A New Spectrophotometric Method for the Determination of Acrolein in Combustion Gases and in the Atmosphere

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▶ The reaction of acrolein with 4hexylresorcinol in an ethyl alcoholtrichloroacetic acid solvent medium in the presence of mercuric chloride results in a blue-colored product with a strong absorption maximum at 605 mµ. Other aldehydes and ketones, including unsaturated aldehydes, do not react to form products absorbing significantly in the same spectral region. Mono-olefins, acetylene, aromatic hydrocarbons, phenols, esters, alcohols, sulfur dioxide, and nitrogen dioxide do not interfere with the determination of the acrolein. This method has been applied to a variety of liquid mixtures and to raw, diluted, and irradiated automobile exhaust effluents.

INFRARED SPECTROSCOPY has been used to determine acrolein resulting from the photolysis of diolefinnitrogen oxide mixtures (14). When complex fuels are burned, the infrared bands characteristic of acrolein are overlapped by the bands attributable to water vapor, other aldehydes, and some types of olefins.

Polarography has been used to analyze for acrolein in cool flame products (4, 7) and in iron foundries and paint and varnish plants (17). However, in complex aldehyde mixtures, the polarographic half-wave potential for acrolein is too close to the value for crotonaldehyde (8, 17), and perhaps other unsaturated aldehydes, to permit a specific analysis for acrolein unless preliminary separations are made (7). For industrial hygiene problems, the sampling procedure necessary is elaborate and time consuming (17).

Acrolein, with other oxygen-containing organic compounds, has been identified in cool flames (θ) and combustion reactions (δ) by gas chromatography, but even when a single pure hydrocarbon is used as the fuel, considerable time and effort are involved (δ). If gasoline is used as the fuel, serious interference with the determination of the oxygenated compounds will occur because of the presence of aromatic and higher molecular weight aliphatic hydrocarbons in the exhaust along with the oxygenates. Under many experimental conditions, the isolation and identification of specific oxygenated compounds by infrared or mass spectrometry also may be necessary. Consequently, gas chromatography, while excellent for the detailed analysis of combustion or photolysis products under many laboratory conditions, is too time consuming and expensive an approach to the specific analysis of acrolein.

Most colorimetric methods for acrolein suffer from interference from other aldehydes. The two colorimetric methods generally considered to have some degree of specificity for acrolein are those using tryptophan (3, 10, 15) or phloroglucinol (11, 16) as the colorproducing reagents. However, studies here showed that they are insufficiently sensitive for the determination of acrolein in the part per million range. Appreciable interference results form the presence of excess amounts of other aldehydes, particularly formaldehyde, as well as from nitrogen dioxide and nitrates.

In the present investigation the use of 4-hexylresorcinol as the reagent, as first proposed by Rosenthaler and Vegezzi (13), has resulted in the development of a very satisfactory spectrophotometric method for acrolein. Previously, this reagent was used in a color-matching procedure to determine acrolein in liquors (13).

This new spectrophotometric method has been applied to the analysis of liquid mixtures containing large excesses of other aldehydes, including other unsaturated aldehydes, and to mixtures containing large quantities of ketones, phenols, and aromatic hydrocarbons. The method has been used to analyze for acrolein in raw automobile exhaust, diluted automobile exhaust gases, and diluted, irradiated exhaust gases.

EXPERIMENTAL

Reagents. The acrolein, α -methylacrolein, and crotonaldehyde samples were analyzed by gas-liquid partition chromatography. The impurity bands could readily be resolved from the major band using a 10-foot column of 20% Carbowax 1540 on firebrick. Calibration curves were not obtained. Instead, the approximation is made that percentage by area is equivalent to per cent by weight. The acrolein had a purity of about

The acrolein had a purity of about 96%. The other 4% consisted almost entirely of acetone and other low molecular weight oxygenated materials. The methylacrolein was 91% pure. About 5% of the remaining material was acrolein, and about 3% was acetone. The crotonaldehyde analyzed at 98+% purity. The other compounds used in checking for possible interference were reagent grade or the best grade commercially available.

4-HEXYLRESORCINOL (m.p. 68° to 70° C.). Five grams of 4-hexylresorcinol dissolved in about 5 ml. of 96% ethyl alcohol to give 10 ml. of solution.

MERCURIC CHLORIDE. Three grams of HgCl₂ in 100 ml. of 96% ethyl alcohol.

SATURATED TRICHLOROACETIC ACID. One hundred grams of the acid (reagent grade) dissolved in 10 ml. of water, by heating in a water bath. The resulting solution had a volume of 70 ml. Even reagent grade trichloroacetic acid has an impurity which affects product intensities. New batches of acid should be carefully checked. It is convenient to prepare large quantities of solution from a single batch of trichloroacetic acid to maintain uniformity of response.

Apparatus. A Cary Model 11 spectrophotometer, or any other generally adequate model using 1- or 5-cm. cells.

Procedures. LIQUID SAMPLES. To 2.5 ml. of ethyl alcohol containing the sample, add 0.05 ml. (about 2 drops) of the 4-hexylresorcinol solution, 0.1 ml. of the HgCl₂ solution, and 2.5 ml. of the trichloroacetic acid solution. Prepare a blank similarly. Heat the resulting solution for 15 minutes at 60° C., remove from the constant temperature bath, and allow to cool for another 15 minutes. Read the absorbance of the resulting blue solution at 605 m μ . If the absorbance is read immediately after the 15-minute heating period, it will be within 10% of the 30-minute value. Heating for only 5 or 10 minutes will result in a somewhat more stable product.

Alternatively, let the reaction mixture remain at room temperature for 2 hours, and then read the absorbance at 605 m μ . If the absorbance is read after only 1 hour, it will be at almost 90% of the maximum absorbance. The solution starts fading after about 3 hours.

AIR ANALYSIS. For acrolein concentrations above 0.1 p.p.m., collect acrolein at flow rates up to 2 liters per minute into at least 2 midget bubblers with glass frits, each containing 10 ml. of ethyl alcohol at ice water temperature. Remove immediately after collection from the ice bath and bring the ethyl alcohol to room temperature. Add reagents, then heat at 60° C. for 15 minutes, cool, and read absorbance at 605 m μ after total of 30 minutes. Alternatively allow solution to react at room temperature for 2 hours.

