doubts concerning the validity of the flask samples. We, following Krogh (*6*), have used the mean of 212 direct laboratory analyses; 20.952 percent by volume. The variability among these samples was ± 0.007 percent by volume with no correlation to observed variations in weather conditions. Krogh suggested a correction of + 0.002 percent by volume for the formation of carbon monoxide in Benedict's apparatus; we believe this correction may be too high. On the other hand, Benedict appears to have reported the abundance of oxygen relative to the total of oxygen, nitrogen, and argon after removal of carbon dioxide. Since this is so, the oxygen abundance in the dry air with normal carbon dioxide would have been 20.946 rather than 20.952 percent by volume.

In 1919, Krogh (*6*) reported an abundance of 20.948 percent by volume for two analyses of atmospheric air in Denmark. In the early 1930's Carpenter (*7*) using equipment similar to that of Benedict analyzed over 1000 samples in eastern United States. The results are almost identical with those of Benedict, but it is not clear whether Carpenter used Benedict's uncorrected value, 20.939 percent by volume, as his standard since he was mainly concerned with variability. Carpenter concluded the oxygen abundance is constant, his standard deviation being about 0.003 percent by volume.

Six analyses of a single large sample collected west of Washington, D.C., by Shepherd (*8*) of the National Bureau of Standards in 1935 ranged from 20.935 to 20.950 percent by volume, the average being 20.946 percent by volume. In 1942, Lockhart and Court (*9*) reported oxygen abundances in Antarctica averaging 20.92 percent by volume and suggested that the low values might be unique to the location. Glueckauf pointed out that they performed no analysis of normal non-Antarctic air to confirm their procedures. To further cast suspicion, their carbon dioxide abundances were many times higher than that found in recent times. Table 1 does not suggest lower values approaching the Antarctica.

All reliable oxygen data since 1910 fall in the range 20.945 to 20.952 percent by volume. The change in atmospheric oxygen since 1910 has been either very small or zero. It is possible that there has been no change even in the third decimal but a more realistic assessment recommends no change in the second decimal place, there being little confidence in differences of the third decimal place. Failure to detect changes in atmospheric oxygen may be consistent with Marshall's view that there is now less cause for alarm about the reduction in photosynthetic production of oxygen (*10*).

Several "doomsday" predictions for the eventual loss of the oxygen from the earth's gas mantle have been proposed and dismissed. Parson (*11*), for example, examined and rejected the views that oxidation of ferrous metals in lower oxidation states to their highest oxidation states and escape of oxygen from the top of the atmosphere would deplete the earth of its oxygen.

It is likely that the burning of fossil fuels would slightly diminish the oxygen content of the atmosphere. Benedict and Krogh showed that there were slight decreases in the oxygen abundance within cities coinciding with high carbon dioxide values. In fact, there is an approximate one-to-one correspondence in the opposite changes of carbon dioxide and oxygen gases when expressed as percent by volume.

Between 1910 and 1967 atmospheric oxygen should have decreased by 0.005 percent by volume as a result of the combustion of fossil fuels (*12*). But the uncertainty in both the 1910 and 1967–70 measurements prevents us from attributing significance to any coincidence between expected and observed changes in atmospheric oxygen. Extrapolating the depletion of oxygen due to fossil fuel burning to the day when all known recoverable reserves are consumed (*13*) leads to an abundance of about 20.8 percent by volume (*14*). The direct effects of this lower value on human respiration would be insignificant since it corresponds to an oxygen partial pressure change equivalent to a rise of about 75 m in altitude.

In summary, the 1967–70 abundance of oxygen in clean air, 20.946 percent by volume of dry air, is statistically the same as all the reliable measurements since 1910; the extreme range among reported values is 0.007 percent of volume. The accuracy of the present oxygen standards is ± 0.006 percent by volume. This latter uncertainty rather than the geographic or instrumental variability may limit the detection of small changes of atmospheric oxygen in the future. Further periodic examination of the oxygen content is planned after more accurate standards are developed.

