Improved Analysis Time and Optimized Sensitivity for EPA Semi-Volatile Methods

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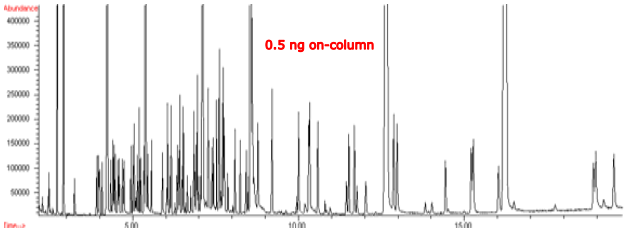
Abstract

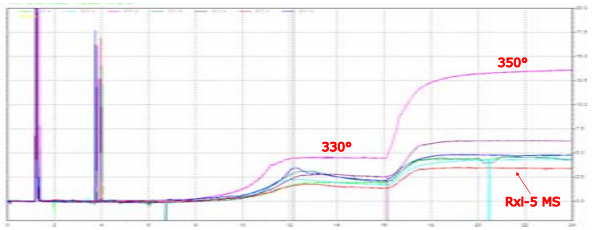
Mass Spectroscopy (MS) is the most common detection system used for Semi-Volatile Organic Analysis (SVOA). The MS provides unique spectral information for accurately identifying components eluting from the capillary column. Several emerging contaminants have required lower levels of detection. Research data on mammalian toxicity, environmental persistence and ground-water mobility of compounds such as, 1,4-Dioxane and N-Nitrosodimethylamine require lower detection limits for further study. Innovative technology has developed and optimized column-making procedures that assure low bleed and unsurpassed inertness. The scope of these analyses was to determine if the new technology could simplify trace-level analysis with mass spectrometric detection methods.

Column Bleed

Lower background noise (signal to noise ratio), especially from column bleed at elevated temperatures, increases overall sensitivity and lowers detection limits. Lower bleed on the MSD makes mass spectral interpretation and identification easier. Therefore when selecting a column for sensitive detection methods, a low bleed column should be utilized.



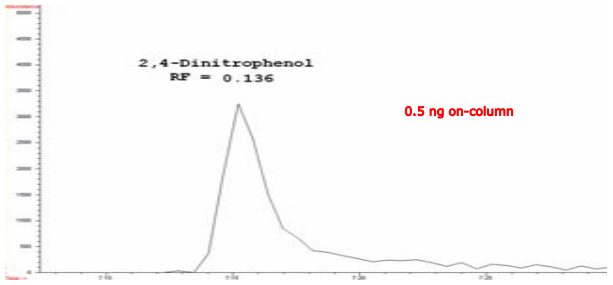
Total Ion Chromatogram of EPA 8270 (93 compounds) on the Rxi-5ms at 0.5 nanogram on column concentration. Low bleed columns allow better sensitivity for late eluting compounds such as the PAHs.



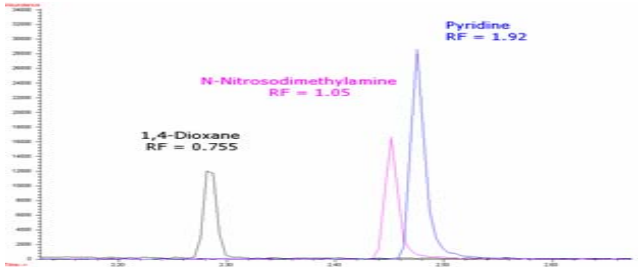
Comparison of various bleed profiles from 30 m x 0.25mm x 0.25µm columns obtained at 135°C starting temperature and at 330°C & 350°C. Rxi-5ms is shown in red. Reference peak is 1ng Tridecane.

Column Inertness

Surface activity in a column is often revealed by the response and peak shape for active analytes such as 2,4-Dinitrophenol and Pyridine. Sub-nanogram quantities of these compounds are a stringent test of column inertness. Below is an Ion Extracted Chromatogram of 2,4-Dinitrophenol at 0.5 ng on column concentration. The limiting factor in this case appears top be related to the injection port.



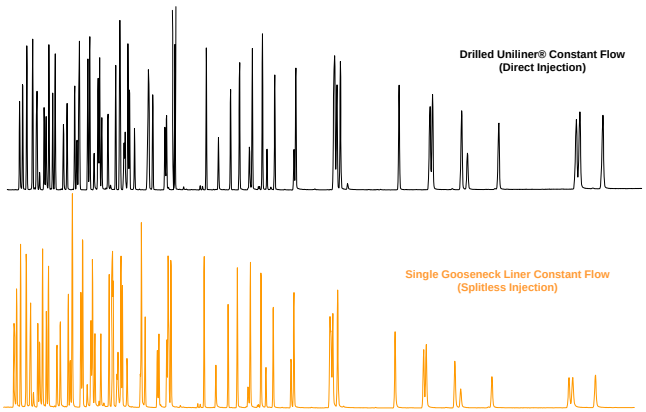
Column Inertness



Ion Extracted Chromatogram of 1,4-Dioxane, NDMA, and Pyridine at 0.5 ng on column concentration.

Sample Transfer

The function of the injection port liner is to shield target compounds from the metal surfaces of the injection port and allow volume for the vaporization of the injected solvent and target compounds. The liner aids in directing compounds to the column. Typical split injections allow for good sample transfer onto the column and the removal of unwanted solvent however there is often some interaction with active metal surfaces during the vaporization phase leading to increased activity. Other drawbacks are discrimination of the late eluting compounds and the possible lose of trace concentration analytes. A splitless injection technique with a drilled Uniliner showed decreased discrimination of late eluting compounds without the usual disadvantages such as increased thermal degradation due to extended dwell times in typical splitless injections. Also, due to nearly complete sample transfer on to the column the loss of trace level compounds can be avoided.