It is not advisable to pass more than 10 liters of gas through the ethyl alcohol at ice water temperature because of the low collection efficiencies obtained for acrolein when large gas volumes are passed through this solvent. This limits this procedure to concentrations above 0.1 p.p.m.

In a convenient procedure for atmospheric sampling, the sample is collected into 10 ml. of reagent mixture at room temperature. The reagent solution is prepared by adding 0.1 ml. of 4-hexylresorcinol solution, 0.2 ml. of 3% mercuric chloride solution, and 5.0 ml. of trichloroacetic acid solution to 5.0 ml. of ethyl alcohol. Separate calibration curves must be prepared. Somewhat higher absorptivities are obtained in this procedure compared to the procedure in which addition or collection is made into ethyl alcohol with subsequent addition of reagents.

For the determination of acrolein in automobile exhaust, 1 or 2 liters of sample is sufficient. About 10 liters of gas sample should be passed through the bubbler train in analysis for 0.1 to 1 p.p.m. of acrolein. Fifty or more liters of gas must be used to analyze for acrolein at concentrations below 0.1 p.p.m.

Plastic bags made of aluminized Scotchpak or Mylar (2) are convenient containers for synthetic or automobile exhaust samples. No significant loss of acrolein in 24 hours was observed in these types of plastic containers.

PHLOROGLUCINOL METHOD

Powick (11) first reported the detection of acrolein by oxidation with 1% hydrogen peroxide, addition of HCl, and then addition of a few drops of phloroglucinol to give a reddishcolored product (pink to violet).

This method was investigated to determine the effect of varying the quantity of reagents used. Under the most favorable conditions, this procedure proved to be only about one tenth as sensitive as the 4-hexylresorcinol method. When the acrolein is collected in alcoholic solution, formaldehyde also reacts to form a yellow product absorbing at $435 \text{ m}\mu$. The formaldehyde absorption is much more intense than the acrolein absorption maximum at $545 \text{ m}\mu$. However, use of an aqueous rather than an alcoholic solution diminishes the reactivity of the formaldehyde with the reagent greatly. Nevertheless, large excesses of formaldehyde still will interfere with the determination of acrolein. Nitrogen dioxide also will interfere by reacting with the phloroglucinol to form a yellow absorption product, as it tends to do generally with phenolic-type reagents.

TRYPTOPHAN METHOD

The reaction of acrolein in alcoholic solution with tryptophan in a hydrochloric acid medium has been described (3, 10, 15). The intensity of absorption of the violet-colored product at 560 m μ is only one fourth or one fifth as great as that obtained in the 4hexylresorcinol method. Formaldehyde and acetaldehyde also react to form yellow- or straw-colored products. The presence of a severalfold excess of formaldehyde and acetaldehyde does not interfere significantly, but large excesses of other aldehydes will. Nitrites and nitrogen dioxide will interfere by reacting with the tryptophan to produce a yellow- or orange-colored product.

The addition of hydrogen peroxide to the other components in the reaction mixture increases the sensitivity of the method appreciably. However, the color produced fades in a few minutes. Furthermore, the intensity of the absorption produced when formaldehyde is substituted for acrolein also is increased markedly.

4-HEXYLRESORCINOL METHOD

4 - Hexylresorcinol Reagent. The quantity of 4-hexylresorcinol reagent solution added to 2.5 ml. of ethyl alcohol containing acrolein was varied from 0.25 to 0.125 ml. No significant change occurs in the intensity of the absorption at 605 m μ when amounts ranging from 0.05 to 0.1 ml. are used. The intensity decreases slightly when 0.125 ml. is used, and the intensity decreases markedly when quantities of reagent solution below 0.05 ml. are used. The quantity of mercuric chloride solution was held at 0.3 ml. of 1%solution (or 0.1 ml. of 3% solution), and 2.5 ml. of trichloroacetic acid solution was used in each determination.

Mercuric Chloride Solution. The quantity of 1% mercuric chloride solution was varied from 0.2 to 0.5 ml. The sample solution was maintained at 2.5 ml., the 4-hexylresorcinol solution at 0.05 ml., and the trichloroacetic solution at 2.5 ml. during these measurements. When 0.2, 0.25, 0.3, 0.35, 0.4, and 0.45 ml. of HgCl₂ solution were added to a sample solution containing 4 μ g. of acrolein, the absorbances obtained were as follows: 0.25, 0.27, 0.28, 0.28, and 0.28. These results indicate that the intensity of the absorption at 605 m μ is relatively insensitive to the quantity of HgCl₁ solution. Furthermore, the use of 0.1 ml. of 3% HgCl₂ solution results in the same absorbance as does 0.3 ml. of the 1% HgCl₂ solution.

The mercuric chloride presumably functions as a catalyst in the reaction. It was thought possible that it acted as an oxidizing agent. However, when such oxidizing agents as ferric chloride, potassium ferricyanide, or hydrogen peroxide were substituted for mercuric chloride, no significant formation of the blue product was observed. Consequently, it does not appear that mercuric chloride actually does function as an oxidizing agent in this reaction.

Trichloroacetic Acid Solution. The quantity of trichloroacetic acid solution added was varied between 2 and 3 ml. The trichloroacetic acid was added to a mixture containing 5 μ g. of acrolein in 2.5 ml. of ethyl alcohol, 0.05 ml. of 4-hexylresorcinol solution, and 0.3 ml. of 1% HgCl₂ solution. The absorbances obtained using 2.0, 2.5, and 3.0 ml. of trichloroacetic solution were 0.23, 0.28, and 0.18. Consequently, the procedure is quite sensitive to the amount of trichloroacetic acid solution used.

Variation of Acidic Media. Acetic, phosphoric, hydrochloric, sulfuric, and trifluoroacetic acids were substituted for the trichloroacetic acid in the experimental procedures. No detectable reaction occurred between acrolein and 4-hexylresorcinol when acetic, phosphoric, or hydrochloric acids were used. Sulfuric acid reacted to produce red-brown products with both the acrolein solution and in the blank solution. Reaction mixtures containing trifluoroacetic acid did form a product absorbing at 598 m μ . However, the intensity of the product formed with trifluoroacetic acid was less than that produced by the use of trichloroacetic acid.

