High-Purity Vapor Generation of Semi-Volatile Chemical Agents for Wearable Sensor Validation

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Introduction

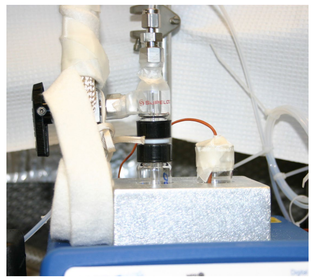
MRIGlobal developed improved methods for the testing of low vapor pressure materials. Testing was conducted on several low vapor pressure highly toxic materials, for A-series and V-series agents. This method generated reproducible vapor streams at stable concentrations, and very low degradation products and impurities for sensor validation

Advanced Vapor Generation

Chemical vapors are frequently generated using a diffusion tube apparatus that has been well characterized and is capable of producing vapor streams at most levels necessary for sensor, decon, or other testing. The diffusion setup is capable of producing chemical vapors at mathematically predicted concentrations based on diffusion tube lengths, bores, number of diffusion tubes, temperature, and dilution flows. Diffusion systems work best with volatile materials, and allow the operator to dial in most concentrations from single ppb to hundreds of ppm at high precision.

Issues arise when working with low vapor pressure materials that require significant temperature increases to produce vapors. While vapor concentration does increase as predicted, so does the production of degradation products. This causes the generated vapor profile to have multiple analytes present, some with very similar structures to the target. This leads to analytical systems monitoring the vapor line possibly not differentiating the target analyte from degradation products, and enabling flawed library references and/or detection limits.

MRIGlobal developed an alternative vapor generation system to overcome the issues associated with diffusion generation of low volatility materials. The advanced setup allows for the generation of chemical vapors at dynamic concentration ranges higher than ever witnessed by diffusion generation, all while maintaining lower temperatures and more pure vapor profiles.



Diffusion Tubes (multiple) in a Diffusion Heater Cell (left), Advanced Setup in Heater Block (right)

Partial Analyte List

Chemical Agent	CAS number	Molecular Weight	~Boiling Point (°C)	Vapor Pressure @ 25°C (torr)
A1	Withheld	--	235	0.0500
A2	Withheld	--	239	0.0407
A3	Withheld	--	258	0.0140
V1	Withheld	--	256	0.0067
V2	Withheld	--	298	0.0021
V3	Withheld	--	298	0.00088
V4	Withheld	--	300	0.00026
V5	Withheld	--	306	0.00025
V6	Withheld	--	335	0.00012

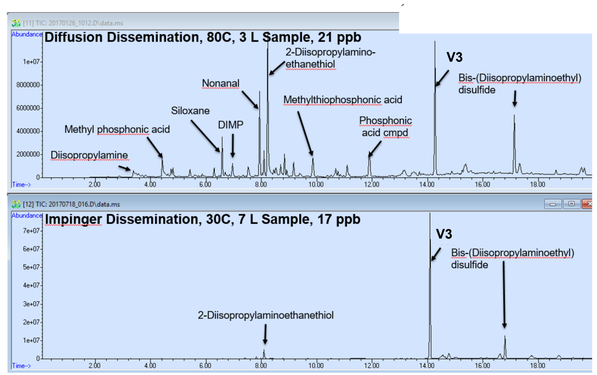
* Predicted values

V3 Dissemination

Method	Temp (C)	ng/L	ppb
Diffusion	75	121	11
Diffusion	80	227	21
Diffusion	80	381	34
Advanced	30	81	7
Advanced	30	737	67
Advanced	30	1548	140

- Data shows the ability to get higher concentrations at lower temperatures using the advanced cell.
- V3 with diffusion is generally tested at 75-80° C, and several degradation products are observed. The advanced data is collected at lower temperatures, and significantly reduces degradation

V3 TD-GCMS Full Scan Data

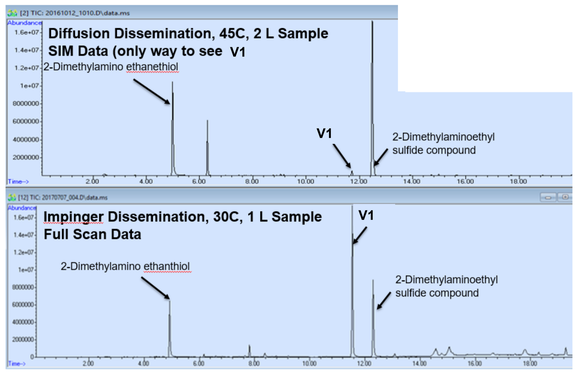


V1 Dissemination

Method	Temp (C)	ng/L	ppb
Diffusion	45	64	5.8
Diffusion	45	97	8.8
Advanced	30	469	54
Advanced	30	1305	149
Advanced	33	2271	260
Advanced	35	4623	618

- Data shows the ability to get higher concentrations at lower temperatures using the advanced cell.
- V1 was originally tested at 45° C, and only seen using extremely sensitive monitoring techniques.. Minor degradation products were seen in the advanced data, at a much lower relative concentration

V1 TD-GCMS Data



V5 Dissemination

Method	Temp (C)	ng/L	ppb
Diffusion	45	16	1
Diffusion	60	14	1
Diffusion	70	19	2
Diffusion	80	22	2
Advanced	25	258	23
Advanced	30	649	59
Advanced	30	1559	141

- Data shows the ability to get higher V5 concentrations than ever witnessed by diffusion.
- V5 vapor by diffusion is typically generated at 60-80° C, with several degradation products present. The advanced vapor is generated at much lower temperatures, with less degradation observed.

Advanced Vapor Generation Summary

Chemical Agent	Temp (C)	ng/L	ppb
V3	30	81	7
		737	67
		1548	140
V1	30	469	54
		1305	149
	33	2271	260
	35	4623	618
V5	25	258	23
	30	649	59
		1559	141
V4	45	3683	333
A1	40	987	122
A2	40	116	14.6
A3	40	161	18.3
V2	49	8291	837
V6	36	1260	108

Concentration Verification

Vapor verification samples were collected by pulling a known volume of the generated vapor stream onto a 10 mm sorbent tube (Markes International, Tenax TA) using a vacuum pump. The tubes were desorbed onto a CWA cold trap using the Markes TD100, and then desorbed and analyzed by GC/MS. TD-GC/MS samples were analyzed on an Agilent 6890N GC and 5975B MS with a Restek RTX-1701, 30m x 250 µm x 1.00 µm column with a split less method. Multi-point calibration curves with R^2 values >0.98 were used for quantitation.

Conclusions

Advanced Vapor Generation Benefits:

- Lower temperatures achieve higher targeted vapor concentrations
- Lower temperatures produce cleaner vapor streams for analytical testing
- Higher concentration vapor streams confirmed vs using traditional diffusion generation
- High-fidelity library creation for new and emerging sensor technologies
- Potential method to characterize degraded vapor streams.

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