Methyl Isocyanate Performance Report

Standard Deviation Measurements using 0-1000 ppm and 0-50 ppb GC methods

Description of Methods and Tests Performed

An ultra-fast GC (zNose™) with electronically variable sensitivity controls can be used to quantify the concentration of methyl isocyanate (MIC) in two different vapor streams with MIC vapor pressure spanning 0-50 ppb and 0-1000 ppm. The sum of all instrument temperatures, sampling times, and sensitivity settings is called a GC Method and two different GC methods are used for the two vapor streams. Precision is the ability to repeat a measurement and is equal to the standard deviation of a replicate set of measurements taken of a constant vapor concentration. At low signal to noise levels, minimum detection level is statistically related (proportional) to the standard deviation.

This report describes the standard deviation of measurements taken with different GC methods, 0-1000 ppm and 0-50 ppb. Standard test vapors were created by spiking air filled tedlar bags with known concentrations of MIC in methanol.. Concentrations of MIC used were at the top and bottom of each method's range.

zNose™ Quantification and Calibration Procedures

The zNose™ is a Gas Chromatograph with a universal (non-specific) detector. The sensitivity of a measurement is controlled by the detector sensitivity and inlet vapor sampling time. Compound Identification is done solely by retention time. An expandable library of compounds and their odors based upon retention time indexing (Kovats indices) to n-alkanes vapor standards is an integral part of system software. MIC has a Kovats index of 839 corresponding to a retention time of 3.2 seconds using a db-624 column and a linear temperature program of 40°C to 140°C at 10°C/second.

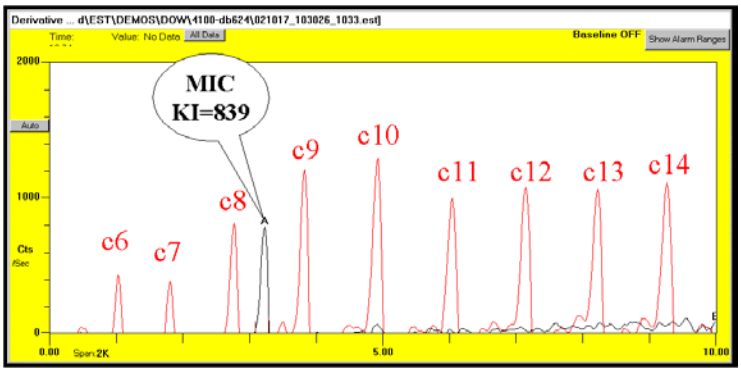

Figure 1- Overlaid n-alkane response to MIC response.

Once an analyte (peak) is identified single- or multi-point response factors are assigned to that analyte based upon the system response (peak areas in counts, cts) to a standard vapor of known concentration. Analyte response factors (e.g. cts/ppm), alarm settings, retention time, and other peak attributes are stored in special peak files. Since response factors are method dependent, peak files are associated with GC method files. .Once calibration is complete the response of the system to each analyte (peak) in a vapor can be displayed with retention time in seconds or Kovats indices and amplitude in user units (e.g. ppm, ppb, pg, ng, etc.) or in detector counts. .

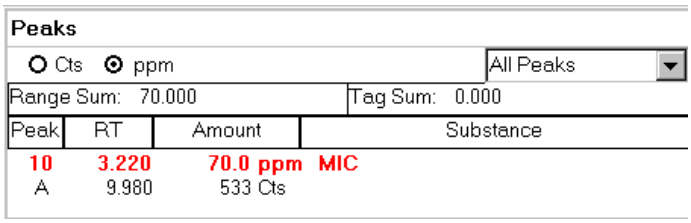

Figure 2- System Response in user units of vapor pressure

Testing 0-1000 ppm Method

High vapor concentrations can overload the GC column, distort peaks, and cause retention shifting. For the 0-1000 ppm method a maximum vapor sample volume of 0.5 milliliter corresponding to a 1 second sample time is recommended. The detector sensitivity setting (temperature) for high MIC vapor pressures was set to 80°C.

