

Naphthalene in Ambient Air by GC/MS-MS Detection

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INTRODUCTION

As the most abundant poly-aromatic hydrocarbon in earth's atmosphere, many agencies are interested in quantifying naphthalene concentrations in ambient air. Naphthalene is classified as a Hazardous Air Pollutant (HAP) by the Environmental Protection Agency (EPA)¹ and identified as a human carcinogen. In 2005, the California Office of Environmental Health Hazard Assessment (OEHHA) adopted a Chronic Reference Exposure Level (CREL) for naphthalene of 9 µg/m³ (1.72 ppbV)². Some states, including Minnesota,³ currently require routine analysis of naphthalene in ambient air and soil gas samples.

Standard methods to measure naphthalene in air include sample collection on cartridges or tubes containing poly-urethane foam (PUF) or XAD resins, with subsequent extraction prior to analysis by either HPLC⁴ or GC/MS⁵. These methods are appropriate for semi-volatile compounds and often require a large volume of air to be sampled for the required sensitivity. Atmospheric naphthalene has also been measured by laser-induced fluorescence⁶ resulting in a linear signal over the calibration range of 5 to 80 ppbv.⁷ While this technique is more direct and avoids the extraction steps of other methods, it may not be useful for samples when a range of volatile compounds is of interest.

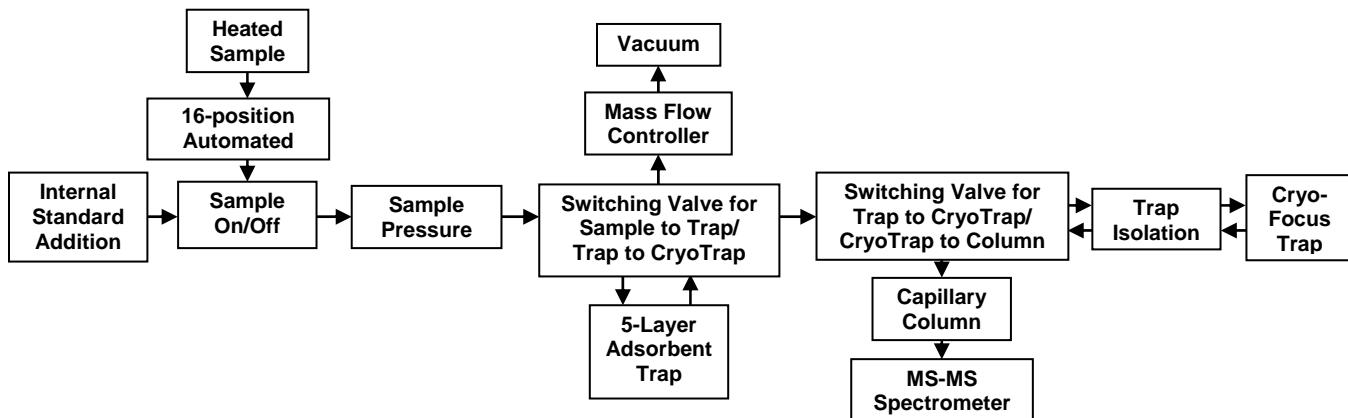
EPA Method TO-15⁸ specifies sample collection with Summa™-style canisters. This approach is attractive because it alleviates time-consuming sample preparation, as the sample is directly loaded in the analyzer without any pretreatment. And other target volatile compounds are measured, along with naphthalene, within the same run.

Mass spectrometry analysis for naphthalene is severely impacted by significant background signals generated from column bleed and sample contaminants that usually distort the target mass spectrum, especially at low concentrations. Naphthalene does not fragment much under normal ionization processes in the mass spec, with the parent ion 128 m/z being very dominant. Even performing Selected Ion Storage or Single Ion Monitoring does not enhance performance much, as backgrounds usually generate significant amounts of 128 m/z not attributable to naphthalene. MS-MS with an ion trap mass spectrometer is perfect for measuring naphthalene. First it ionizes naphthalene and other column coelutors. Then the trap holds onto all ions of mass 128 and ejects out away from the electron multiplier all others. Then the 128 ions are ionized again with enough current to generate daughter ions that become very specific to naphthalene, with daughter ion at 102 m/z being principal. This ion is then employed as the quant ion for naphthalene. The process involves the logical "and" - the target compound must first generate ions at 128 m/z, **AND** then yield ions at 102 m/z. All others are not detected. Background noise is dramatically reduced, greatly enhancing detection of naphthalene.

