



## Solvent Removal Following Oxygen System Cleaning

This paper discusses a number of methods for positively detecting if residual *EnSolv* solvent has been removed from oxygen systems following cleaning operations. *EnSolv*, US Patents 5616549, 5824162, 5938859 & 6176942, European Patent 781842, Canadian Patent 2284792 and additional patents pending, is a precision vapor degreasing and cleaning solvent manufactured by Enviro Tech International, Inc. that is being used by industry for precision cleaning applications ranging from the cleaning of precision medical components to the cleaning of industrial gas systems including oxygen and nitrogen components.

Some of the properties of *EnSolv* are listed in Table 1. Several studies have been conducted to examine the cleaning ability of *EnSolv* and found it to be excellent. However, in addition to cleaning ability, many factors influence the selection of a cleaning solvent. ASTM G 127 "Standard Guide for Selection of Cleaning Agents for Oxygen Systems" lists several of these factors including toxicity, flammability, and material compatibility.

Table I Pertinent Typical Physical Properties of *EnSolv*.

Name	Boiling Point °C/°F	Flash Point	Flammability Limits (%) (based on nPB)	AIT °C ASTM G 72 50/2000 psig	WPEG <sup>1</sup> PPM
<i>EnSolv</i>	69 / 156.2	None	4.6 - 8.2	102/185	100

Testing to determine the toxicity of *EnSolv* is on going. Enviro Tech has set a Manufacturer's Workplace Exposure Guideline of 100 ppm. Testing conducted by the NASA White Sands Test facility has determined that, while *EnSolv* does not demonstrate a flash point when tested in air, it is flammable in oxygen with an AIT of 102°C at 50 psig, and has demonstrated reactivity with liquid oxygen when tested according to ASTM D 2512.

While the user of the solvent should be aware of these issues and should incorporate toxicity and flammability into the decision on solvent selection, there are other criteria that should be considered. For systems where the removal of certain difficult soils is required or for large systems where the cost of the cleaning agent is a consideration, then these considerations might outweigh flammability and toxicity concerns. For example, isopropyl alcohol is used in the cleaning of some oxygen systems because of cost and other environmental considerations, even though it is flammable and therefore not compatible with oxygen. In applications where IPA is used, testing must be done to assure that the IPA is removed to a level below which it represents a hazard. Because of the toxicity and flammability characteristics of *EnSolv* in oxygen, the removal of the chemical to safe levels is required and positive verification must be conducted. Several methods were looked at for removal and positive verification. These included:

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<sup>1</sup> OSHA PEL not established. Enviro Tech International, Inc. recommends a workplace exposure guideline of 100 ppm 8 hour time weighted average (TWA) based on the scientific assessment of toxicological data for the *EnSolv* mixture, n propyl bromide and other compounds. Based on this data *EnSolv* is not expected to be a carcinogen.

- Purging with nitrogen (heated and unheated);
- Purging with a compatible but less effective cleaning solvent i.e. HFE 7100;
- Purging with nitrogen or with solvent followed by sample collection and analysis by Gas Chromatography;
- Purging with nitrogen or solvent followed by detection with a halogen or combustible gas detector.

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Purging with nitrogen without any analysis was discounted since there was no independent verification. Techniques that required instrumental analysis by laboratory instrumentation, such as G.C., were discounted because the expense and specialized skill that was required to conduct the analysis would prevent its effective use in the field. Purging with a compatible solvent was discounted because it lacked any independent verification that the solvent was removed and there would always be questions regarding whether or not solvent had been "swept" out by the HFE 7100. Because of these considerations it was decided to concentrate on a method that involved the purging of the system with an inert fluid, such as nitrogen, followed by detection with either a halogen or a combustible gas detector.

While the use of a halogen detector would be valid, most halogen detectors and combustible gas detectors (CGD) operate on the same principle, that is the change in either thermal or electrical conductivity of a gas passing over a sensor. This change is then sensed and either registered on a meter or by sounding an audible alarm. Whichever detector might be used, the response of the detector to *EnSolv* should be determined prior to employing the technique in the field.

