[6560-01]

ENVIRONMENTAL PROTECTION AGENCY

[40 CFR Part 50]

[FRL 886-4 Docket Number OAQPS 78-8]

PHOTOCHEMICAL OXIDANTS

Proposed Revisions to the National Ambient Air Quality Standard

AGENCY: Environmental Protection Agency.

ACTION: Proposed rule.

SUMMARY: In accordance with the provisions of Sections 108 and 109 of the Clean Air Act as amended, EPA has conducted a review of the criteria upon which the existing primary and secondary photochemical oxidant standards are based. The revised criteria are being published simultaneously with the issuance of this proposed rulemaking. The existing primary and secondary standards for photochemical oxidants are currently set at 0.08 ppm, 1-hour average not to be exceeded more than once per year. As a result of the review and revision of health and welfare criteria, EPA proposes to raise the primary standard level to 0.10 ppm, 1-hour average. EPA also proposes that the secondary welfare-based standard remain at 0.08 ppm, 1-hour average. Other changes proposed in this rulemaking include: (1) changing the chemical designation of the standard from photochemical oxidants to ozone, and (2) changing to a standard with a statistical rather than deterministic form, i.e. allowable exceedances will be stated as an *expected* value, not an explicit value.

During the period between this proposal and final promulgation of the standard, EPA will continue its examination of health and welfare criteria and seek to further involve the public and other affected parties in the final decision on the air quality standard.

DATES: Comments must be received by August 18, 1978. There will be a public hearing at 9:00 a.m. on July 18, 1978. This hearing may be extended into the following day, July 19, as necessary. The standard will be promulgated by the end of September, 1978.

ADDRESS: Send comments to Mr. Joseph Padgett (MD-12), Director, Strategies and Air Standards Division, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

The public hearing will be held at: Environmental Protection Agency, 401 M Street SW., Room 2117, Washington, DC 20460.

FOR FURTHER INFORMATION CONTACT:

Mr. Joseph Padgett, Telephone: 919-541-5204 (FTS 629-5204).

Availability of supporting information: A docket (Number OAQPS 78-8) containing information used by EPA in development of the proposed standard is available for public inspection between 8:00 a.m. and 4:30 p.m. Monday through Friday, at EPA's Public Information and Reference Unit, Room 2922, Waterside Mall, 401 M Street SW., Washington, DC 20460. These materials include the "Air Quality Criteria for Ozone and Other Photochemical Oxidants" and "Control Techniques for Volatile Organic Emissions from Stationary Sources", both issued simultaneously with this proposal. In addition, staff papers pertaining to the form of the ozone standard, risk assessment method, secondary standard, and health panel assessment are also available. These documents can be received upon request from Mr. Joseph Padgett.

Revisions to 40 CFR Part 50, Appendix D, "Measurement Principle and Calibration Procedure for the Measurement of Photochemical Oxidants Corrected for Interferences Due to Nitrogen Oxides and Sulfur Dioxide" and Appendix H, "Interpretation of the National Ambient Air Quality Standard for Ozone" are described elsewhere in this preamble.

Revisions to 40 CFR Part 51 substituting the word "ozone" for "photochemical oxidants" throughout that part, and to Section 51.14 pertaining to control strategies are being proposed by EPA elsewhere in this issue of the FEDERAL REGISTER.

Statements of the environmental, economic, and energy impacts of implementing this standard revision are available upon request from Mr. Joseph Padgett, at the address shown above.

SUPPLEMENTARY INFORMATION:

BACKGROUND

On April 30, 1971, the Environmental Protection agency promulgated in the FEDERAL REGISTER (36 FR 8186) National Ambient Air Quality Standards for photochemical oxidants. The scientific, technical, and medical basis for these standards is contained in the air quality criteria document for photochemical oxidants published by the U.S. Department of Health, Education, and Welfare in March, 1970. Both the primary and secondary standards were set at a level of 0.08 ppm, hourly average not to be exceeded more than once per year. The preamble to the regulation stated:

> "The revised national primary standard of 0.08 ppm is based on evidence of increased frequency of asthma attacks in some asthmatic subjects on days when estimated hourly average concentrations of photochemical oxidant reached 0.10 ppm. A number of comments raised serious questions about the validity of data used to suggest impairment of athletic peformance at lower oxidant concentrations. The revised primary standard includes a margin of safety which is substantially below the most likely threshold level suggested by this data. It is the Administrator's judgment that a primary standard of 0.08 ppm as a 1-hour average will provide an adequate safety margin for protection of public health and will protect against known and anticipated adverse effects on public welfare."

The asthma study cited above as evidence for the original standard is based on work by Schoettlin and Landau. Effect level estimates from this study have changed and are discussed elsewhere in this proposed regulation.

Oxidants are strongly oxidizing compounds which are the primary constituents of photochemical smog. The oxidant found in largest amounts is ozone (O_3), a very reactive form of oxygen. Oxidants also include the group of compounds referred to collectively as peroxycylnitrates (PANs) and other compounds all produced in much smaller quantities than ozone.

Most of these materials are not emitted directly into the atmosphere but result primarily from a series of chemical reactions between oxidant precursors (nitrogen oxides and organic compounds) in the presence of sunlight. The principal sources of organic compounds are the hydrocarbon emissions from automobile and truck exhausts, gasoline vapors, paint solvent evaporation, open burning, dry cleaning fluids, chemical plants and other industrial operations. Nitrogen oxides are emitted primarily from combustion sources such as electric power generation units, gas and oil-fired space heaters, and automobile, diesel and jet engines.

The reductions in emissions of nitrogen oxides and organic compounds are achieved through Federal and State programs which have been formalized in regulations promulgated under the Clean Air Act. The Federal programs provide for the reduction in emissions nationwide through the Federal Motor Vehicle Control Program, the Federal program for control of aircraft emissions, National Emission Standards for Hazardous Air Pollutants, and the development of New Source Performance Standards. The State programs provide for additional control measures through State Implementation Plans in those areas of the country where the Federal programs are not sufficiently stringent to permit attainment of air quality standards.

STATUTORY REQUIREMENTS AFFECTING THIS PROPOSAL

Two sections of the Clean Air Act govern the development of a National Ambient Air Quality Standard. Section 108 instructs EPA to document the scientific basis for the standard, and Section 109 provides guidance on establishing standards and reviewing criteria.

Air quality criteria are required by section 108(a)(2) to accurately reflect the latest scientific information useful in indicating the kind and extent of all identifiable effects on public health or welfare which may be expected from the presence of the pollutant in the ambient air.

Simultaneously with the issuance of these criteria, the Administrator is required to propose primary and secondary ambient air quality standards based upon such criteria. The primary standard is defined in section 109(b)(1) as that ambient air quality standard the attainment and maintenance of which, based on such criteria and allowing an adequate margin of safety, is in the Administrator's judgment requisite to protect the public health. The secondary standard (section 109(b)(2)) must specify a level the attainment and maintenance of which, based on such criteria, is in the Administrator's judgment requisite to protect the public welfare from any known or anticipated adverse effects associated with the presence of the pollutant in the ambient air. These adverse welfare effects are discussed in section 302(h) of the Act, and include effects on soils, water, crops, vegetation, man-made materials, animals, weather, visibility, hazards to transportation, economic values, personal comfort and well-being, and other factors.

The Clean Air Act specifies that National Ambient Air Quality Standards are to be based solely on scientific criteria relating to the level that should be attained to adequately protect public health and welfare. Considerations of cost of achieving those standards or the existence of technology to bring about needed reductions of emissions are not germane to such a determination, as the words of the Act and its legislative history clearly indicate. Section 109(d) directs the Administrator to complete a review of all existing standards and criteria before the end of 1980 and at five-year intervals thereafter, and to revise them in whatever manner that review reveals is necessary. This proposal is the result of such a review.

Assuring attainment and maintenance of ambient air quality standards is the responsibility of the states. Under section 110 of the Act, they are to submit to EPA for approval State Implementation Plans (SIP) that provide for the necessary legal requirements upon sources of the relevant pollutant so as to demonstrate attainment and maintenance of the standards by certain deadlines. In the case of photochemical oxidants, there has been widespread failure to attain the standards. In 1977, Congress amended the Clean Air Act by inserting several sections, mostly found in Part D of the Act as amended, to intensify the effort to attain the oxidant standard. New deadlines were established, and the states are required to submit revised State Implementation Plans by January 1, 1979, for all "non-attainment areas".

The photochemical oxidant (ozone) standard is the only standard scheduled for review and revision before the submission of the 1979 plan revisions. The proposed standard revision will affect the plans. There is nothing in the Act to explain what effect this proposed action should have on the January 1, 1979 deadline or other schedules under the Act. However, based on the nature and extent of changes proposed to the existing standard, including the fact that the standard will not be made more stringent, it is EPA's judgment that this proposed action will in no way impair the states' ability to revise State Implementation Plans by January 1, 1979. Consequently, EPA is concluding that this proposed standard revision does not alter the 1979 SIP submission deadline.

PENDING RULEMAKING PETITIONS

The Agency was petitioned by the American Petroleum Institute and 29 member companies on December 9, 1976, and the City of Houston on July 11, 1977, to revise the criteria, standards and control strategy guidelines for photochemical oxidants. These efforts were already underway when both petitions were filed, and the Agency responded that it was deferring decision on their petitions until the rulemaking was completed. This notice of proposed rulemaking and the accompanying one on control strategy guidelines constitute the action the Agency proposes to take in response to those petitions. The final notices, which will be published by the end of September, 1978, will constitute the Agency's final action on those petitions.

DEVELOPMENT OF AIR QUALITY CRITERIA AND SUMMARY OF GENERAL FINDINGS FROM AIR QUALITY CRITERIA FOR OZONE AND PHOTOCHEMICAL OXIDANTS

On April 20, 1977 (42 FR 20493), EPA announced that it was in the process of reviewing and updating the 1970 criteria document for photochemical oxidants in accordance with provisions of Section 109(d)(1) of the Clean Air Act as amended. The notice called for information and data that would be helpful in revising the document. In the process of developing the criteria document, EPA has provided a number of opportunities for external review and comment. Two drafts of the criteria document have been made available for external review and EPA has received more than 50 written comments on the first draft and approximately 20 on the second draft. The American Petroleum Institute has submitted extensive information that EPA has considered in this standard review. The criteria document was the subject of two meetings of the Subcommittee on Scientific Criteria for Photochemical Oxidants of EPA's Science Advisory Board. Each of these meetings has been open to the public and a number of individuals have presented both critical review and new information for EPA's consideration.

From the extensive review of scientific information presented in the criteria document, findings in several key areas have particular relevance for setting the ozone standard.

1. The concept of a "threshold" may not be an appropriate term for describing the impact of ozone on human health. Since "thresholds" will depend upon who is studied and what is measured, it is unlikely that scientific evidence for a specific effects threshold can be satisfactorily derived for protecting public health. Limited studies can be performed on groups of unusually sensitive persons. Most experimental studies of humans are performed on small numbers of healthy subjects who do not adequately reflect the range of human sensitivity. Toxicological studies usually cannot utilize appropriate models of sensitive human populations. Thus, "thresholds" for sensitive persons are difficult or impossible to determine experimentally, while the "threshold" for healthy persons or animals is not likely to be predictive of the response of more sensitive groups.

2. Ozone is a bronchio-pulmonary irritant which affects the mucous lining, other lung tissues and respiratory functions. It has been demonstrated in clinical and epidemiological studies that ozone does impair the normal function of the human lung and causes clinical symptoms such as chest tightness, cough and wheezing. These effects are estimated to occur at short-term ozone concentrations between 0.15 and 0.25 ppm. The clinical studies data base on these effects is far more extensive than that available in 1970 and these effects have been demonstrated at lower levels than those cited in the 1970 criteria document.

3. Asthmatics experience a higher number of attacks on days when the peak hourly oxidant concentrations reach about 0.25 ppm. This finding is based on a reevaluation of the Schoettlin and Landau study and represents a revision of the 0.10 ppm estimate made in the 1970 criteria document.

4. The key finding from toxicologic studies show increased susceptibility to bacterial infection in laboratory animals exposed to 0.10 ppm ozone and a bacterial challenge. Infection rates are lower for animals exposed only to the bacterial challenge. Other

effects such as biochemical changes, morphological abnormalities, and genetic changes have been shown in some animal studies but the physiological significance of these effects remains to be established.

5. There is a limited amount of data that suggests that ozone may accelerate the aging process in living organisms. Exposure of rabbits to unspecified concentrations of ozone for one hour per week for a year has been reported to induce premature aging symptoms such as premature cartilage calcification, severe depletion of body fat, and general signs of senescence. Inhalation of 0.20 to 0.25 ppm ozone by animals and humans over 30 to 60 minute periods increased the rate of sphering of red blood cells when their blood samples were irradiated, suggesting an acceleration in the aging of the cells.

6. Acknowledgement of the fact that ozone exposure is frequently accompanied by exposure to other pollutants, particularly sulfur dioxide (SO_2), has prompted several investigators to conduct laboratory evaluations of exposure of humans to combinations of O_3 and SO_2.

Exposures to 0.37 ppm O_3 and 0.37 ppm SO_2 simultaneously have been reported to produce enhanced decrements in pulmonary function as compared with either pollutant alone. Other simultaneous exposure tests using O_3 and nitrogen dioxide (NO_2) and O_3, NO_2 and carbon monoxide (CO) produced few important physiological changes and only mild symptoms. These findings suggest the need for an adequate margin of safety as well as the need for more definitive data.

7. There are no health studies that link exposure to ozone or photochemical oxidants to an increase in human mortality. A number of epidemiologic studies have been designed and conducted to demonstrate this effect, but all have been negative or inconclusive.

8. Ozone accelerates the aging of many materials resulting in rubber cracking, dye fading and paint erosion. These effects are related to the total dose of ozone and can occur at very low levels, given long duration exposures. Damage to vegetation occurs as leaf injury, decreased growth and yield, and disruption of reproductive functions.

9. All evidence presently available indicates that around urban centers with severe oxidant problems, the major concern is the formation of photochemical oxidants from man-made organic and nitrogen oxide emissions. Control of these emissions will effect significant reductions in ambient ozone, peroxyacetylnitrate (PAN), aldehydes and photochemical aerosol.

GENERAL APPROACH TO SELECTING THE LEVEL OF THE PRIMARY OZONE STANDARD

Revision of the National Ambient Air Quality Standard for ozone requires certain judgments by EPA about the relationship between concentrations of ozone in the air and possible adverse health effects experienced by the public. This relationship is greatly complicated by the fact that there is variability of response among individuals exposed to ozone, and that there are numerous effects of ozone on health occurring at different levels of exposure. In selecting the proper level for the revised standard, EPA must make judgments relating to four critical areas:

1. The range of demonstrated health effects.
2. The sensitive population.
3. The seriousness of the health effect and the level at which the health effect has been demonstrated to occur.
4. What constitutes an adequate margin of safety to protect the public health.

DEMONSTRATE HUMAN HEALTH EFFECTS AND EFFECTS OBSERVED IN ANIMAL STUDIES

The purpose of this discussion is to describe the health effects attributed to ozone that are of concern in setting an ozone air quality standard. The discussion attempts to put these effects in perspective, and where possible, relate them to common personal experiences of the average person.

Impaired Pulmonary Function and Airway Resistance—Ozone is a bronchiopulmonary irritant which affects the mucous lining, other lung tissue and respiratory functions. Changes in lung function appear as increased airway resistance, reductions in vital capacity, expiratory flow rates and diffusion capacity. These effects are greater in exercising individuals and individuals with hyper-reactive airways (history of developing symptoms during light activity in smog or history of asthma). Changes in lung function are accompanied by clinical symptoms such as coughing, chest tightness, and lower chest soreness.

Because the human respiratory system is endowed with a large capacity, even airway resistance increases of 50 to 100 percent will not ordinarily be perceived in normal individuals. However, a portion of the population with respiratory problems may be operating at the limit of their lung capacity even in normal activity states, and any increase in air flow resistance will affect their ability to perform or aggravate a pre-existing pulmonary disease. For healthy individuals engaged in strenuous activity, a 50 to 100 percent increase in airway resistance might be accompanied by shortness of breath and fatigue. Since these sensations are normally associated with strenuous activity, it would be difficult to detect the air pollution induced effect in healthy persons. In a light activity state, it is unlikely that any observable effect could be noted from changes even as high as 50 to 100 percent increase in flow resistance.

