Group I	Grou	Group II	
Ammonium Potassium	Barium Cadmium Calcium Lead Lithium Magnesium	Nickel Silver Sodium Strontium Zine	

An interesting aspect of these experiments is the fact that ammonium acetate behaves as a base of strength comparable to potassium acetate in acetic acid-chloroform solution, while in water ammonium hydroxide is a much weaker base than potassium, sodium, or lithium hydroxide.

In another series of experiments, alkali metal salts were differentially titrated in the presence of organic bases. In one example, a solution containing 15 mg. of potassium acetate, 15 mg. of pyridine, and 4 mg. of *n*-butylamine was prepared in 10 ml. of glacial acetic acid and 100 ml. of chloroform. This mixture was titrated potentiometrically with 0.01N perchloric acid in *p*-dioxane (Figure 6).

It is evident from this graph that potassium acetate is a stronger base than either *n*-butylamine or pyridine. When ammonium acetate was substituted for potassium acetate, a similar curve was obtained. However, when cations of group II were used instead of those of group I, the basicity of their acetate salts was found equal to that of n-butylamine but stronger than pyridine (Figure 6).

CONCLUSIONS

The experiments described have shown that ammonium and potassium acetates behave as stronger bases than other inorganic acetates studied in the nonaqueous solvent system of acetic acid-chloroform. Thus, a differential titration of sodium acetates and potassium acetates was accomplished.

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Analytical Aspects of Reactions of 2-(2-Pyridyl)-benzimidazole And 2-(2-Pyridyl)-imidazoline with Iron(II)

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The compounds, 2(2-pyridyl)-benzimidazole and 2(2-pyridyl)-imidazoline, of interest because of their structural similarity to 2,2'-bipyridine and o-phenanthroline, were prepared and their reactions with metal cations tested. Both were found to give color reactions with copper(I), copper(II), cobalt(II), iron(II), and iron(III). Most notable were those with iron(II), with which deep red-purple colored complexes were formed. These complexes were studied spectrophotometrically and found to have maximum absorbances at 490 mµ for 2-(2-pyridyl)-benzimidazole at pH 5.7 and 560 mµ for 2-(2-pyridyl)-imidazoline at pH 9.0. The molar extinction coefficients for the 2-(2-pyridyl)-benzimidazole and 2-(2-pyridyl)imidazoline are 3800, and 7800, respectively. The iron complexes could also be extracted with isoamyl alcohol, thus increasing the sensitivity of the color reaction.

N THE course of a study of analytical reagents of the type



where X = O, S, NH and Y = C—OH, C—SH, and N (7-9), 2-(2-pyridyl)-benzimidazole(I) and 2-(2-pyridyl)-imidazoline(II) were prepared and tested. These compounds were of interest because of their structural similarity to bipyridine and o-phenanthroline, reagents for iron. Also, because certain substituted phenanthrolines and diquinolyl did not exhibit reaction with iron, ostensibly because of steric hindrance of the groups adjacent to the nitrogens, the question arose whether the benz- portion of the benzimidazole would exert sufficient hindrance to prevent complex formation. In this, comparison with the imidazoline with no steric hindrance should be revealing.



2-(2-Pyridyl)-benzoxazole(III) was also prepared for purposes of comparison because it was felt that the benz-portion of the benzoxazole would offer less hindrance to coordination reactions of the nitrogen than would occur in the corresponding benzimidazole nitrogen (2).

The reactions of 2-(2-pyridyl)-benzimidazole and 2-(2-pyridyl)imidazoline with metal ions were found to be quite similar to those of bipyridine and o-phenanthroline in that a red complex with iron(II) was formed readily. The colored complex was readily extractable with isoamyl alcohol. That the analogous benzoxazole(III) did not give any reaction with iron(II) was attributed to the lower basicity of the oxazole nitrogen as compared to the imidazole nitrogen.

REAGENTS AND APPARATUS

Preparation of 2-(2-Pyridyl)-benzimidazole. The procedure outlined here is essentially that of Leko and Vlajinats (β) .

