

Analysis of Method TO-14 Target Analytes Using a Cryofocusing High-Speed Gas Chromatograph Interfaced to a High-Speed Time-of-Flight Mass Spectrometer

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ABSTRACT

A high-speed gas chromatograph coupled with a high-speed time-of-flight mass spectrometer was used to gain a six-fold increase in overall rate of analytical throughput for analysis of EPA Method TO-14 target compounds. Duration of chromatograms was 180 seconds. One hundred mass spectra per second, ranging from 35 to 270 mass units, were collected. Single ion chromatograms were searched at appropriate retention times for chromatographic peaks, which were integrated. Thirty-eight of the forty-one TO-14 target compounds were calibrated using standards at five concentrations from 2.5 to 40 ppb. Four grab samples of ambient air were collected at four different locations at an automobile repair facility, and two grab samples were collected less than one minute apart at a site near a chemical plant, just before and just after passage of three large diesel trucks. All samples were analyzed on the same day they were collected. Most of the duplicate analyses were in close agreement. Ability of the high-speed TOF/GC/MS system to perform analyses of TO-14 target compounds rapidly and precisely was demonstrated.

This paper has been reviewed according to US Environmental Protection Agency peer and administrative review policies and approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

INTRODUCTION

Nonpolar and semipolar organic vapors in ambient air can be effectively analyzed by EPA Method TO-14 (1). Whole air samples are collected in Summa-polished™ canisters which are taken to a laboratory where the contents are analyzed by gas chromatography using a variety of nonspecific and specific detectors, including mass spectrometry. Typical analyses take an hour to run, which limits sample throughput to at most eight per day. Fast gas chromatography (FGC), using narrow injection bandwidth (<100 millisecond) and high carrier flow velocity (100 - 200 cm/sec), can increase the speed of analysis, but specially designed detectors must be used to distinguish such narrow peaks from electrical noise. Mass spectrometers and mass selective detectors, unless operated in single ion mode or over a narrow scan range, scarcely respond quickly enough to serve as detectors for even a conventional capillary GC. Typically they can achieve a maximum of perhaps three full scans per second, which is not enough to characterize the one second wide peaks at the front end of a conventional capillary chromatogram. The advent of high-speed time-of-flight mass spectrometry (TOFMS) offers a way to overcome the limitations of conventional GC detectors, and it opens the possibility of much faster GC analyses. Holland and coworkers have designed a high speed TOFMS that can acquire and record up to a thousand full mass spectra per second (2). Use of prototype high-speed TOFMS

instruments has been demonstrated for a variety of analytical applications (3,4,5). The following is an account of the use of this method to analyze volatile organic compounds in whole air samples by a procedure analogous to EPA Method TO-14.

EXPERIMENTAL

Calibration standards were prepared by dynamic mixing of humidified zero air with a commercial mixture containing 10 ppm (nominal) in nitrogen of each compound on the TO-14 target list. A metal bellows pump was used to divert part of the diluted stream from a flow manifold into a Summa-polished™ canister in which it was stored. Pressure of the standard mixture in the canister was up to 30 psig. Pumping rate was controlled by a mass flow controller set low enough to preclude backflow of room air into the manifold. Calibration standards were analyzed by a procedure identical to that used for samples. Calibration standards at five different concentrations 2.5, 7.5, 15, 25, and 40 ppb (nominal), were used. The analytical system was calibrated for thirty-eight of the forty-one TO-14 target compounds. Accurate analysis of benzene was forestalled by background contamination, and 1,2,4-trichlorobenzene and hexachlorobutadiene were not quantitatively eluted because the transfer line heater was not properly regulated.

Samples were collected by opening cleaned and evacuated canisters in places where significant concentrations of TO-14 target compounds were expected. The filled canisters were returned to the laboratory where they were pressurized with ultrazero air to approximately 30 psig. Allowance was made for dilution of the sample by pressurization.

Samples were analyzed by connecting the canister to the Chromatofast Cryofocusing unit and opening the valve to permit sample to flow past the inlet through a tee fitting. A flow from the canister of about 30 ml/min was maintained for three minutes while sample was drawn into the Chromatofast unit at a rate of one ml/min. Control of the injection unit and starting data acquisition by the mass spectrometer were controlled by the microprocessor in the chromatograph.

