## Review of Analytical Methods for Atmospheric Oxidants Measurements

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Instrumental and manual methods currently available for the measurement of atmospheric oxidants are surveyed. Techniques used in the United States are emphasized and their advantages and disadvantages are discussed. Commercial systems are evaluated in terms of general operating principles rather than of specific instruments. The ability of these techniques to meet the measurement requirements defined by U.S. Federal air quality oxidant criteria are discussed. Alternative chemical techniques that may have some advantages over the neutral, buffered KI procedure are discussed. Also some attractive, alternative instrumental procedures that are ozone-specific are presented. These systems are based on chemiluminescence and ultraviolet absorption photometry. Electrochemical and colorimetric methods for total oxidant measurements are compared. Finally, some data are presented on relationships of ozone and total oxidants.

## INTRODUCTION

Before World War II a list of man-made pollutants in the atmosphere would not have included "oxidants" or ozone. In the late 1940s and early 1950s several investigators showed conclusively that oxidants, including ozone, were the products of the solar irradiation of mixtures of hydrocarbons and

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oxides of nitrogen emitted in automotive exhaust.[1] The chemical reactions that ensue lead to the formation of photochemical smog in the Los Angeles basin and to a lesser degree in other localities. Oxidant formation is one of the symptoms of photochemical smog; other, more apparent effects are reduced visibility and eye irritation. Routine measurements of oxidant or ozone have been used as an index of the degree of, or potential for, photochemical smog formation.

Air quality standards and criteria for oxidants are being established at both state and federal levels. For example, recent air quality standards for the State of California state that the acceptable level is exceeded whenever hourly average oxidant values, measured by neutral KI and corrected for $NO_2$, exceed 0.1 ppm on three or more consecutive days. The U.S. Federal air quality criterion has been established at an hourly average of 0.08 ppm oxidant corrected for $SO_2$ and $NO_2$ interferences.[2] The reference method in the *Federal Register* is a measurement of ozone by chemiluminescence. The oxidant "alert" level requiring implementation of first stage control actions is 0.10 ppm for a 1-hr average.[3] This paper surveys current oxidant measurement methods and instrumentation, with emphasis on how these techniques meet the measurement requirements defined by the standards above. Where feasible, advantages and disadvantages of general methods, rather than specific instruments, are discussed. Available methods are classified for convenience as manual laboratory methods (calibration methods), batch techniques designed to determine long-term exposures (e.g. 24 hr), and continuous field methods.

Ozone-specific techniques currently being applied are discussed. The principle reason for pursuing ozone-specific measurements is that, for the ambient atmosphere, the distinction between measured values of ozone and values for total oxidant minus $NO_2$ is not at all clear. Also, any total oxidant method suffers from reducing interferences for which legitimate corrections may not be possible. Finally, ozone is a molecular constituent of the atmosphere, whereas "total oxidant" is a concept that is defined by its effect on a specific chemical system.

## DISCUSSION

### Laboratory or Calibration Methods

The most widely used laboratory procedure for measuring ozone is the 1% neutral buffered potassium iodide method.[4] This version has largely replaced the alkaline KI technique.[5] This method is used for the primary calibration of chemiluminescence ozone analyzers.[2] Advantages of the technique are simplicity, moderate precision for low levels, and a 1:1 molar ratio between

ozone absorbed and iodine produced.[5-11] Furthermore, the neutral KI method responds to a wide variety of oxidizing species such as peroxides, peracids, and peroxyacetyl nitrate. The disadvantages of the technique are a variable stoichiometry factor for oxidants other than ozone, a quantitative negative interference from $SO_2$ and negative interferences from $H_2S$ and other reducing species. Nitrogen dioxide gives a positive response of about 10% of ozone when both are present in equal molar concentrations. Also, the very low concentrations of iodine produced are quite unstable and are readily affected by light or trace impurities. Analysis must be completed soon after sampling, and skilled laboratory techniques must be applied to obtain good precision at low levels of ozone. The lower limit of sensitivity with acceptable precision for the manual method is about 0.05 ppm.

Bergshoeff[7] recently described a modification of the neutral KI procedure that was designed to provide greater stability and more sensitivity. A more efficient absorbing device was used. Excess thiosulfate was added to the reagent to react with the iodine as soon as it was produced. Titration of unreacted thiosulfate with a standard iodine solution then allowed determination of ozone absorbed by difference.

Applications of the neutral KI procedure for absolute ozone measurements have relied upon a 1:1 stoichiometry between moles of ozone absorbed and moles of iodine released. Boyd et al.[8] recently compared neutral KI measurements with absolute gas-phase photometric determinations of ozone at 2537 Å. At relatively high ozone concentrations they obtained a ratio of 1.5 moles iodine released per mole of ozone absorbed. Immediately after this report other investigators examined the stoichiometry. Kopczynski and Bufalini[9] made absolute measurements of ozone by infrared absorption spectrophotometry and obtained a stoichiometry of 1.0 within experimental error. By gas-phase titration of ozone with a standardized sample of nitric oxide in air, Hodgeson et al.[10] also obtained a unity factor. In the most recent study, Behl[11] made absolute ozone measurements in the sub-ppm range with a modified Kruger-type ozone photometer. Again a stoichiometry factor of 1.0 was observed. Experimental evidence, therefore, is predominantly in favor of a stoichiometry of 1.0 for the neutral KI measurement.

