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A New Cuprous Reagent for the Spectrophotometric
Determination of Acetylene*

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TIM-907
Page 2

ABSTRACT

A new spectrophotometric reagent for determining acetylene has been developed. This reagent consists of an acetate-buffered cuprous solution stabilized by gelatin and potassium chloride. Addition of acetylene in acetone to this reagent produces a red color which is stable for at least three days. By trapping acetylene in acetone at -78°C , the method can be used for determining acetylene in gases. Recoveries of 97 ± 2 percent of known quantities of acetylene, trapped from a gas stream, have been obtained.

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INTRODUCTION

Modified Ilsovay reagents (2,4,5,7) have long been used for the colorimetric determination of small amounts of acetylene. Such reagents are usually prepared by hydroxylamine reduction of an ammoniacal cupric solution. Addition of gelatin or other lyophilic colloids is usually made to retard flocculation of the cuprous acetylde sol. Over the last 60 years, many adaptations and modifications of the Ilsovay reagent have been proposed. Yet, reagent instability by air oxidation, precipitation of copper metal by over-reduction and, perhaps most important, flocculation of the cuprous acetylde have not been eliminated.

Substitution of an acetic acid-acetate buffered medium for the usual ammoniacal solution controls the reduction potential of hydroxylamine used to reduce cupric to cuprous in the reagent preparation. Addition of gelatin and potassium chloride stabilizes the suspensoid, and thus prevents flocculation of cuprous acetylde formed from as much as 1000 micrograms of acetylene in 100 ml of solution. The colored colloid is formed within 15 minutes, and is stable for at least three days, if protected from free access to atmospheric oxygen.

EXPERIMENTAL

Apparatus:

Absorbance measurements were made with a Beckman DU Spectrophotometer; absorbance curves were plotted by a Perkin-Elmer Model 202 Recording Spectrophotometer. One centimeter cells were used in both cases.

All titrations for standardization of acetylene solutions were performed automatically with a Sargent Model D Titrator equipped with a glass pH sensing electrode and a metallic silver reference electrode.

The apparatus for concentrating acetylene from a gas stream consists of two acetone filled traps maintained at dry ice-acetone temperature. Each trap has a sintered glass frit to disperse the gas through 30 ml of chilled acetone. A dry ice cooled condenser is used to remove moisture from the gases, and thereby to prevent the glass frits from becoming clogged with ice.

Reagents:

Except where specified, all solutions were prepared from reagent grade chemicals.

Acetylene Stock Solution - Pass commercial grade acetylene through acetone for a few minutes. Dilute 50 ml of the saturated solution to about one liter with acetone. Standardize the solution before each use.

Potassium Chloride-Gelatin - Add 0.40 g of gelatin to 30 g of potassium chloride in 300 ml of water. Heat to dissolve, cool to room temperature and dilute to 500 ml.

Standardization of Acetylene Solution:

This procedure is a modification of the Barnes and Molinini (1) method for acetylenic hydrogen. Add a few drops of a dilute nitric acid solution to 40 ml of silver nitrate solution (500 g per liter). Titrate with standard 0.05 normal sodium hydroxide solution to an arbitrary pH, sufficiently acid to prevent precipitation of silver hydroxide. Add 5 ml of acetylene solution by pipet and retitrate to the same pH value. It should be noted that normal pipetting techniques do not deliver reproducible quantities of acetylene due to volatilization. However, if the pipet is drained into a swirling solution with its tip beneath the surface, such volatilization losses are minimized.

Acetylene concentration is calculated from the nitric acid liberated by reaction of silver nitrate with acetylene; two moles of acid are equivalent to one mole of acetylene.

PROCEDURE

Add the following reagents to a 100 ml volumetric flask in the order given:

1. 25 ml of 0.08M potassium chloride-0.08 percent gelatin.
2. 10 ml of 0.1M cupric chloride.
3. 10 ml of 1M ammonium acetate.
4. 10 ml of 0.3M hydroxylamine hydrochlorine.

Allow about five minutes for the reduction of copper; the solution will be a pale blue - not quite colorless. Failure to allow time for reduction of the copper will retard color formation.

Meanwhile, pass the gas to be analyzed through the cold acetone traps. Remove the traps, transfer their acetone contents to a 100 ml volumetric flask and stopper. Warm the stoppered flask to room temperature then dilute to volume with acetone. Remove a 20 ml aliquot and add to the previously mixed reagent solution. Allow about 15 minutes for complete color development, dilute to volume with water, and determine the absorbance at 552 or 475 millimicrons. Compare to a standard curve prepared by determining the absorbances developed by 20 ml aliquots of various dilutions of acetylene stock solution. It has been noted that the absorbance is sensitive to the order of addition to the reagent mixture. Therefore the acetylene-acetone addition to the mixture must be made in a single 20 ml volume.

RESULTS AND DISCUSSION

The reduction potential of hydroxylamine is pH dependent as is indicated by the half reaction:

Ilsovy's reagent and its modifications can be classified as reduced ammoniacal copper solutions. In order to avoid over-reduction, the reducing power of hydroxylamine was fixed at a definite potential by substituting an acetic acid-acetate buffer system for the ammoniacal system formerly used.

