036, March 1975.
- 3. N. De Nevers and J. R. Morris. Rollback Modelling: Basic and Modified. Journal of the Air Pollution Control Association, Vol. 25, No. 9, Sept. 1975, pp. 943-947.
- 4. Federal Register. Vol. 36, No. 158, Aug. 14, 1971.
- 5. Proceedings of the Smog Chamber Conference. U.S. Environmental Protection Agency, Research Triangle Park, N.C., 1975.
- D. R. Sonten, C. Hopper, and R. Mueller. A Critical Review of the Los Angeles County APCD Method for Simulating Atmospheric Oxidant Based on Smog Chamber Irradiation Experiments. 68th Annual Meeting of the Air Pollution Control Association, Boston, Mass., June 15-20, 1975.
- 7. B. Dimitriades. Oxidant Control Strategies: Part I—An Urban Oxidant Control Strategy Derived From Existing Smog Chamber Data. Environmental Science and Technology, 1975.
- 8. A Critique of the 1975-1976 Federal Automobile Emission Standards for Hydrocarbons and Oxides of Nitrogen. National Academy of Sciences, May 22, 1973.