Decreased Resistance to Infection—This effect is represented by an increased rate of mortality in laboratory animals subjected to both a bacterial challenge and exposures to ozone. According to some studies, the effect may be enhanced by the addition of such stresses as heat, exercise, or the addition of other pollutants in combination with the ozone dose. Despite the lack of confirmatory studies in man, and the uncertainties involved in predicting human effects from animal studies, most medical experts agree that decreased resistance to infection most likely does occur in man and the lack of such evidence is probably due to the difficulty of detecting these responses in epidemiologic studies.

Aggravation of Chronic Respiratory Disease—It is generally accepted by the scientific community that there is a link between ambient oxidant levels and aggravation of pulmonary disease. This link was demonstrated by the Schoettlin and Landau study which related the frequency of asthma attacks to measured ambient photochemical oxidant concentrations. Several studies have investigated the aggravation of emphysema and chronic bronchitis without any definitive links to photochemcial oxidant concentrations.

Air pollution is one of the many stresses which can precipitate an asthma attack or worsen the disease state in persons with chronic cardiopulmonary disease. Other factors which can act like ozone in precipitating attacks include: respiratory infections, passage of cold fronts, seasonal pollens, extreme heat or cold, and even emotional disturbances.

Eye Irritation—Eye irritation is associated with selected chemical species (such as PAN) in the photochemical oxidant mix and other organic vapors. There is no evidence that eye irritation is associated with ozone. Since EPA plans to redesignate the standard from photochemical oxidants to ozone, the eye irritation effect is not a critical one in establishing the standard level.

Biochemical Effects—Experimental exposures of human subjects to ozone have produced changes in blood biochemistry, such as increased fragility of red blood cells and altered enzyme activities in the serum. The significance of these ozone-mediated changes is not yet known, but changes of the magnitude observed in experimental exposures have not yet been linked to any clinical diseases.

Carcinogenic, Mutagenic and Related Effects—Studies have been conducted in an attempt to relate ozone to carcinogenic, mutagenic, and related effects. These studies are not deemed to be important in setting ambient ozone standards because of the failure of researchers to replicate much of the work and because of the questionable significance to man of some effects observed in lower life forms. The criteria document states that the significance of effects such as chromosomal aberrations has not been established. EPA's Science Advisory Board has recommended not including some of the studies in the criteria document lest they receive unwarranted emphasis.

SENSITIVE POPULATION

Clinical and epidemiological studies have shown that asthmatics and other persons with reactive airways appear most sensitive to changes in ozone concentrations and are thus judged to be the principal sensitive group of concern in setting the standard. This is because their airways are hyper-reactive to irritants such as ozone.

Studies have also established that exercise effectively increases the ozone dose delivered to the target tissues in the respiratory tract. Thus, persons engaging in exercise are particularly vulnerable to the acutely irritating effects of ozone. However, the response of these groups to such changes in concentrations has not been systematically studied.

SELECTING THE LEVEL OF THE PRIMARY STANDARD

The language of section 109(b)(1) requires EPA to set a primary standard that, based on the air quality criteria and allowing an adequate margin of safety, is requisite to protect the public health.

Relevant to this charge, the National Academy of Sciences reached the following conclusion in 1974:

> * * * in no case is there evidence that the threshold levels have clear physiological meaning, in the sense that there are genuine adverse health effects at the above some level of pollution, but no effects at all below that level. On the contrary, evidence indicates that the amount of health damage varies with the upward and downward variations in the concentration of the pollutant, with no sharp lower limit.

The House of Representatives Committee on Interstate and Foreign Commerce has observed that the concepts of threshold and adequate margin of safety that underlie the language of section 109(b)(1) of the Clean Air Act are necessary simplifications to permit the Administrator to set standards.

The criteria document confirms that no clear threshold can be identified for health effect due to ozone. Rather, there is a continuum consisting of ozone levels at which health effects are certain, through levels at which scientist can generally agree that health effects have been clearly demonstrated, and down to levels at which the indications of health effects are less certain and harder to identify. Selecting a standard from this continuum is a judgment of prudent public health practice, and does not imply some discrete or fixed margin of safety that is appended to a known "threshold".

The uncertainties with which such a judgment must deal are the result of several factors. First, human susceptibility to health effects varies and we cannot be certain that experimental evidence has accounted for the full range of susceptibility. Second, we cannot be certain that all effects occurring at low ozone levels have been identified and demonstrated. Third, variations in weather create uncertainty as to the expected annual maximum ozone concentrations.

The decision is made more difficult by the fact that the Clean Air Act, as the Administrator interprets it, does not permit him to take factors such as cost or attainability into account in setting the standard; it is to be a standard which will adequately protect public health. The Administrator recognizes, however, that controlling ozone to very low levels is a task that will have significant impact on economic and social activity. It is thus important that the standard not be any more stringent than protection of the public health demands.

Human health effect levels cited in the criteria document from published studies vary from 0.15 to 0.30 ppm. The studies documenting effect levels are presented below:

DEMONSTRATED EFFECT LEVELS IN MAN

Aggravation of asthma	Reduction in pulmonary function	Chest discomfort and irritation of the respiratory tract
0.25 p/m—epidemiologic (schoettlin and Landau).	0.15 p/m to 0.30 p/m clinical (DeLucia and Adams).	0.25 p/m—epidemiologic (Hammer et al.).
	0.25 p/m clinical (Hazucha)	0.15 p/m to 0.30 p/m clinical (DeLucia and Adams).

Although animal studies have described other effects such as decreased resistance to bacterial infection, effect levels cannot be extrapolated to man. Only those effects listed above are considered relevant to estimating a demonstrated effect level in man.

The human health effect category of most concern is aggravation of chronic lung disease and the key study documenting the effect is the Schoettlin and Landau asthma study. Based on a reevaluation of this study, the current criteria document attributes an increase in asthmatic attacks to a level of 0.25 ppm and not 0.10 ppm as presumed when the existing standard was promulgated.

This was a key study in determining the level of the existing standard and was cited in the preamble for the promulgation of the current standard:

> The revised national primary standard of 0.08 ppm is based on evidence of increased frequency of asthma attacks in some asthmatic subjects on days when estimated hourly average concentrations of photochemical oxidant rached 0.10 ppm.

This is an important change in our understanding of that study but does not justify a substantial relaxation of the current standard because new clinical work has documented some effects at concentrations as low as 0.15 ppm.

The study demonstrating the lowest effect level in man is the DeLucia and Adams study of the effects of exercise on lung function and blood biochemistry in six men after 1-hour exposure to 0.15 ppm and 0.30 ppm of ozone via a mouthpiece. For both exposure levels, most subjects demonstrated signs of toxicity (symptoms such as chest tightness, pain on deep inspiration, and cough) during the most stressful exercise protocol, and sensitive subjects exhibited impaired pulmonary function following the most stressful exercise protocol. No effects on the subjects' blood biochemistry were observed following any of the exposures.

Earlier clincial studies document more significant impairment of pulmonary function in sensitive subjects at 0.37 ppm for two-hour exposures. Other clinical studies have described 0.25 ppm or higher as a no-effect level for sensitive lightly exercising subjects.

The effect of reduced resistance to bacterial infection has only been demonstrated in animals. The lowest effect level is for a one-hour exposure to levels of 0.08 ppm to 0.10 ppm. Medical experts agree, and the criteria document concludes, that these studies have definite health implications for man but that such effects in humans may occur at different concentrations. There is no epidemiological evidence that demonstrates the effect of reduced resistance to bacterial infection in man. The criteria document cites numerous epidemiological studies that fail to link increased mortality or increased hospital admissions with ozone or oxidant exposures. Those few studies which do suggest such a link are described as inconclusive in the criteria document, and all these studies are deemed to have serious limitations.

Based on the studies cited in this section, EPA concludes that the *demonstrated* human effects levels as cited in the criteria document vary from 0.15 ppm to 0.30 ppm. Additional opinions were sought from an advisory panel of health experts (referred to hereinafter as the health panel) and other selected medical experts, who were asked to assess the literature reported in the criteria document.

Estimates made by these experts are based on their understanding and interpretation of those health critieria. A summary statement from the health panel has been placed in the docket and is available from EPA at the address given earlier. As an added aid for addressing the uncertainties associated with setting an adequately protective standard, EPA has used an analytic technique of risk assessment. Formal interviews of selected medical experts were evaluated using a methodology known as subjective probability encoding. This analysis estimated the probability of various health effects occurring in sensitive persons at alternative ozone levels. A report which discusses the basis for and application of the analytic method has been placed in the docket and is available from EPA at the address given earlier.

The most probable effect levels for various health effects as estimated by the health panel and by the risk assessment procedure are shown below:

PROBABLE EFFECT LEVEL ESTIMATES—*Estimates for sensitive population segments*

[Parts per million]

	Aggravation of asthma, emphysema, and chronic bronchitis	Reduced resistance in bacteria infection (animal studies)	Reduction in pulmonary function	Chest discomfort and irritation of the respiratory tract
Health panel judgment of effect level.	0.15-0.25	(1)	0.15-0.25	0.15-0.25
Probable (median) effect level as estimated from interviews with health experts	0.17 (0.14-0.25)	0.18 (0.07-0.38)	0.15 (0.07-0.18)	0.15 (0.11-0.18)

[1] Not available.

These estimates are based on the most sensitive population segments. In the case of the risk assessment interviews, the experts were asked to focus not only on the most sensitive population group, but also on a very sensitive portion of that group (specifically, those persons who are more sensitive than 99 percent of the sensitive group, but less sensitive than 1 percent of that group). However, these people should not be considered as medically handicaped as a result of their sensitivity. Their outward appearance may be perfectly normal, but when exposed they could have adverse reaction. The lowest effect level estimate cited by the health panel and those generated through the expert interview process are reasonably consistent, ranging from 0.15 to 0.18 ppm. Based on this data and on the demonstrated effect levels cited in the criteria document, it can be concluded that health effects have been demonstrated at ozone levels of 0.15 ppm.

The criteria document contains several indications of the uncertainties discussed above that have given EPA reason to believe that a standard of 0.15 ppm would not be adequately protective. Of particular importance are: (1) new and replicated animal studies showing reduced resistance to infection at ozone levels of 0.10 ppm; (2) Japanese epidemiological studies reporting an increase in respiratory discomfort and other symptoms in school children at oxidant concentrations below 0.15 ppm.

Evidence of reduced resistance to bacterial infection has not reached the point where it can be meaningfully used to extrapolate concentrations that would similarly affect man. Most experts agree, however, that the effect occurs in humans, and that it is only the concentration at which these effects occur that is uncertain. Further, it is the kind of effect that is serious enough in its implications to raise a need for caution. Thus, there is a need for setting a standard more stringent than the effect level which has been demonstrated in human studies, in order to account in some measure for these unquantified but possibly serious effects.

A similar caution is suggested by the Japanese epidemiological studies. The Science Advisory Board questioned the merit of the studies because there exists the possibility that some of the symptoms observed may have been induced by the subject's knowledge of the prevailing levels. Nevertheless, it would not be wise to totally disregard the studies on the basis of this possibility.

An added uncertainty which must be considered is the variation in air quality concentrations due to prevailing meteorologic conditions. Since EPA's proposed standard will be attained when the expected number of hours per calendar year with concentrations above the standard level is equal to or less than one, there is concern for the magnitude of this one allowable excursion. The probabilities for several alternative standard levels that this excursion will exceed the demonstrated effect level are shown below.

PROBABILITY THAT THE ALLOWABLE STANDARD EXCEEDANCE WILL BE AT OR ABOVE THE DEMONSTRATED EFFECT LEVEL OF 0.15 P/M FOR ALTERNATIVE STANDARD LEVELS

Standard level (p/m)	Probability
0.08	<0.01
0.10	<0.01
0.12	0.08
0.14	0.40

EPA has utilized the analytic technique of risk assessment mentioned earlier in an attempt to address the uncertainties involved both in estimating the health effects levels for sensitive persons and in predicting the air quality expected to result when a given standard level is attained. Using known patterns of variation in ambient air quality, EPA has estimated the probability, at various levels of an ozone standard, that health effects will be experienced. The resulting probability estimates provide a useful tool for comparing the relative protection of various standard levels below the demonstrated effects level of 0.15 ppm.

As mentioned previously, a report discussing the basis for and application of the risk assessment methodology has been placed in the docket. This report has been submitted to the EPA Science Advisory Board for review. However, the review is not yet complete nor has the report received adequate review by others in the scientific community. Consequently, the probability estimates presented therein and summarized below should be considered preliminary.

*Probability that effect threshold will be exceeded 5 times or more in 5 years for alternate standard levels**

Hourly average standard level (1 expected exceedance per year)	(1) Aggravation of asthma, emphysema, and chronic bronchitis	(2) Reduced resistance to bacterial infection (animal studies)	(3) Reduction in pulmonary function	(4) Chest discomfort and irritation of the respiratory tract	Probability of exceeding 1 or more of the thresholds for the individual categories
0.06 ppm	0.02	0.08	0.11	0.03	0.21
0.08 ppm	0.06	0.15	0.19-0.20	0.06	0.36
0.10 ppm	0.16	0.21	0.27	0.15	0.52
0.12 ppm	0.28-0.29	0.26	0.35	0.27	0.67
0.14 ppm	0.40	0.29	0.44	0.39	0.78-0.80

*Probability values expressed as range to reflect range of assumptions regarding distribution of peak ozone values.

In the above table, the right-hand column estimates the probability that the threshold concentration for one or more of the four health effect categories will be exceeded five or more times in five years. The term "threshold" as used in this context applies to people in a narrowly defined range of sensitivity, namely, persons more sensitive than 99 percent of the sensitive population but less sensitive than 1 percent of that group. For a standard level of 0.10 ppm, the probability that persons within this range of sensitivity will experience an effect is about 0.5.

These figures illustrate several important points: (1) all alternative standard levels reflect some risk, (2) there is no sharp break in the probability estimates that would suggest selecting one alternative standard level over another, and (3) the choice of a standard between zero and a level at which health effects are virtually certain (0.15 ppm) is necessarily subjective.

The Administrator has thoroughly considered the demonstrated effects levels, our new understanding of the study that served as the primary basis for the 0.08 standard, and the uncertainties introduced by the various studies discussed in the criteria document. Based upon all these data, it has been determined that a standard of 0.08 ppm does not appear necessary to protect the public health. However, at this time it appears that a standard above 0.10 ppm would not adequately protect public health. It is therefore proposed that the primary standard for ozone be revised to 0.10 ppm. Comments are solicited on whether a less stringent standard could adequately protect public health.

OTHER ASPECTS OF THE STANDARD

Chemical Species of the Standard—EPA is proposing to redesignate the photochemical oxidant standard as an ozone standard. Evidence in the revised criteria document indicates that:

1. The majority of data presented in the revised criteria document is based on ozone exposure. Nearly all of the clinical and toxicological studies are based on effects of ozone.
2. Some more recent epidemiological studies associate adverse effects more closely with ozone than with total oxidants.
3. Effects observed in clinical studies with ozone alone are similar to those effects observed in epidemiologial studies where ozone occurs along the complex mix of urban pollutants. These findings from the health data further suggest that health effects observed during periods of elevated photochemical oxidants concentrations are reasonably attributable primarily to ozone in the ambient air.

The existing standard for photochemical oxidant ostensibly was established for the entire class of this complex mix of compounds. Unfortunately, there are no satifactory methods for accurately and reliably measuring this collective class of pollutants. The reference method used to estimate ambient oxidant levels and to determine compliance with the standard has always measured only a single component of the oxidant mix—ozone. Thus, the chemical designation of the standard and the chemical composition of the pollutant measured to determine compliance have not been stated consistently. Ambient ozone concentrations can range from approximately 65 percent to nearly 100 percent of the total photochemical oxidant concentration; consequently, ozone can be a poor indicator of the quantity and composition of the non-ozone oxidant in the ambient air. Also of concern is the fact that aside from PAN, which is an important constituent of the photochemical oxidant mix, the non-ozone oxidants remain essentially unidentified, cannot be measured, and have not been uniquely associated with adverse effects.

The inconsistencies cited above argue for changing the designation from a total photochemical oxidant standard to an ozone standard.

Promulgation of a Primary Standard for PAN—EPA does not propose to establish a separate standard for PAN at this time. Although PAN is an eye irritant, the health data upon which to base a separate PAN standard are inadequate and routine PAN measurement methods are not available. Most of the studies which have documented the effects of PAN have used ozone or total oxidants as a surrogate for the material causing the adverse effect.

Ozone is not a reliable indicator of PAN. Recorded data shows ozone/PAN ratios ranging from 3:1 to 150:1. This variation in the ratio of ozone to PAN makes it extremely difficult to correlate the eye irritation effects of PAN with specific ozone values. However, it has been shown that at ozone levels of about 0.1 ppm, PAN concentrations will be at a level below those associated with perceptible eye irritation effects. This is true even for low ozone/PAN ratios.