### **Approach:**

A three-phase approach was used in this investigation. In the first phase, the detector response to nitrogen, *EnSolv*, and/or HFE 7100 was investigated to determine if there was interference between the elements of the test. Following this investigation a decision was made as to which purge method to use. In the second phase, following simulated cleaning of a test article with *EnSolv*, the test article was purged with either unheated or heated gaseous nitrogen to remove the *EnSolv*. The removal of *EnSolv* was then verified using a CGD. In the third phase, the CGD was exposed to standard concentrations of *EnSolv* in nitrogen to and the range of response was determined.

### Detector description:

The removal was verified using a TIF Instruments Model TIE 8800 combustible gas detector which responds to the change in the conductivity of a gas. The instrument provides a "Geiger counter" ticking signal that increases in frequency as the concentration of the vapor is increased. The sensitivity is adjustable, and for this testing, the sensitivity was in the upper range. If the detector is saturated, a "siren" type sound is emitted and removal from the source is required to allow the detector to recover. This detector was used since it represented readily available technology that could be easily implemented in the field.

Test article description:

The test article consisted of a 3-foot length of 3/8-inch diameter copper tubing equipped with flare nuts and double flares. Each end of the copper tubing was connected to a ¼ inch NPT brass-bodied ball valve. This test article was chosen since it simulated several critical elements of in-place cleaning operations, yet did not require excessive amounts of solvent to clean. The ball valve used had entrapment areas around the ball and PTFE softgoods which could absorb the solvent. The flared fittings represented additional entrapment areas for the solvent.

Test fluids:

*EnSolv* - provided by Enviro Tech International, Inc.

HFE 7100- provided by 3M Company.

Nitrogen Gas - commercial grade, dry.

**Test Procedure:**

Phase I

The CGD battery was charged and the CGD was adjusted per the manufacturer's directions.

The CGD was exposed to each of the test fluids and the response was noted:

Phase II

The procedure used to evaluate the effectiveness of purging to remove the *EnSolv* from the test article was as follows:

The combustible gas detector (CGD) was prepared for use by turning on the power switch and allowing the unit to warm up. The detector's response was assessed by passing the detector over an open container of *EnSolv*.

The test article, with its valves open, was interfaced to the gaseous nitrogen purge system and a slight purge of unheated nitrogen was passed through the test article.

The CGD was verified to not respond to the test article or the gaseous nitrogen supply by placing the CGD at the end of the test article outlet and recording the response.

Simulated cleaning of the test article was accomplished passing 100 ml of *EnSolv* through the system. The requirement was to pass 100 ml per ft<sup>2</sup> of surface area but since much less than 1 ft<sup>2</sup> of surface area existed in the test article, it was determined that 100 ml would be the evaluation quantity. One hundred milliliters of *EnSolv* were poured into a stainless steel container. The container was closed and pressurized to 80 psig with shop air. *EnSolv* was then sprayed into the test article valve ends until the 100-ml quantity was depleted. The test article valves were cycled to ensure that their seals were wetted with *EnSolv*.

After spraying the test article internal surfaces with *EnSolv*, the test article was interfaced to the nitrogen purge system and excess *EnSolv* purged out of the test article.

The test article was purged with nitrogen for 5 minutes using a set nitrogen purge. The purge pressure was recorded.

After the 5-minute purge, the flow of nitrogen was terminated and the CGD was placed at the end of the test article and the response was recorded.

If there was no response, a gentle purge of nitrogen was introduced into the test article and the CGD response was recorded. The purge pressure was also recorded.

If there was still no response, the purge flow was slightly increased and the monitoring was repeated.

If the CGD responded, a second 5-minute purge was conducted. If there was still a response, the purge and sampling steps were repeated until a total of 30 minutes of purge time had elapsed.

Subsequent tests were performed until 3 separate clean/unheated purge/sample cycles had been completed.

The above steps were repeated using heated nitrogen (to approximately 120°F) for the purge gas until 3 separate clean/heated purge/sample cycles had been completed.