The reagent was chosen to be 0.01M copper, added as cupric chloride, 0.03M hydroxylamine hydrochloride and 0.1M acetate added as ammonium acetate. When copper (II) is completely reduced to copper (I) in this system, a buffer exists consisting of 0.04M acetic acid, 0.06M acetate. As air oxidation slowly uses up the excess hydroxylamine, the buffer changes to 0.06M acetic acid, 0.04M acetate. In this manner, the pH is maintained in the range of 4.6 to 5.0. Addition of a small amount of acetylene to this reagent produces a wine red color. However, larger amounts of acetylene cause coagulation of the colloidal cuprous acetylde. The stabilization of the colloid by the addition of gum arabic or gelatin, as suggested by Geissman, et al. (2) and Pieters (5) was then studied. It was observed that gelatin is much more effective and more convenient to use than gum arabic. When 0.2 percent gelatin is included in the reagent, precipitation is retarded for several hours and as much as 1000 micrograms of acetylene will not cause rapid coagulation. It was observed that when potassium chloride was added to a coagulated solution, the precipitate redispersed immediately. Further examination of this phenomenon revealed that potassium chloride slows the formation of the colloidal red cuprous acetylde but greatly stabilizes the final color in the presence of gelatin. It was found that 0.2M potassium chloride in conjunction with 0.02 percent gelatin allows full color development within 10 minutes and provides a color which is stable for at least three days.

Quantitative recoveries could not be made by passing known quantities of acetylene through four scrubbers containing reagent solution at 0°C. Purser (6) has demonstrated that acetone at dry ice temperature (-78°C) absorbs acetylene effectively.

The effect of acetone upon the color development was studied (Fig 1). Up to at least 30 percent acetone concentration, both the color intensity and the time required for full color development increase with increasing acetone concentration. Concentrations of acetone greater than 40 percent by volume cannot be tolerated in the final solution because of coagulation of the gelatin. As a result, an acetone concentration of 20 percent was chosen as a compromise value for the standard procedure. Absorption spectra of various concentrations of cuprous acetylde in this medium are presented in Fig 2. Absorbances at the 552 millimicron peak and at the 450-500 millimicron plateau are directly proportional to acetylene concentrations from 0.2 to at least 10 micrograms per millimeter.

At 552 millimicrons, the molar absorptivity was found to be dependent on potassium chloride-gelatin and copper chloride concentrations, while ammonium acetate or hydroxylamine concentration variations of ± 20 percent were without significant effect, Table I. At 450-500 millimicrons, although somewhat lower, the absorptivity was found to be independent of ± 20 percent reagent strength variations. The reagent described in the recommended procedure was chosen as a compromise between sensitivity, stability and speed of color development.

In order to check the accuracy and precision of the determination, known amounts of acetylene were pipetted into a 10 percent sodium hydroxide solution. Argon was swept through the solution and thence into the acetone-filled cold traps. The data presented in Table II show that recoveries averaging 96.8 percent with a relative standard deviation of 1.4 percent were achieved. The second trap normally contains less than ten percent of the total acetylene collected. Addition of a third acetone scrubber failed to increase the recovery above the observed 97 percent.

CONCLUSIONS

Difficulties encountered in use of the Ilsoy reagent and its modifications have been overcome. The new reagent, by means of pH control and colloid stabilization, produces a red color with acetylene which adheres to Beer's Law up to at least ten micrograms of acetylene per ml of solution and which is stable for several days. As discussed in a companion report (3), this reagent has proven to be well suited to the determination of traces of acetylene evolved during hydrolysis of lithium samples.

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Table I

Effect of 20 Percent Variation in Reagent Concentration
on Molar Absorptivity of Cuprous Acetylide Sol

<u>Reagent Variation</u>	<u>Molar Absorptivity</u>	
	<u>475 mu</u>	<u>552 mu</u>
None*	2880	4000
0.16M KCl - 0.016% Gelatin	2950	4210
0.24M KCl - 0.024% Gelatin	2950	3920
0.008M Cu	2940	3440
0.12M Cu	2940	4590
0.08M Acetate	2920	3880
0.12M Acetate	3000	4030
0.024M Hydroxylamine - HCl	2920	3920
0.036M Hydroxylamine - HCl	2940	4030

* 0.2M KCl - 0.02% Gelatin, 0.01M Copper, 0.01M Acetate,
0.03M Hydroxylamine, 20% Acetone.

Table II

Recovery of Known Amounts of Acetylene from Argon

<u>C₂H₂ Added, Micrograms</u>	<u>C₂H₂ Found, Micrograms</u>	<u>Percent Recovered</u>
90	86	95.6
172	168	97.7
262	250	95.1
262	254	96.7
326	313	96.0
326	317	97.2
446	431	96.9
446	442	99.2

Ave. Recovery 96.8 Percent

Relative Standard Dev. 1.4 Percent

FIG 1

EFFECT OF ACETONE CONCENTRATION ON RATE
OF COLOR DEVELOPMENT

ABSORPTION SPECTRA OF CUPROUS ACETYLIDE SOLS

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