Despite the lack of a separate PAN standard, those measures taken to reduce oxidant/ozone precursor emissions will also reduce PAN levels. In fact, smog chamber studies indicate that control of oxidant precursor emissions have a greater impact on PAN levels than on ozone/oxidant levels.

Form of the Standard—The current standard specifies that the hourly average ozone concentration must not exceed 160 $\mu g/m^3$ (approximately 0.08 ppm) more than once per year. As discussed in a report placed in the docket and available from EPA at the address given earlier, this deterministic (once-per-year) approach has several limitations, one of which is the fact that it does not adequately take into account the random nature of meteorological variations. The original purpose of permitting a single exceedance was to allow for unique meteorological conditions that were unrepresentative of air quality problems in a given area. Unfortunately, the current standard does not achieve this objective because it specifies in effect that there be zero probability that the second-highest concentration measured in a year exceed the standard level. However, when a single exceedance of the standard is permitted, there is a definite possibility that a second or third exceedance will also occur. If this probability is to be zero, there cannot be even a single exceedance of the standard. This limitation means that compliance with the standard, and consequently pollutant emission control requirements, would be determined on the basis of exceedingly rare adverse weather conditions.

Another fundamental problem with the current standard is that it focuses on a single measured value, the second-highest observation. This value is subject to instrument error, is not a stable statistic, and also will vary in any given area over a period of time. For a given year, the true second-highest value in an area may not be observed because of gaps in the monitoring record. Use of such a random statistic to determine compliance and levels of control can lead to values that are unrepresentative of the true air quality problems in an area.

Because of these and other limitations in the current form of the standard, EPA proposes that the ozone air quality standard be stated in a statistical form. This would mean that the allowable number of exceedances of the standard would be expressed as an average or expected number per year. The standard would be attained when the expected number of hour per calendar year with concentrations above 0.10 ppm is less than or equal to one. The average or expected value would be calculated from data obtained over several years, as explained below.

Definition of When the Standard is Attained—EPA proposes to add Appendix H to 40 CFR Part 50 to explain how to determine when the standard is or is not being attained. The procedure proposed in Appendix H requires that States compute a three-year moving average of the number of hours above the standard and adjust that average for missing data. This would mean that the allowable number of exceedances of the standard, i.e., the times when the standard level is allowed to be exceeded, would be expressed as an expected number of hours during the three-year period. The central feature of this approach is a description of how missing hourly values are handled. The calculations required would add the number of exceedances of the standard expected to be present in the hourly values missing during any calendar year to the actual number of exceedances measured during that year. The three-year average of the expected number of exceedances so computed would have to be equal to or less than one in order to attain the ozone air quality standard.

There is strong similarity between determining attainment of the present oxidant standard and determining attainment of the proposed ozone standard. In both cases, the number of exceedances of the level of the standard is used. The current approach requires that the level of the standard never be exceeded more than once in any year while the proposed form of the standard would permit two or more exceedances in any year provided that the average number of exceedances during the most recent three-year period does not exceed 1. For example, if three successive years of ozone monitoring data showed annual exceedances of 2, 1, and 0, the current standard would not be attained since the first year recorded more than one exceedance. Under the proposed approach, the same exceedance pattern would lead to a decision of attainment since the average number of exceedances for the three years was not above one. Details of the calculations discussed above are given in Appendix H.

A period of three successive years was chosen as the basis for determining attainment for two reasons. First, increasing the number of years increases the stability of the resulting average number of exceedances. Stated differently, as more years are used, the greater the chance of minimizing the effects of an extreme year caused by unusual weather conditions. The second factor is that extending the number of successive years too far increases the risk of averaging data during a period in which a real shift in emissions and air quality has occurred. This would penalize areas showing recent improvement and similarly reward areas which are experiencing deteriorating ozone air quality. Three years is thought by EPA to represent a proper balance between these two considerations.

Another modification that was considered during this review was to change the form of the standard to permit one calendar day in which the hourly standard could be exceeded. This form of the standard has several advantages, including: (1) the requirements for less manipulation and interpretation of data in calculating attainment or non-attainment, (2) reduced time and resources on the part of state and local agencies to validate low concentration values occurring in the evening and morning hours, and (3) greater stability in design statistics needed for control strategy development. However, based on potential conflicts with other air quality management programs such as prevention of significant deterioration, EPA does not propose to make such a change in the form of the ozone standard at this time.

EPA believes the statistical form of the standard coupled with the procedures explained in Appendix H will ameliorate the problems experienced with the present form of the standard. Comments are invited on the form of the standard and the method in Appendix H for determining when the standard is or is not being attained.

Averaging Time of the Standard—EPA does not propose a change in the current one-hour averaging time of the standard. Most clinical studies clearly show impairment of lung function in moderately exercising healthy subjects exposed to ozone for two hours. Since the impact of ozone is related to the total dose delivered to the respiratory tract and since more intense exercise would shorten the time required to deliver an equivalent dose, exposure durations of less than two hours are of concern for protection of individuals engaged in intense exercise. A recent clinical study published last year by DeLucia and Adams confirms this thesis at its shows lung function changes in exercising subjects after a one-hour exposure to relatively low ozone levels.

WELFARE EFFECTS AND THE SECONDARY STANDARD

The Clean Air Act mandates the setting of a national secondary ambient air quality standard to protect the public welfare from any known or anticipated adverse effects associated with the presence of an air pollutant in the ambient air. Ozone and other photochemical oxidants constitute a form of air pollution that affects vegetation and materials. The resultant economic loss has been estimated to be in the range of several hundred million dollars per year nationwide. Nonquantifiable losses to the natural environment occur as well. A report discussing these issues has been placed in the docket and is available from EPA at the address given earlier. The following material summarizes that report. Exposure of vegetation to harmful levels of ozone may result in leaf injury, decreased growth and yield, or reproductive effects. Visible leaf injury is the most readily detectable symptom of ozone exposure and for this reason has commonly been used in attempts to quantify damage to economic crops. Decreases in growth and yield can occur without such visible symptoms; however, since leaf injury is the most readily detectable and frequently reported symptom of ozone damage, this effect provides the best available data base for evaluating alternative standard levels. While it is not currently possible to make definite correlations of foliar injury with reductions in yield, several investigators have suggested that foliar injury rates in the range of 5 to 10 percent could produce detectable reductions in growth or yield, depending on the timing of the injury and other environmental factors. Ozone exposures which may be reasonably expected to produce injury ratings within this range in commercially important crops or indigenous flora are undesirable; therefore, the basis of the secondary National Ambient Air Quality Standard for ozone will be to protect against such exposures.

The effects of ozone on vegetation are not linearly dependent on the dose (product of concentration and exposure duration) sustained by the plant. A given dose applied over a short period of time is more damaging than if it were applied over a longer period. A mathematical model has been used to summarize for several crops the experimental results which depict the variation in foliar response with short-term (0.5-hour to 8-hour) ozone exposures. Based on these results, no commercially important crop is predicted to receive more than 3 percent leaf injury as a result of short-term peak ozone exposures at sites where an hourly average concentration above 0.08 ppm is expected to occur only once per year. Such a level of air quality should thus protect agricultural crops from detectable effects on growth and yield due to short-term peak ozone exposures, even after allowing for possible interaction between ozone and other air pollutants. In addition, studies which have examined the effects of long-term, intermittent ozone exposures on growth and yield of vegetation indicate that no detectable effects are predicted to occur as a result of the long-term pattern of ozone exposures anticipated when an hourly average concentration of 0.08 ppm is expected to be exceeded only once per year.

It should be noted that the above predictions were based on air quality relationships (e.g., the ratio of the 1-hour-average peak concentration to the corresponding 8-hour-average value) which were judged to be representative for urbanized areas where an hourly average concentration above 0.08 ppm is expected to occur only once per year. Equivalent relationships for rural areas have not been quantified, yet there is reason to believe that higher 8-hour-average concentrations may occur at a rural site than at an urban site when both are attaining the same hourly average standard. EPA has attempted to factor this uncertainty into its analysis of alternative hourly average standard levels, but is soliciting comments as to whether the standard should be set for an averaging time of 8 hours rather than 1 hour in order to insure the protection of vegetation in rural areas.

Material damage due to ozone can be described as an acceleration of aging processes, e.g., rubber cracking, dye fading, and paint weathering. In contrast to the effects of ozone on vegetation, these effects appear to be governed by the ozone dose sustained by the material. As a result, the annual average concentration will determine the rate at which material damage occurs, and any nonzero ozone concentration (including natural background levels) will contribute to the deterioration of sensitive materials if the exposure is sustained long enough. In remote areas selected to be as free from man-made influences as possible, annual average ozone concentrations are comparable with those seen in urgan areas, due to strong nighttime scavenging of ozone in urban areas by man-made pollutants. For the above reasons, no effect-based rationale can be offered to decide the level of the secondary standard needed to protect materials. As a result, EPA proposes to evaluate the level of the secondary standard principally on the basis of the air quality required to protect vegetation from growth and yield effects, since there is no level at which some material damage will not occur given sufficient time.

Based on the preceding considerations, EPA proposes to set the secondary ozone air quality standard level at an hourly average concentration of 0.08 ppm expected to be exceeded only once per year.

ECONOMIC, ENERGY, AND ENVIRONMENTAL IMPACTS

As has been noted previously, the Clean Air Act specifically requires that National Ambient Air Quality Standards be based on scientific criteria relating to the level that should be attained to adequately protect public health and welfare. EPA interprets the Act as excluding any consideration of the cost of achieving such a standard in determining the level of the standard. However, in compliance with the requirements of Executive Orders 11821 and 11949 and OMB Circular A-107 and with the provisions of the recently issued Executive Order 12044 for rulemaking proceedings which are currently pending, EPA has prepared an analysis of economic impacts associated with efforts to attain this proposed standard.

Ozone air pollution is a pervasive problem throughout the country. Most urban and many rural areas exceed the existing standard. Even if a less stringent standard (as proposed) is promulgated, most of the major urban areas are not expected to attain the standard in the near-term. Control of the organic precursor materials which generate photochemical oxidants is a major effort in this country and a multi-billion dollar program. The existing control program includes measures to reduce organic emissions from: automobile and truck exhausts, production of chemical and petroleum products, the dry-cleaning industry, most painting operations including the automotive industry, and other industrial operations.

Because the attainment problem in most urban areas is so severe, the proposed relaxation of the standard is not expected to change the level of control requirements in the near-term. However, the move to a 0.10 ppm standard would eliminate the need for major control programs in many rural and wilderness areas which currently exceed the standard.

With the proposed relaxation of the standard, the longer-range outlook does indicate that many urban areas will achieve the standard by 1987. However, even with aggressive control programs, it will be very difficult for some urban areas to achieve the proposed standard within the next 10 years.

In addition, a document has been prepared assessing the impacts that efforts to attain the proposed standard may have on the nation's energy requirements. Control of oxidant precursors will often be accomplished by recovery of organic materials that would otherwise be emitted to the atmosphere, or by more efficient combustion. Because of such energy savings, this document concludes that oxidant precursor control measures may well lessen the nation's energy requirements.

Furthermore, environmental impacts associated with control of oxidant precursors have been examined in a document available in docket number OAQPS 78-8. This study indicates that modifying the current standard as proposed should have minimal environmental impacts.

Copies of the above-mentioned analyses of the economic, energy, and environmental impacts involved in the proposed ozone standard are available from EPA at the address given earlier.

REVISIONS TO PART 50 REGULATIONS

In addition to the revised standard, this action necessitates two other revisions to Part 50 as follows:

1. In Appendix D, as well as in the table of sections for Part 50, the title is revised to read as follows: Appendix D—Measurement Principle and Calibration Procedure for the Measurement of Ozone in the Atmosphere. The substitution of "ozone" for "photochemical oxidants corrected for interferences due to nitrogen oxides and sulfur dioxide" is a result of the proposed change in the chemical designation of the standard.
2. Appendix H, "Interpretation of the National Ambient Air Quality Standard for Ozone", is added because additional guidance is necessary to understand the statistical nature of the revised standard.

REVISIONS TO PART 51 REGULATIONS

Elsewhere in this issue of the FEDERAL REGISTER three revisions to Part 51 are proposed concurrently with the revision to the photochemical oxidant standard. They are as follows:

1. The term "photochemical oxidants" will be changed to "ozone" throughout Part 51.
2. Section 51.14, "Control strategy: Carbon monoxide, hydrocarbons, photochemical oxidants, and nitrogen dioxide", is being revised to allow the states to use any of four analytical techniques in the place of Appendix J to calculate the percent hydrocarbon reduction needed to attain the ozone standard.
3. Appendix J is being deleted from Part 51.

With regard to SIP development under Part 51, the proposed ozone standard should have little impact on the attainment status designation of most areas. However, where sufficient data is available to support a change in designation, either the State or EPA may initiate such a change under the terms of section 107 of the Clean Air Act after the standard is promulgated. The proposed standard may impact the control strategies needed in some areas. These impacts will need to be analyzed on a case-by-case basis and EPA will provide guidance on this matter when the standard is promulgated. The standard will not substantially affect New Source Review requirements.

FEDERAL REFERENCE METHOD

The measurement principle and calibration procedure applicable to reference methods for measuring ambient ozone concentrations to determine compliance with the standard are not affected by the proposed amendments. Elsewhere in this issue of the FEDERAL REGISTER, however, EPA is proposing to replace (supersede) the current calibration procedure with a new, superior calibration procedure based on ultraviolet photometry. The measurement principle and the current calibration procedure are set forth in Appendix D of 40 CFR Part 50 (as amended in the February 18, 1975 issue of the FEDERAL REGISTER, 40 FR 7042). Reference methods—as well as equivalent methods—for monitoring ozone are designated in accordance with 40 CFR Part 53 (40 FR 7044). A list of all methods designated by EPA as reference or equivalent methods for measuring ozone is available from any EPA regional office, or from EPA, Department E (MD-76), Research Triangle Park, NC 27711.

PUBLIC PARTICIPATION

EPA has solicited public comment and critique on draft revisions to the criteria document as well as comments on several staff position papers describing possible modifications to the standard. Comments on the two draft revisions of the criteria document have been considered in the final document published simultaneously with the issuance of this proposal. An explanation of how EPA addressed each of these comments will be provided as a part of the docket number OAQPS 78-8 prior to promulgation of this standard. On December 30, 1977, EPA announced in the FEDERAL REGISTER (42 FR 65264) a public meeting to discuss issues related to possible revisions of the national ambient air quality standard for photochemical oxidants. In that notice, EPA announced the availability of staff papers describing preliminary recommendations: (1) redesignating the standard from oxidant to ozone; (2) proposing not to set a separate standard at this time for peroxyacetylnitrate (PAN); (3) redefining the standard in a statistical, rather than deterministic, form; (4) retaining the one-hour averaging time for the standard; and (5) establishing the standard level somewhere in the range between 0.08 ppm and 0.15 ppm. The public meeting was held January 30, 1978; a transcript of the meeting is available through docket number OAQPS 78-8. During the meeting and afterwards, comments were received which addressed the aforementioned issues as well as other topics related to the standard or to control measures required to attain the standard. The greatest area of controversy was with the interpretation of health data. Industrial groups criticized much of the available data as incomplete, unreliable, or not applicable to the determination of health effects threshold. Most of these groups maintained that there exists little evidence for health effects below 0.25 ppm. As discussed elsewhere in this proposed regulation, EPA does not agree with this judgment of a demonstrated effect level. Comments from other groups such as the American Lung Association argued that hyperreactive asthmatics may suffer health effects below 0.15 ppm and suggested that there may not be a no-effect threshold for ozone.

The use of the "risk" analysis approach to aid in selecting a standard was generally supported. However, there were several criticisms of the specific methodology selected by EPA. The American Petroleum Institute (API) doubted that the population considered at risk could be adequately characterized. The health department of the city of Houston, Texas did not feel the probability encoding technique was valid for extending the range of knowledge beyond experimental data. The API also called on EPA to seek peer review of the entire risk assessment methodology. We have accepted the API's suggestion for further review of the methodology, as mentioned earlier, and have submitted the material to the EPA Science Advisory Board for review. We have also been cooperating with the API by providing them with information on all aspects of the development of the risk assessment methodology. We do not agree with the city of Houston on the lack of the utility of the probability encoding technique. The approach is probably the best technique for quantifying an expert's knowledge of uncertainty. Some measure of this uncertainty is extremely useful as input for establishing an adequately protective standard.