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## Smog Aerosol: Infrared Spectra

*Abstract.* *Infrared spectra of smog aerosol are similar to those of sulfuric acid aerosol, but they do not show the prominent CH and carbonyl bands of organic aerosols from terpenes. Some features of the smog aerosol spectra are not present in the spectra from either type of synthetic aerosol.*

It has been clear for many years that the symptoms of photochemical air pollution (smog) are caused by a variety of chemical reaction products. One such product is ozone; it causes plant damage, odor, rubber cracking, and probably respiratory discomfort, but it does not cause either eye irritation or light scattering. Almost all the reaction products so far identified are small molecules which are much too volatile to form a light-scattering aerosol at ambient air dilutions. Two notable exceptions to this rule have been discovered in laboratory studies of these reactions. One is the reaction of higher-molecular-weight olefins either with ozone or with nitrogen oxides and solar ultraviolet irradiation. Went (*1*) has suggested that terpene hydrocarbons react in this way to produce the blue haze over forested areas. Gasoline-type hydrocarbons (particularly olefins) might conceivably behave in a similar fashion. The second reaction is caused by ultraviolet irradiation of hydrocarbon, nitrogen oxides, and sulfur dioxide (*2*). Some of the sulfur dioxide is oxidized to sulfuric acid which then condenses with water vapor to form an aerosol. Although both these aerosol-forming mechanisms have been well established in laboratory work it has been difficult to extrapolate these findings to the atmosphere where reactant concentrations are much lower (*3*).

The amounts of sulfur dioxide necessary to form a laboratory aerosol comparable to that seen in ambient air have been unrealistically high, especially in view of the exceptionally low concentrations of sulfur oxides in southern California. There has never been a good quantitative comparison of the terpene aerosol produced in the laboratory with natural aerosols. Further complications arise because the degree of light scattering is heavily dependent on the particle size as well as the total mass. We have devised a technique for comparing synthetic aerosols with natural smog aerosol by infrared spectrophotometry. We now describe results obtained with this technique.

The active part of the infrared beam of a model 137 Perkin-Elmer infrared spectrophotometer has the shape of the entrance slit and is only about 14 mm high by about 1.5 mm wide at the location of the sample holder. If a sample is concentrated to an area which just matches this size, very small amounts of sample will yield usable spectra. A small impactor was constructed to collect natural and synthetic aerosols and to test this idea. This impactor is of conventional single-stage design with provisions for adjustment of the slit width and for use of various impaction surfaces. The slit is 14 mm long to match the infrared beam. For analysis by infrared absorption the first requirement for the substrate is that it be at least partially transparent to infrared radiation. It should also be chemically inert, nsoluble, easily cleaned, and strong. So far we have used T-12 (a blend of calcium and barium fluorides obtained from Harshaw), Teflon, and polyethylene. The T-12, although marble-like in appearance, transmits infrared to about 12 μm wavelength. Most of the work was done with a disk about 5 mm thick; more recently a 3-mm thick disk has been used with much improved transmission in the 10- to 12-μm region.

It quickly proved possible to obtain infrared spectra of ambient polluted air (Fig. 1). Several fairly distinctive groups of bands are apparent, and although some similarities with the spectrum of sulfuric acid are apparent, the agreement with this spectrum is not complete. It seemed that the impacted aerosol reacted with the surface, because the spot could not be wiped off but had to be polished out of the disk. Furthermore, the spectrum changed when the disk was allowed to stand for several hours. In particular, the two peaks at 8.7 and 9.1 μm increased on standing while the bands at 3.1 and 5.9 μm decreased.

A flow photoreactor was used to make synthetic aerosols from mixtures of pollutants. This equipment has been described (*4*). The reactor, made from borosilicate tubes 6 inches in diameter, provides for irradiation with simulated sunlight of a stream of purified air containing metered amounts of hydrocarbons, nitrogen oxides, and sulfur dioxide. With a flow rate of 2.37 liter/min, the 141-liter volume provides a residence time of 1 hour. Blacklight fluorescent lamps provide irradiation with maximum intensity near 350 nm. The input and output streams can be analyzed for a variety of reactants and products. In addition to the aerosol impactor a forward light-scattering photometer was used to monitor total scattering as a measure of aerosol. Scattering by natural smog was also measured with the photometer to provide a reference.