In spite of some difficulties in the manual neutral KI method, it has been designated as the official reference method for calibrating ozone sources and oxidant instruments.[2] A typical system used for dynamic neutral KI calibration is shown in Figures 1 and 2. The neutral KI bubbler train receives samples from a manifold that is fed ozone from a constant ozone source. Other instruments or methods to be calibrated against the neutral KI method obtain samples from other points on the manifold. An ozone source, such as that shown in Figure 1, has recently been described.[12] The source produces a stable ozone output for prolonged periods and may be used as a secondary

standard for the calibration of air monitors after an initial primary calibration of the source by the neutral KI method. The source operates at a constant air flow in the 1 to 5 liters per minute range. The ozone output may be changed continuously from 0 to 1 ppm by variable shielding of the photolysis lamp envelope.
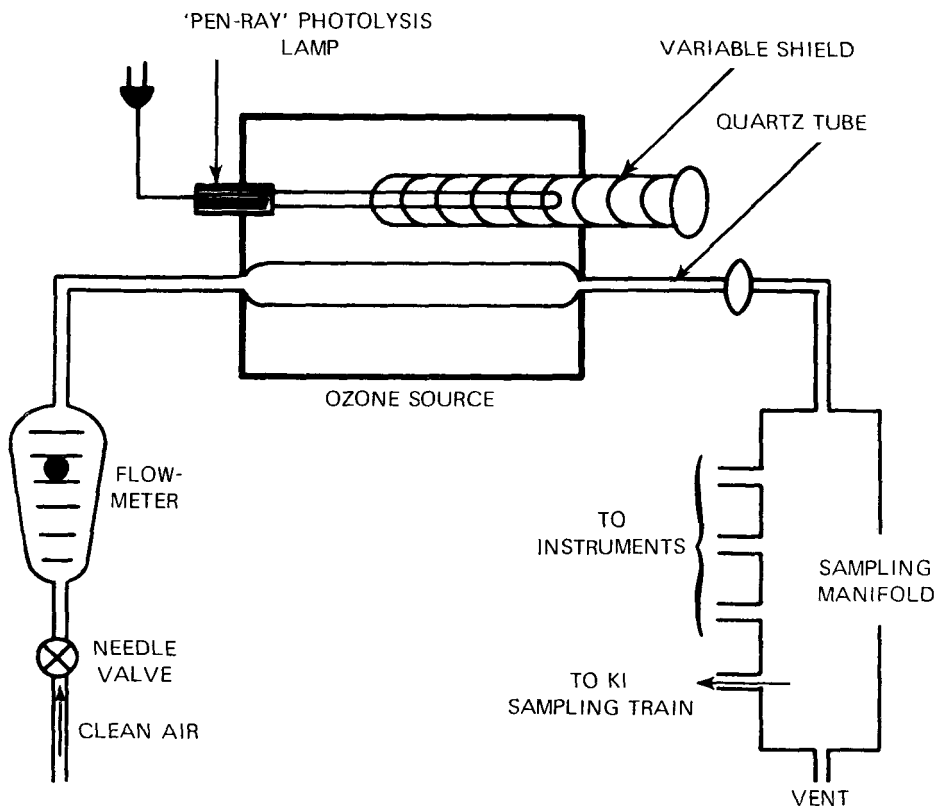


FIGURE 1    Ozone source for iodometric calibration.

In spite of the predominant use of neutral KI, alternative chemical methods have been proposed and applied. The ferrous ammonium sulfate method[13] as modified by Cohen *et al.*[14] is an example. During sampling, ferrous ion is oxidized to ferric ion; the color is then developed with ammonium thio-cyanate at the time of color measurement. Because the ferric ion is much more stable in solution than the triiodide ion, one of the main sources of

FIGURE 2   **KI** sampling train.

difficulty in the neutral KI method is eliminated. Ferrous ammonium sulfate responds to a wide variety of oxidants. The molar absorptivities for color measurement, based on absorbed ozone, are equivalent to or greater than those for neutral KI.[14] Effenberger[15] states that the interference from $NO_2$ is less with the ferrous reagent than with the KI reagent. Because of different absorptivities and different reaction rates in solution, a total oxidant value obtained from a mixed oxidant sample by use of the ferrous r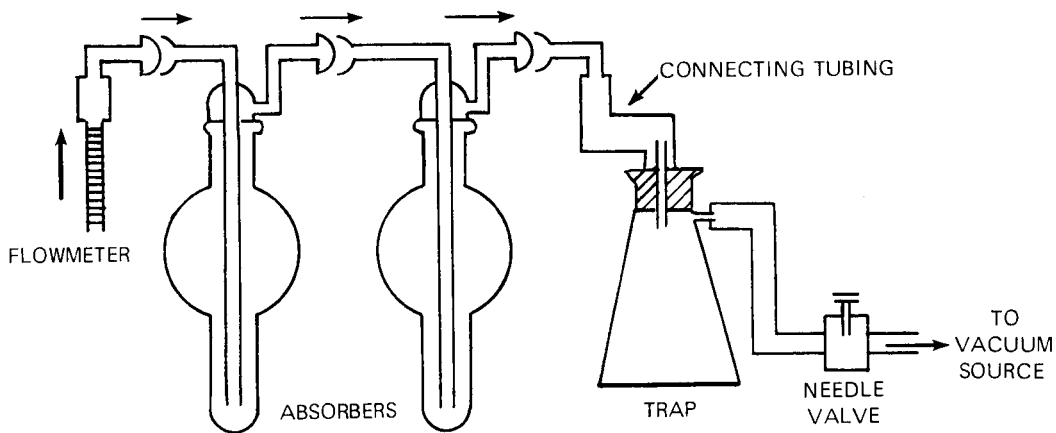eagent should be somewhat different than that obtained by neutral KI. Unfortunately, few quantitative data have been presented on sensitivity, precision, and stoichiometry of and effects of reducing interferences on the ferrous ammonium sulfate method. Comparing color development of the ferrous reagent with that of neutral KI by use of a variable ozone source, Cohen and Bufalini[16] reported that the molar absorptivity for the ferrous reagent increased greatly at low ozone concentrations. This anomalous finding might just as easily have resulted from deviations in the KI method at low concentrations.