Changes in the form of the standard and the chemical designation of the standard received little criticism as a result of the public review process. The recommendation not to promulgate a PAN standard at the present time was not challenged.

A number of comments were received regarding implementation of the air quality standard. Representatives of industry and areas with high ozone concentrations felt that the current air quality standard could not be attained. The principal reasons cited were high natural background levels of ozone and transport of ozone from other locations. In addition, comments were made that the hydrocarbon abatement strategies required for implementing a stringent standard were unproven, ineffective, and excessively destructive of social and economic activity. Since these factors are not related to health and welfare criteria, they are not germane to the establishment of the standard, but are important considerations in developing state implementation plans. EPA will assure that these comments are given proper attention.

Dated: June 9, 1978.

DOUGLAS M. COSTLE,
Administrator.

EPA proposes to amend Part 50 of Chapter I, Title 40, of the *Code of Federal Regulations* as follows:

1. Section 50.9 is revised as follows:

§ 50.9 National primary and secondary ambient air quality standards for ozone.

(a) The level of the national primary ambient air quality standard for ozone measured by a reference method based on Appendix D to this part and designated in accordance with Part 53 of this chapter, or by an equivalent method designated in accordance with Part 53 of this chapter, is 0.10 part per million (196 $\mu g/m^3$). The standard is attained when the expected number of hours per calendar year with concentrations above 0.10 part per million (196 $\mu g/m^3$) is equal to or less than one, as determined by Appendix H.

(b) The level of the national secondary ambient air quality standard for ozone, measured as in § 50.9(a) is: 0.08 part per million (157 $\mu g/m^3$). The standard is attained when the expected number of hours per calendar year with concentrations above 0.08 part per million (157 $\mu g/m^3$) is equal to or less than one, as determined by Appendix H.

2. In Appendix D, as well as in the table of sections for Part 50, the title is revised to read as follows' Appendix D—Measurement Principle and Calibration Procedure for the Measurement of Ozone in the Atmosphere.

3. Appendix H is added as follows:

Appendix H—Interpretation of the National Ambient Air Quality Standard for Ozone

1. *General.*—This Appendix explains how to determine when the expected number of hours per calendar year with concentrations above 0.10 part per million (196 $\mu g/m^3$) is equal to or less than one. An expanded discussion of these procedures and associated examples are contained in the "Guideline for Interpretation of the Ozone Air Quality Standard." For purposes of clarity in the following discussion, it is convenient to use the term "exceedance" to describe an hourly ozone measurement that is greater than the level of the standard. Therefore, the phrase "expected number of hourly values with concentrations above the level of the standard" may be simply stated as the "expected number of exceedances."

The basic principle in making the above determination is relatively straight-forward. Most of the complications that arise in determining the expected number of annual exceedances are consequences of accounting for incomplete sampling. In general, the average number of exceedances per calendar year must be less than or equal to 1. In its simplest form, the number of exceedances at a monitoring site would be recorded for each calendar year and then averaged over the past three calendar years to determine if this average is less than or equal to 1.

2. *Interpretation of expected number of exceedances.*—The ozone standard states that the expected number of exceedances per year must be less than or equal to 1. The statistical term, "expected number" is basically an arithmetic average. The following example explains what it would mean for an area to be in compliance with this type of standard. Suppose a monitoring station records an ozone value for every hour of the year during the past 3 years. At the end of each year, the number of hours with concentrations above 0.10 part per million is determined and this is averaged with the results of previous years. As long as this arithmetic average remains "less than or equal to 1" the area is in compliance.

3. *Estimating the number of exceedances for a year.*—In general, a value is not available for each hour of the year and it will be necessary to account for these missing values when estimating the number of exceedances for a particular calendar year. It should be noted that the purpose of these computations is to determine if the expected number of exceedances per year is less than or equal to 1. Thus, if a site has two or more observed exceedances each year, the standard is not attained and it is not necessary to use the procedures of this section to account for incomplete sampling.

The term "missing value" is used here in the general sense to describe all hours that do not have an associated ozone measurement. In some cases, a measurement might actually have been missed but in other cases no measurement may have been scheduled for that hour.

Many State and local air pollution control agencies deliberately design their schedules so that missing data associated with instrument maintenance occur at times when there is virtually no chance of violating the standard. Also, in some areas the seasonal pattern of the pollutant is so pronounced that entire months may be omitted because it is extremely unlikely that the standard would be exceeded. To avoid unfairly penalizing such areas, some allowance must be made to allow for hours that were not actually measured but would certainly have been below the standard. This introduces a complication in that it becomes necessary to define under what conditions a missing hourly value may be assumed to have been less than the level of the standard. The following criteria shall be used for ozone.

A missing hour of ozone data shall be assumed to be less than the level of the standard if either of the following conditions is met:

(a) An individual missing hourly value shall be assumed to be less than the level of the standard if both the hour preceding and the hour following this missing value have values that do not exceed 75% of the level of the standard.

(b) In cases where consecutive missing hours occur, a missing hour shall be assumed to be less than the level of the standard if no hourly value for that same hour of any day in the particular month in question has exceeded 75% of the standard level based upon the most recent three calendar years of available monitoring data.

Let z denote the number of missing values that is assumed to be less than the standard. Then to establish that the ozone standard has been met, the following formula shall be used to estimate the number of exceedances for the year:

$$e = v + \frac{v}{n} (N-n-z) \qquad (1)$$

Where:

N=the number of hours in the year,
n=the number of hourly ozone measurements,
v=the number of hourly values above the level of the standard,
z=the number of hours assumed to be less than the standard level, and
e=the estimated number of exceedances for the year.

The estimated number of exceedances shall be rounded to one decimal place (fractional parts equal to 0.05 round up).

The above equation may be interpreted intuitively in the following manner. The estimated number of exceedances is equal to the observed number of exceedances (v) plus an increment that accounts for incomplete sampling. There were (N-n) missing hourly values for the year but a certain number of these, namely z, were assumed to be below the standard. Therefore, (N-n-z) missing values are considered to include possible exceedances. The fraction of measured values that are above the level of the standard is v/n. It is assumed that this same fraction applies to the (N-n-z) missing values and that

$$\frac{v}{n} (N-n-z)$$

of these values would have also exceeded the level of the standard.

4. *Use of multiple years of data.*—Ideally, the expected number of exceedances for a site would be computed by knowing the probability that the site would record 0,1,2,3 . . . exceedances in a year. Then each possible outcome could be weighted according to its likelihood of occurrence and the appropriate expected value, or average, could be computed. In practice, this type of situation will not exist because ambient data will only be available for a limited number of years.

Consequently, the expected number of exceedances per year at a site shall be computed by averaging the estimated number of exceedances for each year of available data during the past three calendar years. In other words, if the estimated number of exceedances has been computed for the calendar years of 1974, 1975, and 1976 then the expected number of exceedances is estimated by averaging those three numbers. If this average is greater than 1, then the standard has been exceeded at this site. It suffices to carry one decimal place in this computation. For example, the average of the three numbers 1, 1 and 2 is 1.3 which is grater than 1. If data is not available for each of the last three years then this average shall be computed on the basis of available data from the remaining years in that period.

Authority: Sections 109 and 301 of the Clean Air Act, as amended (42 U.S.C. 7409, 7601).

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[6560-01]

[40 CFR Part 50]

[FRL 914-1 Docket Number OAQPS 78-8]

MEASUREMENT OF OZONE IN THE ATMOSPHERE

Calibration of Ozone Reference Methods

AGENCY: Environmental Protection Agency.

ACTION: Proposed rulemaking.

SUMMARY: Appendix D to 40 CFR Part 50 prescribes a measurement

principle upon which reference methods for the measurement of ozone[1] in the atmosphere must be based. This appendix also specifies a procedure to be used for calibrating those ozone reference methods. EPA now has evidence that at least one other calibration procedure for ozone reference methods is significantly more accurate and less variable than the procedure currently specified in Appendix D. Accordingly, EPA is proposing an amendment to 40 CFR Part 50, Appendix D, to replace (supersede) the current calibration procedure with the new, superior calibration procedure which is based on ultraviolet photometry.

DATES: Comments relative to the proposed amendment must be received by August 18, 1978.

ADDRESS: Send comments to: Mr. Larry J. Purdue, Department E (MD-76), Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

FOR FURTHER INFORMATION CONTACT:

Mr. Larry J. Purdue, Telephone 919-541-3076 (FTS 629-3076).

SUPPLEMENTARY INFORMATION:

INCIDENTAL INFORMATION

This proposal is indirectly related to EPA's proposal to change the National Ambient Air Quality Standard for photochemical oxidants (ozone) specified in 40 CFR Part 50, which appears elsewhere in this issue of the FEDERAL REGISTER.

BACKGROUND

Part 50 of Title 40, Chapter I of the Code of Federal Regulations specifies the National Ambient Air Quality Standards for several air pollutants including ozone. Appendixes to Part 50 provide information concerning the reference methods which are used to measure those pollutants. In particular, Appendix D to Part 50 describes a measurement principle upon which ozone reference methods must be based and a calibration procedure to be used for calibrating such methods. It is the latter—the calibration procedure prescribed for reference methods for ozone—that would be changed by the amendment being proposed herein.

The calibration procedure presently contained in Appendix D is based on assay of ozone with 1% neutral buffered potassium iodide (NBKI) and is known as the "NBKI procedure". In the October 6, 1976, issue of FEDERAL REGISTER (41 FR 44049), EPA published a notice indicating that EPA was aware of some inherent shortcomings with the NBKI procedure. In addition, the notice described evidence to suggest that one or more alternative calibration procedures may be superior to the NBKI procedure. The notice also indicated EPA's intention to investigate this situation by testing, evaluating, and soliciting public comment on the alternative procedures, and to propose to revise or replace the NBKI procedure as appropriate based on the results of that investigation. The amendment to 40 CFR Part 50, Appendix D, being proposed today is a direct result of that course of action. Interested readers are referred to the October 6, 1976, notice for additional background information.

TESTS

The October 6, 1976, FEDERAL REGISTER notice described 3 candidate procedures which were likely to be superior to the NBKI procedure. These were identified as gas phase titration (GPT) with excess nitric oxide, ultraviolet photometry (UV), and GPT with excess ozone, and were set forth as alternates A, B, and C, respectively, in Attachment A to that notice. Subsequent to the drafting of the notice, a fourth promising procedure, based on a boric acid potassium iodide technique and identified as the "BAKI procedure", became available.

The performance (precision and accuracy) of each of these 4 procedures has been laboratory tested by EPA and compared. The tests were conducted with volunteer technicians from both within and outside EPA. Each volunteer was asked to become familiar with and then use the procedure being tested. The results from each volunteer were compared quantitatively to a highly stable, controlled laboratory reference system. Results from all of the volunteers were then used to estimate the precision (variability) and accuracy (bias) for each method.

TEST CONCLUSIONS

Interpreting the results of these tests is difficult because of a number of variables which were impossible to control. The primary uncertainty is in estimating the representativeness of the test data to the actual performance of the procedure in real applications. Most of the procedures are dependent on the accuracy and reliability of the required equipment and apparatus, and on the capability and skill of the operator. These factors are difficult to quantify. Nevertheless, EPA believes certain conclusions are valid, based on statistical and judgemental evaluation of the test data as well as information from other sources.

Briefly, the UV calibration procedure showed very low calibration variability in the tests. Its accuracy is believed to be excellent because it is a direct measurement of ozone based on the well-established ozone absorption coefficient. Also, independent comparisons of the procedure among various researchers agree within a few percent. The other three procedures showed considerably greater variability in the tests than the UV procedure, probably reflecting their relative complexity and large equipment dependence. While the test showed no significant average bias for the BAKI procedure, the two GPT procedures were shown to have an average positive bias of 7 to 8% with respect to the UV reference.

Additional information concerning the test results can be obtained from a summary report which summarizes the test results of all four procedures. More specific information concerning the tests and test results is given in the individual test reports for each procedure. All of these test reports can be obtained upon request from Department E (MD-76), Environmental Monitoring and Support Laboratory, Environmental Protection Agency, Research Triangle Park, N.C. 27711 and will be available in a docket [Number OAQPS 78-8] for inspection and copying at the United States Environmental Protection Agency, Public Information Reference Unit, Room 2922 (EPA library), 401 M Street, Washington D.C. 20460.

SUMMARY OF COMMENTS RECEIVED

The October 6, 1976 FEDERAL REGISTER notice specifically solicited public comments on the three alternative calibration procedures set forth in the notice, and on EPA's proposed course of action. Comments were received from 12 respondents, representing 5 air pollution control agencies and 5 industrial organizations. While many of the respondents recognized inadequacies in the present version of the NBKI procedure and generally supported EPA's intended course of action, several of the respondents expressed a desire to retain the present procedure or to adopt a modified KI procedure demonstrated to have improved accuracy and precision. In general, these respondents indicated the need for an inexpensive, easy to perform procedure compatible with existing equipment. Some respondents offered evidence of acceptable performance of the NBKI procedure in the respondents' agency or laboratory.

Several of the respondents favored adoption of the UV photo-metric procedure as the primary calibration procedure because it appears to be the least complex, the most direct, and the least operator-dependent of the alternative procedures under consideration.

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[1] The term "ozone" is used herein to be consistent with another EPA action proposing to substitute "ozone" for "photochemical oxidants corrected for interferences due to nitrogen oxides and sulfur dioxide," which is currently used in Part 50.

The GPT procedures were generally judged to be the least desirable alternatives because they are considered too difficult to perform. There was some concern for the reliability of the required standards (NO standard for GPT, O_3 absorption coefficient for UV) and the availability of the required equipment. The effect of water vapor and other potential interferences on the GPT and UV procedures was also questioned. A few of the respondents felt that certain statements in the notice regarding the performance of the NBKI procedure and the consistent agreement between the UV and GPT procedures were in conflict with the results of the various studies cited in the notice.

Some comments were received regarding the use of ozone generators and ozone analyzers as transfer standards and the effect of atmospheric pressure on the performance of these devices. Several respondents showed concern that the additional documents cited in the notice (e.g. the Transfer Standard Document and the Technical Assistance Documents) were not available for public review at the time of publication of the FEDERAL REGISTER notice.

A more detailed summary of all of the comments received and EPA's response to them is available from Department E at the address specified at the beginning of this notice.

SUPERSESSION OF NBKI PROCEDURE

As noted in the October 6, 1976, notice, EPA was aware of shortcomings with the prescribed NBKI procedure—substantial variability and an apparently positive but unpredictable bias. The tests of the four alternate calibration procedures confirmed EPA's surmise that at least one of the procedures was sufficiently superior to the NBKI procedure to consider supersession. However, although accuracy and precision are of primary importance, many other factors had to be considered as well before supersession by a new procedure could be proposed—factors such as complexity, cost and availability of equipment, field portability, operator training, evaluation of benefits to be obtained, and overall impact to user agencies. Another question was whether or not to consider replacing the NBKI procedure by more than one new calibration procedure to provide flexibility of choice by users.

EPA has carefully considered all these factors as well as all public comments, and is proposing what it believes to be the optimum course of action. The proposed changes are as follows:

(1) Supersede the NBKI calibration procedure with a procedure based on UV photometry for the calibration of reference methods for ozone. (As noted in the October 6, 1976, notice, no Standard Reference Material is availabe for ozone. Hence, ozone concentrations established via the UV procedure would be tantamount to primary ozone standards, and the UV procedure itself is thus often referred to as a "UV standard" for ozone.)

(2) Allow the independent use of the BAKI procedure in lieu of the UV procedure for 18 months after promulgation of the amendment, with the recommendation that the BAKI technique be related to a UV standard whenever possible.

(3) Specifically allow the use of alternative procedures as transfer standards if they meet certain transfer standard performance guidelines to be set forth by EPA. A transfer standard would be any device or procedure which can be referenced to a UV ozone standard and then used at another location to reproduce ozone standards. A practical transfer standard would offer some important advantages—such as lower cost, ruggedness, easier operation, or convenience—over direct use of the UV procedure.

RATIONALE FOR PROPOSED CHANGES

Of all the procedures tested, the UV procedure clearly has the best performance—low variability, high accuracy, and minimum operator involvement. From a scientific viewpoint, it is perhaps the most ideal technique presently available for assaying pure ozone concentrations below 1 ppm. While the procedure is not without some practical disadvantages, these appear to be relatively few and minor, and EPA believes they are adequately minimized as discussed below. Therefore, the UV procedure appears to be the logical choice to replace the NBKI procedure.

