

QUICK TESTS FOR ACETYLENE IN OXYGEN RICH LIQUID STREAMS

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This paper discusses two adaptations of the older, general, "Illosvay" type acetylene determinations, which we have used to advantage at our Fortier Plant in Louisiana. These are in part modifications of the Bureau of Mines Work⁽¹⁾ on Urban Air Sampling for Acetylene Contamination, and also, of what was then our normal analysis, using the Linde "Rapid Acetylene Analyzer."

Development of these methods was done by R. E. Gallinghouse and G. L. Smith of our Fortier Plant Analytical Group.

We will not take time to labor through the minutia of these methods, "Cook Book" style. Rather, I will outline the basic principles and steps, referring to the appended methods for details. I will also discuss the time saving advantages of these tests.

Both of these modified tests rely on the adsorption of Acetylene on the surface of cold silica gel and on the color development of copper Acetylide in the presence of sulfate ions. We have classified these methods as follows:

- I. QUALITATIVE TEST FOR ACETYLENE IN OXYGEN RICH LIQUIDS.
- II. QUANTITATIVE DETERMINATION OF ACETYLENE IN OXYGEN RICH LIQUIDS.

The former might appropriately be classed as a yes/no method at the level of 0.005 ppm C_2H_2 in the liquid sample whereas the latter provides a quantitative measure of the C_2H_2 concentration in the range 0.1 to 0.8 ppm Acetylene.

Qualitative test for acetylene

As indicated previously, acetylene is adsorbed directly from the liquid sample onto silica gel. Without desorption, the gel is immersed in Illosvay Solution. The adsorbed acetylene is reacted with ammoniacal cuprous sulfate to produce copper acetylide, which is orange in color in presence of the sulfate ions.

Since chlorine and particularly oxygen develop colors with Illosvay solutions, these must be removed from the gel tube prior to immersion of the gel in the Illosvay solution. This is done with a small nitrogen purge, predetermined to purge the oxygen without desorption of acetylene from the gel.

This test can be carried out in approximately five minutes and has become the basic test for Reboiler

and additional condenser surveillance at our Fortier Plant.

Because of the yes/no results at the 0.005 level, we begin additional liquid purges at this level and operate our Oxygen Plants in the "no trace" area almost exclusively.

Quantitative determination of acetylene (0.1 to 0.8 ppm Range)

Again we adsorb the acetylene on the surface of cold silica gel and purge the gel oxygen free. Here, however, we warm the gel and desorb the acetylene into a warm nitrogen stream, followed by absorption in Illosvay solutions. The copper acetylide, thus formed, is held suspended, through the addition of gelatin, for uniform color development. These developed colors are compared to color standards for determination of the acetylene content of the liquid sample.

The color standards used in this test are prepared as APHA color standards, (cobaltous Chloride and Potassium Chloroplatinate mixtures) to match known concentrations of copper acetylide. We operate with prepared standards equivalent to 0.1, 0.5, and 0.8 ppm C_2H_2 , although other standard colors could be prepared and utilized.

This method, though somewhat more time consuming than the Qualitative Test can still be done in approximately 15 minutes. This compares with times of 45 minutes to 90 minutes by methods we previously used. This represents not only a saving of operator time but also means that adequate action may be taken without the delay inherent in older methods.

We feel that these tests, because of their speed and simplicity, can become effective backup even for plants with continuous analysis of reboiler liquid. A routine testing program can indicate analyzer drift, problems in continuous sampling, or just supply a confidence check of the on stream analyzer.

For the plant operating without continuous reboiler-additional condenser sampling, these methods provide a short, reliable way to maintain surveillance through frequent analyses. The qualitative test, with its yes/no result is particularly useful here since its 5 minute time requirement imposes a minimum operator work load.

Literature cited

1. U. S. Bureau of Standards—Summary Technical Report Number 7273., Hughes and Gordon. Analytical Chemistry, January, 1959.

APPENDIX I

Qualitative test for acetylene in oxygen rich liquids

1. Principle

Acetylene is adsorbed onto the surface of cold silica gel from the liquid sample. Acetylene reacts with ammonical cuprous sulfate to produce copper acetylide which is orange in color in the presence of sulfate ions.

2. Interferences

Chlorine and oxygen interfere by coloration of the Illosvay solution.

3. Apparatus

- a. Test Tube, Straight 16 x 150 mm.
- b. Dewar Flask, 1000 ml capacity, calibrated for 250 ml
- c. Silica Gel Tube. See Figure 1.

4. Reagents

- a. Hydrochloric Acid, dilute 1:1
- b. Illosvay number 1—Add 40 gm $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ to 160 ml NH_4OH in 500 ml of water and make up to 1000 ml with water.
- c. Illosvay number 2—Dissolve 70 grams of Hydroxylamine Sulfate in water and make up to 1000 ml with water.
- d. Silica Gel, 3-8 mesh
- e. Distilled Water

5. Procedure

- a. The bulb portion of the silica gel tube is filled with silica gel. (3-8 mesh)

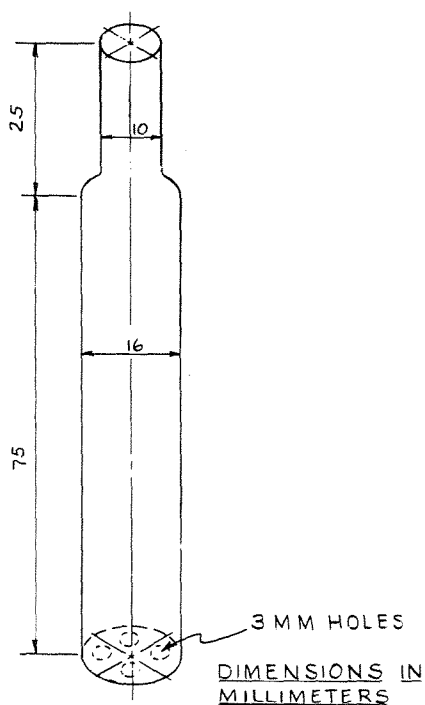


Figure 1. Silica gel tube for qualitative test.