Reaction Time and Temperature. About a 2-hour reaction time at room temperature is necessary for the intensity of the absorption at 605 m_{μ} of the product to reach its maximum value (Table I). If a loss of about 10% in intensity can be tolerated, 1 hour of reaction time at room temperature is sufficient. The intensity slowly diminishes after 3 hours, decreases to 90% of the maximum value after 4 hours, and decreases to less than 50% of the maximum value after 18 hours.

The reaction mixtures also were heated at 60° C. for times varying between 5 and 30 minutes. These mixtures were cooled and read immediately after the heating period, and

Table I. Effect of Heating and Reaction Time on Intensity of Absorption at 605 M μ

| Heating | | Reaction Time, Minutes | | | | |
|----------------------------|------------------------|------------------------|--------|--------|------|------|
| Per., Min. ^a | End of heating per. | 30 | 60 | 120 | 180 | 240 |
| | | | Absort | bance" | | |
| 0 | | 0.39 | 0.60 | 0.69 | 0.65 | 0.61 |
| 5 | 0.31 | 0.54 | 0.66 | 0.70 | 0.66 | 0.63 |
| 10 | 0.52 | 0.64 | 0.71 | 0.71 | 0.66 | 0.63 |
| 15 | 0.62 | 0.68 | 0.70 | 0.69 | 0.63 | 0.60 |
| 20 | 0.66 | 0.68 | 0.68 | 0.66 | 0.60 | 0.56 |
| 30 | 0.65 | 0.65 | 0.66 | 0.62 | 0.56 | 0.52 |

• For 10 μ g. of acrolein in reaction mixture.

Heated at 60°.

 Table II.
 Wave-Length Maxima and Absorptivities for Products Formed by

 Aldehydes and Ketones with 4-Hexylresorcinol Reagent

| | | Absorptivities, a | |
|---|---|--|---|
| Substance | $\lambda_{max}, M\mu^{a}$ | λ _{max} | 605 mµ |
| Acrolein α-Methylacrolein ^e 2-Butenal 2-Methyl-2-butenal Formaldehyde Acetaldehyde Propanal Butanal 2-Methylpropanal | 605, 525, * 410 480 540, 500, 385, 345 405 543, 455 545, 450 540, 455, 400 540, 455, 400 530, 450 | 0.35, 0.04, 0.02 0.015 0.009, 0.01, 0.04, 0.04 0.006 0.0001, 0.0001 0.0001, 0.0002 0.0015, 0.0003, 0.0003 0.001, 0.0003, 0.0003 | 0.35 0.001 0.002 0.001 0.00001 0.00005 0.00005 0.00005 0.00005 |
| Pentanal Glyoxal Acetone 2-Butanone 3-Pentanone 3-Buten-2-one 2,3-Butadione Benzaldehyde Furfural | 542, 450, 400 540 550 615, 535, 395 550, 440, 400 570, 455 650, 550, 445 | 0.0007, 0.0002, 0.0002 0.0001 0.00002 0.0001 0.0001 0.00005, 0.0002, 0.01 0.00005, 0.0002, 0.01 0.00005, 0.0015, 0.0015 0.00035, 0.003 0.01, 0.004, 0.005 | 0.0001 0.00001 0.00001 0.00001 0.00001 0.00005 0.0002 0.0002 0.0002 |

• For total reaction times between 30 minutes and 2 hours.

* Shoulder at 525 m μ . • α -Methylacrolein product had a band at 605 m μ owing to presence of acrolein impurity.

after total reaction times of 30, 60, 120, 180, and 240 minutes (Table I). A heating period of 15 minutes is about optimum. However, the intensities obtained varied only slightly when the heating period was varied between 10 and 30 minutes. Heating periods of less than 15 minutes resulted in lower intensities immediately after heating and after 30 minutes' total reaction time, but in somewhat more stable products over a 4-hour period (Table I).

Reaction mixtures that were heated and exposed to light decreased to less than one third of their maximum absorbances at 605 m μ after 24 hours. Reaction mixtures kept in the dark attained the same maximum absorbances as those reacting in the light. However, light accelerates the rate of fading to a small extent.

Nature of Spectra of Reaction Product. The product formed by the reaction of the acrolein with the 4-hexylresorcinol has a strong absorption maximum at 605 m μ , which is not shifted with time, nor by varying the concentration of the acrolein or the other reactants. The main absorption band is fairly narrow for a band in the visible region of the spectrum. It has a half band-width of about 50 m μ . A weak shoulder appears at 525 m μ , and a very weak maximum occurs at 410 m μ (Figure 1).

The absorbance of the maximum at 605 m μ is linear with concentration in at least the 1- to 30- μ g. range of acrolein in the reaction mixture. The absorptivity of the reaction product is about 0.35 μ g.⁻¹ ml. cm.⁻¹, based on the acrolein concentration in micrograms per milliliter of the reaction mixture.

Possible Interfering Substances with 4-Hexylresorcinol. ALDEHYDES AND KETONES. The absorption maxima, absorptivities at these maxima, and absorptivities at 605 m μ for the products formed with 4-hexylresorcinol of a number of aldehydes and ketones are given in Table II.

The interference from saturated aliphatic aldehydes and ketones in one or two hundredfold excess over acrolein is negligible. Similarly, glyoxal, 2,3butanedione, 3-buten-2-one, and benzaldehyde do not react with 4-hexylresorcinol to form a product absorbing significantly at 605 m μ .



Figure 1. Absorption spectra of product formed by reaction of acrolein with 4-hexylresorcinol reagent

| | | | 3(|) μς | j. c | ъf | acro | ein |
|-------|---|------|----|------|------|----|-------|-----|
| _ | — | | 5 | μg. | of | a | crole | in |

 α , β -Unsaturated aldehydes, other than acrolein, react with 4-hexylresorcinol to form products with characteristic absorption spectra. However, the intensity of these bands is much less than that possessed by the acrolein product in the visible region. Consequently, acrolein can readily be determined in at least a tenfold excess of α , β -unsaturated aldehydes.

These α , β -unsaturated aldehydes, along with 3-buten-2-one, form products with 4-hexylresorcinol which absorb appreciably in the ultraviolet. These products may be useful in identifying or analyzing these compounds in many oxygenated mixtures.