Following the first set of tests, subsequent tests included an additional step to further evaluate the test article cleaning status after no response by the CGD has been noted. The test article line was "locked up" by closing the valves for 5 minutes, then reopening the test article valves and re-sampling with slight gaseous nitrogen flow. It was thought that residual *EnSolv* might be present in the softgoods and entrapment areas of the valves and fittings, which may be released during a quiescent period.

### Phase III:

Three standard concentrations of *EnSolv* in nitrogen were prepared; 10 ppm, 100 ppm, and 1000 ppm.

The CGD battery was charged and the CGD was adjusted per the manufacturer's directions.

The CGD was exposed to each of the three standards and the response was noted.

### **Test Results:**

#### Phase I

The CGD responded to both HFE 7100 and *EnSolv* and would not discriminate between the two chemicals. The detector did not respond to the nitrogen gas unless the flow was very high and directed directly into the sensor.

## Phase II

The first ambient temperature gaseous nitrogen test was conducted on 11/19/98. After 100 ml of *EnSolv* were sprayed through the test article, the test article was connected to an unheated gaseous nitrogen source and the residual liquid *EnSolv* was purged from the test article with unheated gaseous nitrogen at about 20 psig dynamic pressure. The test article was then purged with unheated gaseous nitrogen for 5 minutes at a static purge pressure setting of 50 psig, which resulted in a dynamic purge pressure on the nitrogen supply gauge of 25 psig. At the end of the purge interval with no flow through the test article, the CGD was placed at the outlet of the test article valve. No response was noted. The gaseous nitrogen flow was increased to approximately 10 psig dynamic flow and a slight CGD response was noted when the test article valves were cycled closed then open. The test article was then purged for an additional 5 minutes at approximately 25 psig dynamic pressure. After this second purge, CGD sampling with a 10 psig dynamic flow showed no further response, even when the test article valves were cycled.

The first heated gaseous nitrogen test was conducted on 11/19/98. After 100 ml of *EnSolv* were sprayed through the test article, the test article was connected to a heated gaseous nitrogen source and the residual liquid *EnSolv* was purged from the test article with heated gaseous nitrogen at about 25 psig dynamic pressure for a few seconds. The test article was then purged with heated gaseous nitrogen for 5 minutes at a dynamic purge pressure setting of approximately 5 psig, which resulted in sustained gas temperature during the purge of about 95°F. During the purge at 3½ to 4 minutes elapsed time, the test article valves were cycled twice. During the first cycle of each valve, liquid was discharged from the outlet end of test article. At the end of the purge interval with no flow through the test article, the CGD was placed at the outlet of the test article valve. No response was noted. The gaseous nitrogen flow was increased to approximately 3 - 4 psig dynamic flow and a significant CGD response was noted when the test article valves were cycled closed then open. The test article was then purged for an additional 5 minutes at approximately 3 - 4 psig dynamic pressure, which resulted in a sustained gas temperature of approximately 110°F. After this second purge, CGD sampling with a 3 - 4 psig dynamic flow showed no further response even when the test article valves were cycled.

Test results from 11/20/98 are as follows:

The test article was flushed with 100 ml of *EnSolv* by spraying it through the test article. The test article was connected to an unheated gaseous nitrogen source and the residual liquid *EnSolv* was purged from the test article with unheated gaseous nitrogen at about 20 psig dynamic pressure. The test article was then purged with unheated gaseous nitrogen for 5 minutes at a static purge pressure setting of 50 psig, which resulted in a dynamic purge pressure on the nitrogen supply gauge of 25 psig. At the end of the purge interval with no flow through the test article, the CGD was placed at the outlet of the test article valve. No response was noted. The gaseous nitrogen flow was increased to approximately 5 psig dynamic flow and a slight CGD response was noted when the test article valves were cycled closed then open. The test article was then purged for an additional 5 minutes at approximately 25 psig dynamic pressure. After this second purge, CGD sampling with a 5 psig dynamic flow showed no further response even when the test article valves were cycled. The test article valves were closed

and the test article was maintained in a "locked up" configuration for five minutes. The test article outlet valve was opened with the upstream valve still closed. No response was noted by the CGD. The upstream valve was then opened, which introduced a 5 psig dynamic flow of gaseous nitrogen through the test article, and the CGD saturated. The test article valves were closed and the CGD was allowed to recover to its background level, then the valves were reopened. The CGD response was again "off scale". A third unheated gaseous nitrogen purge was completed at approximately 25 psig dynamic pressure. Subsequently, no response was noted at the end of the third purge at a 5 psig dynamic flow. The test article valves were again "locked up" for 5 minutes. This time, only a momentary response of the CGD was noted when the test article valves were cycled. With a 5 psig dynamic pressure on the test article, cycling of either valve produced a momentary response on the CGD. A fourth purge cycle was considered but was not performed.