Several chemical methods recently proposed for ozone are based on olefin cleavage reactions and analysis of cleavage products. Bravo and Lodge[17] used 4,4'-dimethoxystilbene as the reagent and analyzed for the product, anisaldehyde, by Sawicki's method.[18] This method is reportedly specific for ozone among the oxidizing components. The biggest drawback in routine application of this technique is the use of trifluoroacetic acid and trifluoro-acetic anhydride in the color-development step. Hauser and Bradley[19] used 1,2-di-(4-pyridyl)ethylene as the olefin and they analyzed for the product, pyridine-4-aldehyde, by colorimetry. By reference to neutral KI, 1 mole of ozone yielded 1.23 moles of aldehyde for ozone concentrations below 1 ppm. Using a different kind of absorber and propionic acid rather than acetic acid, Bergshoeff[7] observed a one to one stoichiometry between ozone and aldehyde for this procedure. This technique shows some sensitivity to $H_2O_2$ and peroxyacetyl nitrate, but any interference with ozone measurement is probably insignificant at ambient levels of these compounds. The reducing compounds, $SO_2$ and $H_2S$, do not interfere. The use of glacial acetic acid is a drawback for routine application but is not nearly as serious a problem as the use of trifluoro-compounds in the previous method. Finally, West[20] has been investigating the ozonolysis of 1-olefins, followed by analysis for formaldehyde as a function of ozone concentration. Very few details of this method are available.

The phenolphthalein method[21] has been used for measurement of atmospheric total oxidant. The colorless reagent is oxidized to the highly colored phenolphthalein, followed by color measurement in the visible region. Because of its sensitivity to pH and to temperature changes, this technique has been largely replaced by the neutral KI method.

## Batch or Exposure Methods

In the laboratory methods just described, sampling normally lasts 10 to 30 min. The next section discusses instruments designed to give a continuous analog signal proportional to oxidant concentration in the atmosphere. Many air monitoring applications, however, require a 24-hr or longer average oxidant or ozone concentration at a given point. An example is initial survey work, which requires only an indication of relative oxidant concentration at several points in an area. High accuracy is generally not of great importance. Techniques for such analyses must meet several requirements. They must be capable of sampling unattended in the field during the averaging period. They must yield a reaction product or property that is stable during sampling and during transport to a central laboratory, where analysis is usually performed. Requirements for specificity and temperature independence usually become more stringent with such long sampling periods. Finally, a very important requirement is that the technique be fairly simple and inexpensive. It is obvious that expensive, continuous oxidant analyzers would not be suitable for an initial survey of an urban area in which simultaneous, daily averages are to be obtained at 20 to 30 different points. Two exposure-type techniques are the 24-hr bubbler boxes[22] previously used by the National Air Surveillance Network (NASN) of the Environmental Protection Agency (EPA), and the rubber-cracking method.

In the NASN procedure, a box containing glass absorbers with fritted impingers, prescrubbers and filters, a downstream trap, a critical orifice leak, and a sample pump was used for sampling ambient air at 200 $cm^3$/min over a 24-hr period in the field. The sample solution was returned to the laboratory for analysis. NASN used ferrous ammonium sulfate reagent, since the stability of the ferric ion produced allowed considerable lapse of time between sampling and analysis. The minimum calculated sensitivity was 0.0012 ppm average for a 24-hr sampling period. In areas where sulfur dioxide was present, a chromium trioxide[23] or similar scrubber was used. The use of a chromium trioxide scrubber introduces problems that are discussed later in more detail. Long-term sampling can introduce problems such as enhancement of interferences, variations in flow and temperature, instability of reagent, and scrubber inefficiency. To demonstrate the usefulness of a 24-hr technique, results should be correlated with average values obtained by integrating the output of a continuous oxidant analyzer. Some work was done within NASN to correlate measurements by the 24-hr ferrous method and by continuous oxidant analyzers. Poor correlations were obtained and the collection of 24-hr samples for total oxidant has been discontinued.

Another survey method which has been used frequently is the rubber-cracking technique.[24,25] This is a simple, inexpensive method of surveying

an area to determine points of high relative ozone concentration or to determine whether ozone levels exceed a certain value. Because of high imprecision, uncertain nature of the calibration, and the possibility of interference from free radicals or other reactive species in the atmosphere, the rubber-cracking method should not be used to obtain quantitative average ozone concentrations over an extended period.

The most accurate way to obtain 24-hr average oxidant or ozone values would be to integrate the output of a continuous analog system. Although the cost of present instrumentation would prohibit this approach for field surveys, the development of simple, analog instrumental systems for pollutant monitoring is not beyond present technology. If a simple, inexpensive monitor can be realized, the necessary integration could be performed by attaching an inexpensive tape recorder to the analog instrument. This recorder would integrate the signal over fixed periods and store digital signals on tape. The tape could be returned or used to relay data to a central location for processing to give 24-hr averages, daily maxima and minima, or whatever reduction is required.

## Continuous Oxidant Instrumentation †

Commercial total oxidant instruments in use today are all based on the oxidation of a potassium iodide solution and detection of the iodine produced by either colorimetric or electrochemical methods. Thus these analyzers are subject to the same kind of interferences as the neutral KI method, although the degree of interference may vary for the individual systems.