EXPERIMENTAL METHODS

The analytical system employed follows the block diagram in Figure 1 and is based on the Varian 240 Ion Trap Mass Spectrometer (Varian, Inc. Walnut Creek, Ca). The valving system is designed and assembled by Lotus Consulting (Long Beach, CA). Air samples are introduced through heated gas sampling lines using a 16-position automated sampler and trapped onto a low-volume, multi-bed adsorbent trap with a mass flow controller setting the sample size. Internal standard is also added to the adsorbent trap through a sample loop.

Figure 1. Block Diagram of Ultra Trace Toxics System



The trapped analytes are then desorbed and transferred to a cryo-focus trap to reduce the effective volume, prior to introduction to a Varian CP-Select 624 column (60m x 0.25mm ID, 1.4 μm film thickness) in a temperature-programmed Varian 450 Gas Chromatograph for separation. Three electronic flow controllers regulate helium carrier gas flow to the column, helium purge of the adsorbent trap, and air purge through the sample loop used for the screening analysis of samples prior to TO-15 analysis by a Flame Ionization Detector (FID). A digital flow controller is used to purge nitrogen through the tubing used to bring the sample to the adsorbent trap and the internal standard loop whenever sample is not being loaded. The nitrogen flow also purges the concentrator sample lines as the internal standard is transferred to the adsorbent trap. The column effluent flows through a transfer line assembly at elevated temperature into a Varian 240 Ion Trap mass spectrometer.

The Varian 240 was upgraded to full MS-MS capability by installation of a hardware key to activate MS-MS. The precursor ion is set to 128 m/z, with a “resonant” wave form option selected. The excitation amplitude is determined through Automated Method Development where a test run is made with test amplitudes selected. The optimum choice is when the 128 precursor ion nearly disappears in the spectrum, yielding the optimum signal for the 102 m/z quant ion. An amplitude setting of 1.25 volts is the result for conditions used. The switch between full scan and MS-MS is time-programmed to occur at 55 minutes, just after elution of hexachlorobutadiene and before elution of naphthalene.

A naphthalene gas standard at approximately 1000 ppbV was custom blended with a standard TO-15 mix (Spectra Gases, Branchburg, NJ) and is used to prepare calibration standards by serial dilution into stainless steel canisters using pressure. The naphthalene starting material had been dissolved in bromoform, resulting in an elevated concentration for this target from normal levels.

RESULTS AND DISCUSSION

Selectivity of MS-MS for Naphthalene

Figures 2-5 illustrate the process for selecting naphthalene in a complex chromatogram with variable backgrounds from column bleed and sample contaminants. When all ions are included in the chromatogram, every species within the scan range are displayed, as in Figure 2. When a single ion (128 m/z) is chosen, naphthalene becomes quite apparent at 55.2 minutes, but so

Figure 1. Reconstructed Ion Chromatogram of Late Eluting Analytes, ~100 ppbV

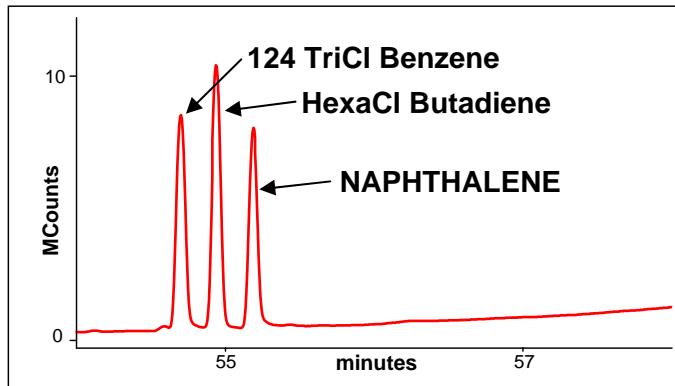
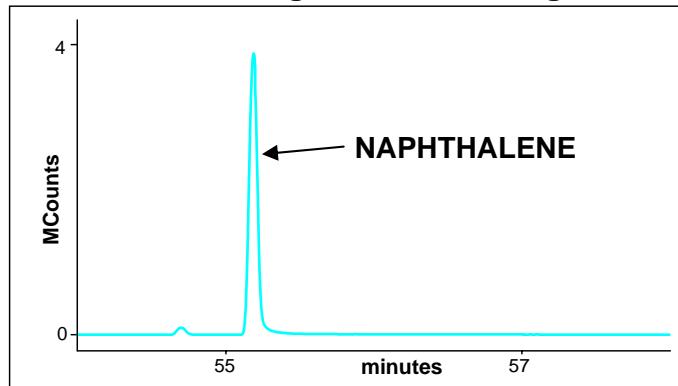


Figure 3. 128 m/z Chromatogram from RIC, akin to Single Ion Monitoring



can other unrelated ions. By processing the column effluent into the ion trap set to perform MS-MS at the precursor ion of 128 m/z (the dominant molecular ion for naphthalene), and then look for ions within the range of $58\text{-}128\text{ m/z}$, the target peak becomes quite selective to only naphthalene (Figure 4). By narrowing into just the major daughter ion at 102 m/z , only naphthalene is seen because only molecules that have ions at 128 m/z , and then break apart into ions at 102 m/z , are detected (Figure 5).