EPA is also convinced that the UV procedure is the only procedure which should be promulgated to replace the NBKI procedure—for several reasons: First, since no primary ozone concentration standards (e.g. Standard Reference Materials) are available, the calibration procedure is actually a means for obtaining primary ozone standards. In this important respect, singularity is necessary for uniformity and comparability, and to avoid conflicts or discrepancies which could arise if more than one independent standard were allowed. Second, none of the other procedures can match the precision and accuracy of the UV procedure. And finally, flexibility to use alternate techniques is adequately—and possibly better—provided by allowing their use as transfer standards. As a transfer standard, an alternative technique would have to be tested for performance and related to a UV ozone standard. Thus, accuracy would be determined by the UV procedure, not the alternative technique, and each user would have to determine and control the variability of the technique under his own individual conditions of use.

The UV procedure has not been widely used by air monitoring agencies in the past, and many agencies are not familiar with the procedure and may not own a UV photometer meeting the requirements of the procedure. Also, the availability of UV photometers is somewhat limited presently (a situation which should improve shortly after promulgation of the procedure). In view of this situation, and in response to a number of the public comments, EPA proposes an 18-month transition period to allow agencies to acquire the necessary equipment, become familiar with the UV procedure, and phase it into their calibration and quality control programs. During this 18-month period, use of the BAKI procedure would be acceptable until the UV procedure can be implemented. The BAKI procedure is very similar to the currently prescribed NBKI procedure, and any agency equipped for and familiar with the NBKI procedure should have no trouble adapting to the BAKI procedure. Unfortunately, the BAKI procedure shares some of the same problems associated with the NBKI procedure (general variability). But the tests showed low bias, and the variability of the BAKI should be easier to control because the BAKI procedure is much less sensitive to such factors as color development time, impinger type, and water vapor effect.

In addition, EPA is proposing and advocating the use of transfer standards for calibration of field-sited ozone analyzers. Transfer standards would have to be related to primary ozone standards obtained by the UV procedure, but would offer several important advantages such as the following:

1. The UV calibration photometer could be permanently located in a laboratory and operated by an experienced, responsible person under laboratory conditions to maximize the precision and accuracy of the procedure. This would also spare the photometer from possible physical damage from being moved about to field locations.
2. Agencies would have flexibility to select a transfer standard technique or device of their choice, and still have comparability to the UV ozone standard.
3. Costs could be reduced by using a single UV photometer to certify as many transfer standards as needed by the agency. Small agencies may even avoid the purchase of a photometer if they could gain access to one through a cooperating larger agency, a State or Regional EPA Office, an agency cooperative, or by commercial certification of transfer standards.
4. Transfer standards could be designed to better survive the demands

of frequent transportation and field use.

5. Transfer standards could be used to intercompare UV photometers among various agencies to assure accuracy.

6. Transfer standards may also be more convenient, easier to operate, and less expensive.

Finally, EPA emphasizes that the proposal to supersede the NBKI procedure arises more from the demonstrated superiority of the UV procedure than from the degree of unreliability of the NBKI procedure itself. Thus supersession is specifically not intended to imply that ambient ozone measurements obtained with reference (or equivalent) methods calibrated with the NBKI procedure are categorically invalid or useless.

EFFECT ON NATIONAL AMBIENT AIR QUALITY STANDARD FOR PHOTOCHEMICAL OXIDANTS

EPA believes that supersession of the NBKI calibration procedure with the U.V. procedure requires no revisions to the oxidant standard (or proposed new ozone standard) for the following reasons; Because of the substantial variability and unpredictable bias in the NBKI procedure the exact magnitude of any bias which may exist cannot accurately be determined. Thus no precise quantitative factor is available for use as a basis for revision of the standard. (For the same reason, no factor is available to "correct" or "adjust" previously obtained data.)

Comparative studies cited in the October 6, 1978 notice suggest that the differences between the NBKI procedure and the GPT and UV procedures generally do not exceed 10 percent. This degree of bias is not sufficient to warrant revision of the standard and is adequately accounted for within the margin of safety included in the standard at the time of promulgation (36 FR 8186, April 30, 1971). EPA will continue to study health and other effects related to ozone using this new calibration procedure. If any evidence becomes available to indicate that revision of the standard should be considered, EPA will address the issue at that time.

EFFECT ON CURRENTLY DESIGNATED REFERENCE AND EQUIVALENT METHODS

As noted in the October 6, 1976, notice, replacement of the calibration procedure specified in Appendix D of 40 CFR Part 50 would not affect the design or performance characteristics of existing reference methods for ozone. Thus the only effect of the change would be on the calibration procedure described in the operation manuals associated with the analyzers. EPA proposes to provide a reasonable period of time—probably 6 months after final promulgation—for manufacturers to revise their manuals, have EPA approve the revised manual, and to distribute revised manuals (or manual supplements) to all analyzer owners. Also, since the two equivalent methods which have been designated to date prescribe the NBKI calibration procedure, EPA sees no reason why they could not be treated in the same way. If all manufacturers respond promptly, there would be no impact (other than the change in calibration procedure itself) to owners of designated ozone analyzers.

NEW UV CALIBRATION PROCEDURE

Unlike the currently prescribed NBKI procedure, the new UV calibration procedure is quite simple. After generating a stable, dynamic ozone concentration with an ozone generator, the operator assays it by passing a portion of the gas flow through the cell of the UV photometer. The photometer readings are then used in a formula to calculate the ozone concentration, which, as noted earlier, is effectively a primary ozone standard. (Some photometers do the calculations automatically.) The primary burden on the operator is to insure (1) that the photometer is operating correctly, (2) that the apparatus is set up properly and is clean and leak-free, and (3) that the calculations are accurate. While none of these are particularly difficult, EPA is preparing a Technical Assistance Document which will explain these tasks and provide other detailed information about the procedure. A draft form of this document will be available from the address specified at the beginning of this notice.

The photometer is obviously of critical importance to the procedure and must have a precision within 0.005 ppm or 3% of the concentration, whichever is greater. While a calibration photometer can be assembled from laboratory components, EPA recommends the purchase of a commercial photometer which is either designed specifically for this calibration procedure, or which can be readily adapted to it. EPA is presently aware of 2 such commercial photometers (available from Dasibi Environmental Corp., Glendale, California, and Science Applications, Inc., La Jolla, California) and expects others will become available in the future.

UV photometers of the type used in ambient ozone analyzers are likely to be suitable as calibration photometers. (Conversion of an ambient UV analyzer to a calibration photometer is covered in the Technical Assistance Document mentioned above.) However, it is important to differentiate between the use of a UV photometer as an ambient analyzer and its use as a calibration photometer. This distinction is predicated more on operational differences than on any specific physical differences. EPA proposes to require that a photometer to be used for calibration be dedicated exclusively to such use, be maintained under meticulous conditions, and be used only with clean, calibration gases. UV analyzers used for ambient monitoring should always be calibrated with an independent calibration photometer or a certified transfer standard. A UV analyzer should not be considered to be "self-calibrated" even though it contains a UV photometer which meets the specifications of the UV calibration procedure.

NEW BAKI CALIBRATION PROCEDURE

As noted earlier, the BAKI procedure is an improved form of the currently prescribed NBKI calibration procedure. Its independent use would be allowed only for calibration of ozone analyzers (not transfer standards) on a temporary basis during a 18-month transition period to permit agencies to adopt the new, UV calibration procedure. However, the BAKI procedure has considerable variability and is distinctly inferior to the UV procedure. Therefore, EPA would urge agencies to adopt the UV procedure as soon as practical. And, when possible, the BAKI procedure should be related to the UV procedure to improve the overall accuracy.

Following the 18-month period, the BAKI procedure would not be authorized for independent use, but could be used as a transfer standard. As such, it would have to be related to the UV procedure, and its variability and accuracy would have to be monitored and controlled. Thus agencies which find the BAKI procedure advantageous could continue to use this procedure as a transfer standard.

TRANSFER STANDARDS

As indicated earlier, EPA intends to specifically allow transfer standards for calibrating ozone analyzers, and has noted a number of advantages which might be realized by their use. Transfer standards for ozone could include any of the alternate techniques (GPT, BAKI) as well as devices such as ozone analyzers and stable ozone generators. EPA recommends that agencies consider the use of transfer standards where advantageous. But transfer standards are not without pitfalls and disadvantages of their own. EPA is preparing a fairly comprehensive guideline/Technical Assistance Document on transfer standards for ozone. This document is available (in draft form), and a copy may be requested by writing to the address given for comments. If the use of transfer standards for ozone proves to be successful and widely accepted, EPA intends to consider extending the concept to SO_2, NO_2, and CO. Comments on the use of transfer standards and on the transfer standard guideline are welcome.

USE OF NEW PROCEDURES PRIOR TO PROMULGATION OF AMENDMENT

As indicated in this proposal, the UV calibration procedure—and to a lesser extent the BAKI procedure—are believed to be scientifically superior to the currently prescribed NBKI calibration procedure. And it is very likely that the UV procedure (and the BAKI procedure on a temporary basis) will be promulgated to supersede the NBKI procedure. Accordingly, agencies which have the capability and desire to commence using these procedures immediately would not be discouraged from doing so. Immediate use of transfer standards could also be considered on the same basis.

PUBLIC PARTICIPATION

All documents and information relevant to this rulemaking are being placed in Docket No. OAQPS 78-8, the docket for the proposed amendments to the standards for photochemical oxidants. That docket will be available for public inspection during the hours 8:00 to 4:30 at the Public Information Reference Unit, Room 2922, 401 M Street SW., Washington, D.C.

Comments on any aspect of this proposed amendment are solicited from interested persons or agencies. Comments should be submitted to Mr. Larry J. Purdue at the address given at the beginning of this notice. Comments should be received within 60 days of the date of publication for due consideration prior to final promulgation. Copies of all comments received will be added to the docket.

In addition interested persons may make comments on the proposal orally at the public hearing on the ozone standard scheduled for July 18, 1978.

Dated: June 9, 1978.

DOUGLAS COSTLE,
Administrator.

It is proposed to amend Part 50 of Title 40, Code of Federal Regulations as follows:

1. Appendix D is revised to read as follows:

APPENDIX D—MEASUREMENT PRINCIPLE AND CALIBRATION PROCEDURE FOR THE MEASUREMENT OF OZONE IN THE ATMOSPHERE

AUTHORITY: Section 109, 301 of the Clean Air Act as amended (42 USC 57409, 7601).

MEASUREMENT PRINCIPLE

1. Ambient air and ethylene are delivered simultaneously to a mixing zone where the ozone in the air reacts with the ethylene to emit light, which is detected by a photomultiplier tube. The resulting photocurrent is amplified and is either read directly or displayed on a recorder.

2. An analyzer based on this principle will be considered a reference method only if it has been designated as a reference method in accordance with Part 53 of this chapter and calibrated as follows:

CALIBRATION PROCEDURE

1. Principle. The calibration procedure is based on the photometric assay of ozone (O_3) concentrations in a dynamic flow system. The concentration of O_3 in an absorption cell is determined from a measurement of the amount of 254 nm light absorbed by the sample. This determination requires knowledge of (1) the absorption coefficient (α) of O_3 at 254 nm, (2) the optical path length (l) through the sample, (3) the transmittance of the sample at a wavelength of 254nm, and (4) the temperature (T) and pressure (P) of the sample. The transmittance is defined as the ratio I/I_0, where I is the intensity of light which passes through the cell and is sensed by the detector when the cell contains an O_3 sample, and I_0 is the intensity of light which passes through the cell and is sensed by the detector when the cell contains zero air. It is assumed that all conditions of the system, except for the contents of the absorption cell, are identical during measurement of I and I_0. The quantities defined above are related by the Beer-Lambert absorption law,

$$\text{Transmittance} = \frac{I}{I_0} = e^{-\alpha c l} \qquad (1)$$

where:

α=absorption coefficient of O_3 at 254 nm=308±4 $\text{atm}^{-1}\ \text{cm}^{-1}$ at 0°C and 760 torr.(1,2,3,4,5,6,7)

c=O_3 concentration in atmospheres

l=optical path length in cm

In practice, a stable O_3 generator is used to produce O_3 concentrations over the required range. Each O_3 concentration is determined from the measurement of the transmittance (I/I_0) of the sample at 254 nm with a photometer of path length l and calculated from the equation,

$$c(\text{atm}) = -\frac{1}{\alpha l}(\ln I/I_0) \qquad (2a)$$

or,

$$c(\text{ppm}) = -\frac{10^6}{\alpha l}(\ln I/I_0) \qquad (2b)$$

The calculated O_3 concentrations must be corrected for O_3 losses which may occur in the photometer and for the temperature and pressure of the sample.

2. Applicability. This procedure is applicable to the calibration of ambient air O_3 analyzers, either directly or by means of a transfer standard certified by this procedure. Transfer standards must meet the requirements and specifications set forth in Reference 8.

3. Apparatus. Figure 1 illustrates a basic dynamic UV calibration system and shows the suggested configuration of the components listed below. All connections between components in the calibration system downstream of the O_3 generator should be of glass or Teflon®. Additional information regarding the assembly of a UV photometric calibration apparatus is given in Reference 9. For certification of transfer standards which provide their own source of O_3, the transfer standard may replace the O_3 generator and possibly other components shown in Figure 1; see Reference 8 for guidance.

3.1 UV photometer. The photometer consists of a low-pressure mercury discharge lamp, (optional) collimation optics, an absorption cell, a detector, and signal-processing electronics, as illustrated in Figure 1. It must be capable of measuring the transmittance, I/I_0, at a wavelength of 254 nm with sufficient precision such that the standard deviation of the concentration measurements does not exceed the greater of 0.005 ppm or 3% of the concentration. Because the low-pressure mercury lamp radiates at several wavelengths, the photometer must incorporate suitable means to assure that no O_3 is generated in the cell by the lamp, and that at least 99.5% of the radiation sensed by the detector is 254 nm radiation. (This can be readily achieved by prudent selection of optical filter and detector response characteristics.) The length of the light path through the absorption cell must be known with an accuracy of at least 99.5%. In addition, the cell and associated plumbing must be designed to minimize loss of O_3 from contact with cell walls and gas handling components. See Reference 9 for additional information.

3.2 Air flow controllers. Devices capable of maintaining constant air flow within ±2%.

3.3 Ozone generator. Device capable of generating stable levels of O_3 over the required concentration range.

3.4 Output manifold. The output manifold should be constructed of glass, Teflon®, or other relatively inert material, and should be of sufficent diameter to insure a negligible pressure drop at the photometer connection and other output ports. The system must have a vent designed to insure atmospheric pressure in the manifold and to prevent ambient air from entering the manifold.

3.5 Two-way valve. Manual or automatic valve, or other means to switch the photometer flow between zero air and the O_3 concentration.

3.6 Temperature indicator. Accurate to ±1°C.

3.7 Barometer or pressure indicator. Accurate to ±2 torr.

4. Reagents.

4.1 Zero air. The zero air must be free of contaminants which would cause a detectable response from the O_3 analyzer, and it should be free of NO, C_2H_4, and other species which react with O_3. A procedure for generating suitable zero air is given in Reference 9. As shown in figure 1, the zero air supplied to the photometer cell for the I_0 reference measurement must be derived from the same source as the zero air used for generation of the ozone concentration to be assayed (I measurement). When using the photometer to certify a transfer standard having its own source of ozone, see Reference 8 for guidance on meeting this requirement.

5. Procedure.

5.1 General operation. The calibration photometer must be dedicated exclusively to use as a calibration standard. It should always be used with clean, filtered calibration gases, and never used for ambient air sampling. Consideration should be given to locating the calibration photometer in a clean laboratory where it can be stationary, protected from physical shock, operated by a responsible analyst, and used as a common standard for all field calibrations via transfer standards.

5.2 Preparation. Proper operation of the photometer is of critical importance to the accuracy of this procedure. The following steps will help to verify proper operation. The steps are not necessarily required prior to each use of the photometer. Upon initial operation of the photometer, these steps should be carried out frequently, with all quantitative results or indications recorded in a chronological record either in tabular form or plotted on a graphical chart. As the performance and stability record of the photometer is established, the frequency of these steps may be reduced consistent with the documented stability of the photometer.

5.2.1 Instruction manual: Carry out all set up and adjustment procedures or checks as described in the operation or instruction manual associated with the photometer.

5.2.2 System check: Check the photometer system for integrity, leaks, cleanliness, proper flowrates, etc. Service or replace filters and zero air scrubbers or other consumable materials, as necessary.