In the electrochemical instruments, air containing ozone is pulled through the electrochemical cell; ozone reacts with the electrolyte (a neutral buffered KI:KBr solution) to release free halogen, which, in turn, is reduced at the working electrode, causing a current to flow in an external circuit. Each molecule of ozone reacting in neutral solution is equivalent to two electrons.

$$O_3 + 2I^- + H_2O = I_2 + O_2 + 2OH^-$$

$$2e^- + I_2 = 2I^-$$
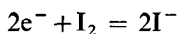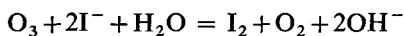
The theoretical current obtained may be calculated from Faraday's constant; the concentration of $O_3$ (C) in parts per million by volume; and the air flow rate (F) in ml/min. If contact and reaction efficiencies are 100%, the current produced at 25°C and 1 atmosphere pressure is:

$$I(\mu A) = 0.1315 \times F \times C$$

† Mention of a specific company or product does not constitute endorsement by the Environmental Protection Agency.

Two electrochemical versions now in use employ different type cells. In the cell used by Brewer and Milford[26] a polarization voltage is applied across inert electrodes to produce a thin layer of hydrogen at the working electrode. Free halogen produced is reduced by the hydrogen, temporarily depolarizing the electrode and causing a current to flow to re-establish balance. The polarization current flowing is equivalent to halogen reduced. In this cell, electrolyte is consumed and must continually be replenished from a reagent reservoir. The galvanic cell developed by Hersch and Deuringer[27] does not use an applied voltage, but operates as a fuel cell in which iodine is reduced at the cathode while carbon is oxidized at the carbon anode. This cell reuses the electrolyte indefinitely. Commercial versions of the Brewer cell are made by the Atlas and the Mast[28] instrument companies. Beckman has marketed an instrument utilizing the Hersch cell.

The electrochemical instruments suffer 100% interference from $SO_2$,[29] as well as some interference from other reducing species in the atmosphere, such as $H_2S$. For the Brewer cell, the $NO_2$ interference equivalent which has commonly been used is approximately 0.06 molar ozone response per mole of $NO_2$ added. In a recent study, Tokiwa et al.[30] measured the $NO_2$ interference equivalents in the presence of varying ozone concentrations. Nitrogen dioxide interference equivalents were found to vary from 0.081 to 0.025 as the ozone concentration was changed from 0 to 0.60 ppm.[30] Interference factors from 0.03 to 0.20 mole ozone per mole of $NO_2$ have been reported for the galvanic cell.[27,29] These numbers are approximate; for any individual device the factors should be determined independently.

These systems also respond to other strongly oxidizing species such as peroxides, peroxyacids, and peroxyacyl nitrates.[31] The coulometric yields, based on referencing electrochemical currents to simultaneous neutral buffered KI ozone values, are approximately 100% for the Hersch cell[27] and 75% for the Brewer cell.[31]

Continuous colorimetric oxidant analyzers are of the type first described by Littman and Benoliel.[32] The colorimetric analyzers normally use 20% neutral buffered KI reagent. Air containing ozone is drawn into the analyzer at a fixed flow rate with an air pump. The reagent pump draws the neutral KI reagent countercurrently to the air stream in a contact column, where mixing and reaction occur. After leaving the contact column the reagent flows through a cell where absorption at 360 nm, characteristic of the triiodide ion, is measured with a double-beam ratioing photometer. Used reagent is circulated to a solution storage tank, through a charcoal filter to remove residual iodine, and then back to the absorber column for further use. Widely used commercial colorimetric systems are made by Beckman and Technicon. More recently, Litton Industries have marketed their model 410 colorimetric oxidant analyzer.

Colorimetric oxidant analyzers suffer the same kind of interferences previously discussed for the neutral KI method. When more concentrated KI formulations are employed, the interference from $NO_2$ becomes greater. Cherniack and Bryan[29] reported that the interference equivalent for $NO_2$ in 20% KI solution becomes approximately 30% of an equimolar concentration of ozone. Tokiwa et al.[30] measured $NO_2$ interference equivalents in 20% KI and observed values from 0.34 to 0.19 over an ozone concentration range of 0 to 0.61 ppm. In 10% KI the variation in interference equivalent with ozone concentration was less, and the average value of the equivalent was 0.22. The degree of interference from $NO_2$ is a function of the contact design and thus should be determined for each instrument. It would not be surprising to find that the extent and rate of reactions of oxidizing species other than $NO_2$ vary with KI reagent strength and ozone concentration. However, the total concentration of other oxidizing species in the atmosphere is probably low compared with that of ozone, so that the overall effect would be a small perturbation on the total oxidant value.

Two techniques have been proposed for selectively removing ozone upstream of the KI solution and thus determining by difference ozone and other oxidants, including $NO_2$. In the scheme of Bufalini,[33] the air stream is periodically titrated in the gas phase with trans-butene-2 which quantitatively reacts with and removes ozone without affecting other oxidants. The method of Cohen et al.[34] is designed for separating the effects of $NO_2$ and ozone by using a treated cotton-wool plug that quantitatively removes ozone while passing $NO_2$. Little information is available on applications of either of these techniques.

Comparison of results from electrochemical and colorimetric instruments has occupied several investigators. Cherniack and Bryan[29] compared a continuous colorimetric analyzer with the Mast meter, a galvanic cell sensor, and the Kruger ozone photometer in both laboratory calibration and field sampling studies. By least-square analyses of many data points they obtained correlation coefficients of 77% and 89% between the colorimetric oxidant readings and the galvanic and Mast sensors, respectively, after correcting for calibration differences. They did not correct for $NO_2$ or $SO_2$ interferences. The variance between electrochemical and colorimetric data was also considerable. Potter and Duckworth[35] observed that the Mast ozone meter gave results 15% lower, on the average, than the colorimetric analyzer in field operations, again without correcting for $NO_2$. In a more recent study, Siu et al.[36] obtained agreement between the Mast analyzer and colorimetric results, within standard deviation limits, by simultaneously measuring $NO_2$ and applying correction factors. The factors subtracted were 35% of the $NO_2$ from the colorimetric data and 5% from the Mast data. In an extensive field study in Pasadena, California, Tokiwa et al.[30] obtained valid simul-

taneous measurements for electrochemical and colorimetric oxidants and $NO_2$ concentrations for a total of 1170 hr. After correction for $NO_2$ interference, the colorimetric oxidant data were higher than the electrochemical data by factors of 10% or less.

