Dragon, Karen E. (CDC/NIOSH/EIDIV)

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Sent: Tuesday, October 03, 2006 11:38 AM
To: NIOSH Docket Office (CDC)
Cc: Eileen.Kiefer@MSANet.com; Zane.Frund@MSANet.com
Subject: NIOSH Docket -008: Water vapor interference with cyclohexane detection in the IR at high flowrates and 80% RH
Attachments: MSA C6 comments.pdf

Please see the attached letter for comments submitted to NIOSH Docket-008 for the Industrial PAPR Concept paper.

Regards,
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NIOSH Docket Office, Reference: NIOSH DOCKET -008
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Reference: NIOSH DOCKET -008: Water vapor interference with cyclohexane detection in the IR at high flowrates and 80% RH

The new NIOSH Concept for Industrial PAPR eliminates the high and low humidity pre-equilibration before gas service life testing. Instead, the as-received cartridges are tested at low and high humidity. As well, NIOSH selected cyclohexane as the representative organic vapor in order to eliminate testing with carbon tetrachloride, an EPA regulated carcinogen and greenhouse gas.

Because of these needed changes, there is now a technical problem with the new requirement of cyclohexane testing at high flowrates and high relative humidities. The current cyclohexane test method, CET-APRS-STP-CBRN-0301, utilizes an infrared spectrometer detector for the downstream concentration. Unfortunately, water vapor overlaps the cyclohexane signal, resulting in a false leak. Figure 1 shows a cartridge run at 1000 ppm C_6H_{12}, 80% RH, and 100 lpm per the STP. The service time was only 3 minutes before the IR absorbance corresponding to 5 ppm breakthrough was reached, but after subtracting out the water vapor interference, the true breakthrough was 41 minutes. This is a 38 minute service time discrepancy caused by the detection method.

Fig. 1: IR Cyclohexane breakthrough curve

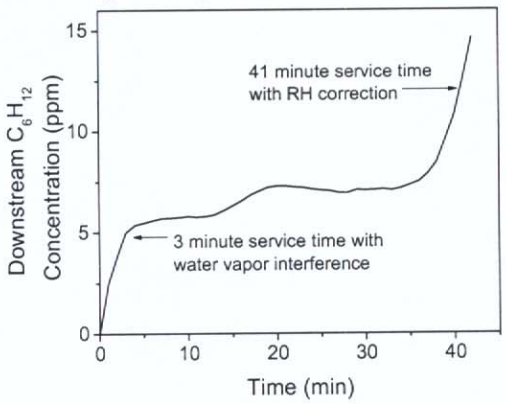

Fig. 1: Cyclohexane service life testing was performed at 1000 ppm C_6H_{12}, 80% RH, and 100 lpm using an infrared spectrometer downstream detector per CET-APRS-STP-CBRN-0301. Water vapor interference caused a 38 minute loss in service time.

In order to confirm that the initial "leak" was caused by water vapor and not cyclohexane, another service time test was performed. This time the breakthrough was monitored simultaneously with IR, as well as a gas chromatograph equipped with a flame ionization detector (GC-FID). Since the FID burns the sample, water vapor does not interfere with the signal. Results are shown in Figure 2 and confirm that the true service time is 42 minutes.

Fig. 2: Cyclohexane breakthrough monitored with IR and GC-FID

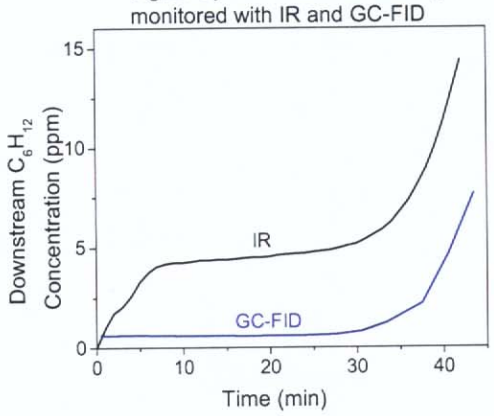

Fig. 2: Cyclohexane service life testing was performed at 1000 ppm C_6H_{12}, 80% RH, and 100 lpm using a GC-FID as well as an IR spectrometer. The initial leak seen in the IR as cyclohexane is not confirmed by GC-FID.

In order to quantify the humidity interference in the IR, clean air at varying relative humidities was sampled by the detector. Figure 3 illustrates the water vapor absorbance relative to the 5 and 10 ppm cyclohexane signals, calibrated with bag mixes in 40% RH air.

Fig. 3: IR Response to Water Vapor at 3.4 μm

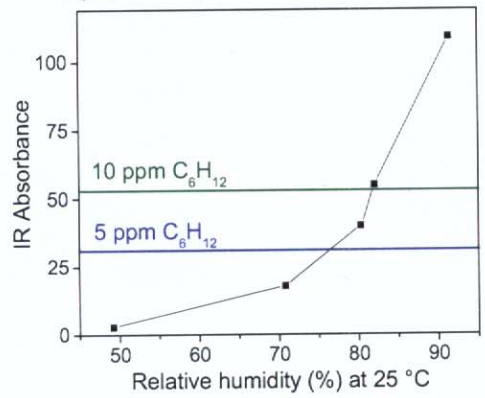

Fig. 3: The IR response to clean air at varying RH. The IR was set to 3.4 micron wavelength, as called out in CET-APRS-STP-CBRN-0301.

According to Figure 3, the downstream relative humidity at our test conditions was 75-80% RH. Why was this interference not observed for previous CBRN-APR cyclohexane testing at 80% RH? The reason is that 64 lpm is the highest flowrate that has been tested. At low flowrates, activated carbon effectively adsorbs both organic vapors and water vapor, reducing the effluent relative humidity below 65%. When the flow is raised, however, the carbon selectively adsorbs

cyclohexane and more water is allowed to pass through the bed. Thus, at high flowrates a higher downstream relative humidity is observed than at low flow rates.

We also examined IR detection wavelengths at high humidity for ammonia (10.9 μm) and methylamine (12.9 μm) to determine the effect of water vapor interference. At 85% RH, the ammonia concentration was negligible, 1.2 ppm, and the methylamine concentration was 3.4 ppm. With 12.5 and 10 ppm breakthrough limits, respectively, we do not anticipate a problem with using an IR detector for those challenge agents.

Recommendations:

1) A gas chromatograph detector should be used for the Industrial PAPR test procedure for cyclohexane.
2) Cyclohexane breakthrough concentrations should be 10 ppm for both PAPR cartridges and canisters.

Sincerely,

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