

**Performance of the
Varian 240 Ion Trap Mass Spectrometer
in the Measurement of Volatile Organic Compounds
by EPA Method TO-15**

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INTRODUCTION

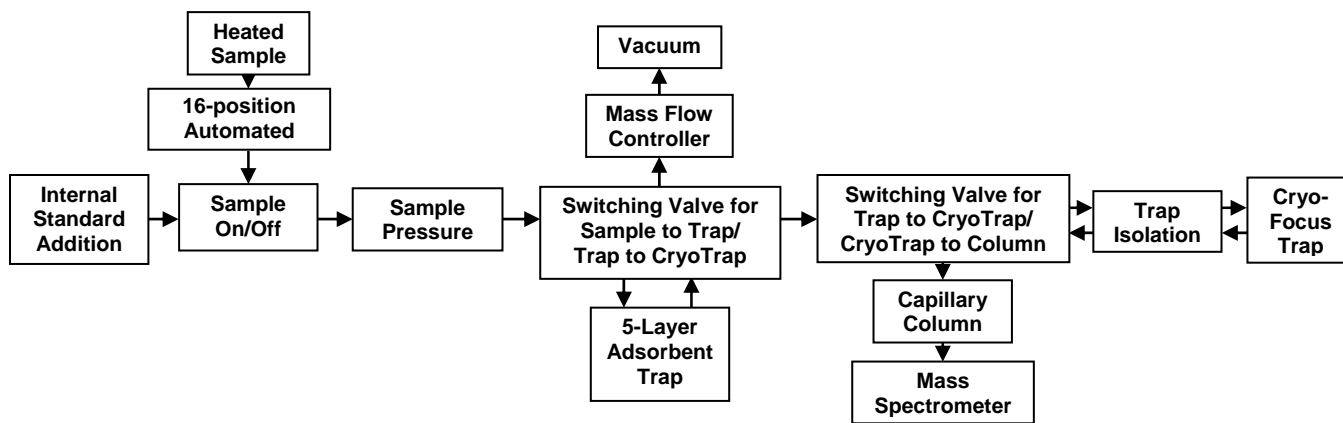
EPA Method TO-15 for the analysis of volatile organic compounds in air collected using stainless steel canisters requires detection by mass spectrometry, using either a linear quadrupole or an ion trap analyzer.¹ The linear quadrupole instrument acts as a mass filter. As electric fields are varied, ions over a range of masses individually proceed to the detector, while others are lost. While linear quadrupole mass spectrometers are more commonly used for the TO-15 application, the ion trap mass spectrometer is significantly more sensitive because mass fragments are formed, ionized and separated in the same location prior to being counted, resulting in minimal losses. Historically, ion trap technology posed challenges such as space-charge effects. Ions contained in the trap travel in stable trajectories prior to exiting to an electron multiplier unless too many ions are present, in which case electrostatic interactions between the charged particles can result in potential losses in mass resolution or mass shifts. In addition, due to proton transfer reactions affecting fragment ions of lower masses, spectral distortion is a concern with regard to identification of unknowns using mass spectral library databases. Through axial modulation, automatic gain control, and design modifications, modern ion trap instruments have overcome many of these limitations.²

Specifically, the Varian 240 MS (Varian, Inc., Walnut Creek, CA) exhibits greater sensitivity, increased trap capacity, and reduced background over the companion model, the Varian Saturn 220 MS. Combined with the sample concentrator designed by Lotus Consulting and Varian 3800 Gas Chromatograph, the resulting analysis system, the Ultra Trace Toxics System, is capable of measurements over a linear range of 0.025 to 100 ppbV, achieves single digit pptV method detection limits for most of the compounds routinely measured by TO-15, and eliminates carryover of high concentration analytes in subsequent analytical runs. A reduction in degree of spectral distortion has also been observed.