The very weak absorption bands formed at 540 and 450 m μ by saturated aldehydes continue to increase in intensity for several days. The products formed by 2,3-butanedione, 3-buten-2one, and other ketones exhibit similar behavior. The absorptivities obtained within an hour and after one or more days are given in Table III. Although the intensities increase very appreciably, they are still weak compared to the intensity of the 605-m μ band of the acrolein product.

The rate of formation of the products between the saturated aldehydes and 4-hexylresorcinol is affected by light. For example, the absorbances at 540 m μ for the products of 4-hexylresorcinol with formaldehyde and propionaldehyde reacting in the dark and light are 0.04, 0.06, 0.53, and 0.80, respectively, for milligram quantities of these two aldehydes after a 2-hour reaction time.

DIOLEFINS. Mono-olefins do not react appreciably with 4-hexylresorcinol.

The diolefins do not form products which absorb significantly unless milligram quantities of the diolefins are used. 1,3-Butadiene and 1,3-pentadiene do react to form products with maxima at 605 mµ after a 30-minute reaction time which have absorptivities of only 0.005 and 0.007 µg.⁻¹ ml. cm.⁻¹ Consequently, appreciable excesses of 1,3-butadiene or 1,3-pentadiene will interfere somewhat with the determination of acrolein. However, in practice, such excess concentrations will not be present in most air pollution applications. Unlike acrolein, the diolefins form products whose bands continue to increase in intensity with time over long reaction periods. 2-Methyl-1,3-butadiene reacts less readily with 4-hexylresorcinol than do the straight-chain conjugated diolefins, but it does form a product with band maxima at 630, 540, and 395 m μ having absorptivities of only 0.0001, 0.0002, and 0.0002.

Aromatic Hydrocarbons AND PHENOLS. Quantities of benzene, mxylene, phenol, o-cresol, or m-cresol in the 900- to 1200-µg. range, when reacted with 4-hexylresorcinol, gave no detectable coloration. Since a quantity of absorbing material which produces as little as 0.02 to 0.03 absorbance unit on the spectrophotometer can be seen as a visible coloration in the 500- to 600-mu region, the absorptivities must be less than 0.0001. Consequently, only very large excesses of the more volatile aromatic hydrocarbons and phenols could offer any interference whatsoever with the determination of acrolein.

SULFUR DIOXIDE AND NITROGEN DIOXIDE. When as much as a milligram of sulfur dioxide is reacted with the 4-hexylresorcinol reagent, no visible coloration is observable. Nitrogen dioxide does react with the phenolic reagent to form a yellow product with a maximum at about 310 to 320 m μ . When 1-mg. amounts of nitrogen dioxide are added to the reagent, a strong absorption band is observed in the ultraviolet. However, the tail of this band extends only to about 550 m μ .

Analysis of Liquid Mixtures. A liquid mixture was prepared consisting of 1.25 µg. of acrolein, 53 µg. of crotonaldehyde, 170 μ g. of formaldehyde, and 84 μ g. of acetaldehyde. About 1 mg. of nitrogen dioxide was added also. This mixture reacted to produce an absorption spectra with maximum at 605, 535, 500, and 380 mµ. The crotonaldehyde product is responsible for the absorption bands with maxima at 535, 500, and the shoulder at 380 m μ . The nitrogen dioxide is responsible for the strong ultraviolet band. Separate measurements on formaldehyde and acetaldehyde definitely show that in the concentrations at which they exist in

the mixture, their products would not absorb significantly. The absorbance at 605 m μ corresponds to 1.30 μ g. of acrolein, in good agreement with the actual amount of acrolein present.

A second aldehyde mixture was prepared consisting of 4.5 μ g. of acrolein, 993 μ g. of formaldehyde, 193 μ g. of acetaldehyde, 189 μ g. of propanal, 192 μ g. of butanal, 197 μ g. of 2-methylbutanal, and 192 μ g. of pentanal. The absorbance at 605 m μ corresponded to 4.6 µg. of acrolein. The products formed also had maxima at 543 and 454 m μ with absorbances of 0.26 and 0.09 owing to the saturated aldehydes in the mixture. After three days, the absorption spectra of the reaction products of this mixture had maxima at 540 and 450 m μ with absorbances of 0.65 and 0.66. A mixture consisting of the saturated aldehydes alone at the same concentrations had absorbances at 540 and 450 mµ of 0.66 and 0.66, in almost exact agreement with the values found for the complete mixture.

A complex mixture was prepared containing acrolein along with several ketones, alcohols, esters, and phenols. The exact composition was 5 μ g. of acrolein, 1016 μ g. of acetone, 1006 μ g. of 2-butanone, 1012 μ g. of propyl alcohol, 1018 μ g. of *tert*-butyl alcohol, 1056 μ g. of ethyl acetate, 1003 μ g. of propyl acetate, 1010 μ g. of phenol, and 954 μ g. of *m*-cresol. The absorption spectra of the reaction products of the mixture with 4-hexylresorcinol had only the single maximum at 605 mµ with an absorbance corresponding to 4.7 μ g. of acrolein. A mixture containing the other components, but not the acrolein, did not react to form products absorbing in the visible region. A second such liquid mixture was prepared containing 5 μ g. of acrolein along with over 100 µg. of various ketones and phenolic substances. The acrolein was determined in this mixture to within 5% of the known amount. Consequently, acrolein can be analyzed for in mixtures containing large excesses of ketones, alcohols, esters, or phenols within $\pm 5\%$.

A liquid mixture was prepared containing 4.5 μ g. of acrolein, 973 μ g. of 1-hexene, 1027 μ g. of 2-hexene, 949 μ g. of 2-methyl-1-pentene, 1020 μ g. of benzene, 970 μ g. of toluene, 1072 μ g. of o-xylene, 1049 μ g. of m-xylene, and 1001 μ g. of p-xylene. This mixture also analyzed to give the acrolein concentration present to within 5%.

Collection Efficiencies for Source and Atmospheric Sampling. Either ethyl alcohol or a combined reagent mixture can be used as a collection medium. The combined reagent is a satisfactory medium for use with the large gas volumes needed for atmospheric acrolein analysis.