Figure 4. Reconstructed Ion Chromatograms for Full Scan and MS-MS

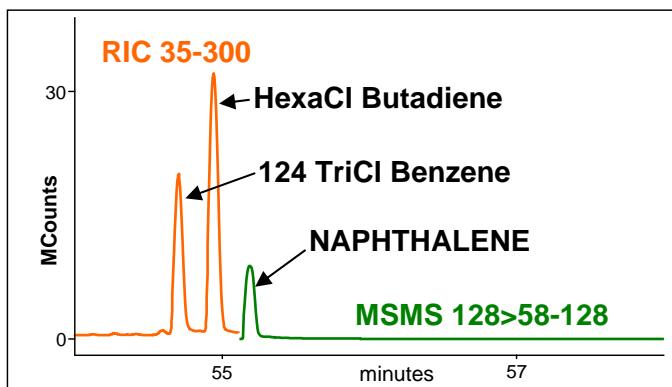
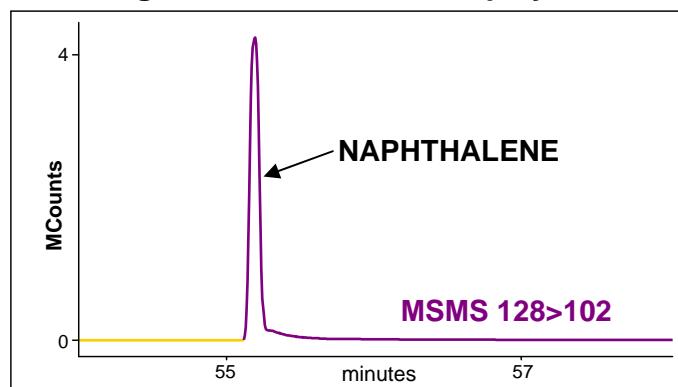


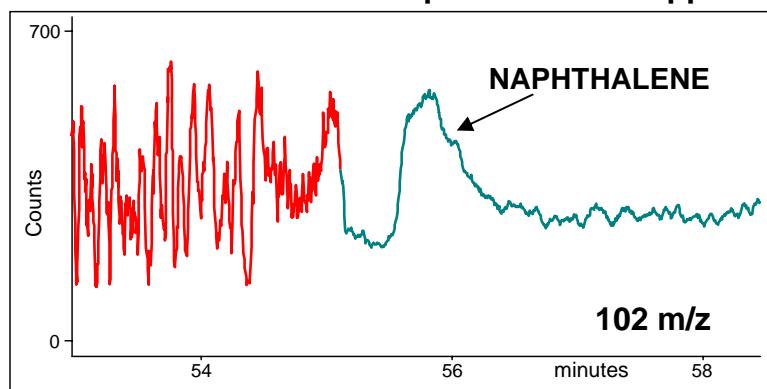
Figure 5. Ion 102 m/z displayed



Sensitivity of MS-MS to Naphthalene

The MS-MS process of selective detection for naphthalene also significantly reduces noise around the eluting peak, as nearly all interferences are fully eliminated in the ion trap prior to the multiplier. The major change in noise allows significantly lower detection limits to be achieved readily. Figure 6 illustrates the signal-to-noise enhancement for a 0.01 ppb V standard with MS-MS in **BLUE**, especially when compared with noise during normal MS operations shown in **RED**.

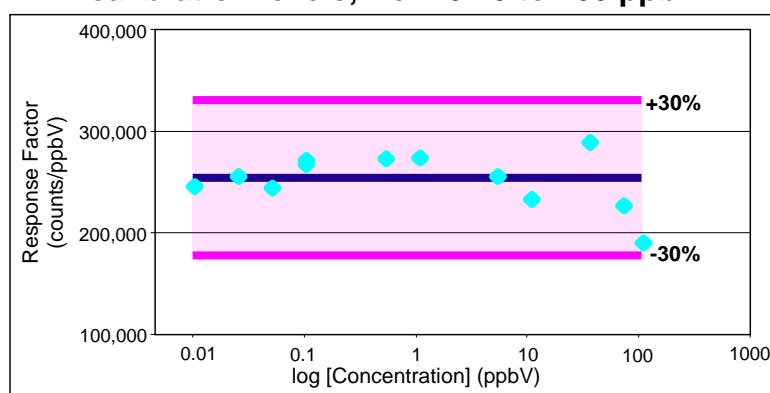
Figure 6. Dramatic Change in Noise between Normal MS and MS-MS Operations - 0.01 ppbV