One mole (123 grams) of α -picolinic acid and 1 mole (108 grams) of o-phenylenediamine were allowed to react in a distilling flask immersed in an oil bath kept at a temperature of 175° to 185° C. for 3 hours. The flask was then stoppered and the product distilled under atmospheric pressure at a temperature of about 310° C. Direct heat rather than immersion in an oil bath was used for heating the flask for distillation. The resultant product, recrystallized twice from an alcohol-water mixture, gave a melting point of 216° to 219° C. (literature melting point, 216° to 218° C.). The compound was slightly soluble in water and ter and the retrachloride, benzene, and ether.

Preparation of 2-(2-Pyridyl)-imidazoline. The procedure outlined here is essentially the same as that for 2-(2-pyridyl)-benzimidazole with few exceptions.

One mole (123 grams) of α -picolinic acid and 1 mole (60 grams) of ethylenediamine were allowed to react in a distilling flask immersed in an oil bath kept at a temperature of 150° to 160° C. for 4 hours. The flask was then stoppered and the product distilled under atmospheric pressure using direct heat. The resultant product was a thick, green, oil which was induced, by scratching the side of its container, to crystallize as white crystals. The compound was recrystallized twice from petroleum ether (boiling point 90° to 100° C.), giving a melting point of 96° to 98° C. Oxley and Short give 97° to 98° C. (6).

The compound is soluble in water and virtually all organic solvents.



10γ of iron per ml.

Reagent Solutions. Reagent solutions of 2-(2-pyridyl)-benzimidazole and 2-(2-pyridyl)-imidazoline having the concentration of 20 mg. per ml. were prepared in 95% ethyl alcohol and used in aliquots as needed. An alcoholic solution of either reagent is stable for an indefinite period.

Metal Ion Solutions. Reagent grade nitrates of aluminum, barium, bismuth, cadmium, calcium, cobalt, copper, indium, lead, magnesium, manganese, mercury, nickel, potassium, silver, sodium, strontium, and zinc, the chloride of tin, and the sulfate of niobium were used to make solutions which contained 50 mg. of metal per ml. for use in testing for the specificity of the reagents as well as for interferences to the reactions with iron.

Standard Iron Solution. Exactly 3.500 grams of Thorn Smith standard ferrous iron(II) ammonium sulfate (99.9%) pure was dissolved in 500 ml. of iron-free distilled water. A few drops of concentrated sulfuric acid were also added to prevent hydrolysis. The resulting solution had an iron concentration of 1.00 mg. per ml.

Buffer Solution. A sodium acetate-acetic acid buffer solution was prepared by dissolving 225 grams of sodium acetate and 250 ml. of acetic acid in distilled water and diluting up to 1 liter (1). This buffer solution was used to maintain the pH between 5.0 and 5.8 in the solutions to be analyzed spectrophotometrically. Hydroxylamine Reducing Solution. A 10% aqueous solution of c.p. hydroxylamine hydrochloride was used as the reducing agent in all of the runs. One milliliter of this solution was added in each determination to keep the iron in a reduced state.

Isoamyl Alcohol. The isoamyl alcohol used as the extracting solvent was dried over calcium chloride and fractionated through a 3-foot helices-packed distilling column.

Apparatus. All pH measurements were carried out using a Model G Beckman pH meter.

All colorimetric measurements were made with the Beckman DU quartz spectrophotometer equipped with 1.000-cm. cells.

REACTIONS WITH METALS

Qualitative tests of 2-(2-pyridyl)-benzimidazole with several metals were carried out in both acidic and basic media. Results show that only mercury(II), copper(I), iron(II), and cobalt(II) give any perceptible reaction in either acid or basic regions. Mercuric ion gives a white precipitate, copper and cobalt give light brown to orange colors, the iron(II) gives an intense red color. No noticeable reaction in either acidic or basic media was observed with any of the other metals tested. The qualitative procedures used for the above tests are those outlined by Irving, Butler, and Ring (1).

Qualitative tests were performed in both acidic and basic media with 2-(2-pyridyl)-imidazoline. Results show that only mercury(II), copper(I), cobalt(II), iron(III), and iron(II) give any perceptible reaction in either acid or basic media. Mercury(II) ion gives a white precipitate, cobalt, iron(III), and copper(I) ions give a deep yellow color, copper(II) gives a deep bluish color, and iron(II) gives a red-purple color. No noticeable reaction in either acidic or basic media was observed with any of the other metals tested.