Although ethyl alcohol is a convenient collection medium, it does suffer from disadvantages because the acrolein is held in the ethyl alcohol only by its solubility in this solvent.

Table III.Increase in Absorptivities with Time for Absorption Bands of Products
of Aldehydes and Ketones with 4-Hexylresorcinol

| | | | Absorptivities, | |
|------------------|--|----------------------------|----------------------------|----------------------------|
| Substance | λ_{max} ., $M\mu^a$ | 1 hour ^b | 1 day | 3 days |
| Formaldehyde | 543 | 0.0001 | 0.0003 | 0.0015 |
| | 450 | 0.0001 | 0.0004 | 0.0025 |
| Acetaldehyde | 545 455 | 0.0001 0.0002 | 0.0001 0.0007 | 0.00015 0.0015 |
| Propanal | 540 455 400 | 0.0015 0.0003 0.0003 | 0.005 0.002 0.002 | 0.005 0.0035 0.003 |
| Butanal | 540 450 400 | 0.001 0.0003 0.0003 | 0.003 0.001 0.0015 | · · · · · · · |
| 2-Methylpropanal | 539 450 | 0.0007 0.0003 | 0.0008 0.0008 | |
| Pentanal | 542 450 400 | 0.0007 0.0002 0.0002 | ••• | 0.0035 0.0025 0.0025 |
| Acetone | 550 | 0.00002 | 0.00005 | |
| 3-Buten-2-one | 615 535 395 | 0.00005 0.0002 0.01 | 0.00015 0.0006 0.015 | · · · · · · · |
| 2,3-Butanedione | 540 440 400 | 0.0007 0.0015 0.0015 | 0.0025 0.003 0.0035 | · · · · · · · |
| Benzaldehyde | $\begin{array}{c} 570\\ 455 \end{array}$ | 0.00035 0.003 | 0.001 0.015 | |

^a Most maxima observed were constant within ± 1 or 2 m μ ; however, some shifted by ± 5 m μ over 3 days of reaction time. Values given are for 1-hour reaction period. ^b Most data in this column obtained for reaction times between 0.5 and 1 hour; how-

^o Most data in this column obtained for reaction times between 0.5 and 1 hour; however, a few absorbances were read after a 2-hour reaction period.

Large gas volumes tend to displace the acrolein down the train of bubblers at ice water temperature. However, ethyl alcohol can be used for the collection of acrolein from the small gas volumes needed to analyze raw automobile exhaust. Use of the ethyl alcohol at dry ice-acetone temperature does permit efficient collection at concentrations below 0.1 p.p.m.

In a bubbler train with ethyl alcohol at ice water temperature as the collection medium, at least 80% and usually 90% of the acrolein in raw automobile exhaust samples of 1 to 3 liters total sample volume is collected in the first bubbler (Table IV).

The collection efficiency decrease appreciably if 10 liters of auto exhaust gas (~ 10 p.p.m. by volume of acrolein) or a synthetic mixture of 0.1 p.p.m. of acrolein is collected in ethyl alcohol. Two series of runs were made using automobile exhaust gas pulled through the bubbler train at flow rates of 0.2, 0.5, and 2.0 liters per minute. In one series the usual midget bubblers with coarse glass frits and cylindrical outer containers were used. In the other series the solution was placed in a bulbshaped section at the bottom of the bubbler. The outer container expanded into a large vapor chamber above the solution. However, this change in con-

| Table IV. | Collection | Efficiencies | of | Acrolein into | Ethyl | Alcohol-Co | ooled ice | Water |
|-----------|------------|--------------|----|---------------|-------|------------|-----------|-------|
| | | | ٦ť | emperatures | | | | |

| Sample Vol., L. | Flow Rate, L./Min. | Celi Length, Cm. | Abs 1st bubbler | orbance of Solut 2nd bubbler | ion 3rd bubbler | |
|---|--|----------------------------|--|---|--|--|
| | | Raw A | UTO EXHAUST | | | |
| $ \begin{array}{c} 1\\ 1\\ 2.5\\ 10.0\\ 10.0\\ 10.0\\ 10.0\\ 10.0\\ 10.0\\ 10.0\\ \end{array} $ | $\begin{array}{c} 0.2 \\ 0.2 \\ 0.2 \\ 0.5 \\ 2.0 \\ 0.5 \\ 2.0 \\ 0.5 \\ 2.0 \end{array}$ | 1 1 1 1 1 1 | $\begin{array}{c} 0.21 \\ 0.22 \\ 0.21 \\ 0.57 \\ 0.63 \\ 0.54 \\ 0.455 \\ 0.44 \\ 0.45 \end{array}$ | $\begin{array}{c} 0.02 \\ 0.02 \\ 0.03 \\ 0.29 \\ 0.37 \\ 0.26 \\ 0.205 \\ 0.135 \\ 0.19 \end{array}$ | 0.09 0.12 0.11 0.075 0.095 0.07 | |
| 0.1 P.P.M. Acrolein in Air | | | | | | |
| $10.0 \\ 10.0 \\ 20.0 \\ 50.0$ | $2.0 \\ 2.0 \\ 2.0 \\ 2.0 \\ 2.0$ | 1 5 5 1 | $\begin{array}{c} 0.02 \\ 0.11 \\ 0.215 \\ 0.025 \end{array}$ | $\begin{array}{c} 0.015 \\ 0.07 \\ 0.145 \\ 0.025 \end{array}$ | 0.07 0.03 | |

| Table | ۷. | Collection | Efficiencies | of | Acrolein | into | Reagent | Mixture |
|-------|----|------------|--------------|----|----------|------|---------|---------|
| | | | | | | | | |

(Sample, 0.1 p.p.m. acrolein in air; flow rate, 2 liters per minute)

| Vol. | Collection | Ab | sorbance of Soluti | on |
|------|------------|-------------|--------------------|-------------|
| L. | Temp. | 1st bubbler | 2nd bubbler | 3rd bubbler |
| 50 | Ice water | 0.615 | 0.105 | 0.03 |
| 43 | Ice water | 0.485 | 0.085 | 0.02 |
| 50 | 25° C. | 0.56 | 0.075 | 0.015 |