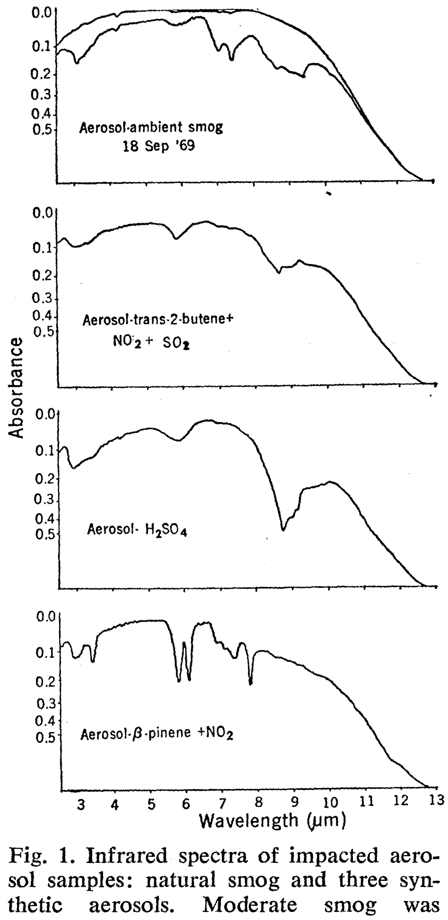

Fig. 1. Infrared spectra of impacted aerosol samples: natural smog and three synthetic aerosols. Moderate smog was present in the air on the campus at the University of California at Riverside when the sample which gave the lower curve in the top section was taken. The upper curve in the top section gives the spectrum of the T-12 substrate with no aerosol.

The two types of aerosol described at the beginning of this report were made in the photoreactor with the following conditions:

1) Trans-2-butene, 10 ppm: nitrogen dioxide, 0.5 ppm; sulfur dioxide, 4 ppm; residence time, 1 hour; 2-hour impaction (Fig. 1).

2) β-Pinene, 10 ppm: nitrogen dioxide, 5 ppm; residence time, 1 hour (Fig. 1).

In both cases the photometer indicated a light scattering about one order of magnitude greater than for smog aerosol, which was judged subjectively to be "moderate." Both experiments were, therefore, quantitatively unrealistic but nevertheless qualitatively quite useful. The β-pinene aerosol spectrum shows a distinct CH absorption band at 3.4 μm which is absent from the other three spectra and testifies to the organic character of this aerosol. This spectrum also has a strong carbonyl band at 5.8 μm. The two sharp absorbancies at 6.1 and 7.8 μm are near those for nitrate groups, although this assignment should be verified. Nitric acid is much too volatile to form an aerosol, so that the nature of the nitrate is uncertain. A spectrum of the aerosol from α-pinene was similar.

Several incidental observations bear on the interpretation of these results. Since the natural aerosol etched the T-12 crystal, a sample was impacted on *p*H paper and found to be about *p*H 4 or 5, as would be expected for a sulfuric acid aerosol but not for an organic polymer. Examination under low magnification revealed numerous, obviously solid particles of various shapes and colors. These are clearly different from either the sulfuric acid or terpene aerosols and are probably just suspended dust of relatively large diameter.

Ordinary road dust may well be the source of this, and it may contribute a great deal to the total weight of particulate without making much contribution to loss of visibility. High-particulate weight-loadings sometimes occur with little loss of visibility if the average particle size is large (*5*). The extremes which Lundgren reported were seen on windy days and were most likely suspended sand. Samples taken with our impactor on clear windy days also showed this solid particulate, but the infrared spectrum showed no bands.

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## Tryptophan Operon: Structural Gene Mutation Creating a "Promoter" and Leading to 5-Methyltryptophan Dependence

*Abstract.* *A strain carrying the mutation* trpA515, *which maps in the "unusual" region (between the genes* trpA *and* trpB*) of the tryptophan operon of* Salmonella typhimurium *is capable of utilizing anthranilic acid as a growth factor only in the presence of the analog 5-methyltryptophan, normally a potent growth inhibitor. The reason for this peculiar phenotype is the creation by* trpA515 *of a transcription-initiating signal in the "unusual" region.*