Standard Deviation at 971 ppm

A 40 mL septa sealed vial was spiked with 10 µliter of MIC diluted 100-to-1 in methanol to produce a MIC vapor pressure of 971 ppm at 22.5°C. Replicate measurements were taken on the vial. Each measurement removed a small amount of vapor from the vial causing a small reduction of the vial vapor pressure with each measurement. .

The single-point response factor was 11.78 cts/ppm and standard deviation after removing the systematic decrease due to vapor sampling was 415 cts or approximately 35 ppm.

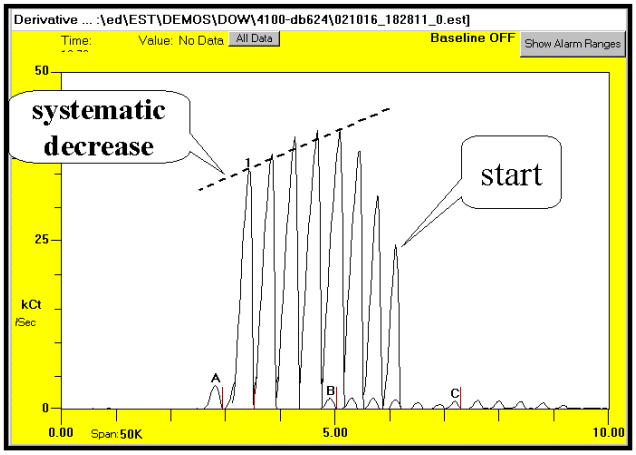

Figure 3- Horizontally offset replicate measurements of vial containing 971 ppm MIC .using 0-1000 ppm method

Standard Deviation at 70 ppm

Precision was also tested at the low end of the 0-1000 ppm scale. A tedlar bag containing 500 milliliters of air was spiked with 9 µliters of MIC diluted 100 to 1 in methanol and this created a 70 ppm standard vapor.

The single-point response factor was 16.87 cts/ppm and standard deviation after removing the systematic decrease was 7.6 cts or approximately 0.6 ppm.

Note: The instability of MIC vapor with time might be due to the reactive chemical nature of MIC to react with or permeate (leak) through the walls of the tedlar bag

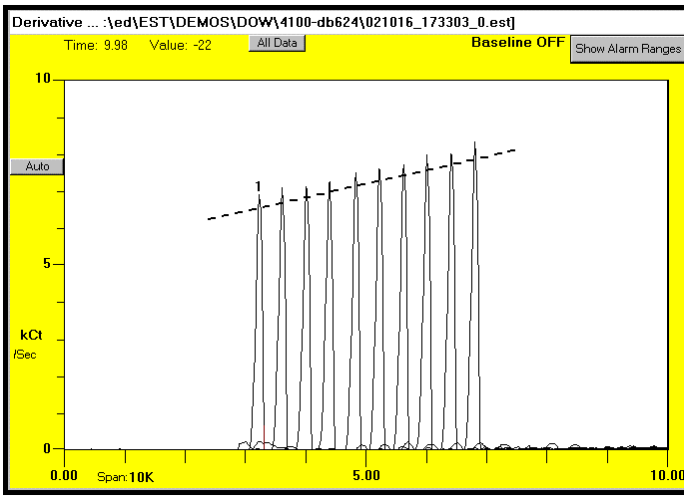

Figure 4- Horizontally offset replicate measurements using a 70 ppm MIC vapor standard with 0-1000 ppm method.

Standard Deviation at 5 ppm

After a 16 hour waiting period (overnight) the tedlar bag was again tested and the concentration of MIC had decreased to approximately 5 ppm and 10 replicate runs gave a standard deviation of 0.25 ppm.