EXPERIMENTAL METHODS

The analytical system employed follows the block diagram in Figure 1. 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) of a temperature-programmed Varian 3800 Gas Chromatograph for separation. Three electronic flow controllers regulate helium carrier gas flow to the column, the helium purge of the adsorbent trap, and the 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 to either a Varian Saturn 220 or a Varian 240 Ion Trap mass spectrometer. The MS acquisition parameters selected, such as the emission current used for ionization and the total number of target ions trapped, minimize possible space charge effects.

A gas standard containing 63 volatile organic compounds at approximately 1000 ppbV (Spectra Gases, Branchburg, NJ) is used to prepare calibration standards by serial dilution into stainless steel canisters using pressure. Data reported follow the requirements of EPA Method TO-15 for mass spectral abundance criteria using bromofluorobenzene, internal standard area responses, precision of relative response factors for calibration curves, and other parameters.

RESULTS AND DISCUSSION

Overall System Performance Comparison

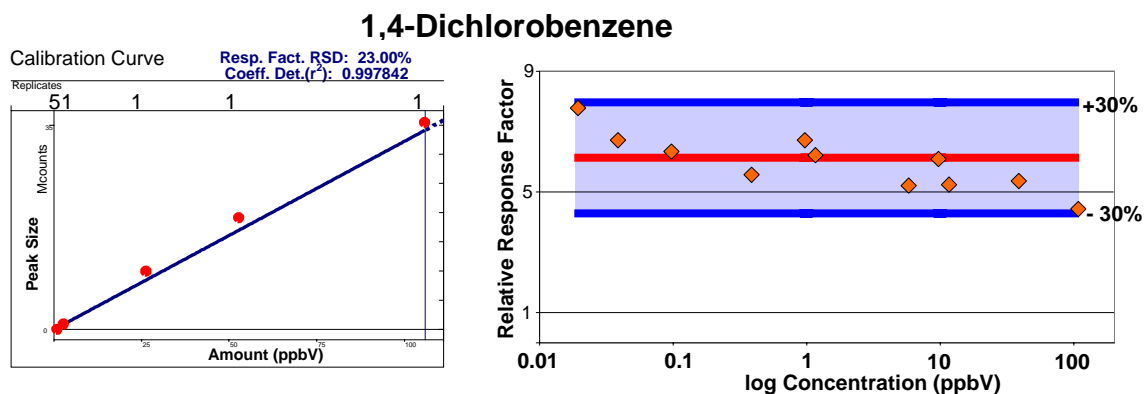
The performance of the Varian Saturn 240 MS is compared to the Varian 220 MS as significant design modifications were made between the two models. These included expanding the capacity of the ion trap so that interactions between ions was significantly reduced resulting in an extended linear range. The Varian Saturn 220 MS exhibits a reproducible linear range from 0.20 to 20 ppbV for virtually all of the 63 compounds studied, whereas the Varian 240 MS calibration range extends from less than 0.025 to 100 ppbV for the majority of compounds. Standards with concentrations down to 0.033 ppbV are tested using the Varian Saturn 220 MS with acceptable results. In order to achieve this level of sensitivity, however, the sample flow rate to the adsorbent trap has to be increased, resulting in a sample volume of 600 mL. This illustrates the enhanced performance of the Varian 240 MS with regard to sensitivity resulting from a change in the geometry of the trapping field dipole of the ion trap that delivers 100% of the ions in the trap to the electron multiplier. Operation of the Varian Saturn 220 MS results in 50% of ions emptying to the electron multiplier. Method detection limits (MDLs) of single digit pptV are typical for the majority of the 63 analytes studied using the Varian 240 MS as indicated in Table 1.