- a. The sample point is purged until a representative stream sample can be withdrawn.
- b. Connect the gel sample tube to the sample point with rubber tubing.
- c. Draw 250 ml of the liquid sample through the silica gel and collect in the calibrated Dewar flask.
- d. At the end of the sampling remove the silica gel tube from the sample point.
- e. Attach the silica gel tube to a pure nitrogen purge and purge for 2 minutes at a rate of 500-600 cc/minute.
- f. During the purging make up a solution of equal parts (5 ml each) of Illosvay number 1 and 2 in a test tube.
- g. At the end of the purge drop the silica gel tube into the test tube containing the Illosvay solution.
- h. If a definite orange coloration does not develop on first few particles of silica gel an acetylene concentration of less than 0.005 ppm acetylene should be reported. Conversely, the appearance of an orange coloration indicates an acetylene concentration in excess of 0.005 ppm.
- i. Rinse silica gel from tube and clean tube in 1:1 dilute hydrochloric acid.
- j. Dry and refill tube with silica gel for the next sample.

APPENDIX II

Quantitative determination of acetylene in oxygen rich liquid streams

1. Principle

Acetylene in liquid oxygen is adsorbed onto the surface of cold silica gel. The acetylene is then desorbed from the silica gel with a stream of nitrogen and is swept into an absorber containing ammonical cuprous sulfate. The acetylene concentration is determined by comparing the resulting yellow color with a set of calibrated color standards.

2. Apparatus

- a. Comparison cells
- b. Dewar flask (1000 ml capacity) calibrated for 625 ml
- c. Heater, Automerse
- d. Water Bath
- e. Timer
- f. Scrubber, Vigreux
- g. Color Standards, 0.1 to 0.8 ppm C_2H_2
- h. Silica Gel Sample Tube. See Figure 2.

3. Reagents

- a. Distilled Water
- b. Hydrochloric Acid, dilute 1:1
- c. Illosvay Number 1. Add 40 gm of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ to 160 ml of NH_4OH in 500 mls H_2O and make up to 1000 mls with water.
- d. Illosvay Number 2. Dissolve 70 gm of Hydroxylamine sulfate in water and make up to 1000 mls with water.
- e. Alcohol, N-Amyl.
- f. Gelatin, 0.5% in water.
- g. Silica Gel, 3-8 mesh

4. Procedure

- a. Fill the inner portion of the tube with 3-8 mesh silica gel. (This gel must be kept dry until used.)
- b. Purge the liquid sample point until a representative stream sample can be drawn.
- c. Connect the sample tube to the liquid oxygen sample point with rubber tubing.

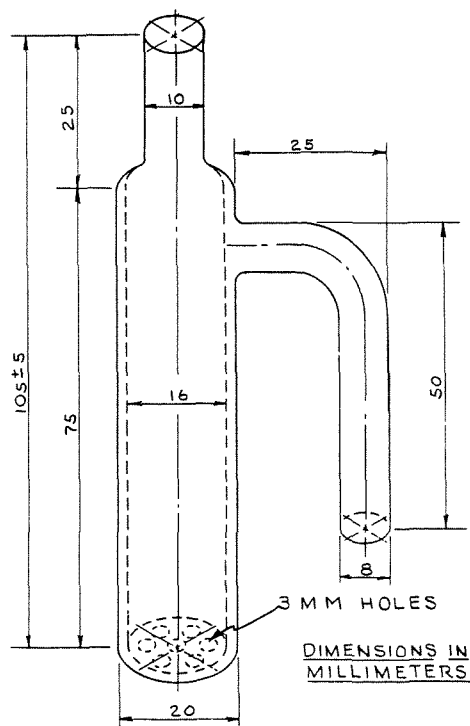


Figure 2. Silica gel tube for quantitative test.

- d. Draw 625 ml of the liquid sample through the silica gel, collecting and measuring the sample in the calibrated Dewar flask.
- e. At the end of the sampling, remove the sample tube from the sample point.
- f. Attach the silica gel tube to a pure nitrogen purge and purge exactly 3 minutes at 500-600 cc/minute flow.
- g. During this purging, make a solution of equal parts (10 ml each) of Illosvay Number 1 and Number 2 in the scrubber. Add 5 ml of the gelatin solution and 5 drops N-Amyl Alcohol.
- h. At the end of the 3 minute purge, connect the outlet from the gel tube to the scrubber inlet.
- i. Immerse the gel sample tube bulb in the hot water bath. (Near boiling.)
- j. Purge through the scrubber for exactly 7 minutes at a flow rate of 500-600 cc/minute.
- k. Empty the contents of the scrubber into a comparison cell and place the cell between the proper color standards. Estimate the acetylene concentration by comparison to the nearest matching color standard.
- l. After completing the test, rinse the scrubber and comparison cell with 1:1 hydrochloric acid, rinse with distilled water and dry for the next test.