5.2.3 Linearity test: Test the photometer for linearity by dilution. Generate and assay an O_3 concentration near the upper range limit of the system (0.5 or 1.0 ppm), then accurately dilute that concentration with zero air and reassay it. Repeat at several different dilution ratios. Compare the assay of the original concentration with the assay of the diluted concentration divided by the dilution ratio, as follows

$$E = \frac{A_1 - A_2/R}{A_1} \times 100\% \qquad (3)$$

where:

E=linearity error, percent

A_1=assay of the original concentration

A_2=assay of the diluted concentration

R=dilution ratio=flow of original concentration divided by the total flow

The linearity error must be less than 5%. Since the accuracy of the measured flowrates will affect the linearity error as measured this way, the test is not necessarily conclusive. Additional information on verifying linearity is contained in Reference 9.

5.2.4 Intercomparison: When possible, the photometer should be occasionally intercompared, either directly or via transfer standards, with calibration photometers used by other agencies or laboratories.

5.2.5 Ozone losses: Some portion of the O_3 may be lost upon contact with the photometer cell walls and has handling components. The magnitude of this loss must be determined and used to correct the calculated O_3 concentration. This loss must not exceed 5%. Some guidelines for quantitatively determining this loss are discussed in Reference 9.

5.3 Assay of O_3 concentrations.

5.3.1 Allow the photometer system to warm up and stabilize.

5.3.2 Adjust the flowrate through the photometer absorption cell, F_p, to a convenient value so that the cell can be flushed in a reasonably short period of time (2 liter/min is a typical flow). The precision of the measurements is inversely related to the time required for flushing, since the photometer drift error increases with time.

5.3.3 Adjust the flowrate into the output manifold to a value at least 1 liter/min greater than the total flowrate required by the photometer and any other flow demand connected to the manifold.

5.3.4 Adjust the flowrate of zero air, F_Z, to a value at least 1 liter/min greater than the flowrate required by the photometer.

5.3.5 With zero air flowing in the output manifold, actuate the two-way valve to allow the photometer to sample first the manifold zero air, then F_Z'. The two photometer readings must be equal ($I=I_o$).

NOTE: In some commercially available photometers, the operation of the two-way valve and various other operations in section 5.3 may be carried out automatically by the photometer.

5.3.6 Adjust the O_3 generator to produce an O_3 concentration as needed.

5.3.7 Actuate the two-way valve to allow the photometer to sample zero air until the absorption cell is thoroughly flushed and record the stable measured value of I_o.

5.3.8 Actuate the two-way valve to allow the photometer to sample the ozone concentration until the absorption cell is thoroughly flushed and record the stable measured value of I.

5.3.9 Record the temperature and pressure of the sample in the photometer absorption cell. (See Reference 9 for guidance.)

5.3.10 Calculate the O_3 concentration from equation 4. An average of several determinations will provide better precision.

$$[O_3]_{OUT} = \left(\frac{-1}{\alpha l} \ln \frac{I}{I_0}\right) \left(\frac{T}{273}\right) \left(\frac{760}{P}\right) \times \frac{10^6}{L} \qquad (4)$$

where:

$[O_3]_{OUT}$=O_3 concentration, ppm

α=absorption coefficient of O_3 at 254 nm=308 atm^{-1} cm^{-1} at 0°C and 760 torr

l=optical path length, cm

T=sample temperature, K

P=sample pressure, torr

L=correction factor for O_3 losses from 5.2.5=(1-fraction O_3 lost)

Note.—Some commercial photometers may automatically evaluate all on part of equation 4. It is the operator's responsibility to verify that all of the information required for equation 4 is obtained, either automatically by the photometer or manually. For "automatic" photometers which evaluate the first term of equation 4 based on a linear approximation, a manual correction may be required, particularly at higher O_3 levels. See the photometer instruction manual and Reference 9 for guidance.

5.3.11 Obtain additional O_3 concentration standards as necessary by repeating steps 5.3.6 to 5.3.10 or by Option 1.

5.4 Certification of transfer standards. A transfer standard is certified by relating the output of the transfer standard to one or more ozone standards as determined according to section 5.3. The exact procedure varies depending on the nature and design of the transfer standard. Consult Reference 8 for guidance.

5.5 Calibration of ozone analyzers. Ozone analyzers are calibrated as follows, using ozone standards obtained according to section 5.3 or by means of transfer standards.

5.5.1 Allow sufficient time for the O_3 analyzer and the photometer or transfer standard to warmup and stabilize.

5.5.2 Allow the O_3 analyzer to sample zero air until a stable response is obtained and adjust the O_3 analyzer's zero control. Offsetting the analyzer's zero adjustment to +5% of scale is recommended to facilitate observing negative zero drift. Record the stable zero air response as "Z".

5.5.3 Generate an O_3 concentration standard of approximately 80% of the desired upper range limit (URL) of the O_3 analyzer. Allow the O_3 analyzer to sample this O_3 concentration standard until a stable response is obtained.

5.5.4 Adjust the O_3 analyzer's span control to obtain a convenient recorder response as indicated below:

$$\text{recorder response (\% scale)} = \left(\frac{[O_3]_{OUT}}{URL} \times 100\right) + Z \qquad (5)$$

where:

URL=upper range limit of the O_3 analyzer, ppm

Z=recorder response with zero air, % scale

Record the O_3 concentration and the corresponding analyzer response. If substantial adjustment of the span control is necessary, recheck the zero and span adjustments by repeating steps 5.5.2 to 5.5.4.

5.5.5 Generate several other O_3 concentration standards (at least 5 others are recommended) over the scale range of the O_3 analyzer by adjusting the O_3 source or by Option 1. For each O_3 concentration standard, record the O_3 concentration and the corresponding analyzer response.

5.5.6 Plot the O_3 analyzer responses versus the corresponding O_3 concentrations and draw the O_3 analyzer's calibration curve or calculate the appropriate response factor.

5.5.7 *Option 1:* The various O_3 concentrations required in steps 5.3.11 and 5.5.5 may be obtained by dilution of the O_3 concentration generated in steps 5.3.6 and 5.5.3. With this option, accurate flow measurements are required. The dynamic calibration system must be modified as shown in Figure 2 to allow for dilution air to be metered in downstream of the O_3 generator. A mixing chamber between the O_3 generator and the output manifold is also required. The flowrate through the O_3 generator (F_O) and the dilution air flowrate (F_D) are measured with a reliable flow or volume standard traceable to NBS. Each O_3 concentration generated by dilution is calculated from:

$$[O_3]'_{OUT} = [O_3]_{OUT} \left(\frac{F_O}{F_O + F_D}\right) \qquad (6)$$

where:

$[O_3]'_{OUT}$=diluted O_3 concentration, ppm
F_O=flowrate through the O_3 generator, liter/min
F_D=diluent air flowrate, liter/min

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8. "Transfer Standards for Calibration of Ambient Air Monitoring Analyzers for Ozone", EPA Publication available in draft form from EPA, Department E (MD-76), Research Triangle Park, N.C. 27711.

9. "Technical Assistance Document for the Chemiluminescence Measurement of Ozone", EPA Publication available in draft form from EPA, Department E (MD-76), Research Triangle Park, N.C. 27711.

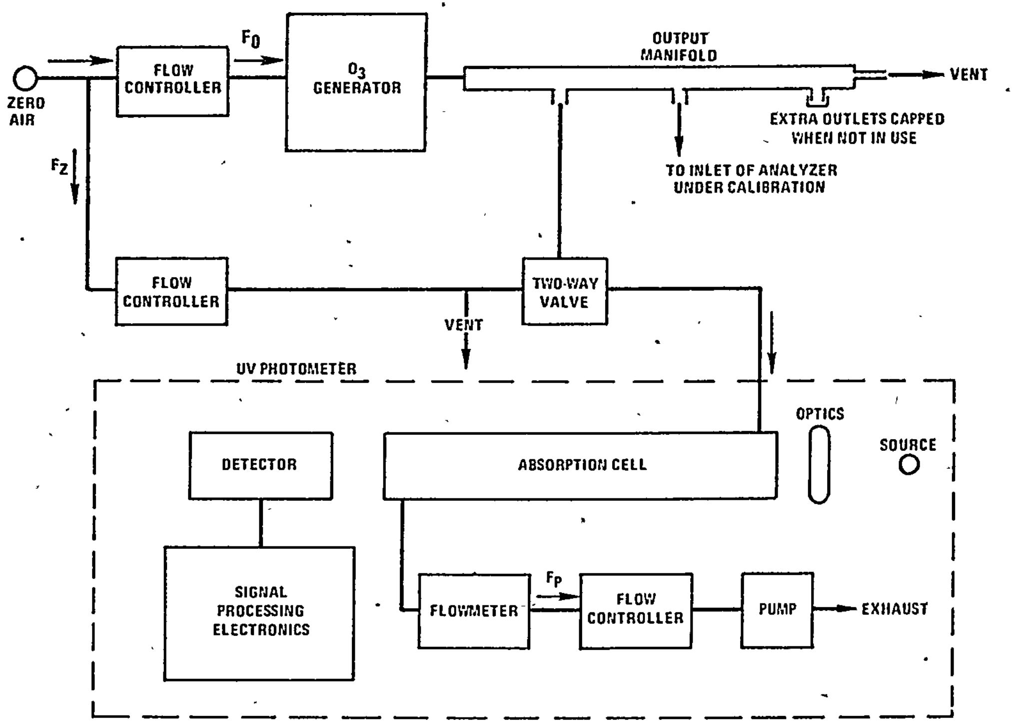

Figure 1. Schematic diagram of a typical UV photometric calibration system.

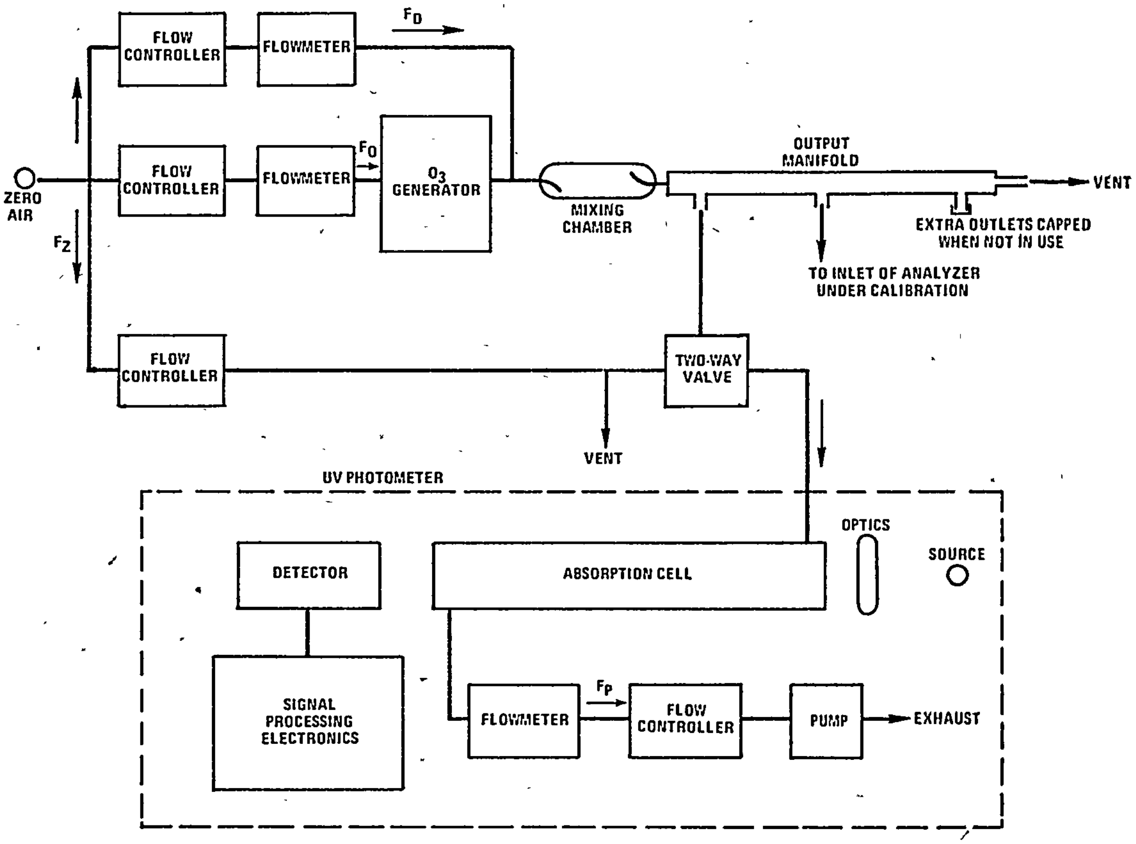

Figure 2. Schematic diagram of a typical UV photometric calibration system (OPTION 1)

Temporary Alternative Calibration Procedure—(Boric Acid-Potassium Iodide). This procedure may be used as an alternative to the Ultraviolet Photometry procedure for direct calibration of ozone analyzers—but not to certify transfer standards—until [18 months after the date of final promulgation]. After that time this procedure can be used only as a transfer standard in accordance with the guidance and specifications set forth in Reference 4, "Transfer Standards for Calibration of Ambient Air Monitoring Analyzers for Ozone".

1. Principle. This calibration procedure (1) is based upon the reaction between ozone (O_3) and potassium iodide (KI) to release iodine (I_2) according to the stoichiometric equation: (2)

$$O_3+2I^-+2H^+\rightarrow I_2+H_2O+O_2 \qquad (1)$$

The stoichiometry is such that the amount of I_2 released is equivalent to the amount of O_3 absorbed. Ozone is absorbed in a 0.1M boric acid (H_3BO_3) solution containing 1% KI, and the I_2 released is measured spectrophotometrically as the triiodide ion (I_3^-) at a wavelength of 352 nm. The output of a stable O_3 generator is assayed in this manner, and the generator is immediately used to calibrate the O_3 analyzer. The O_3 generator must be used immediately after calibration and without physical movement, and it is recalibrated prior to each use. Alternatively, the O_3 analyzer may be calibrated by assaying the O_3 concentrations using the prescribed procedure while simultaneously measuring the corresponding O_3 analyzer responses. Ozone concentration standards may also be generated by an optional dilution technique. With this option, the highest O_3 concentration standard is assayed using the prescribed procedure. The additional O_3 concentration standards required are then obtained by dilution.

2. Apparatus. Figures 1 and 2 illustrate a typical BAKI O_3 calibration system and show the suggested configuration of the components listed below. All connections between components downstream of the O_3 generator should be of glass, Teflon®, or other relatively inert material.

2.1 Air flow controller. Device capable of maintaining a constant air flowrate through the O_3 generator within ±2%.

2.2 Air flowmeter. Calibrated flowmeter capable of measuring and monitoring the air flowrate through the O_3 generator within ±2%.

2.3 Ozone generator. Device capable of generating stable levels of O_3 over the required concentration range.

2.4 Output manifold. The output manifold should be constructed of glass, Teflon®, or other relatively inert material and should be of sufficient diameter to insure an negligible pressure drop at the analyzer connection. The system must have a vent designed to insure atmospheric pressure in the manifold and to prevent ambient air from entering the manifold.

2.5 Impingers. All glass impingers with the specifications indicated in Figure 2 are recommended. The impingers may be purchased from most major glassware suppliers. Two impingers connected in series are used to insure complete collection of the sample.

2.6 Air pump and flow controller. Any pump and flow control device capable of maintaining a constant flowrate of 0.4–0.6 liter/min through the impingers may be used. A critical orifice as described by Lodge *et al.* (3) is recommended. The orifice should be protected against moisture and particulate matter with a membrane filter or moisture trap containing Drierite®, silica gel, or glass wool. The air pump must be capable of maintaining a pressure differential of at least 0.6–0.7 atmospheres across the critical orifice. Alternatively, a needle valve could be used with the pump to adjust the flow through the impingers. A flowmeter is then recommended to monitor the flow. The needle valve-flowmeter combination should be protected against moisture and particulate matter with a membrane filter or moisture trap.

2.7 Thermometer. Accurate to ±1°C.

2.8 Barometer. Accurate to ±2 torr.

2.9 Volumetric flasks (Class A). 25, 100, 200, 1000-ml.

2.10 Pipets (Class A). 1, 2, 3, 5, 10, 15, 20, and 25-ml volumetric.

2.11 Spectrometer. Capable of measuring absorbance at 352 nm with an absolute accuracy of ±1% and linear response over the range of 0–1.0 absorbance units. The photometric accuracy may be checked using optical glass filters which have certified absorbance values at specified wavelengths. Matched 1-cm or 2-cm cells should be used for all absorbance determinations.