Table 1. TO-15 Analysis Results using Varian Saturn 220 MS versus Varian 240 MS

	Varian Saturn 220 MS	Varian 240 MS
Calibration Range	0.20 – 20 ppbV	0.025 to 100 ppbV
Sample Volume	210 mL	300 mL
Reporting Limits	0.21- 0.55 ppbV	0.025 – 0.054 ppbV (low curve) 0.25 – 0.28 ppbV (high curve)
Selected MDLs:		
Carbon disulfide	0.133 ppbV	0.004 ppbV
Hexane	0.085 ppbV	0.003 ppbV
Benzene	0.056 ppbV	0.003 ppbV
Trichloroethene	0.053 ppbV	0.001 ppbV
Toluene	0.036 ppbV	0.001 ppbV
o-Xylene	0.021 ppbV	0.006 ppbV
1,3,5-Trimethylbenzene	0.038 ppbV	0.004 ppbV

Data obtained using both Varian mass spectrometers meet EPA Method TO-15 performance criteria such as the requirement that the relative standard deviation (RSD) of the relative response factors (RRFs) be less than 30% as illustrated for 1,4-Dichlorobenzene in Figure 2.

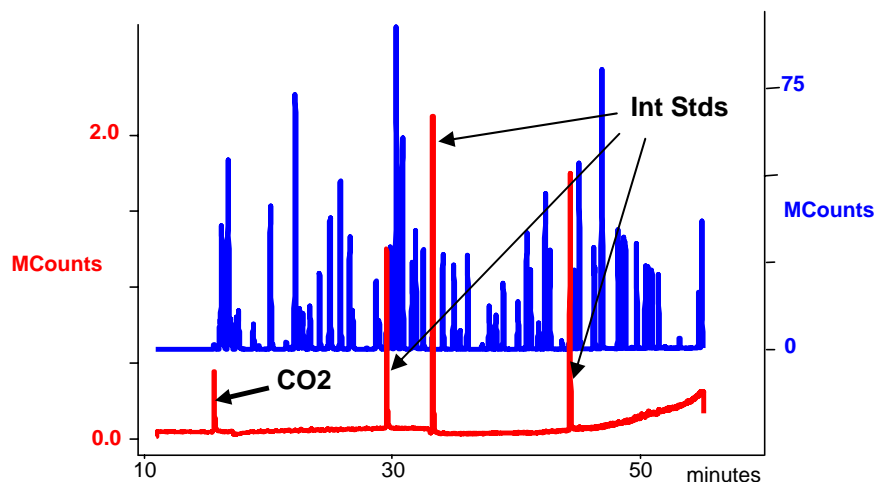
Figure 2. Typical Cartesian Calibration Plot for 9 levels versus Typical Semi-log Plot of RRF for 11 calibration levels over very wide range 0.025 – 100 ppb V/V



Cleanliness of the Analytical System

As high sample throughput is a requirement for many laboratories performing the analysis of volatiles in air, there is a desire to minimize blank runs to remove contamination from the system after the analysis of high concentration samples. Because several sections of the analytical system are constantly purged with either helium or nitrogen when they are not being used for sample loading, carryover from previous samples is effectively eliminated. The reconstructed ion chromatogram for a 100 ppbV standard run just prior to a nitrogen blank is shown in figure 3 to illustrate the cleanliness of the analytical system.

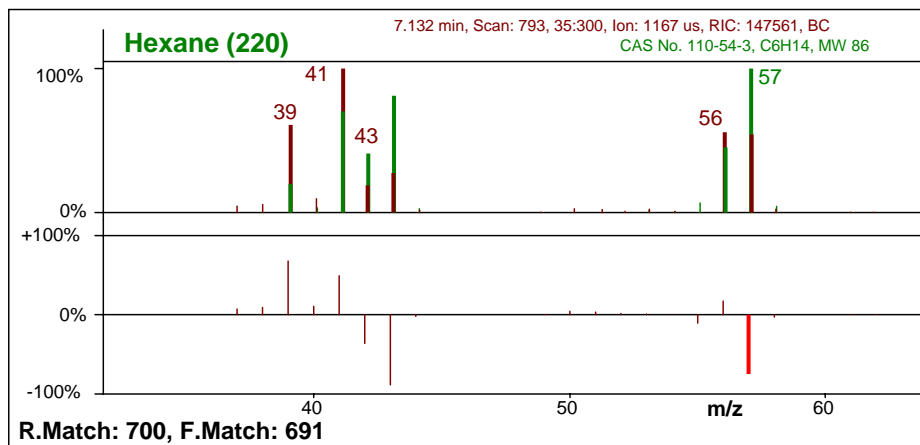
Figure 3. 100 ppbV TO-15 Standard Followed Immediately by a Nitrogen Blank