STRUCTURE OF THE METAL COMPLEXES

Leko and Vlajinats $(4, \tilde{o})$ have prepared and analyzed the silver, copper(II), and mercury(II) salts of the 2-(2-pyridyl)-benzimidazole and give the following formulas based upon the analysis: $(C_{12}H_9N_3)$. CuCl₂, $(C_{12}H_9N_3)$. HgCl₂, and $(C_{12}H_9N_3)$. Ag.







Some of the commonly used anions were tried to precipitate the iron complex. Only the perchlorate of the ferrous salt of 2(2-pyridyl)-benzimidazole gave a precipitate in neutral solution. The resultant brick-red salt gave the following analysis: reported, C = 51.0%, H = 3.31%, and N = 15.2%; calculated, C = 51.3%, H = 3.2%, and N = 15.1%. This corresponds to the formula Fe(C₁₂H₉N₃)₃(ClO₄)₂, indicating that three reagent molecules react with each iron molecule, much as does 2-(2-bipyridine) and o-phenanthroline.

Several anions were added to solutions containing the iron complex of 2-(2-pyridyl)-imidazoline, but no precipitate was obtained in either acidic or basic solution. However, since the reagent has the same general structure as the 2-(2-pyridyl)-benzimidazole as well as the same general reactive properties, it can be assumed that the iron complex has the same structure.

COLOR REACTION

When an alcoholic solution of the reagents 2-(2-pyridyl)-benzimidazole or 2-(2-pyridyl)-imidazoline is added to an aqueous solution containing iron(II) ions, an intense red color is formed. The alcoholic solution of the reagent has no color itself. However, the intensity of the color produced depends upon several varying factors. The effect and nature of these factors are listed below.

Wave Length of Maximum Absorption. Spectral transmittance curves were run on aqueous solutions of the iron complexes of 2-(2-pyridyl)-benzimidazole and 2-(2-pyridyl)-imidazoline from 350 to 700 m μ at several pH values. From the curves represented in Figures 1 and 2 it can be seen that the wave length of maximum absorption varies with the pH. For the 2-(2-pyridyl)-benzimidazole iron complex, 490 m μ was found to be the wave length of maximum absorption in the pH region from 4.0 to 6.0 and 545 m μ as the wave length of maximum absorption in the pH range above pH 10.

For 2-(2-pyridyl)-imidazoline-iron complex, 560 m μ was chosen as the wave length of maximum absorption for the pH range 9.0 to 11. The wave length of maximum absorption as well as the color sensitivity increases with the pH.

Effect of pH. Several measurements were taken on the colored 2-(2-pyridyl)-benzimidazole complex at various pH values 2.0 to 10. The absorbance increased with pH to a maximum

at pH 5.0. The density reading remained constant in the pH range 5.0 to 6.0. Above this pH value a turbidity was noted which persisted until a pH of 11 was reached, where a deep purple color was obtained and could be maintained above this pH. It was found that the pH could be maintained between 5.0 and 6.0 by the use of a sodium acetate-acetic acid buffer solution. The higher pH's were obtained by using sodium acetate and sodium hydroxide solution.

The color intensity of the red-purple complex of iron and 2-(2pyridyl)-imidazoline increased with the pH until a pH of 9 was reached. Above pH 9 the sensitivity of the color reaction did not increase but was maintained at a constant value.

Reducing Agents. Sodium sulfite and hydroxylamine hydrochloride were tried as reductants for the iron. It was found that the hydroxylamine hydrochloride was most satisfactory for the reduction of iron or for the prevention of any oxidation of the reduced iron. The relatively small amounts used and the speed of reduction warrant the use of this reductant.

Color Stability. A solution of the iron complex of 2(-2-pyridyl)benzimidazole, containing hydroxylamine as a reductant and kept at a pH of about 5.5 with the buffer solution, was found to give the same extinction reading after standing in a stoppered flask for a period of weeks. This same solution at pH 11 to 12 could be preserved only for about 24 hours.

A solution of the iron complex of 2-(2-pyridyl)-imidazoline containing hydroxylamine as a reductant and maintained at a pH of 9.0 with sodium acetate and sodium hydroxide would give a reproducible extinction reading after standing in a stoppered flask for not longer than a week.