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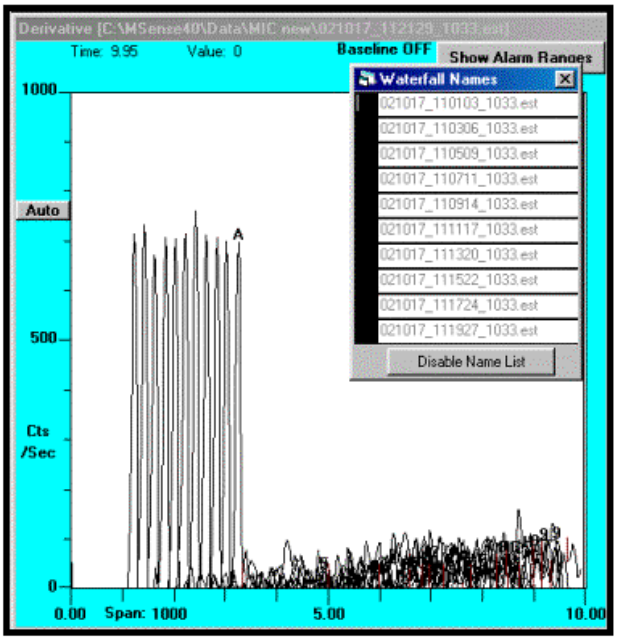

Figure 5- Replicate measurements on 70 ppm tedlar bag after 12 hours.

Standard Deviation at 54.4 ppm

A new tedlar bag with a concentration of 54.4 ppm was created and again replicate measurements taken using the 0-1000 ppm method. The response factor was 13.38 cts/ppm and the standard deviation of 7 replicate runs was 2.2 ppm.

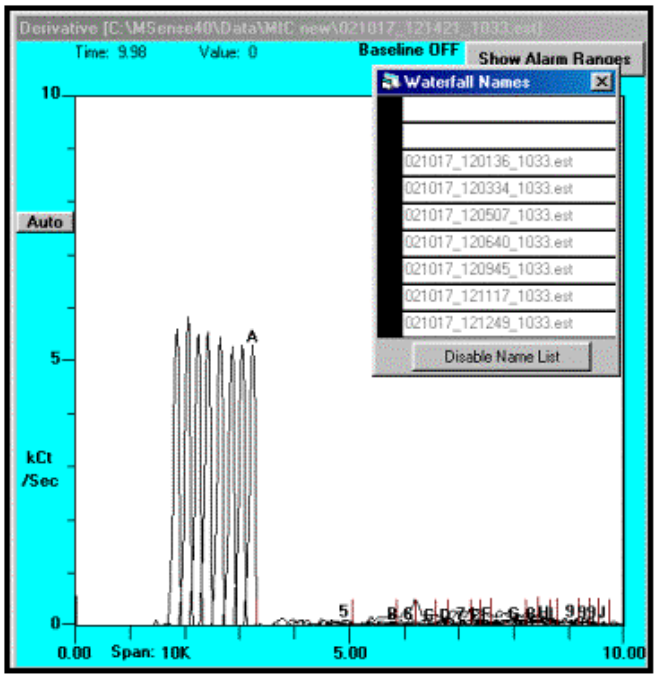

Figure 6- Horizontally offset replicate measurements on 54.4 ppm MIC concentration in tedlar bag usingt 0-1000 ppm method.

Testing 0-50 ppb Method

Low vapor concentrations require a larger sample volume for preconcentration and additional detector sensitivity. For the 0-50 ppb method a maximum vapor sample volume of 15 milliliter corresponding to a 30 second sample time was used. Sample times longer than this do not increase sensitivity for MIC due to breakthrough in the preconcentrator trap. The detector sensitivity setting for the 0-50 ppb method was 10°C.

Standard Deviation at 55 ppb

. Vapor standards with concentrations in the ppb range required a second 100X dilution of the original 100-to-1 methanol solution. Injecting 7 microliters of this into a tedlar bag containing 500 milliliters of air produced a vapor concentration of 55 ppb. Measurements taken using the 0-50 ppb method produce a response factor of 47.3 cts/ppb and after removing systematic loss the standard deviation of 7 replicate measurements was 1.05 ppb.