The double mutant *trpA49 trpA515* is one of several 5-methyltryptophan (5MT)-dependent derivatives of *trpA49*, a mutant for the first gene of the tryptophan (*trp*) operon of *Salmonella typhimurium.* The mutation *trpA49* maps at the extreme operator-proximal end of *trpA* (Fig. 1) and has been characterized as an amber mutation with an extreme polar effect on the expression of the distal genes of the operon (*1, 2*). Mutants for the *trpA* gene are capable of utilizing anthranilic acid (AA), a substrate for phosphoribosyl transferase (PRT), the second enzyme of the tryptophan pathway, as a growth factor. One consequence of the polar effect of *trpA49* is to lower drastically the level of PRT, thus giving a strain which grows slowly on LAA, that is, minimal medium supplemented with anthranilic acid (2 μg/ml) (Table 1, No. 6). The double mutant *trpA49 trpA515* arose spontaneously on LAM, which is LAA supplemented with 5MT (100 μg/ml). When tested for its growth characteristics, it showed the peculiar property of growing better on AA supplement in the presence of 5MT than in its absence (Table 1, No. 4). This behavior was entirely unexpected since 5MT is a potent growth inhibitor at the concentration we used. This analog of tryptophan acts both as a false feedback inhibitor of anthranilate synthetase (AS), the first enzyme of the tryptophan biosynthetic pathway (*3*) as well as a false corepressor (*4, 5*), thus mimicking the role of tryptophan in these two respects.

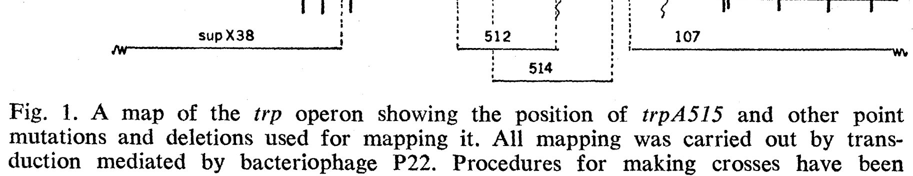

Fig. 1. A map of the *trp* operon showing the position of *trpA515* and other point mutations and deletions used for mapping it. All mapping was carried out by transduction mediated by bacteriophage P22. Procedures for making crosses have been described (*7*). The *trp* structural genes code for the following enzymes: *trpA*, anthranilate synthetase (AS); *trpB*, phosphoribosyl transferase (PRT); *trpE*, indoleglycerol phosphate synthetase (InGPSase); *trpD*, β component of tryptophan synthetase; *trpC*, α component of tryptophan synthetase. The "unusual" region (unus) is defined by a group of mutations deficient in both AS and PRT (*1, 2*; see text). P1 represents the *trp* promoter and P2 the low efficiency "promoter-like" element first described by Bauerle and Margolin (*15*). O indicates the *trp* operator (*trpO*). Deletion of *supX* suppresses the mutation *leu500* (*15*); *cysB* leads to a requirement for cysteine.

Figure 1 is a map of the *trp* operon showing the order of the structural genes and controlling elements. The enzymes for tryptophan biosynthesis and their corresponding genes are listed in the legend to Fig. 1. Both AS and PRT are required in a complex to carry out the first reaction of tryptophan biosynthesis (chorismic acid $\dashrightarrow$ AA) but PRT, complexed or free, carries out the second reaction (AA $\dashrightarrow$ *N*-5′phosphoribosyl anthranilate) (*1, 6*). As a rule, mutations in *trpA* will lead to the loss of AS, and mutations in *trpB* to the loss of PRT activity. Mutations in the "unusual" region (Fig. 1) result in a simultaneous deficiency for both activities and lead to slow or no growth on AA supplement (*1, 2*). A'though it has been proposed that they correspond to the initial portion of *trpB* (*1*), their status is unclear at present (*2*), and we retain the original designation of *trpA* (*7*) for mutants of this class.

When the double mutant *trpA49 trpA515* was used as a donor to transduce the strain carrying the deletion *trpBEDC107* (Fig. 1) and recombinants were selected on minimal (M) medium supplemented with indole (10 μg/ml), a substrate of tryptophan synthetase, three distinct classes were found: (i) donor type; (ii) slow AA-utilizing, 5MT-sensitive recombinants shown by genetic analysis to carry only *trpA49* (Table 1, No. 6); and (iii) recombinants with a novel phenotype shown, by genetic tests, to carry only *trpA515*. Recombinants of this last class showed an absolute dependence on 5MT for growth on AA supplement (Table 1, No. 1); and, unlike the double mutant *trpA49 trpA515* they reverted to prototrophy and yielde
prototrophic recombinants when crosse
to *trpA49*. Figure 1 summarizes the r
sults of crosses between *trpA515* ar
the various point mutations ar
deletions indicated. Prototrophic
combinants were obtained in all cros
except those against the deleti
*trpA514*, clearly positioning *trpA5*
within the "unusual" region. In sim
crosses of the double mutant *trp*
*trpA515* against the mutations and
letions shown in the figure, only t
against *trpA49* and the deletion *trpA*