The third unheated test was a repeat of the second unheated test, except only two unheated 5-minute purges were required to bring the test article to a condition where the CGD would only respond momentarily to valve cycling after the 5-minute "lockup" interval.

Test results from 11/23/98 are as follows:

The second heated test was performed as follows: After 100 ml of *EnSolv* were sprayed through the test article, the test article was connected to a heated gaseous nitrogen source and the residual liquid *EnSolv* was purged from the test article with heated gaseous nitrogen at about 25 psig dynamic pressure for a few seconds. The test article was then purged with heated gaseous nitrogen for 5 minutes at a dynamic purge pressure setting of approximately 3 psig, which resulted in sustained gas temperature during the purge of about 87<sup>B</sup>F. (The temperature of the test cell and the nitrogen K-bottle was 37<sup>B</sup>F at the start of the test day.) During the purge at 3½ to 4 minutes elapsed time, the test article valves were cycled twice. At the end of the purge interval with no flow through the test article, the CGD was placed at the outlet of the test article valve. No response was noted. The gaseous nitrogen flow was increased to approximately 3 - 4 psig dynamic flow and a significant CGD response was noted. As a result, another 5-minute purge cycle was performed at approximately 3 psig and 87<sup>F</sup> gas temperature. After this second purge, CGD sampling with a 3 - 4 psig dynamic flow showed no further response, even when the test article valves were cycled. The test article valves were closed and the test article was maintained in a "locked up" configuration for five minutes. The test article outlet valve was opened with the upstream valve still closed. No response was noted by the CGD. The upstream valve was then opened, which introduced a 3-psig dynamic flow of heated gaseous nitrogen through the test article, and the CGD responded momentarily. With a 3-psig dynamic pressure on the test article, cycling of either valve produced a momentary response on the CGD.

The third heated test was conducted in essentially the same manner as reported above. After 100 ml of *EnSolv* were sprayed through the test article, the test article was connected to a heated gaseous nitrogen source and the residual liquid *EnSolv* was purged from the test article with heated gaseous nitrogen at about 25 psig dynamic pressure for a few seconds. The test article was then purged with heated gaseous nitrogen for 5 minutes at a dynamic purge pressure setting of approximately 3 psig, which resulted in sustained gas temperature during the purge of about 92<sup>F</sup>. During the purge at 3½ to 4 minutes elapsed time, the test article valves were cycled twice. At the end of the purge interval

with no flow through the test article, the CGD was placed at the outlet of the test article valve. No response was noted. The gaseous nitrogen flow was increased to approximately 3 - 4 psig dynamic flow and a significant CGD response was noted. As a result, another 5-minute heated gaseous nitrogen purge cycle was performed. After this second purge, CGD sampling with a 3 - 4 psig dynamic flow continued to show further CGD response, so a third 5-minute purge was conducted. At the end of the third purge cycle, CGD sampling with a 3 - 4 psig dynamic flow showed no further response, even when the test article valves were cycled. The test article valves were closed and the test article was maintained in a "locked up" configuration for five minutes. The test article outlet valve was opened with the upstream valve still closed. No response was noted by the CGD. The upstream valve was then opened, which introduced a 3-psig dynamic flow of heated gaseous nitrogen through the test article, and the CGD responded momentarily. Subsequent closing and opening of the test article valves did not produce additional CGD response so testing was terminated.