Linear Range

The enhanced sensitivity performance of the Varian 240 MS results from a change in the geometry of the trapping field dipole of the ion trap so that it delivers 100% of the ions in the trap to the electron multiplier. The expanded capacity of the ion trap, so that interactions between ions are significantly reduced, results in a greatly extended linear range. Figure 7 demonstrates a linear range, with EPA guidelines of $\pm 30\%$, from 0.01 to 100 ppbV, or 4 orders of magnitude.

Figure 7. Response Factor versus log [Concentration] for 11 calibration levels, from 0.10 to 100 ppbV



Method Detection Limit

The enhanced sensitivity through MS-MS directly translates into an achievement of very low detection limits. Table 1 lists raw data from consecutive runs of a 0.004 ppbV standard and the computation employed to generate a method detection limit of 8.5 pptV (0.0085 ppbV) for naphthalene.

Table 1. Detection Limit Calculation for Naphthalene

| <u>Area Counts</u> | <u>Area Counts</u> |
|--------------------|--------------------|
| 9561 | 11711 |
| 9913 | 9853 |
| 9844 | 9558 |
| 10015 | 9500 |

$$LOD = \frac{t * s}{m} = \frac{3 * 719}{254462} = 0.0085 \text{ ppbV}$$

where m = average response factor

t = t-factor for 99% confidence level; 3 for >7 replicates

s = standard deviation of at least five replicates

Typical Example of Ambient Air

A positive hit for naphthalene in ambient air is shown in Figures 8 and 9. Chromatograms are generated with a sample loading of 300 ml.

Figure 8. MS-MS Chromatogram at 102 m/z for ambient sample at 1.12 ppbV

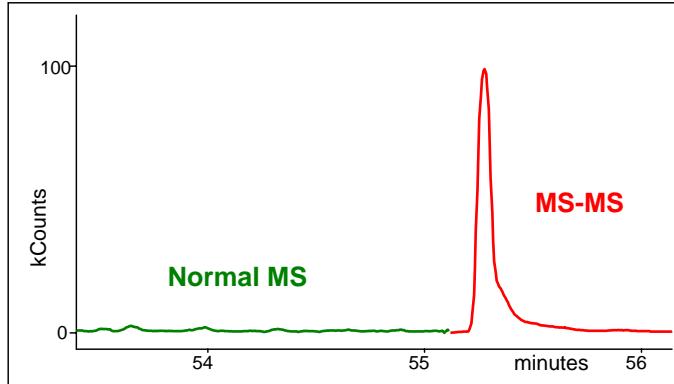
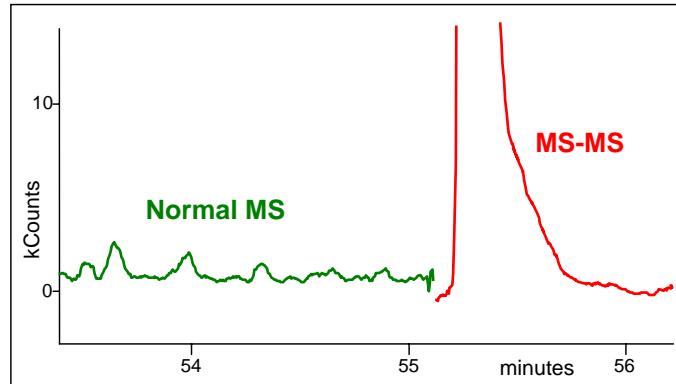


Figure 9. Expanded Scale of Figure 8



SUMMARY

The selectivity and sensitivity gains achieved with MS-MS significantly enhance the performance for measuring naphthalene in ambient air, especially at very low levels. An extremely wide linear calibration range offers high sensitivity with a method detection limit for naphthalene at 8.5 pptV, while being capable of analyzing compound concentrations up to 100 ppbV without diluting samples or changing instrument operating conditions. Sample throughput is improved by the ability to avoid reruns due to samples being outside a narrower operating range. And since this method is “whole air” sample processing direct into the Ultra Trace Toxics System, sample preparation for analysis is minimal. Full rejection of ions, other than naphthalene, that coelute with this target ensures that proper quantitation is achieved without inclusion of these interferences that could yield a wrong, elevated result. And this measurement can be performed simultaneously with normal TO-15 analyses.

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