A Varian 3400 Star Fast GC™ equipped with a Chromatofast Cryointegrator™ injection system was connected directly to a prototype Leco FCD-1000™ time-of-flight mass spectrometer. The temperature of the methylsilicone-coated column was programmed from 60 to 180°C at a nominal rate of 35°/minute (32°/minute actual). Initial hold time was 0.2 min, and duration of chromatograms was 180 seconds. One hundred mass spectra per second, ranging from 35 to 270 mass units, were collected. The single ion chromatograms corresponding to the base peaks of TO-14 target list compounds were searched for chromatographic peaks at appropriate retention times. Peaks were integrated on-screen by hand, and peak areas and heights were imported into a Lotus spreadsheet for tabulation and graphical representation. The baseline of each ion chromatogram used in quantitation was sampled over a range of several seconds in a region apparently free of peaks, and the minimum detectable peak height was taken to be three times the standard deviation of the baseline for that chromatogram. Lesser peaks were treated as "below detection limit". Detection limits ranged from 0.13 ppb for Freon 12 to 38.1 ppb for benzyl chloride. Most detection limits were below 5 ppb. Much higher detection limits resulted when there was excessive scatter on the calibration plot. The average of all detection limits was 4.3 ppb. By contrast, Method TO-14, using samples 100 times larger has detection limits of about 0.2 ppb.

RESULTS AND DISCUSSION

Four grab samples of ambient air were collected at different locations in an automobile repair facility. Two samples were also collected less than one minute apart at a site near a chemical plant just before and just after passage of three large diesel trucks. All samples were analyzed the same day they were collected. Figure 1 shows data from a sample collected in the parking lot of the auto repair shop. Four compounds were detected, all at low concentrations. In the service writer's office (Figure 2) and in the shop behind the office (Figure 3) concentrations were substantially higher. Duplicate analyses were run on these samples and good agreement was observed. Concentrations inside the paint locker of the body repair shop where the stench was virtually intolerable were highest of all, even with the exhaust fan in operation (Figure 4).

A sample was taken at the gate of a chemical plant and analyzed in duplicate, again showing close agreement (Figure 5). Immediately after the fifth sample was taken, three large diesel trucks passed the gate, whereupon a sixth sample (the second at the site) was collected within less than a minute. Concentrations of all compounds found in the first sample at that site were larger in the second sample (Figure 6), which suggests that they probably originated from heavy truck traffic in the area rather than from the chemical plant.

CONCLUSIONS

Ability of the high-speed TOF/GC/MS system to perform analyses of TO-14 target compounds rapidly and precisely was demonstrated. Duplicate analyses were generally in close agreement. Sensitivity was about 20 times less than for Method TO-14 using samples 100 times smaller. Since column capacity decreases with increasing flow velocity, it is not possible to increase sample size to that used in Method TO-14. On the other hand, narrow injection bandwidth enhances sensitivity because peaks are taller. The optimum sensitivity of FGC/TOFMS analysis has not yet been realized. Slightly larger sample size with improved technique may result in sensitivity nearly equivalent to Method TO-14. In any case, a useful method for rapid screening and preliminary evaluation of TO-14 samples has been demonstrated.