Effect of Reagent Concentration. In Figure 3, it has been attempted to show the effect on the color development of the variation of the reagent 2-(2-pyridyl)-benzimidazole-iron ratio from 2 to 1 up to 8 to 1 and also the effect of a great excess. As can be seen from the plot, it is necessary to have a reagent-iron ratio of 6 to 1 for maximum color development rather than the stoichiometric ratios of 3 to 1. A greater excess of reagent over the 6 to 1 ratio has no effect upon the absorbance readings. The gradual slope of the curve also points out that a relatively weak complex is being formed.

The relative stability of the 2-(2-pyridyl)-imidazoline appears to be even less than that of the 2-(2-pyridyl)-benzimidazole since, in order to obtain maximum color development at any pH, there must be a great excess of reagent present. The relative position of this curve also appears in Figure 3. Both of these curves were run at pH values giving maximum color development.

Metal Ion	Conen of Fe	Concn. of Metal	U U	
Tested	$\gamma/Ml.$	Ion, γ/Ml .	DA^{a}	$D_{B^{cb}}$
Blank	500	0	0.343	0.150
Copper	500	500	0.050	0.130
Nickel	500	500	0.005	0.080
Cobalt	500	500	0.030	0.115
Zinc	500	500	0.300	0.150
Manganese	500	500	0.345	0.150
Copper	Ó	500	0.004	0.005
Nickel	Ó	500	0.001	0.001
Cobalt	0	500	0.001	0.002
Zinc	Ō	500	0.000	0.000
Manganese	ō	500	0.000	0.000
$a \dot{A} = 2 \cdot (2)$	nyridyl)-benzim	idazole		
b B = 2-(2-b)	-pyridyl)-belizini -pyridyl)-imidaz	oline.		

The preliminary study of interferences revealed that a number of metal ions, such as copper, cobalt, and nickel, seemed to consume reagent. Although these ions did not themselves exhibit any characteristic color when mixed with the reagents, their presence resulted in more or less bleaching the iron-reagent color. When a great excess of reagent was used, no bleaching effect was noted. A study was made of this reaction.

Equimolar concentrations of the ferrous ion and of the metal to be studied in relation to iron were added to a volumetric flask.

Sufficient reagent solution was added so that there was a ratio of 3 moles of reagent to 1 of iron. One milliliter of hydroxylamine solution was also added, the pH was adjusted to 5.2 in the case of the 2-(2-pyridyl)-benzimidazole and to pH 9.0 in case of the 2-(2-pyridyl)-imidazoline, and the solution was diluted to volume. This serves as a sort of competition reaction. A blank was run on the iron, and separately upon each tested metal as well to ensure that no erroneous reading would be obtained from a color produced by that metal. The absorbance readings were recorded for each experiment and the results can be seen in Table I.



Sensitivity. The conformity of the colored solution of 2-(2pyridyl)-benzimidazole to Beer's law was studied over a concentration range from a lower limit of about 0.5γ of iron per ml. to a maximum concentration of about 40γ per ml. Beer's law was followed very closely as can be seen from Figure 4. From this, then, a molecular extinction coefficient was calculated to be about 2600 at 490 m μ (pH 5.5) and 3800 at 545 m μ (pH 11).

The 2-(2-pyridyl)-imidazoline iron complex also conformed to Beer's law in a concentration range from 0.05 to about 15γ of iron per ml. as shown in Figure 4. The molecular extinction coefficient calculated at 560 m μ (pH 9) was 7800. This compares favorably with 2-2'-bipyridine and o-phenanthroline (10).

Effect of Diverse Ions. The 2-(2-pyridyl)-benzimidazole and 2-(2-pyridyl)-imidazoline method for the colorimetric determination of iron is comparatively free from interference by most of the anions and cations. Only a few cause any appreciable interference as can be seen from Table II.

2-(2-PYRIDYL)-BENZIMIDAZOLE. The method used for the study of the effect of diverse ions on the color development was as follows:

In each case, exactly 2 ml. of the standard iron solution containing 200γ of iron are added to a 100-ml. volumetric flask (this is 20γ of iron per ml.). Then 6 ml. of the sodium acetateacetic acid buffer solution were added. Varying amounts of the metal ion solution to be studied were then added. An alcoholic solution of the reagent was added until the deep red color of the iron complex appeared to remain constant, and then a slight excess was added. The absorbance of the resultant solution was then read at 490 m μ after about 15 minutes. All readings were compared with the Beer's law curve to determine the extent of interference. The results can be observed in Table II.