Reduction of Spectral Distortion

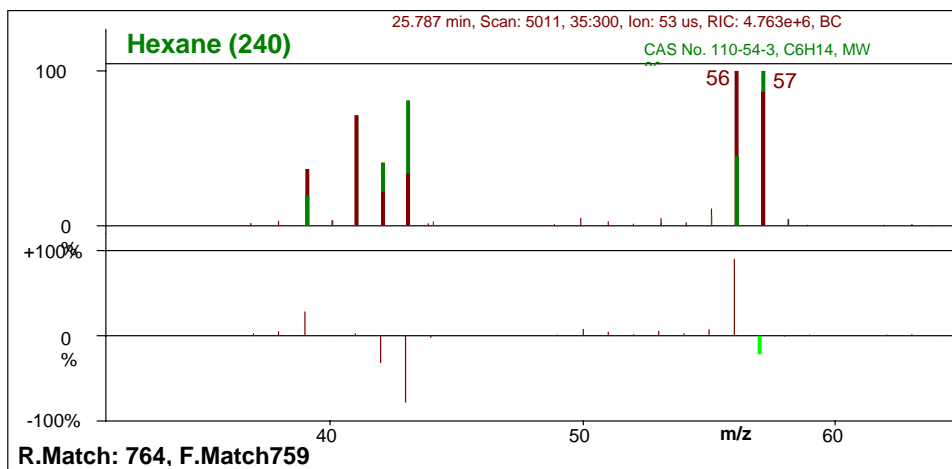
A reduction in spectral distortion is observed when comparing mass spectra generated by the Varian Saturn 220 MS to the Varian 240 MS. This is especially apparent for hydrocarbon compounds that are typically susceptible to proton transfer reactions. The experimental spectrum of hexane from the Varian Saturn 220 MS, along with the difference between the experimental and NIST library spectra is shown in Figure 4. A NIST library search generated a forward match value of 691 and reverse match of 700, with hexane as the 18th most likely identification for the compound. This is compared to the hexane spectrum collected by the

Figure 4. Varian Saturn 220 MS Generated Sample Spectrum for Hexane (brown) compared to NIST library spectrum (green), with the difference between spectra below.



Varian 240 MS shown in Figure 5, which resulted in a forward match value of 764 and reverse match of 759, with hexane being the fifth most likely identification for the compound on a

Figure 5. Varian 240MS Generated Sample Spectrum for Hexane (brown) compared to NIST library spectrum (green), with the difference between spectra below.



NIST library search. Thus, the degree of spectral distortion observed has been reduced in the latest model of ion trap mass spectrometer. This is especially important in the identification of unknown compounds, or tentatively identified compounds. These compounds are not routinely analyzed, and therefore not compared to spectra generated from standards, but their identification is often requested and in some states required as part of the analysis of volatiles in air by TO-15.

SUMMARY

While linear quadrupole mass spectrometers are more commonly used in the analysis of volatile organic compounds by EPA Method TO-15, the Varian 240 Ion Trap mass spectrometer has proven to offer a high level of performance. An extensive linear calibration range offers high sensitivity with method detection limits typically at single digit pptV values with the simultaneous capability to analyze compound concentrations up to 100 ppbV providing a high level of throughput by reducing instrument time for running diluted samples. In addition, system cleanliness following high concentration samples and generation of spectra that can be used for reliable library identification of unknowns illustrate the suitability of the Ultra Trace Toxics System for the analysis of volatile compounds in air.

REFERENCES

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