All of the instruments described can measure ozone with acceptable precision at the 0.01-ppm level. Thus, the electrochemical and colorimetric oxidant analyzers meet the sensitivity requirements set by U.S. Federal air quality criteria. These instruments are all subject to the same type of interferences, although the magnitude of the interferences, particularly from $NO_2$, will vary among the various monitors. Regardless of which instrument is used, air quality standards call for correction or compensation for interferences from $NO_2$ and $SO_2$.

In order to apply the $NO_2$ correction to total oxidant concentrations, simultaneous measurements of $NO_2$ must be made. The available continuous $NO_2$ instruments are probably the least satisfactory of all the ambient air monitors in use today. The federal air quality criteria for $NO_2$ have been based on a 24-hr collected sample rather than on continuous analysis.[2] It has been common practice to apply a constant factor in the $NO_2$ correction over the entire range of ozone concentrations. The work of Tokiwa *et al.*[30] indicates that such a correction may not be adequate in all cases. For those colorimetric instruments using 20% KI, the total $NO_2$ correction is large, and the observed variation in interference equivalent with ozone concentration is significant. For the electrochemical sensors and colorimetric units that use weaker KI solutions, the $NO_2$ correction is sufficiently small that the use of an average interference equivalent should be adequate in the corrected oxidant measurement. Another problem remaining is that predominant evidence indicates that electrochemical oxidant values are lower than colorimetric oxidants obtained in field measurements even after applying $NO_2$ correction factors. Many wet-chemical oxidant analyzers are in use and will continue to be used for determining air quality. For this reason, more field information and evaluation are needed to determine the frequency with which $NO_2$ interference and subsequent corrections may cause an over- or underestimation of incidents in which air quality standards are exceeded.

Among the most serious problems in using neutral KI-based automatic analyzers, whether electrochemical or colorimetric, is the quantitative interference from sulfur dioxide. As long as the $SO_2$ concentration is low compared to that of oxidant, and $SO_2$ concentration is measured simultaneously, a correction to the oxidant reading is feasible. This approach is used in California because of the low-sulfur fuel requirements, but for a large portion of the urban environment of the United States a correction is not possible. In areas like the East Coast, Chicago, Cleveland, and St. Louis, normal $SO_2$ levels are equivalent to or higher than oxidant levels. Figure 3 represents
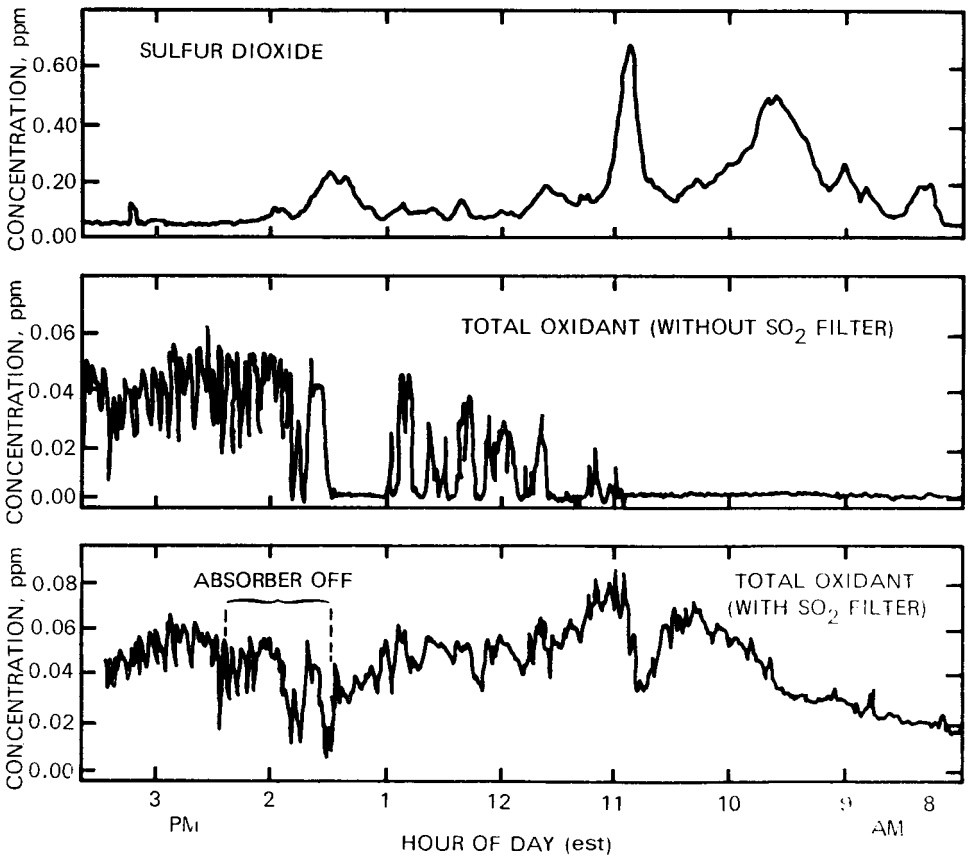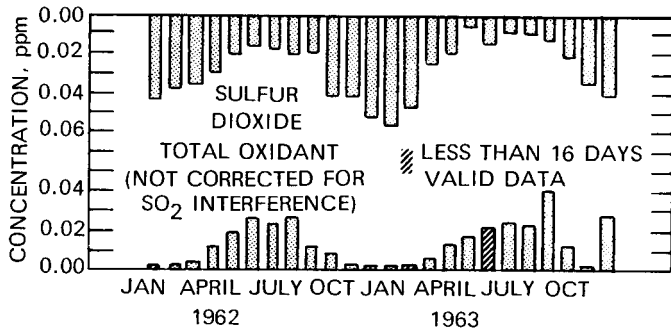
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FIGURE 3   Effect of sulfur dioxide on recorded total oxidant measurements.