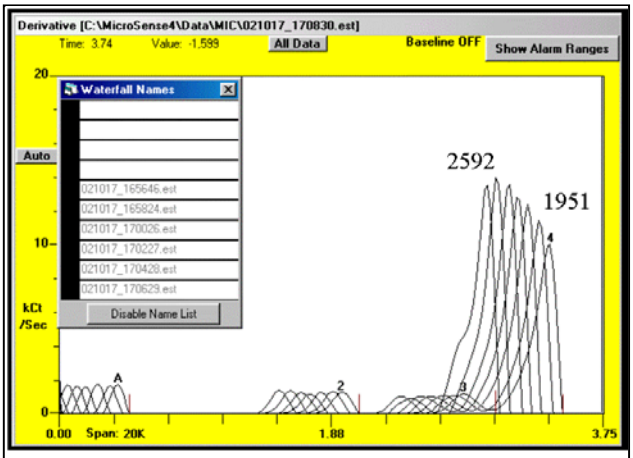

Figure 7- Horizontally offset replicate measurements using 0-50 ppb method and 55 ppb MIC.

Standard Deviation at 39 ppb

. Injecting 5 microliters of this into a tedlar bag containing 500 milliliters of air produced a vapor concentration of 39 ppb. Measurements taken using the 0-50 ppb method produce a response factor of 56 cts/ppb and after removing systematic loss the standard deviation of 7 replicate measurements was 1.15 ppb.

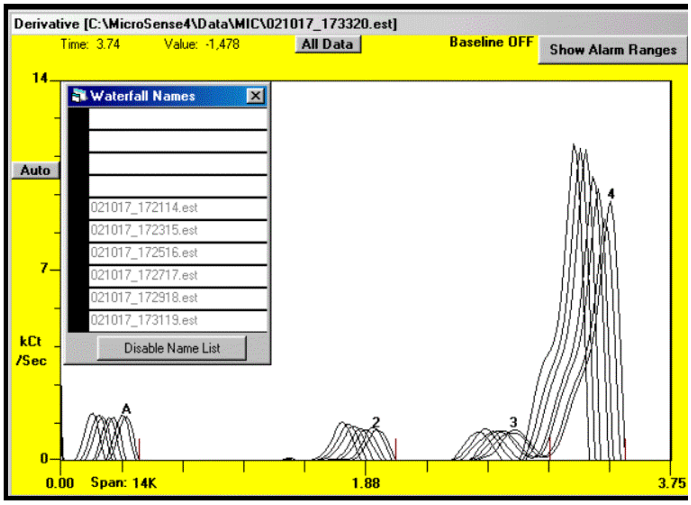

Figure 8-Horizontally offset Replicate measurements of 39 ppb using 0-50 ppb GC method.

Standard Deviation at 7.8 ppb

Injecting 2 microliters of this into a tedlar bag containing 1000 milliliters of air produced a vapor concentration of 7.8 ppb. Measurements taken using the 0-50 ppb method produce a response factor of 64 cts/ppb and after removing systematic loss the standard deviation of 7 replicate measurements was 0.26 ppb

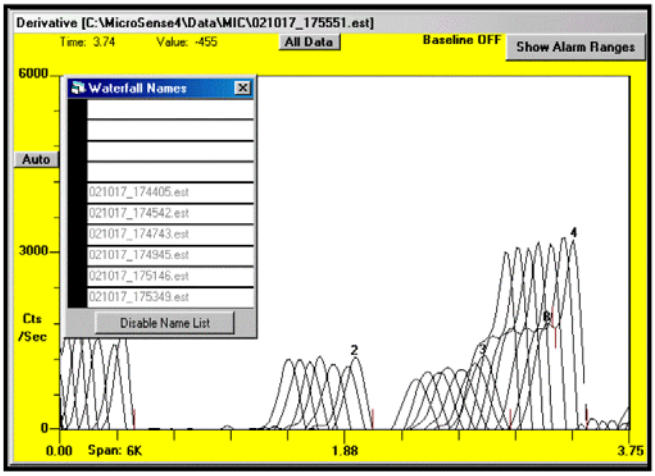

Figure 9- Horizontally offset replicate measurements of 7.8 ppb using 0-50 ppb GC method

Potential Interference

Sources of interference are chemicals that may exist in the background vapors. Toluene and xylenes (3-types) were evaluated and compared to methyl isocyanate. The results are shown in Figure 10 where vertically offset traces are compared together with the n-alkanes and MIC vapors.