3. Reagents.

3.1 Zero air. The zero air must be free of contaminants which will cause a detectable response on the O_3 analyzer or which might react with 1% BAKI. Air meeting this requirement may be obtained by: (1) passing it through silica gel for drying; (2) treating it with O_3 to convert any nitric oxide (NO) to nitrogen dioxide (NO_2); (3) passing it through activated charcoal (6–14 mesh) and molecular sieve (6–16 mesh, type 4A) to remove any NO_2, hydrocarbons, and traces of water vapor; and (4) passing it through a 2-micron filter to remove any particulate matter.

3.2 Boric acid (H_3BO_3), ACS reagent grade.

3.3 Potassium iodide (KI), ACS reagent grade.

3.4 Hydrogen peroxide (H_2O_2), ACS reagent grade, 3% or 30%.

3.5 Potassium iodate (KIO_3), ACS reagent grade, certified 0.1N.

3.6 Sulfuric acid (H_2SO_4), ACS reagent grade, 95% to 98%.

3.7 Distilled water. Used for preparation of all reagents.

3.8 Absorbing reagent. Dissolve 6.2 g of boric acid (H_3BO_3) in approximately 750 ml of distilled water in a nonactinometric 1000-ml volumetric flask. The flask may be heated gently to speed dissolution of the H_3BO_3, but the solution must then be cooled to room temperature or below before proceeding with the reagent preparation. [While the H_3BO_3 solution is cooling, prepare the hydrogen peroxide (H_2O_2) solution according to the directions in 3.9.] When the H_3BO_3 solution has cooled, add 10 g of potassium iodide (KI) to the H_3BO_3 solution and dissolve. Add 1 ml of 0.0018% H_2O_2 solution (see 3.9) and mix thoroughly. Within 5 minutes after adding the peroxide, dilute to volume with distilled water, mix, and determine the absorbance of this BAKI solution at 352 nm against distilled water as the reference. The pH of the BAKI solution must be 5.5±0.2.

Set the absorbing solution aside for 2 hours and then redetermine the absorbance at 352 nm against distilled water as the reference. If the resultant absorbance from this second determination is at least 0.010 absorbance units/cm greater than the first determination, the absorbing reagent is ready for use. If no increase or an increase of less than 0.010 absorbance units/cm is observed, the KI reagent probably contains an excessive amount of a reducing contaminant and *must be discarded.* In this event, prepare fresh absorbing reagent using a different numbered lot of KI. If unacceptable absorbing reagent results from different lots of KI, test the possibility of contamination in the H_3BO_3 by using a different numbered lot of H_3BO_3.

3.9 Hydrogen peroxide solution (0.0018%). Pipet 3 ml of 30% or 30 ml of 3% hydrogen peroxide (H_2O_2) into approximately 200 ml of distilled water in a 1000-ml volumetric flask, dilute to volume with distilled water, and mix thoroughly. To prepare the 0.0018% solution, pipet 2 ml of the above solution into 50 ml of distilled water in a 100-ml volumetric flask, dilute to volume with distilled water, and mix thoroughly. This 0.0018% H_2O_2 solution must be prepared fresh each time a fresh batch of absorbing reagent is prepared. Therefore, the remaining contents of both volumetric flasks should be discarded after treatment of the BAKI absorbing reagent (see 3.8).

3.10 Standard potassium iodate solution (0.1N). Use a commercial standard solution of potassium iodate (KIO_3) having a certified normality.

3.11 Sulfuric acid (1N). Dilute 28 ml of concentrated (95–98%) sulfuric acid (H_2SO_4) to volume in a 1000-ml volumetric flask.

4. Procedure.

4.1 Assemble an ozone calibration system such as shown in Figure 1.

4.2 Assemble the KI sampling train such as shown in Figure 2. All connections between the various components must be leak tight and may be made using grease-free ball joint fittings, heat-shrinkable Teflon® tubing, or Teflon® tube fittings. The connection to the O_3 output manifold should be made using 6 mm (1/4 in.) Teflon® tubing not to exceed 1.5 meters in length.

4.3 Calibrate all flowmeters and critical orifices under the conditions of use against a reliable flow or volume standard such as a NBS traceable bubble flowmeter or wet-test meter. Correct all volumetric flowrates to 25°C and 760 torr as follows:

$$F_R = F_S \times \frac{P_S - P_{H_2O}}{760} \times \frac{298}{T_S + 273} \qquad (2)$$

where:

F_R=flowrate corrected to reference conditions (25° C and 760 torr), liter/min

F_S=flowrate at sampling conditions, liter/min

P_S=barometric pressure at sampling conditions, torr

P_{H_2O}=vapor pressure of H_2 at T_S, torr (For wet volume standard. For a dry standard, P_{H_2O}=O)

T_S=temperature at sampling conditions, °C

4.4 KI calibration curve.

4.4.1 Prepare iodine standards, fresh when needed, as follows:

A. Accurately pipet 10 ml of 0.1N standard potassium iodate (KIO_3) solution into a 100-ml volumetric flask containing approximately 50 ml of distilled water. Add 1 g of potassium iodide (KI) and 5 ml of 1N sulfuric acid (H_2SO_4), dilute to volume with distilled water, and mix thoroughly.

B. Immediately before use, pipet 10 ml of the iodine (I_2) solution prepared in step A above into a 100-ml volumetric flask and dilute to volume with absorbing reagent. Then further dilute this solution by pipetting 10 ml of it into a 200-ml volumetric flask and diluting it to volume with absorbing reagent.

C. In turn, pipet 5, 10, 15, 20, and 25 ml aliquots of the final I_2 solution prepared in step B above into a series of 25-ml volumetric flasks. Dilute each to volume with absorbing reagent and mix thoroughly. To prevent I_2 losses by volatilization, the flasks should remain stoppered until absorbance measurements are made. Absorbance measurements (see 4.4.2) should be taken within 20 minutes after preparation of the I_2 standards.

4.4.2 Determine the absorbance of each I_2 standard at 352 nm. Also measure the absorbance of a sample of unexposed absorbing reagent. Determine the net absorbance of each I_2 standard as:

$$\text{net absorbance} = \left(\begin{array}{c}\text{sample}\\ \text{absorbance}\end{array}\right) - \left(\begin{array}{c}\text{unexposed}\\ \text{reagent}\\ \text{absorbance}\end{array}\right) \qquad (3)$$

4.4.3 For each I_2 standard, calculate the net absorbance/cm as:

$$\text{net absorbance/cm} = \frac{\text{net absorbance}}{b} \qquad (4)$$

where:

b=spectrophotometer cell path length, cm

4.4.4 For each I_2 standard, calculate the I_2 concentration in mole/liter as:

$$[I_2]_i = N_{KIO_3} \times \frac{1\ \text{eq}\ I_2}{1\ \text{eq}\ KIO_3} \times \frac{1\ \text{mole}\ I_2}{2\ \text{eq}\ I_2} \times \frac{10}{100} \times \frac{10}{100} \times \frac{10}{200} \times \frac{V_i}{25} \qquad (5a)$$

or,

$$[I_2]_i = N_{KIO_3} \times V_i \times 10^{-5} \qquad (5b)$$

where:

$[I_2]_i$=concentration of each I_2 standard, mole I_2/liter

N_{KIO_3}=normality of KIO_3 (from 3.10), eq-liter

V_i=volume of I_2 solution (from step 4.4.1.C)=5, 10, 15, 20, or 25 ml

4.4.5 Plot net absorbance/cm (y-axis) versus the mole I_2/liter (x-axis) for each I_2 standard and draw the KI calibration curve. Calculate the slope of the curve in liter mole^{-1} cm^{-1} and record as S_c. The value of the slope should be 25,800±600. If the slope is not within this range, and the photometric accuracy of the spectrophotometer meets the specifications given in 2.11, repeat the procedure using freshly prepared I_2 standards. If the slope is still not within the specified range, repeat the procedure using a different lot of certified 0.1N KIO_3 to prepare the I_2 standards.

4.5 Calibration of the ozone generator.

4.5.1 Adjust the air flow through the O_3 generator to the desired flowrate and record as F_o. At all times the air flow through the generator must be greater than the total flow required by the sampling systems, to assure exhaust flow at the vent.

4.5.2 With the O_3 generator off, flush the system with zero air for at least 15 minutes to remove residual O_3. Pipet 10 ml of absorbing reagent into each of 2 impingers and connect them into the sampling train as shown in Figure 2. Draw air from the output manifold of the O_3 calibration system through the sampling train at 0.4-0.6 liter/min for 10 minutes. Immediately transfer the exposed solutions to clean spectrophotometer cells. Determine the net absorbance (sample absorbance-unexposed reagent absorbance) of each solution at 352 nm within three minutes. Add the net absorbances of the two solutions to obtain the total net absorbance. Calculate the indicated O_3 concentration (system blank) as equivalent O_3 concentration according to 4.5.4. If the system blank is greater than 0.005 ppm O_3, continue flushing the O_3 generation system for an additional 30 minutes and redetermine the system blank. If the system blank is still greater than 0.005 ppm O_3, the zero air probably contains traces of an oxidizing contaminant, and the activated charcoal and molecular sieve (see 3.1) should be replaced.

4.5.3 Adjust the O_3 generator to generate an O_3 concentration in the range of interest and allow the system to equilibrate for about 15 minutes. The uncalibrated O_3 analyzer to be calibrated can conveniently be used to indicate the stability of the O_3 generator output. When the O_3 generator output has stabilized, pipet 10 ml of absorbing reagent into each impinger. Draw O_3 from the output manifold of the O_3 calibration system through the sampling train at 0.4-0.6 liter/min. Use a sample time of between 10 and 30 minutes such that a total net absorbance between 0.1 and 1.0 absorbance units is obtained. (At an O_3 concentration of 0.1 ppm and a sampling rate of 0.5 liter/min, a total net absorbance >0.1 absorbance units should be obtained if a sampling time of 20 minutes and 1-cm spectrophotometer cells are used.) Immediately after collection, transfer the exposed solutions to clean spectrophotometer cells. Determine the net absorbance (sample absorbance—unexposed reagent absorbance) of each solution at 352 nm within three minutes. Add the net absorbances of the two solutions to obtain the total net absorbance.

4.5.4 Calculation of ozone concentration.

4.5.4.1 Calculate the total volume of air sampled, corrected to reference conditions of 25°C and 760 torr as:

$$V_R = F_R x t_S$$

where:

V_R=volume of air sampled, corrected to reference conditions, liter

F_R=sampling flowrate corrected to reference conditions, liter/min

t_S=sampling time, min

4.5.4.2 Calculate the I_2 released in moles as:

$$\text{mole}\ I_2 = \frac{\text{total net absorbance} \times 0.01}{S_c \times b} \qquad (7)$$

where: total net absorbance=sum of net absorbances for the two solutions

0.01=volume of absorbing reagent in each impinger, liter

S_c=slope of KI calibration curve, liter mole^{-1} cm^{-1}

b=spectrophotometer cell path length, cm

4.5.4.3 Calculate the μl of O_3 absorbed as:

$$\mu l\ O_3 = \text{mole}\ I_2 \times \frac{1\ \text{mole}\ O_3}{1\ \text{mole}\ I_2} \times \frac{24.47\ l\ O_3}{\text{mole}\ O_3} \times \frac{10^6\ \mu l\ O_3}{l\ O_3} \qquad (8a)$$

or,

$$\mu l\ O_3 = \text{mole}\ I_2 x 24.47 x 10^6$$

4.5.4.4 Calculate the O_3 concentration in ppm as:

$$\text{ppm}\ O_3 = \frac{\mu l\ O_3}{V_R} \qquad (9)$$

4.5.5 Repeat steps 4.5.3 and 4.5.4 at least one more time at the same O_3 generator setting. Average the two (or more) determinations and record the average along with the O_3 generator setting.

4.5.6 Adjust the O_3 generator to obtain other O_3 concentrations over the desired range. Determine each O_3 concentration using the procedure given above. Five or more O_3 concentrations are recommended. Plot the O_3 concentrations versus the corresponding O_3 generator settings and draw the O_3 generator calibration curve. 4.6 Calibration of the ozone analyzer.

4.6.1 Allow sufficient time for the O_3 analyzer to warm-up and stabilize.

4.6.2. Allow the O_3 analyzer to sample zero air until a stable response is obtained and adjust the O_3 analyzer's zero control. Offsetting the analyzer's zero adjustment to +5% of scale is recommended to facilitate observing negative zero drift. Record the stable zero air response as "Z".

4.6.3 Using the O_3 generator as calibrated above and the same F_o, generate an O_3 concentration near 80% of the desired upper range limit (URL) of the O_3 analyzer.

4.6.4 Allow the O_3 analyzer to sample this O_3 concentration until a stable response is obtained. Adjust the analyzer's span control to obtain a convenient recorder response as indicated below:

$$\text{recorder response (\% scale)} = \left(\frac{[O_3]_{OUT}}{URL} \times 100\right) + Z \qquad (10)$$

$[O_3]_{OUT}$ = O_3 concentration at the output manifold, ppm URL = upper range limit of the O_3 analyzer, ppm, Z = recorder response with zero air, % scale.

Record the O_3 concentration and the O_3 analyzer response. If substantial adjustment of the span control is necessary, recheck the zero and span adjustments by repeating steps 4.6.2 through 4.6.4.

4.6.5 Generate several other O_3 concentrations (at least 5 others are recommended) over the scale range of the O_3 analyzer by adjusting the O_3 generator settings (preferably the same settings as used in 4.5) or by Option 1. For each O_3 concentration, allow for a stable analyzer response, then record the response and the corresponding O_3 concentration.

4.6.6 Plot the O_3 analyzer responses versus the corresponding O_3 concentrations and draw the O_3 analyzer's calibration curve or calculate the appropriate response factor.

4.6.7 *Option 1:* The various O_3 concentrations required in step 4.6.5 may be obtained by dilution of the O_3 concentration generated in 4.6.3. With this option, accurate flow measurements are required. The dynamic calibration system must be modified as shown in Figure 3 to allow for dilution air to be metered in downstream of the O_3 generator. A mixing chamber between the O_3 generator and the output manifold is also required. The flowrate through the O_3 generator (F_O) and the dilution air flowrate (F_D) are measured with a reliable flow or volume standard traceable to NBS. The highest O_3 concentration standard required (80% URL) is assayed according to the procedure in 4.5. Each O_3 concentration generated by dilution is calculated from:

$$[O_3]'_{OUT} = [O_3]_{OUT} \left(\frac{F_O}{F_O + F_D}\right) \qquad (11)$$

where: $[O_3]'_{OUT}$ = diluted O_3 concentration, ppm; F_O = flowrate through the O_3 generator, liter/min; F_D = diluent air flowrate, liter/min.

NOTE.—Direct calibration of the O_3 analyzer may also be accomplished by assaying the O_3 concentrations using the procedure in 4.5 while simultaneously measuring the corresponding O_3 analyzer responses as specified in 4.6.

REFERENCES

1. D. L. Flamm, "Analysis of Ozone at Low Concentrations with Boric Acid Buffered KI," *Environ. Sci. Technol.*, *11*, 978 (1977).

2. B. E. Saltzman and N. Gilbert, "Iodometric Microdetermination of Organic Oxidants and Ozone," *Anal. Chem.*, *31*, 1914 (1959).

3. J. P. Lodge, Jr., J. B. Pate, B. E. Ammons, and G. A. Swanson, "The Use of Hypodermic Needles as Critical Orifices in Air Sampling," *J. Air Poll. Control Assoc.*, *16*, 197 (1966).

4. "Transfer Standards for Calibration of Ambient Air Monitoring Analyzers for Ozone," EPA Publication available in draft form from EPA, Department E (MD-76), Research Triangle Park, N.C. 27711.