Instrument Test Conditions

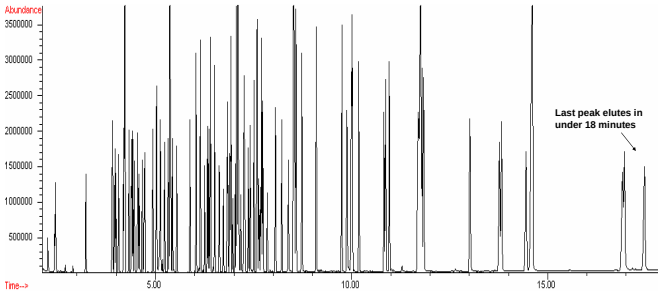
Care was taken when determining carrier gas flow rates for the GC/MS system. The GCMS system is under vacuum and if the flows are set too high sensitivity is compromised. A general rule for typical bench-top MS systems is 1.0 ml/min plus or minus 0.2 ml/min. Also, of concern are the resolutions of compounds with similar quantitation ions. The goal is to reduce the overall analysis time yet still maintain good peak shape and resolution while meeting the method criteria.

Calibration
5, 10, 25, 50, 80 and 100 µg/mL standards
40 µg/mL internal standard concentration

Instrument Conditions
Column: Rxi-5 MS (30m x 0.25mm, 0.25 µm film)
Carrier gas: 1.2 mL/min Helium constant flow
Injection port temperature: 250 °C w/ Drilled Uniliner
Splitless Injection: 1 µL; 0.1min splitless hold
MS transfer temperature: 280 °C
Temperature program: 40 °C (0.5 min), 25 °C /min to 245 °C (0 min), 6C/min to 330 °C (5 min)

Analyses performed on HP6890 w/5973 MS

EPA 8270 TIC



Total Ion Chromatogram of 93 EPA 8270 compounds at 10 µg/mL (10ng on column).

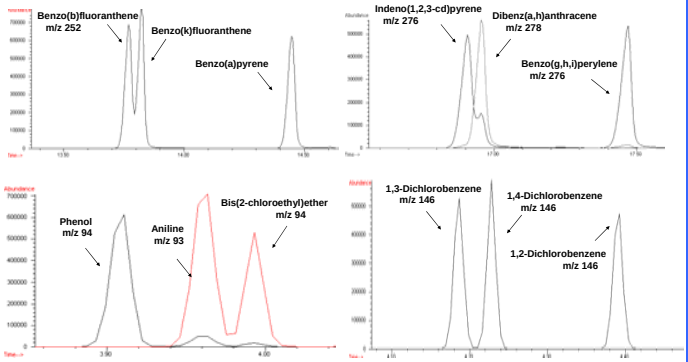
SPCCs	5	10	25	50	80	100	AVG
N-nitroso-di-n-propylamine	1.113	1.128	0.968	1.059	1.115	0.965	1.058
hexachlorocyclopentadiene	0.187	0.188	0.179	0.213	0.242	0.213	0.204
2,4-dinitrophenol	0.151	0.205	0.185	0.230	0.239	0.226	0.206
4-nitrophenol	0.251	0.311	0.269	0.318	0.350	0.300	0.300

Average Response Factor information for EPA 8270 SPCCs. The minimum acceptable average RF for these compounds is 0.05.

Percent Relative Standard Deviation (%RSD) information for EPA 8270 CCCs. Analytes were analyzed at 6 points and no points across the calibration range listed were dropped.

CCCs	5	10	25	50	80	100	%RSD
Acenaphthene	1.327	1.341	1.206	1.128	1.171	1.102	8.31
1,4-Dichlorobenzene	1.533	1.564	1.453	1.478	1.501	1.403	3.87
Hexachlorobutadiene	0.177	0.180	0.173	0.180	0.189	0.173	3.32
Diphenylamine	1.350	1.283	1.173	1.255	1.306	1.186	5.30
Di-n-octyl phthalate	1.488	1.629	1.583	1.673	1.750	1.573	5.58
Fluoranthene	1.343	1.410	1.274	1.297	1.427	1.264	5.21
Benzo(a)pyrene	1.179	1.215	1.171	1.208	1.318	1.176	4.57
4-Chloro-3-methylphenol	0.346	0.357	0.328	0.354	0.383	0.330	5.76
2,4-Dichlorophenol	1.174	1.194	1.010	1.076	1.148	1.021	7.17
2-Nitrophenol	0.799	0.844	0.723	0.772	0.816	0.735	6.01
Phenol	1.777	1.907	1.704	1.836	1.849	1.707	4.55
Pentachlorophenol	0.232	0.245	0.219	0.260	0.306	0.265	12.04
2,4,6-Trichlorophenol	0.237	0.234	0.220	0.242	0.257	0.222	5.81

Separation of Critical Pairs



Conclusion

These analyses demonstrated that a Drilled Uniliner results in a more inert sample pathway and significantly reduces injection port discrimination. Utilization of a thin film Rxi-5 MS column helps reduce column bleed and the inert nature of the column should lead to more sensitive detection limits. The sub-18 minute analysis times for EPA 8270 were achieved while maintaining excellent peak shapes and good resolution of critical pairs. The shorter analysis time was also achieved while maintaining EPA 8270 method criteria. Even shorter analysis times may be achievable with 0.18mm ID columns by combining these two unique items.