Table VI. Absorptivity of Acrolein **Collected Directly into Reagent Mixture**

| | Total Time | Reac- | |
|---------|------------|---------|----------|
| Collec- | Held at | tion | |
| tion | Ice Water | Per. at | |
| Per., | Temp., | 25° C., | Absorp- |
| Min.• | Min. | Min. | tivities |
| 5 | 40 | 30 | 0.50 |
| 10 | 40 | 30 | 0.49 |
| 13 | 0 | 43 | 0.52 |
| 25 | 0 | 55 | 0.53 |

°0.1 p.p.m. acrolein in air passed through bubblers at 2 liters/minute. °Heating at 60° C. for 15 minutes; all samples allowed to react at 25° C.

for 30 minutes. • For collection into 10 ml. of reagent solution. Multiply by 2 to put on same basis as results obtained using 5 ml. of solution.

figuration in the outer container did not affect the collection efficiency. Furthermore, the collection efficiencies observed appeared to be independent of flow rate in at least the 0.2 to 2 liters per minute range (Table IV). Only 60% of the acrolein was collected in the first bubbler. Ninety per cent of the acrolein was collected by the first two bubblers in a train containing three bubblers (Table IV).

The collection efficiency becomes progressively poorer as larger gas volumes pass through ethyl alcohol. When 20 liters of 0.1 p.p.m. of acrolein in air was passed through the bubbler train, only 50% of acrolein was collected in the first bubbler and 83% in the first two bubblers. Finally, when 50 liters of 0.1 p.p.m. of acrolein in air

was passed through the ethyl alcohol collecting medium, only about 20% of the theoretical amount of acrolein used was collected in each of three bubblers (Table IV).

All of the above work was done using ethyl alcohol at ice water temperature. In a determination made with the ethyl alcohol at room temperature, about 20% of the acrolein normally collected in the first bubbler at ice water temperature is carried over to the second bubbler.

The results given above indicate that ethyl alcohol should not be used to collect acrolein from more than 10 liters of total gas volume. Ice water should always be used to cool the ethyl alcohol. Under these conditions as little as 0.1 p.p.m. can be analyzed for, if 5-cm. cells are used. Raw automobile exhaust can readily be analyzed for acrolein with these collection conditions.

A more generally satisfactory collection medium for low concentrations of acrolein is the mixture made up by adding 4-hexylresorcinol, mercuric chloride, and trichloroacetic acid solutions to ethyl alcohol in the usual manner. This reagent mixture when used in a bubbler train collects 70 to 80% of the acrolein in the first bubbler and 95% of the acrolein in the first two bubblers even when 40 to 50 liters of gas is passed through the bubblers (Table V). This collection efficiency is obtained both at ice water and room temperatures. The absorptivities obtained in this procedure are almost 50% higher than those resulting from addition or collection of acrolein in ethyl alcohol (Table VI). Consequently, a separate calibration curve is necessarv when using the combined reagent.

The reagent mixture if stored in a freezer or refrigerator can be used for at least a week. Reagent kept at room temperature should be prepared fresh each day. Ethyl alcohol should have an indefinite life as a collection medium and may be useful when the sample collected is to be used for multiple analyses of several substances. However, the high collection efficiency of the reagent mixture even at room temperature may make it the most desirable collection medium in most analyses for acrolein.

APPLICATIONS TO AIR POLLUTION

Analysis of Raw Automobile Exhaust Samples. A number of samples of cruise and mixed cruise and deceleration (actually a downhill-coast type of cycle) cycles were obtained from the exhaust of an automobile mounted on a chassis dynamometer. The samples were collected into aluminized Scotchpak bags of about 2 cubic feet capacity (2) or directly into bubblers containing ethyl alcohol as the collect-



Figure 2. Absorption spectra of product formed by reaction of 1 liter of cruise exhaust gases with 4-hexylresorcinol reagent

ing solution cooled to ice water temperature. The sample volumes used varied from 1 to 4 liters of exhaust gas. The samples collected in bags later were pulled out of the bags through two bubblers each again containing 10 ml. of ethyl alcohol cooled to ice water temperature.

The effect of storage of the gas sample in the bags on the acrolein analysis was tested by removing samples collected an hour or two previously, the following day, and several days later. The absorbances obtained were as follows: 1 hour, 0.21; 24 hours, 0.21; 48 hours, 0.19. In another set of determinations the absorbances obtained were as follows: 1 hour, 0.27; 24 hours, 0.23; 72 hours, 0.13. Consequently, the samples can be stored for at least 24 hours.

Results obtained for acrolein in automobile exhaust are given in Table VII. Since the results were obtained at various times over a 2-month period, and the fuel and engine conditions were varied, these values are intended only as an indication of the concentrations of acrolein present in auto exhaust. No correlation with engine cycle should be attempted. The concentrations of acrolein obtained arc in the range of 5 to 10 p.p.m. by volume. Previous work using pure hydrocarbon in fuels in the engine indicated that 10 to 15% of the peak area in gas chromatographic analyses of cruise exhaust for oxygenated compounds is attributable to acrolein (5). If approximately equal sensitivities can be assumed for the major oxygenated components, then the acrolein concentrations obtained would be in the 5 to 10 p.p.m. by volume range also.

Samples collected in the bags maintained their acrolein concentrations for at least 24 hours, but the nitrogen dioxide concentration in the gas phase diminished rapidly. This was indicated by the rapid decrease in the absorption in the ultraviolet (Figure 2).

A weak absorption maximum or shoulder was perceptible in the 530to 540-m μ range of the spectra formed by automobile exhaust with 4-hexylresorcinol (Figure 2). This absorption was much less intense than the band resulting from the acrolein product. The absorption probably is due to the presence of saturated aldehydes and possibly crotonaldehyde in the exhaust.

An attempt was made to analyze raw exhaust by the tryptophan method. The use of 2 liters of exhaust sample resulted in no absorption attributable to the acrolein product.

Analysis of Diluted Raw Automobile Exhaust. When raw automobile exhaust was diluted nine hundredfold with air, analysis showed an acrolein content of 1 to 2 p.p.h.m. (Table VI). After one or more days of reaction, weak absorption maxima were found in the 540- and 450-m μ regions, probably indicating the presence of other aldehydes.