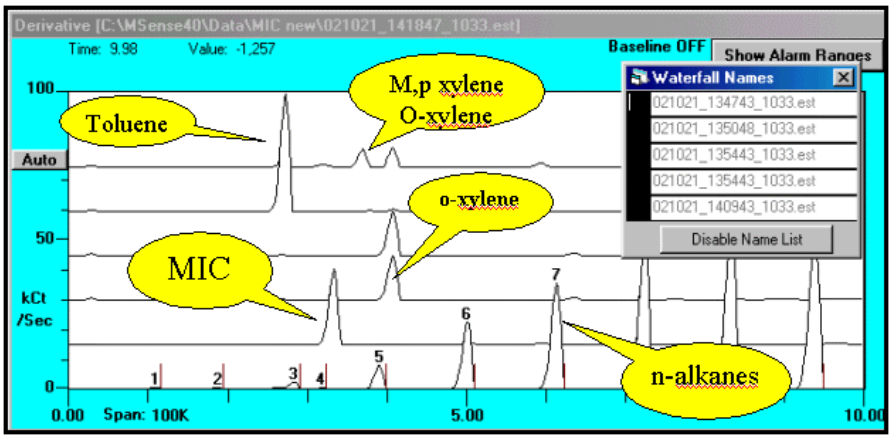

Figure 10- Vertically offset analyses of MIC and potential Interference from toluene and xylenes.

Using the n-alkanes the retention times of all compounds are indexed as shown in the following table of Kovats indices.

Compound	***Kovat Index***
Benzene	681
Toluene	787
Methyl Isocyanate	840
m,p-xylene	881
o-xylene	917

Using software supplied with the zNose retention time alarm bands can easily be defined such that there is no interference or overlap of the alarms for each of the compound.

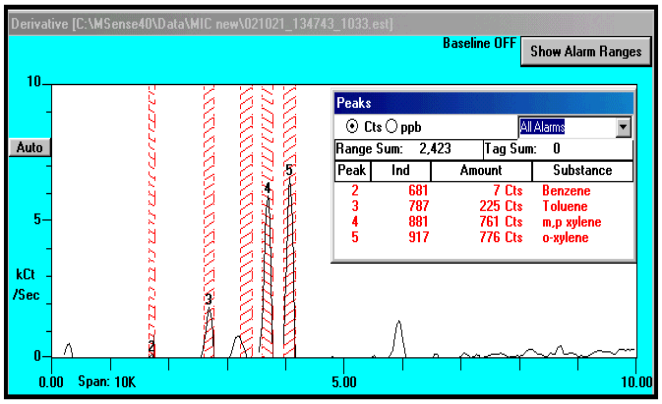

Figure 11- Alarm regions for MIC showing no interference with toluene and xylenes.

Summary of Results

The measurement results are summarized in the following tables. Vapor pressure listed is the partial pressure MIC calculated using the temperature and vapor concentration of MIC in the standard test vapor. The response factor shown is the average of all single measurements.

Range 0-1000 ppm RF(avg)=13.8 Cts/ppm	
Vapor Pressure (ppm)	**Std Deviation (ppm)**
971	**35**
70	**0.6**
55	**2.2**
5	**0.25**

Range 0-50 ppb RF(avg)=13.8 Cts/ppm	
Vapor Pressure (ppb)	**Std Deviation (ppb)**
55	**1.05**
39	**1.15**
7.8	**0.26**