For the determination of iron in solution, the following ions may be present in concentrations of at least 600γ without causing an error greater than 2%: aluminum, acetate, bismuth, barium, cadmium, calcium, chloride, cobalt, copper, indium. fluoride, iodide, lanthanum, lead, magnesium, manganese, nickel, niobium, phosphate, potassium, sodium, strontium, sulfate, tin, and zinc. The ions which give serious interference are silver, mercury(II), and tartrate, when present in any concentration.

2-(2-PYRIDYL)-IMIDAZOLINE. Essentially the same procedure was followed in the study of the effect of diverse ions with 2-(2pyridyl)-imidazoline as was followed with the 2-(2-pyridyl)benzimidazole. The only exceptions were that only half the concentration of iron was used (10γ of iron per ml.) and that the study was made at pH 9.0 and 560 m μ . The results observed can be seen in Table II.

The ions which give serious interference are mercury(II), silver, and the metals which give hydroxides at this pH. These latter interferences may be eliminated by the use of some complexing agent as tartrate or citrate.

Effect of Extraction. The extraction of the ferrous complex of 2-(2-pyridyl)-benzimidazole was tried with several of the common organic extractants. The only satisfactory extractant found was isoamyl alcohol. Isoamyl alcohol will extract the colored complex completely at any pH. It was found that when the color from 100 ml. of solution was extracted into 10 ml. of the isoamyl alcohol, the sensitivity was increased threefold. This increase in the sensitivity allowed, by extraction, the extension of the lower limit of the concentration range in aqueous solution to about 0.05γ per ml.

The ferrous complex of 2-(2-pyridyl)-imidazoline was not extracted by any of the organic extractants tried, at any pH. However, the colored complex would extract into isoamyl alcohol if perchlorate ion were present. This probably means that the perchlorate of the complex is more soluble in isoamyl alcohol than it is in water. The following equations best describe the reaction [R = 2-(2-Pyridyl)-imidazoline]:

$$Fe^{+2} + SO_4^{--} + 3R \xrightarrow{OH^-} FeR_3SO_4 \text{ (not soluble in isoamyl alcohol, but soluble in water)}$$

 $\operatorname{Fe}R_3\operatorname{SO}_4 + 2\operatorname{ClO}_4^- \longrightarrow \operatorname{Fe}R_3(\operatorname{ClO}_4)_2 + \operatorname{SO}_4^-$ (soluble in water but more soluble in isoamyl alcohol)

The extraction with isoamyl alcohol also increases the sensitivity of the color reaction with this reagent.

RECOMMENDED PROCEDURES

For the determination of iron with 2-(2-pyridyl)-benzimidazole, transfer to a 50-ml. volumetric flask an aliquot of the unknown solution containing a quantity of iron which is within the concentration range illustrated by the Beer's law curve (Figure 4). Then add 1 ml. of the 10% solution of hydroxylamine hydrochlo-

	Table II.	Effect of Ions	
	Concn. of Ion,	Max. Interfe	renceª, % Fe
Ion plus Fe	$\gamma/\mathrm{Ml}.$	A	В
Aluminum	600	None	None
Acetate	600	None	None
Barium	600	None	None
Cadmium	600	2	None
Calcium	600	1	None
Chloride	600	$\overline{2}$	2
Cobalt	300	ī	ī
Conner	600	ĩ	5
Fluoride	600	None	None
Indium	600	None	None
Iodide	600	None	None
Lead	600	1	5
Magnesium	600	None	None
Manganese	600	None	None
Mercury	70	Interferes	Interferes
Nickel	600	1	None
Niohium	600	None	None
Nitrate	600	1	None
Perchlorate	600	Interferes	None
Potassium	600	None	None
Silver	70	Interferes	Interferes
Sodium	600	None	None
Strontium	600	1	None
Sulfate	600	None	None
Tartrate	100	Interferes	None
Tin	300	3	2
Zinc	600	None	None
a A = 2 - (2 - 1)	pyridyl)-benzimidaz	ole, $B = 2 \cdot (2 \cdot \text{pyrid})$	yl)-imidazoline.