Analysis of Irradiated Automobile Exhaust. When diluted exhaust was analyzed after several hours of irradiation by two banks of fluorescent lights external to an aluminum and Mylar chamber (12), acrolein concentrations in the irradiated exhaust were slightly higher than in the diluted exhaust (Table VII). In one run involving an initial hydrocarbon concentration of about 8 p.p.m. in the diluted exhaust, the acrolein concentration in both bubbler and plastic bag samples was 0.07 p.p.m.

The absorption spectra produced by the reaction of irradiated exhaust gases with the reagent showed appreciable absorption in the 520- to 540-m μ range of the same order as the absorption at

Table VII. Analyses for Acrolein in Raw, Diluted, and Irradiated Automobile Exhaust Gases

| Type of Auto Exhaust | Collection Method | Total Gas Vol., L. | Concn. of Acrolein, P.P.M. by Vol. |
|-------------------------|----------------------|-----------------------|--|
| Cruise | Bubblers | 4 | 8.3 |
| Cruise | Plastic bag | 1 | 8.7 |
| Decel. (coasting) | Plastic bag | 1 | 7.0 |
| Cruise and decel. | Bubblers | 1 | 7.0 |
| Diluted ^b | Bubblers | 50 | 0.025 |
| Irradiated ^b | Bubblers | 50 | 0.03 |
| Diluted | Bubblers | 50 | 0.015 |
| Irradiated ^e | Bubblers | 50 | 0.025 |
| Irradiated | Bubblers | 50 | 0.02 |
| Irradiated ⁴ | Bubblers | 30 | 0.07 |
| Irradiated ^d | Plastic bag | 30 | 0.07 |
| | | | |

• 30-m.p.h. cruise exhaust samples collected at about same time.

^{b.e} Samples collected from dilution system and irradiation chamber at about same time and after several hours of irradiation.

⁴ Total hydrocarbon concentration in diluted auto exhaust about 8 p.p.m. in this run; totals in other runs were 3 to 4 p.p.m.

605 m μ in the first hour or two of reaction time. However, unlike the 605m μ peak, the absorption in the 520to 540-m μ region continues to increase in intensity during the first day and no appreciable fading occurs for several days. The rate of increase in intensity of this band, unlike the one at 605 m μ , is increased by the presence of light. The absorbance attained after 24 hours was as high as 0.25. Usually, however, the absorbance was in the 0.10 to 0.15 range.

DISCUSSION

Since 1,3-butadiene forms a product with 4-hexylresorcinol which has an absorption maximum at 605 m μ , some discussion of the degree of interference by 1,3-butadiene with the acrolein analysis is necessary. 1,3-Butadiene passing into the atmosphere reacts through photo-oxidation to form most of the acrolein produced by atmospheric reactions. The concentrations of other conjugated diolefins which form acrolein through photo-oxidation probably are too small to be significant. In view of the rather rapid rate of photo-oxidation of butadiene in the presence of nitrogen oxides (14), it is not likely to coexist with acrolein in community atmosphere to any appreciable extent. Gas chromatographic analyses of raw automobile exhaust indicate that the 1,3butadiene exists at concentrations of less than 20 p.p.m. by volume in integrated raw exhaust samples (9). Since the absorptivities of acrolein and 1,3-butadiene at 605 m μ are 0.35 and 0.005, respectively, even a severalfold excess of 1.3-butadiene over acrolein would not result in a serious error in the analysis for acrolein.

Crotonaldehyde may exist in about equal concentration or in slight excess to acrolein in combustion gases (5, 7). Since the absorptivities of acrolein and crotonaldehyde at 605 m μ are 0.35 and 0.0002, even a severalfold excess of crotonaldehyde over acrolein would not cause a significant error in the determination of acrolein.

The absorption in the 520- to 540m μ region formed when irradiated exhaust gases are reacted with the 4hexylresorcinol reagent for 24 hours could be due to aldehydes other than acrolein in the irradiated gases. The general wave-length position of this band and its intensification with time and exposure to light all suggest such an assignment. However, such an assignment becomes less certain when the situation is considered from the quantitative viewpoint.

Even if the lowest absorbances observed of about 0.10 are used as the basis for calculation, 32 p.p.m. by volume of aldehyde, calculated as formaldehyde, would have to be present. Analyses for formaldehyde by the chromotropic acid method on the irradiated exhaust gave concentrations of 0.4 to 0.6 p.p.m. by volume (1).

If the saturated aldehydes above acetaldehyde are considered as primarily responsible for the observed absorption, a reasonable average absorptivity such as 0.003 results in a calculated concentration of 3 to 4 p.p.m. by volume. This concentration also seems excessive, considering that the total initial olefin concentration probably would not reach 1 p.p.m.

The crotonaldehyde product has a shoulder at 540 m $_{\mu}$ with an absorptivity of about 0.015 after a 24-hour period. This is a higher intensity than those shown by the products formed by the saturated aldehydes. About 1 p.p.m. of crotonaldehyde would have to be present to account for the observed absorption. The crotonaldehyde concentration is unlikely to exceed 0.05 p.p.m. If this is so, the contribution from the crotonaldehyde reaction product to the observed absorption in the 520- to 540-m $_{\mu}$ region would be small.

It is possible that the concentration of various aldehydes in the irradiated exhaust is somewhat higher than seems reasonable to assume on the basis of the presently available data. If so, the absorption band possibly may result from the aldehydes other than acrolein in the irradiated exhaust. Ozone, alkyl nitrates, nitroalkanes, higher nitroalkenes, and peroxyacetyl nitrate do not react with 4-hexylresorcinol to form products absorbing in the visible. On the basis of present data, it is possible that an as yet unidentified species may be responsible for most of the absorption observed in the 520- to 540-m_µ region when irradiated exhaust gases undergo reaction for a 24-hour period with the 4-hexylresorcinol reagent.