simultaneous measurements of oxidant and $SO_2$ taken from data obtained in Cincinnati in 1962–63.[37] Correction to the oxidant reading in such situations is not possible.

The prevalent method for making oxidant measurements with KI-based instruments in areas of high $SO_2$ employs a paper impregnated with chromium trioxide for removal of $SO_2$.[23] This technique may introduce new problems into the oxidant measurement and must be applied with some precautions. Nitric oxide passing through the scrubber is oxidized to nitrogen dioxide, yielding an interference from total oxides of nitrogen. The efficiency of the scrubber for oxidizing NO to $NO_2$ may decrease during the lifetime of the scrubber. In this event, a correction for total $NO + NO_2$ may become too large. The requirements on the scrubber system are stringent: to quantitatively pass one very reactive compound ($O_3$) while removing all of another reactive species ($SO_2$). Very little information has been published on performance of the scrubber under real or simulated atmospheric conditions. Our own laboratory experience has shown that such scrubbers must first be conditioned with high concentrations of ozone to remove reactive sites where ozone may be consumed. Continuous exposure of a conditioned scrubber to humid, polluted air even for as short a time as 24 hr has caused a decrease in the efficiency of the scrubber for ozone passage. A certain amount of moisture exposure was required before the scrubber removed $SO_2$ quantitatively. After exposure of a scrubber to humid air for a time sufficient to make the surface wet, the efficiency for $SO_2$ removal decreased and ozone was partially removed. Under some conditions the lifetime of the scrubber may be only a few days. If the chemical scrubber described here is used, it must be conditioned initially and should be replaced after a periodic interval of one week or less, depending on ambient conditions.

If sensitivity and specificity factors are equivalent for various instruments, other parameters such as mechanical operability, down-time, stability of zero and calibration, maintenance requirements, cost, and size may determine the instrument of choice for oxidant measurements. All the instruments described above are the wet-chemical type and thus have some common disadvantages. These instruments are particularly susceptible to mechanical problems inherent in maintaining reagent purity, reagent circulation and flow rate, air flow, and air-solution contact. For more detailed information on instrument performance, the reader is referred to reports on field evaluations of oxidant monitors.[29,38]

## Continuous Ozone Instrumentation

This section describes a number of instrumental gas-phase methods that have

recently been applied to measure atmospheric ozone. Some commercial monitors applying these techniques have recently become available.

Three different chemiluminescence techniques have been applied to measure atmospheric ozone. Regener[39] published a method in 1960 for the chemiluminescence detection of ozone in the upper atmosphere. He later reported a surface ozone monitor that uses the chemiluminescence approach.[40] In Regener's approach, chemiluminescence is obtained on reaction of ozone at a surface of Rhodamine-B dye adsorbed on activated silica gel. The chemiluminescence intensity measured with a photomultiplier tube is a linear function of ozone concentration passing over the surface. This technique is sensitive to less than 0.001 ppm, and no atmospheric interferences have been observed.[41] Prototype Regener monitors built under EPA contract[42] have shown excellent performance in extended field evaluations.[38] The construction of the automated monitor, however, is complicated by the necessity of incorporating frequent internal calibration cycles to compensate for changes in the sensitivity of the chemiluminescence surface.

The gas-solid chemiluminescence approach has been largely supplanted by gas-phase chemiluminescence techniques that have improved response characteristics.[43] In 1965, Nederbragt[44] measured ozone in the vicinity of nuclear accelerators by applying an atmospheric pressure chemiluminescent reaction between ozone and ethylene. Later this technique was described in more detail by Warren and Babcock.[45] A schematic of the Nederbragt detector is shown in Figure 4. Air (1 liter/min) and ethylene (10–20 cm$^3$/min) mix near the cathode of a photomultiplier. Sample is pulled through the cell at atmospheric pressure with a small air pump. The chemiluminescence from the ozone-ethylene reaction is in the 4300 Å region.[43] No atmospheric interferences have been observed and no filter is needed between the reaction cell and the photocathode. The chemiluminescence intensity is a linear function of ozone concentration and the sensitivity is about 0.001 ppm. Prototype monitors of this type have been constructed by EPA and one was included in the Los Angeles field study.[38] Correlations among the Nederbragt, Regener, and oxidant instruments are described below. Commercial versions of the Nederbragt detector are now being offered by several companies, including Bendix, McMillan, Melabs and REM. This gas-phase approach is the reference technique described in the *Federal Register*[2] for corrected oxidant measurements.