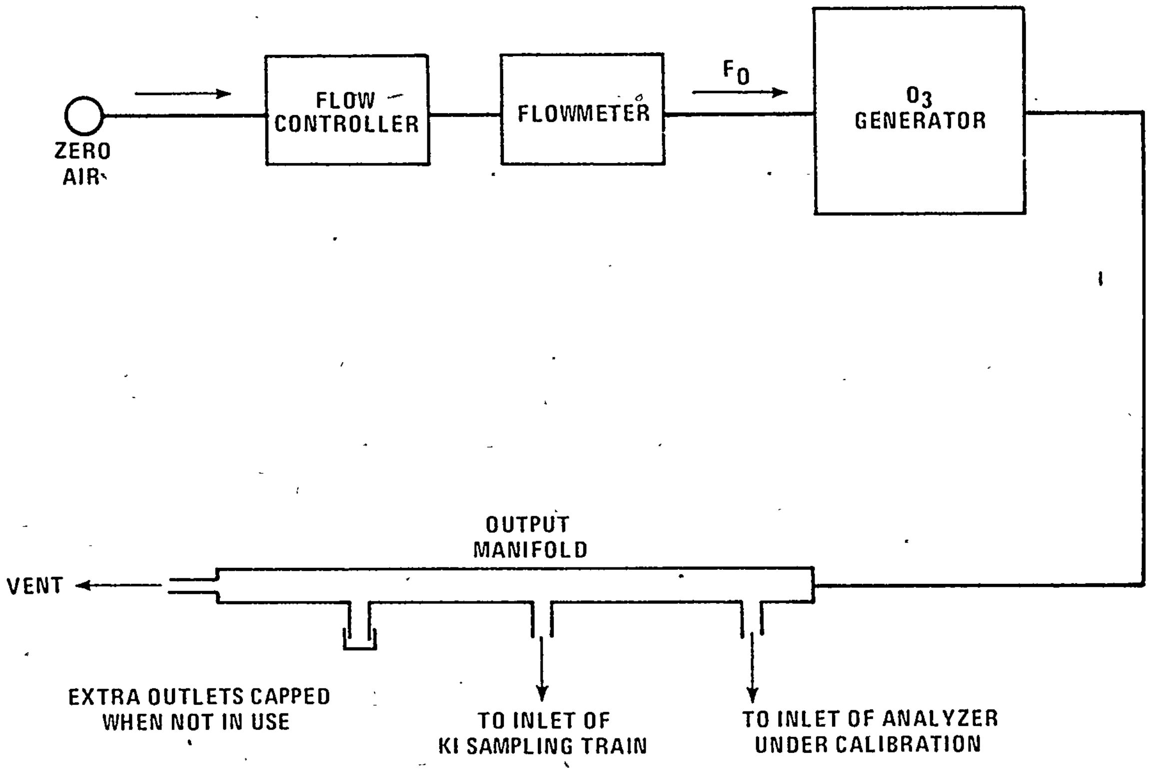

Figure 1. Schematic diagram of a typical BAKI calibration system.

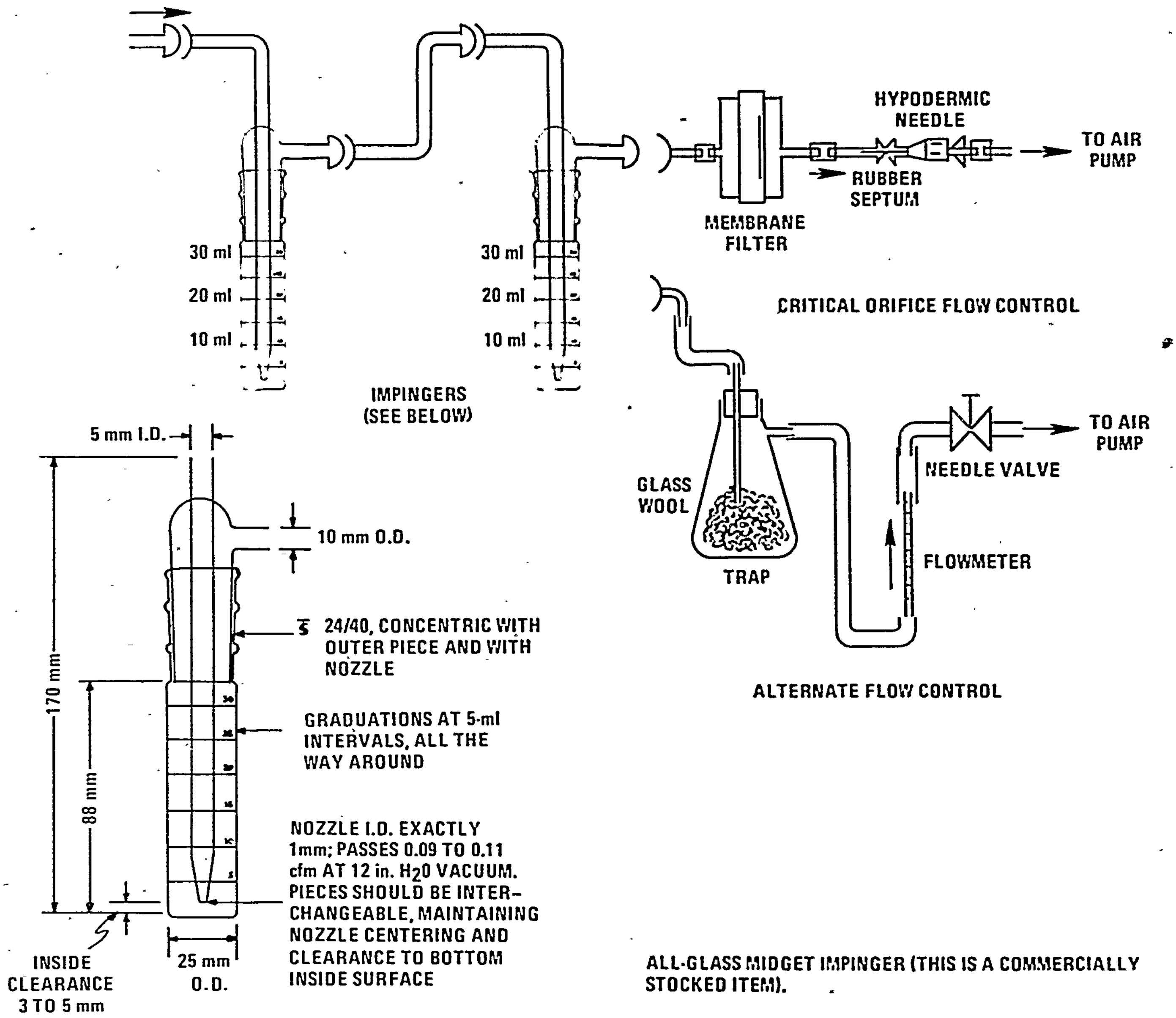

Figure 2. KI sampling train.

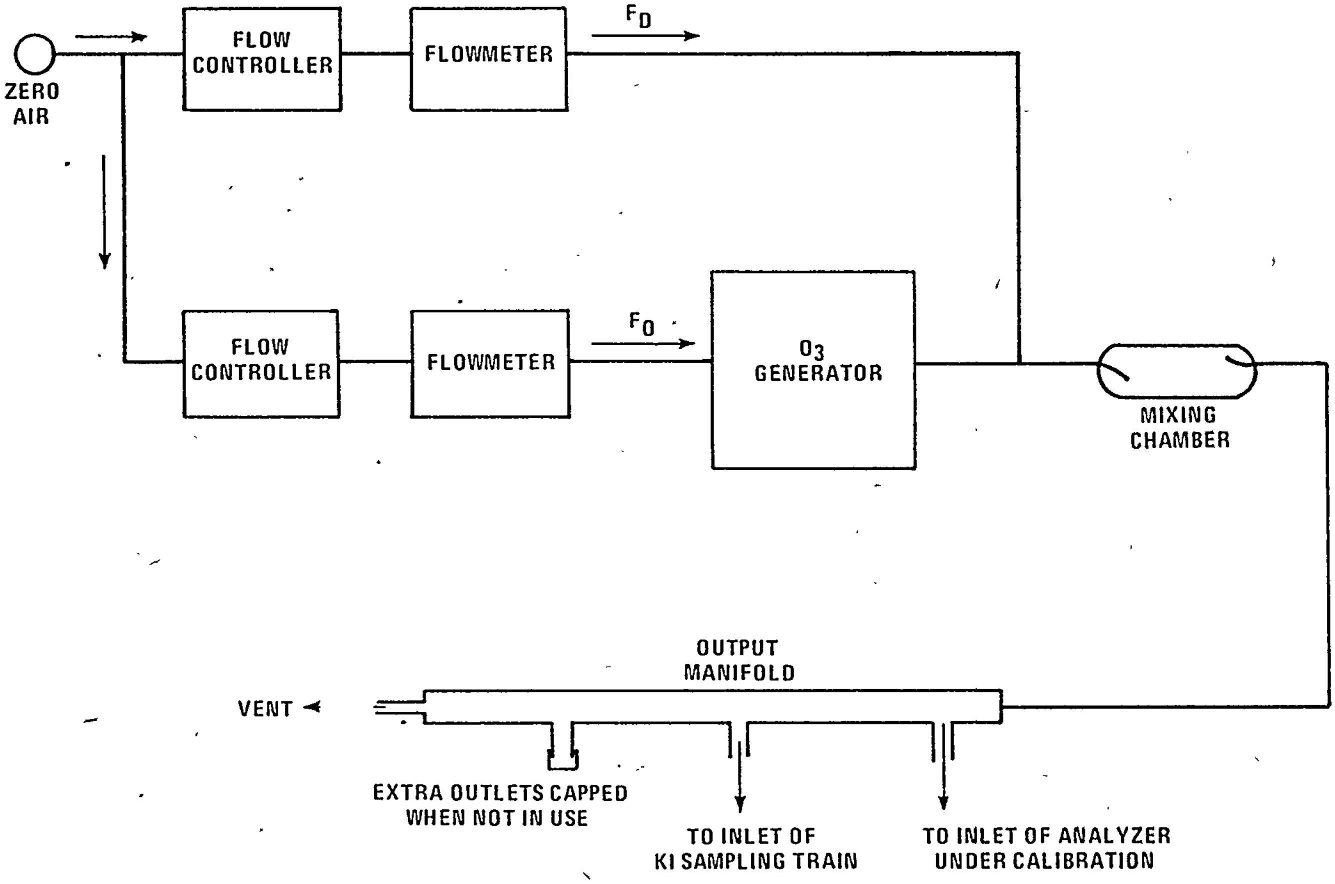

Figure 3. Schematic diagram of a typical BAKI calibration system (Option 1).

[FR Doc. 78-17154 Filed 6-21-78; 8:45 am]

[6560-01]

[FRL 914-2]

[40 CFR Parts 51 and 52]

REQUIREMENTS FOR PREPARATION, ADOPTION, AND SUBMITTAL OF IMPLEMENTATION PLANS

Approval and Promulgation of Implementation Plans

AGENCY: Environmental Protection Agency.

ACTION: Proposed rule.

SUMMARY: In this action, the Administrator proposes to make certain revisions to the procedures for preparation of State Implementation Plans for photochemical oxidants. Specifically, he proposes the following actions:

1. Change the terms "photochemical oxidant(s)" and "oxidant(s)" to "ozone" throughout Parts 51 and 52.

2. Delete Appendix J of 40 CFR Part 51 and revise 40 CFR 51.14 with respect to the method for calculating needed reductions in hydrocarbon emissions.

The terms "photochemical oxidants" and "oxidants" are being changed to "ozone" to be consistent with EPA's proposal to redesignate the photochemical oxidants standard as an ozone standard. The redesignation of the standard, along with the reasons for it, will be proposed as a separate Federal Register action. Thoughout the rest of these actions the word "ozone" will be used in place of "oxidant", except when reference is made to existing language in the *Code of Federal Regulations*.

Appendix J is being deleted to make the Part 51 regulations consistent with EPA's current policy on development of State Implementation Plans (SIPs) to meet the ozone standard. States will be allowed to use any of four prescribed techniques to relate ozone concentrations to hydrocarbon emissions. The techniques will be set forth in the proposed revisions to 40 CFR 51.14(c)(4).

DATES: Comments must be received by August 18, 1978. Comments submitted will facilitate internal distribution and public availability.

ADDRESSES: Persons may submit written comments on this proposal to: U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Control Programs Development Division (MD 15), Research Triangle Park, N.C. 27711, Attention: Mr. Darryl D. Tyler.

EPA will make all comments received within 30 days of publication of this proposal available for public inspection during normal business hours at: EPA Public Information Reference Unit, 401 M Street, SW., Room 2922, Washington, D.C. 20460.

FOR FURTHER INFORMATION CONTACT:

Joseph Sableski, Chief Plans Guidelines Section, Control Programs Development Division (919-541-5437).

SUPPLEMENTARY INFORMATION

In connection with the review of the NAAQS and associated SIP requirements for ozone, EPA has determined that certain changes in 40 CFR Part 51 are appropriate.

APPENDIX J

Petitions to EPA from the American Petroleum Institute (and 29 member companies) on December 9, 1976, and the City of Houston on July 11, 1977, recommended revisions to the method of calculating needed hydrocarbon reductions specified in Appendix J. EPA has studied various methods by which these calculations can be made and has determined that Appendix J of 40 CFR 51 no longer represents the only acceptable analytical relationship between hydrocarbons and ozone. Therefore, Appendix J is being proposed for deletion.

SECTION 51.14

The Administrator is also proposing to amend 40 CFR 51.14(c)(4) to allow the use of alternate analytical relationships for determining the hydrocarbon reductions necessary to meet the ozone standard. EPA is conducting further studies and will propose alternatives or a replacement for Appendix J when the studies are concluded. During the interim period, for the purposes of SIP control strategy development, any one of four modeling techniques may be used. EPA has published a document entitled, "Uses, Limitations and Technical Basis of Procedures for Quantifying Relationships Between Photochemical Oxidants and Precursors" (November, 1977; EPA 450/2-77-021a) which references analytical techniques that States must consider. These techniques include the following:

(1) Photochemical grid models—These models are based on the most accurate available physical and chemical principles underlying the formation of ozone.

(2) Empirical Kinetics Modeling Approach (EKMA)—This model represents a compromise between rigorous treatment of chemical and physical principles underlying the formation and dispersion of ozone and the extensive data requirements necessary to represent such principles in model form. EKMA is not as accurate or flexible as the grid models. However, it does reflect reality to a greater extent than the empirical and statistical approaches.

(3) Empirical and Statistical Models—These models reflect observer relationships between ozone and other variables. However, they do not imply cause-effect relationships; hence, their applicability to estimating the impact of substantial control programs is limited because the conditions, under which the relationships in the model have been derived, will be altered by control programs.

(4) Proportional Rollback—This model assumes a linear relationship between hydrocarbon emissions and ambient concentrations of ozone. Proportional rollback appears to be useful as a lower bound for estimates of hydrocarbon controls needed to attain the ozone standard in most U.S. cities.

EPA will also make available computer programs and other aids to enable States to use the techniques described above.

Background concentrations and transport of ozone from upwind locations can impact upon high levels of ozone in or near an urban area during afternoon hours. Therefore, consideration of background and transport should be made in applying any of the techniques to develop an ozone control strategy. Means for measuring transported ozone and interpreting the measurements, as well as procedures for assessing the impact of transport in an urban area are described in the EPA document referenced above. In developing the ozone control strategy for a particular area, States may assume that the ozone standard will be attained at upwind locations.

IMPACT

In accordance with Agency policy as set forth in 39 FR 37419, EPA has reviewed the proposed changes and determined that they do not constitute "significant" revisions or modifications (as defined in 39 FR 37419) and therefore do not require an environmental impact statement.

Dated: June 9, 1978.

DOUGLAS M. COSTLE,
Administrator.

In Title 40, Chapter I, EPA proposes to amend Subchapter C as follows:

PART 51—REQUIREMENTS FOR PREPARATION, ADOPTION, AND SUBMITTAL OF IMPLEMENTATION PLANS

1. Wherever the terms "Photochemical oxidant(s)" or "oxidant(s)" appear in Part 51, they are changed to read "ozone."

2. Appendix J is deleted and reserved.

3. Section 51.14(c)(4) is revised to read as follows:

§ 51.14 Control strategy: Carbon monoxide, hydrocarbons, photochemical oxidants, and nitrogen dioxide.

* * * * *

(c)

* * * * *

(4) In selecting an appropriate model to determine the amount of hydrocarbon reductions necessary to demonstrate attainment of the ozone standard, one of the following techniques must be applied:

(i) Photochemical grid models—These models are based on the most accurate available physical and chemical principles underlying the formation of ozone.

(ii) Empirical Kinetics Modeling Approach (EKMA)—This model represents a compromise between rigorous treatment of chemical and physical principles underlying ozone formation and dispersion and the extensive data requirements that would be necessitated by such an approach.

(iii) Empirical and Statistical Models—These models reflect observer relationships between ozone and other variables.

(iv) Proportional Rollback—This model assumes a linear relationship between hydrocarbon emissions and ambient concentrations of ozone.

In developing ozone control strategies for a particular area, background concentrations and ozone transported into an area must be considered. States may assume that the ozone standard will be attained in upwind areas.

PART 52—APPROVAL AND PROMULGATION OF IMPLEMENTATION PLANS

4. Wherever the terms "photochemical oxidant(s)" or "oxidant(s)" appear in Part 52, they are changed to read "ozone".

AUTHORITY: Sections 110 and 301(a), Clean Air Act, as amended (42 U.S.C. 7410, 7601).)

[FR Doc. 78-17155 Filed 6-21-78; 8:45 am]