A wide variety of phenolic reagents have been used in the development of analytical procedures for aldehydes. Molecules such as 1,8-dihydroxynaphthalene-3,6-disulfonic acid (chromotropic acid) or simply 2,7-dihydroxynaphthalene react rather specifically with formaldehyde in highly acidic media to give a product absorbing in the 500-m μ region (18). Other aldehydes give yellow products or do not react. Formaldehyde, along with other aldehydes, reacts with phloroglucinol and resorcinol in alkaline solution. Oxidation of acrolein to the epihydrin aldehyde and reaction with phloroglucinol (11) or resortinol in hydrochloric acid solution provides a method of rather poor sensitivity, but fair specificity for acrolein (11). The relative merits of 4-hexylresorcinol, resorcinol, dimethyldihydroresorcinol, and 5-methylresorcinol have been investigated (13), and 4-hexylresorcinol was found to be most satisfactory. In the present work the substitution of

4 - tert - butylpyrocatechol for 4hexylresorcinol resulted in no detectable color formation in the reaction. A yellow product of low intensity was formed when 2-methylresorcinol was substituted for 4-n-hexylresorcinol. Acrolein reacts with 4-ethylresorcinol to form a weakly absorbing yellow-green product with a weak maximum at 600 m μ . 4-Cyclohexylresorcinol reacts with acrolein to form a band system very similar in position and intensity to that formed with 4-hexylresorcinol.

All of these experimental data indicate that condensation of acrolein with phenolic reagents is favored by the two hydroxy groups meta to each other with an alkyl group blocking the position ortho to one hydroxy group and para to the other group, and by the use of a strongly acidic reaction medium. Aside from acrolein, molecules of about the same size and those having some structural features in common with acrolein, such as crotonaldehyde, methylacrolein, propanal, butanal, and 1,3-butadiene, are the next most reactive species with this reagent. Although these structural details are suggestive, the exact nature of the reaction products has not yet been elucidated.

The failure to form the blue reaction product when acetic, phosphoric, hydrochloric, or sulfuric acids are used indicates that the trichloroacetic acid provides more than the proper acidity. Apparently the trichloroacetic or trifluoroacetic acids actually participate in some way in the blue reaction complex formed.

The results given on diluted and irradiated exhaust concentrations of acrolein lead to several conclusions. First, incomplete combustion in the engine forms a good part of the acrolein in the irradiated exhaust. Photo-oxidation of mono-olefins does not result in acrolein as a product (14). Only the photooxidation of 1,3-butadiene and pentadienes can produce acrolein (14). Consequently, the combustion process in this instance does play a significant part in contributing to the atmospheric concentration of acrolein. The same situation probably exists for crotonaldehyde. However, the combustion process does not necessarily play as important a role as does photo-oxidation with respect to the atmospheric concentration of other aldehydes.

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Determination of Nonaromatic Unsaturates in Automobile Exhaust by Spectrophotometric Titration

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A procedure has been devised for the determination of C₄ and higher molecular weight olefins in automobile exhausts and other gas mixtures. It takes advantage of the high molar absorptivity of the free tribromide ion in ultraviolet. It is sensitive for concentrations ranging between 25 and 1000 The results obtained by this p.p.m. procedure are consistent and reproducible.

A^S A RESULT of research on the mechanism of smog formation, it is generally agreed that olefins discharged into the atmosphere from automobiles constitute a major source of smog (2, 4). These olefins undergo photochemical reactions in sunlight to form compounds which irritate eyes, damage crops, and reduce visibility. Since recent evidence strongly suggests that olefins in the size range of four to six carbon atoms are dominant in the development of smog manifestations (1, 5), we have developed a method for the rapid estimation of these olefins in exhaust samples, at the same time minimizing the interference from the relatively large quantities of ethylene and propylene present in exhaust gases.

The procedure, described below, has proved valuable in this connection, particularly in research on the relation of automobile exhaust composition to fuel composition. It involves the absorption of the hydrocarbons from the gas phase with carbon tetrachloride and the subsequent determination of olefins by

standard bromometric methods, with slight modifications. The method is applicable for olefin concentrations ranging between 25 and 1000 p.p.m. by volume. The olefin recovery ranged between 80 and 105% for compounds having five or more carbon atoms in the molecule; approximately 50% of the C₄ olefins are recovered, and the presence of ethylene does not affect the results.

PROCEDURE

Apparatus and Reagents. Beckman Model DU spectrophotometer, with hydrogen discharge lamp and 1-cm. silica cells.

CARBON TETRACHLORIDE. The solvent used was Mallinckrodt analytical reagent or Baker analyzed reagent. These reagents did not show absorption at 290 microns.

TITRATING REAGENT. Standard bromate-bromide solution (0.1N) was prepared by dissolving 5.58 grams of potassium bromate and 19.80 grams of potassium bromide in distilled water and diluting to 2 liters. The normality of the solution was checked against 0.1N sodium thiosulfate. The 0.01N bromate-bromide solution was prepared by diluting the 0.1N solution 1 to 10.

STANDARD REAGENT SOLVENT. This solvent was prepared by mixing the following reagents:

| Glacial acetic acid | 50 ml |
|--------------------------|---------|
| Methanol | 20 m! |
| Coned, hydrochloric acid | 1.2 ml. |
| 40% potassium bromide | 2 ml. |
| 20% aqueous zinc sulfate | 4 mi. |

DILUTE REAGENT SOLVENT. For use when the olefin concentration in the gas stream was lower than 100 p.p.m. by volume, a more dilute solution of standard reagent was prepared as follows:

| Standard reagent | 100 ml. |
|---------------------|---------|
| Glacial acetic acid | 175 ml. |
| Methanol | 75 ml. |

Collection and Analysis of Samples. In the study of the olefin content in the exhaust vapors of automobiles, representative portions of the exhaust stream were diverted into an accumulator tank installed in the trunk of a testing vehicle. Sampling procedure and time interval between sample collection and analysis were kept constant, since these factors have a marked influence on olefin recoveries. Exhaust samples were withdrawn from the storage facility through Ascarite traps into evacuated 2-liter flasks with double stems and ground, leakproof glass stopcocks. One of the stems was used for collection of the gas sample; the other was covered with a serological stopper for the introduction of the absorbing solution. The flasks were wrapped completely with black masking tape, which prevented light exposure and thereby retarded oxidation processes during subsequent handling. Twenty milliliters of carbon tetra-

chloride were then added to the flask by inserting a hypodermic needle through a serological stopper and injecting the liquid with a syringe.

After the bulbs had been shaken on a mechanical shaker for 30 minutes, the absorbing solution was transferred into a 50-ml. volumetric flask. The 2-liter flask was washed with two 14-ml.