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ride to reduce the iron. Add approximately 3 to 5 ml. of the sodium acetate-acetic acid buffer solution, or until the pH is between 5.0 and 6.0. Add an alcoholic solution of the reagent until the red color of the complex appears to be constant and then add a slight excess (2 ml.). Bring the volume up to 50 ml. with distilled water, and read the extinction values on the spectrophotometer.

When the concentration of iron is below about 2γ per ml., the sensitivty can be increased by extracting the color from the prepared aqueous solution into isoamyl alcohol. Depending on the concentration of iron as well as the volume of aqueous solution the volume of extractant can be varied.

Essentially the same procedure is used for the determination of iron with 2-(2-pyridyl)-imidazoline, except that the determination is made at about pH 9 rather than at pH 5; pH 9 is obtained by the use of about 2 grams of sodium acetate and a few drops of 3N sodium hydroxide. Also, when extracting with isoamyl alcohol, an excess of perchlorate (as sodium perchlorate) should be used to the amount of iron present, so that the colored complex will extract.

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Use of Molybdates for Estimating Amount of Olefinic-Type Hydrocarbons in Air

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The estimation of micro quantities of olefinic hydrocarbons is important in studies of atmospheric pollution, as these hydrocarbons oxidize under proper conditions in the air, giving compounds that can cause crop damage, eye irritation, and reduced visibility. The gradual color change from yellow to green accompanying reduction of complex and simple molybdates in acid media has been used by others for measuring the amount of carbon monoxide in air. The same color change can be produced in molybdates by olefins and forms the basis for a method of measuring the approximate amount of C₃ and heavier olefinic hydrocarbons in the air. The method employs inexpensive equipment and should find useful application in air-pollution work.

THE determination of olefinic-type unsaturation in petroleum L products by bromine number has long been a routine test. However, the method was developed for relatively large quantities of sample and large proportions of olefins in the sample. The determination of micro quantities of olefinic hydrocarbons is important in studies of atmospheric pollution, since these hydrocarbons can oxidize under proper conditions in the air and cause crop damage, eye irritation, and reduced visibility (2, 5-7, 10, 12). Large tonnages of olefins are released daily into the air from petroleum production, refining, and marketing, as well as from automobiles. Hydrocarbons have been shown to be the largest source of organic material emitted to atmosphere in Los Angeles (10). There is at present no established method for determining the amount of olefinic-type hydrocarbons in the air.

Polis, Berger, and Schrenk (15) of the U.S. Bureau of Mines devised a colorimetric procedure for determining relatively large amounts of carbon monoxide in air using phosphomolybdic acid. It was shown that certain olefins were effective in causing color production in this test. An extremely sensitive test for carbon monoxide was described by Shepherd (16). This test was based on color production in silica gel impregnated with ammonium molybdate, sulfuric acid, and palladous sulfate. Although certain precautions are taken in practice to prevent olefin interference, the impregnated silica gel can be made to give an intense green color with olefins (17). A procedure was developed in this laboratory for estimating minute amounts of C_3 and heavier olefinic-type

hydrocarbons in the air based on a similar color reaction. This involved development of a highly sensitive, yet stable, molybdate reagent.

PRINCIPLE OF METHOD

If an air sample is drawn through a finely divided caustic material as, for instance, Ascarite, various acidic substances such as carbon dioxide, nitrogen dioxide, aldehydes, organic acids, peroxides, sulfur dioxide, and hydrogen sulfide can be largely removed. Furthermore, if the air which has been drawn through Ascarite is sampled in a freeze-out trap such as that proposed by Shepherd (18) which uses liquid oxygen refrigerant, carbon monoxide and hydrogen will not be collected because of their extremely low boiling points. All olefins, however, except ethylene and propylene, exist as solids at this low temperature. Ethylene cannot be collected in substantial quantity because of its appreciable vapor pressure, although some may be retained in the freeze-out trap under proper conditions. A certain amount of acetylene also may be collected in the trap (18). Since the largest general source of acetylene to atmosphere is the automobile exhaust, in which acetylene constitutes about 5% of the hydrocarbons (13), neglecting acetylene can introduce only a small error. Olefins in automobile exhaust gases comprise approximately half of the hydrocarbons from this source.

A colorimetric reagent was devised with a view to maximum sensitivity and as uniform a color intensity for various types of