Fontijn et al.[46,47] have developed a gas-phase technique that utilizes the chemiluminescent reaction between nitric oxide and ozone at low pressures.

$$NO + O_3 \rightarrow NO_2{}^* + O_2$$
$$\downarrow$$
$$NO_2 + h\nu \; (6000 \text{ Å} \rightarrow I.R.)$$
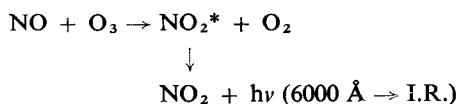
If one of the components is in excess, the chemiluminescence intensity obtained is proportional to the concentration of the second reactant. Air sample is mixed with reactant gas inside a low pressure (1–5 Torr) reaction chamber closely coupled to the photocathode of an infrared sensitive photo-multiplier. Sensitivity is 0.005 ppm for detection of either NO or $O_3$, and no atmospheric interferences are observed when the appropriate light filter is

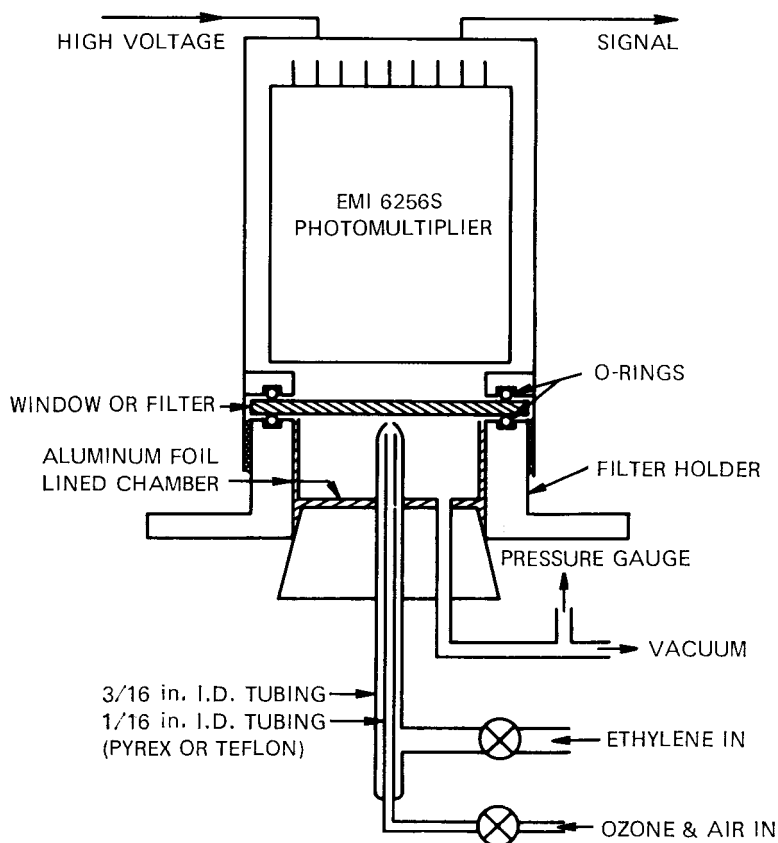FIGURE 4   Nederbragt chemiluminescence ozone detector.

used. One advantage of this sensor over the other chemiluminescence types is that the same instrument may be used to measure NO or $O_3$. A disadvantage is the requirement of low pressure operation. Little application has been made of this approach for ozone measurements, but Fontijn's detector is being used extensively for the measurement of oxides of nitrogen.

B

Specific determination of atmospheric ozone may be accomplished by use of u.v. absorption measurements at 2537 Å.[48,49] Interferences may be eliminated in a double-beam instrument by passing the air to the reference cell through a tube, coated on the inside walls with potassium permanganate, to selectively remove ozone. This is perhaps the most direct way of monitoring ozone in the atmosphere. The advantage of this method over chemiluminescence is that the measurement for ozone can be absolute since the absorption coefficient is well known. The Kruger ozone photometer was available in the past, but because of electrical and thermal instability it was not extensively used. A much-improved instrumental version which uses the u.v. photometric approach has recently been marketed by the DASIBI Corp. The details of this instrument are described by Behl.[11]

## Ozone Versus Total Oxidant Relations

A key question that relates present air quality criteria for total oxidant to the development of ozone-specific instrumentation concerns the relationship of ozone to total oxidants measured by neutral KI methods in the field. The extensive data of Cherniack and Bryan[29] showed an average ratio of 0.98 for ozone measured with the Kruger photometer to total oxidants measured with a colorimetric analyzer. This ratio was obtained even though the positive interference from $NO_x$ was not subtracted from the colorimetric data. Furthermore, these results were obtained in Los Angeles, where concentrations of photochemical oxidants should be highest. This study also showed that concentrations of total oxidants measured by the electrochemical sensors were lower, on the average, than those measured with the ozone photometer. A comparison has been made between chemiluminescence measurements of ozone and total oxidant data obtained in Cincinnati and in Bayonne, N.J.[50] Data obtained in Cincinnati on Regener chemiluminescence versus Mast systems, both dynamically calibrated by neutral KI, showed frequent incidents in which chemiluminescence data for ozone exceeded Mast values of total oxidant. These results were obtained both with and without use of the chromium trioxide scrubber. Similar results were obtained in Bayonne where average chemiluminescence ozone concentrations exceeded colorimetric total oxidant data. In both locations, humid, polluted conditions and high $SO_2$ concentrations were prevalent, and proper functioning of the $CrO_3$ scrubber was suspect. In extended studies in Philadelphia and Denver, Richter et al.[51] observed many occasions during which chemiluminescence ozone values exceeded those for total oxidant measured by colorimetric or electrochemical methods.

The latest and most extensive comparative study has been performed in

downtown Los Angeles over a three-month period during the fall of 1970.[38] Ozone data were obtained with both Nederbragt and Regener chemiluminescence systems. Total oxidant data were obtained with a colorimetric analyzer (20% KI) and an amperometric oxidant recorder. Nitrogen dioxide was measured with an automated colorimetric (Saltzman) instrument. Unfortunately, the $NO_2$ data could not realistically be applied to correct the total oxidant data because of excessive down-time of the $NO_2$ analyzer and uncertainties in the calibration procedure. Sulfur dioxide measurements were made with colorimetric, conductimetric, coulometric and flame photometric analyzers. The preliminary results of this study have recently been reported[52] and it is worthwhile to summarize some of the pertinent conclusions here:

Correlation coefficients between the two different chemiluminescence analyzers were 99% regardless of time of day.

