

# AVOID MISLEADING ANALYSES

Possible masking of acetylene in liquid oxygen by presence of Carbon Dioxide in excess of its solubility.

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The use of a modified Illosvey solution for a colorimetric check for acetylene in oxygen has been the industry standard now for some time. We have, in the past few months, found that under certain conditions the Illosvey technique will give a negative reading even though the acetylene may be present.

The potential problem first came to our attention in a small nitrogen gas producing plant. As part of standard operating procedures, periodic Illosvey-type analyses for acetylene were being made and reported to the home office. These analyses consistently showed no evidence of acetylene. Also, as part of a production monitoring program, liquid samples from the re-boiler were being taken in batch samplers and returned to our laboratories for complete analysis. This analysis from time-to-time indicated the presence of acetylene, sometimes as high as 1 to 1½ ppm. A possible clue to the reason for this discrepancy between the two analyses was indicated in the laboratory's analysis by the presence of CO<sub>2</sub> greatly in excess of its solubility limit in LOX whenever acetylene was also present.

## The laboratory technique

The theory was immediately postulated that the acetylene was being adsorbed by the solid CO<sub>2</sub>. The laboratory technique used to test the theory is described below:

Three liters of pure LOX in a four-liter wide-mouthed dewar were permitted to reach equilibrium conditions. A loose-fitting cover was placed over the mouth of the dewar. After the liquid became quiescent, a predetermined quantity of gaseous acetylene was injected with a hypodermic syringe slowly into the gaseous oxygen just above the liquid surface. The quantity of acetylene was calculated to produce 1 ppm concentration in the LOX. Some time was permitted for the acetylene to go into solution and then, after stirring, the LOX was tested for acetylene. As the coloration did not come up to the 1 ppm level, additional gaseous acetylene was injected. It is believed that some of the acetylene was lost by solidification on the wall of the dewar. This mixture was then permitted to sit overnight and the Illosvey check the next morning gave a good, sharp coloration of about 1 ppm. This mixture was decanted into a small-necked dewar and kept as a reference mixture. A second sample was then prepared in the wide-mouthed dewar using the procedure just described.

The next step was injecting CO<sub>2</sub> into this second mixture, using the same technique as for the acetylene. It was quite evident that the size of particle or flake of CO<sub>2</sub> produced in the LOX was much larger than found in LOX produced in an air separation plant. We believe, however, that if the phenomena was one of adsorption, and if our experiment was successful using the larger particles of CO<sub>2</sub> having a correspondingly re-

duced surface area, the conclusions reached would be valid in the working plants. After injection of the CO<sub>2</sub> to a level of approximately 1,000 ppm, the same bright coloration persisted when checked for the presence of acetylene. We certainly do not expect this high a level of CO<sub>2</sub> in the plant, but it was convenient from a laboratory standpoint and would also offset to a degree the loss of surface area because of the larger particles.

Both the reference sample and the working sample were then permitted to sit overnight. Before the next Illosvey checks were made, the liquid level in both dewars was brought back up to the three-liter mark. After 24 hours the coloration of the Illosvey solution was about one-half as intense as originally in the LOX containing CO<sub>2</sub>; after 48 hours the coloration was still less, but still positive; and after 72 hours the coloration was essentially nil. The reference sample at all times showed a test coloration of essentially the same intensity as when first prepared.

## Recovering the CO<sub>2</sub>

The next problem was to recover the CO<sub>2</sub> from the LOX. A 75 cc. stainless steel vessel was fitted with a small stainless steel porous metal cylindrical filter in the outlet and both the inlet and outlet equipped with a valve. The filter had about a 15 micron pore size. This size would have been too large to have filtered CO<sub>2</sub> from liquid produced in a plant, but was sufficiently small to filter out the CO<sub>2</sub> particles produced by our technique. In the meantime, the CO<sub>2</sub> particles were allowed to settle as much as possible in the dewar and all visible CO<sub>2</sub> particles adhering to the walls were broken loose with a glass stirring rod. The CO<sub>2</sub>-free LOX was carefully dipped from the top of the dewar until the level was down to about 1 liter. The residue was slowly poured through the filter. It went in cloudy and came out clear and again tested negative with respect to acetylene. This filter cylinder was then valved off and permitted to warm up. A cylinder pressure of about 10 psig resulted.

Analysis of the gas so produced proved that the filter technique worked fairly well as the sample contained 38% CO<sub>2</sub>, with the bulk of the remainder being oxygen. As the ratio of CO<sub>2</sub> to acetylene was about 1,000 to 1 in the original mixture, we therefore expected to find about 380 ppm of acetylene in the gas—but the analysis showed only 20 ppm, 5% of that expected.

The chemists are "back at the drawing board" reviewing their techniques; the plant, after revising operating procedure, is operating at a CO<sub>2</sub> level below its solubility.

*Ed. Note: Actual presentation of this paper was done by F. K. Kitson at Montreal.*