### Phase III:

The CGD was exposed to 10 ppm of *EnSolv* in nitrogen. The detector gave a positive response within 5 seconds. The response was characterized by an increase in the ticking rate well above the background rate. The CGD was exposed to 100 ppm of *EnSolv* in nitrogen. The detector response was immediate and the detector rapidly saturated as characterized by a siren-type signal. Exposure to 1000 ppm would give similar results.

### **Discussion:**

#### Phase I

The results of the Phase I testing indicate that the CGD (and other similar detectors) are unable to discriminate between the two solvents. Therefore, procedures that incorporate two-solvent cleaning, (i.e., *EnSolv* is used to remove certain soils and the HFE 7100 is used to perform final cleaning operations) need to incorporate steps to remove the *EnSolv* and verify removal prior to conducting the final cleaning operations. This is essential given the number and type of contaminants that solvents are required to remove and the limitations in cleaning abilities of replacement solvents, which is driving processes to consider multiple cleaning solvents to assure removal of all contaminants.

#### Phase II

In general, the results showed that an effective nitrogen purge could remove *EnSolv* from systems. If the nitrogen is heated then the amount of time and number of purges required is shortened. A critical element of the purge is that prior to final certification it should be shown that after the system is "locked-up" for some period of time that no residual *EnSolv* remains.

Entrapment did occur and must be considered in cleaning of oxygen systems. ASTM G 93, "Standard Practice for Cleaning Methods and Cleanliness Levels for Materials and Equipment Used in Oxygen-Enriched Atmospheres," and other documents recommend that systems be disassembled prior to cleaning to avoid entrapment. In the minimum, when piping systems are cleaned the valves and other components should be removed and replaced with Spool pieces and the components

cleaned separately by completely disassembling the component and cleaning it to remove oils, greases, soils and particulate.

In addition to entrapment, there was evidence of some absorption by softgoods (plastics and elastomers) in the system. The absorption of *EnSolv* by softgoods represents a problem for three reasons:

- First, the absorbed solvent could slowly off gas residual solvent over time representing a potential toxicity hazard;
- Second, the potential for material incompatibility exists between *EnSolv* and system softgoods which could change the material properties and lead to system leaks and malfunctions;
- Third, *EnSolv* absorbed into softgoods could render what would normally be considered a compatible softgood, incompatible and represent a flammability hazard to the system.

To avoid these problems, each user must examine their systems and processes and ensure that softgoods are removed, extra care is taken in removal of residual solvent, and/or the softgoods are compatible with *EnSolv*.

### Phase III

Test results from Phase III indicate that the detector used is quite sensitive to the presence of *EnSolv* in concentrations that are below the levels of concern from toxicity considerations and are well below the levels where flammability is an issue. Other detectors may vary in sensitivity and any detector used should be tested and the response to *EnSolv* determined prior to use. Detectors should only be used in good condition and should be routinely checked against standard concentrations in addition to a field test each day of use.

### **Conclusions:**

The detector used is quite sensitive to the presence of *EnSolv* in concentrations that are below the levels of concern from toxicity considerations and are well below the levels where flammability is an issue. However, the detector used was not able to distinguish between HFE 7100 and *EnSolv*.

An effective nitrogen purge can remove *EnSolv* from systems. The use of heated nitrogen reduces the amount of time and number of purges required.

### **Recommendations:**

Any detector used should be tested and the response to *EnSolv* determined prior to use. Detectors should only be used in "good" condition and should be routinely checked against standard concentrations in addition to a field test each day of use.

Procedures that incorporate two solvents for cleaning, (i.e., *EnSolv* is used to remove certain soils and the HFE 7100 is used to perform final cleaning operations) need to incorporate steps to remove the *EnSolv* and verify removal prior to conducting the final cleaning operations.

Each user must examine their systems and processes and ensure that either softgoods are removed, extra care is taken in removal of residual solvent, and/or the softgoods are compatible with *EnSolv* to prevent system toxicity and flammability hazards resulting from absorption by softgoods.

Prior to final certification, it should be shown that after the system is "locked-up" for some period of time that no residual *EnSolv* remains.

Systems and system components should be completely disassembled prior to cleaning with *EnSolv*. For piping systems, components should be removed and replaced with spool pieces and the components and piping cleaned separately.