

MEMORANDUM

To: AIR QUALITY CONSULTANTS

From: John Sliwinski
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Re: Vinyl Chloride Detection Limits
GC-MSD SCAN Mode

Date: 02.09.24

Target chemicals exhibit the best detection limits when determined in Selected Ion Monitoring (SIM) mode. If normal full characterization is carried out in SCAN mode, selectivity and sensitivity can be enhanced by employing target ion verification analysis (TIVA) developed by OSB Lab which permits integration of target ion reconstructed chromatograms manually or by downloading of ion areas using computer software to the EXCEL spreadsheet.

TIVA requires that ion areas be multiplied by a suitable constant (MF) to generate equivalent total ion counts (TIC) as integrated areas. The MF is obtained experimentally for each target chemical using calibration gas standard TIC areas divided by the selected ion areas. This is possible because ion ratios for each chemical remain intrinsically constant. TIVA is a similar but limited substitute for SIM mode. TIVA has a significant advantage at the nominal detection limit (NDL) where coelution or background interferences mask the recovery of any target compound run in SCAN mode.

The method detection limit (MDL) is a statistically defined decision point such that measured results falling at or above this point are interpreted to indicate the presence of analyte in the sample with a specified probability (99%), and assumes that there are no known sources of error in identification or biases in measurement.

MDLs are deliberately determined at a stable response-to-concentration level to provide reliable interlaboratory comparable bench marks. The NDLs are determined at the detection threshold level (presence/absence) to demonstrate statistically the absence of an analyte in SCAN mode.

Organic chemicals exhibit different sensitivity (response) at the mass selective detector. This is primarily due to the formation of a unique mass fragment distribution for each compound. The sensitivity or response is concentration dependent but not always a simple linear relationship throughout a broad concentration range. Response may not be continuous or predictable between zero and the MDL test value (5-10 times the estimated MDL). Many chemicals exhibit high detection thresholds due to poor fragmentation or artifact formation.

Vinyl Chloride has been chosen to illustrate how detection limits are reported by OSB Lab in SCAN mode and how they are affected by the sample volume collected. Experiments were done on two analytical systems defined as MSD 5972 and MSD 5973N.

	ION AREAS			
	MSD 5972		MSD 5973N	
CONCENTRATION (Nanograms)	ION 62	ION 64	ION62	ION64
3.285	0.06602	0.00535	0.2829	0.0880
6.570	0.1944	0.0435	0.5575	0.1707
13.14	0.4346	0.1076	1.154	0.3675
26.28	0.8949	0.2578	2.384	0.7501
52.56	1.689	0.5235	4.799	1.504

It is evident that one instrument is more sensitive than the other, therefore detection limits will vary by instrument in addition to any coelution or background interferences. If we assume that TIVA is carried out for Vinyl Chloride determined in SCAN mode then NDL may be set at 3.2ng and MDL at 26.3ng.

VINYL CHLORIDE	EQUIVALENT AIR CONCENTRATION $\mu\text{g}/\text{m}^3$							
VOLUME SAMPLED (L)	1		5		10		50	
	NDL	MDL	NDL	MDL	NDL	MDL	NDL	MDL
		3.2	26.3	0.64	5.26	0.32	2.63	0.064

If the sample is split, the detection limit is increased by the split factor. The following convention has been adopted at OSB Lab:

- Blank* = Below integration threshold but presence or absence was not verified by manual search
- < = Manual search for compound verified as below MDL
- <(TRACE) = Characteristic ions present but too low to be quantified
- <(ND) = Characteristic ions are not present therefore Not Detected

The detection limit represented by MDL is set deliberately conservative for reliable quantitation but assumes no coelution or background interference. *Blank* means that Autointegration or Paraintegration carried out by the software did not recognize that compound. *Less Than (<)* means that the analyst examined the peak fragmentation pattern and determined that the compound was present but below the MDL value. *Less Than (TRACE)* means the analyst examined the fragmentation pattern and determined that the compound may be present but the ion areas were too low to be reliable for quantitation (3.285ng for MSD 5972 could be reported as *TRACE*). *Less Than (ND)* means the fragmentation pattern did not show any target ion areas to be present.

The detection limit represented by TIVA NDL is set deliberately low or at *TRACE* level to demonstrate that the compound would likely not be present below that value or always present at or above that value.