Correlation coefficients between chemiluminescence ozone and electrochemical total oxidant were 92% during daytime hours (0800–1800 hr).

Correlation between ozone and colorimetric total oxidant was 70% for day time hours.

Correlation coefficients between ozone and total oxidant corrected for $SO_2$ and $NO_2$ interferences were poorer than those above. These results were probably due to uncertainties in the $NO_2$ data and imprecision in the $SO_2$ measurements at low concentrations (0.005–0.03 ppm).

The mean chemiluminescence ozone concentration was equal to 98% of the mean colorimetric total oxidant for the 3-hr interval of maximum total oxidant concentrations (1100–1400 hr).

Mean ozone levels were 126% of electrochemical total oxidant over the same interval.

The interference from sulfur dioxide, as measured by flame photometry and coulometry, averaged 10% of the total oxidant during the daily 1-hr interval of maximum oxidant concentrations.

Figure 5 shows the average diurnal variation in ozone and total oxidant data for October, 1970, in downtown Los Angeles.

In summary, none of the data cited indicate that measurement of total oxidant minus oxides of nitrogen provides a unique characterization of the atmosphere when compared to the measurement of ozone alone. The measured value of total oxidant may be even lower than that of ozone because of problems with scrubbers and reducing interferences. It seems probable that in the ambient atmosphere total concentrations of other oxidants, such as peroxides, peracids, and peroxyacyl nitrates, are so low compared with ozone concentrations that their contribution to measured total oxidant is negligible within the experimental precision of such instruments.
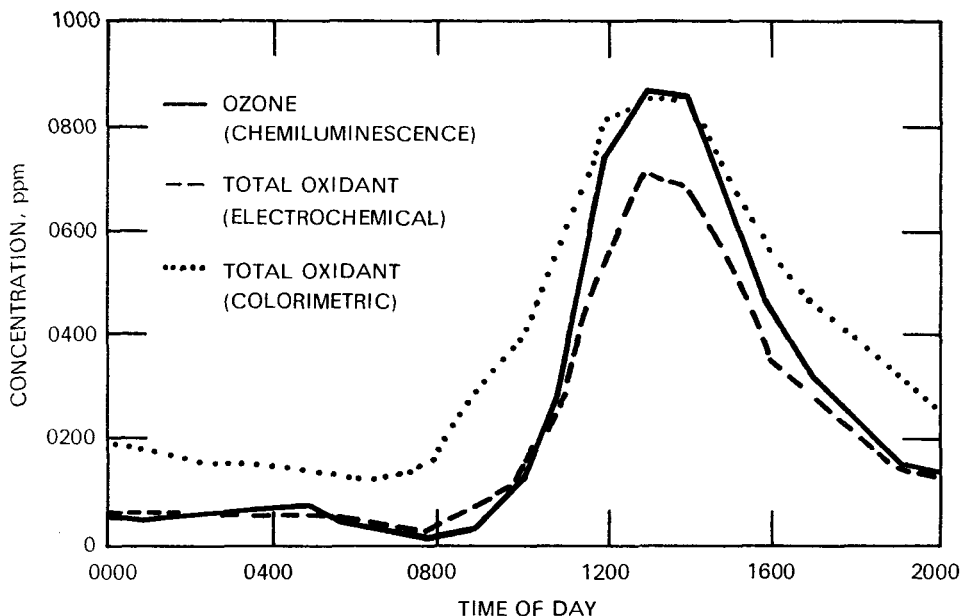
FIGURE 5   Ozone-oxidant diurnal averages, October 1, 1970 to October 31, 1970.

## CONCLUSIONS

The 1 % neutral buffered KI procedure has proved to be a reliable and handy reference method for calibration of oxidant analyzers and ozone sources at levels above 0.05 ppm. The 1:1 stoichiometry of ozone to iodine has been confirmed by several independent methods. Other reagents, such as ferrous ammonium sulfate or certain olefins, may offer greater stability and precision to lower levels. Data at present are lacking.

Batch exposure techniques, such as the 24-hr bubbler box, offer very simple systems for survey work, but little faith can be placed in such measurements until they are demonstrated to correlate with data from continuous monitors.

Commercial oxidant analyzers, whether electrochemical or colorimetric, are capable of making the measurements required by U.S. Federal standards in areas of low $SO_2$ and with concurrent measurements of $NO_2$. The variable $NO_2$ interference equivalent still imposes a problem for those situations in which the magnitude of the $NO_2$ correction is large. Colorimetric analyzers have shown closer agreement with specific ozone measurements than electrochemical analyzers. On the basis of size, cost, and simplicity of operation, however, the electrochemical analyzers are advantageous. In order to avoid

problems inherent in chemical scrubbers, specific ozone analyzers are recommended for areas where $SO_2$ concentrations may be high.

Available data indicate that, within the experimental precision of the analyses, the specific measurement of ozone gives concentrations that are equivalent to values of total oxidant minus $NO_x$ obtained by neutral KI techniques. This has been true even in areas where concentrations of photochemical oxidants should be highest. In highly polluted eastern areas of the United States measured oxidant values may be even lower than those of ozone because of scrubber problems or effects of reducing interferences. More data should be obtained on relationships of ozone and total oxidant in urban areas of the midwest and east where levels of $SO_2$ are high.

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