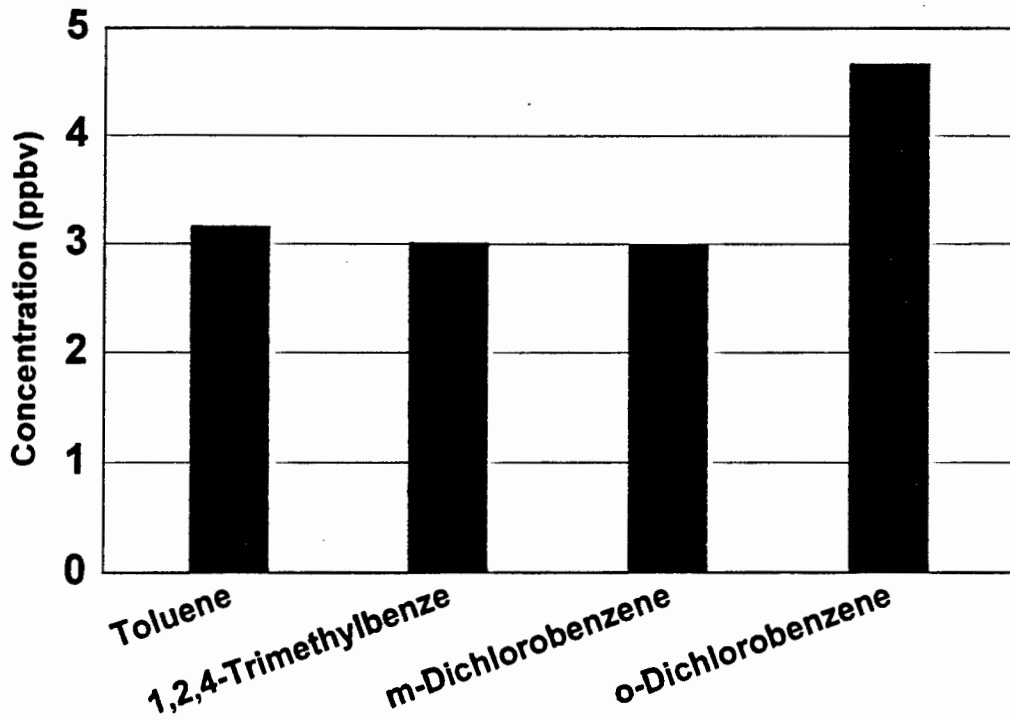
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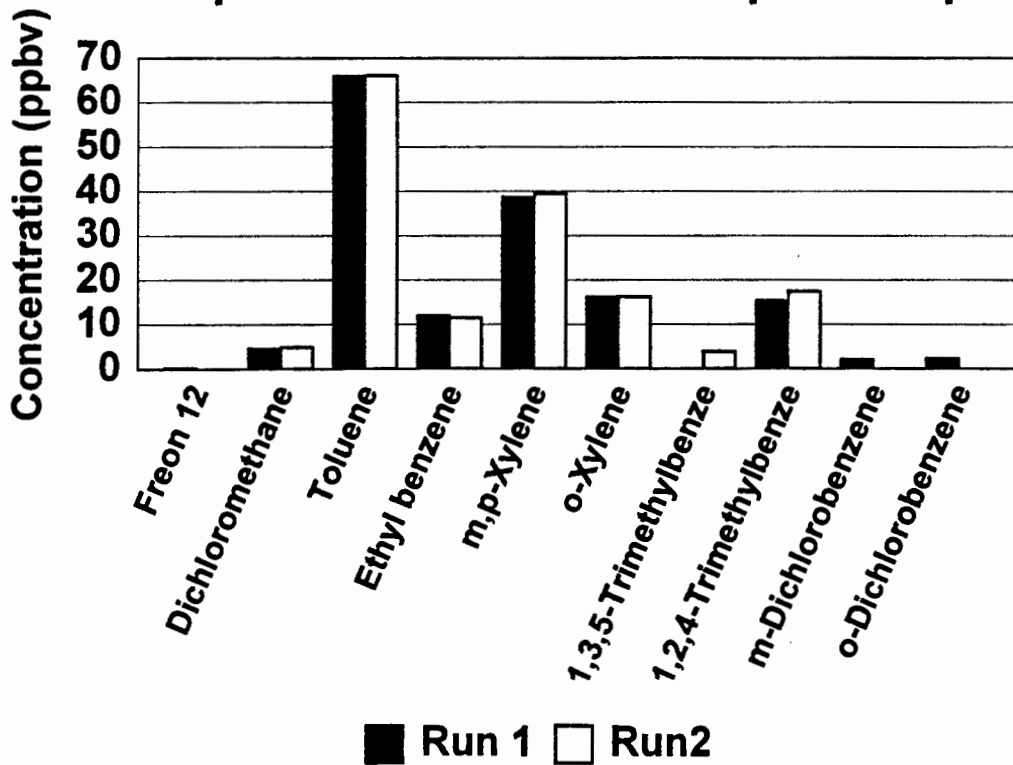
CAPTIONS FOR FIGURES

- Figure 1. Analysis of a sample collected in the parking lot of an automobile repair shop.
- Figure 2. Duplicate analyses of a sample collected in the office of an automobile repair shop.
- Figure 3. Duplicate analyses of a sample collected inside an automobile repair shop.
- Figure 4. Analysis of a sample collected inside the paint locker of an automobile body shop.
- Figure 5. Duplicate analyses of a sample collected at the gate of a chemical plant.
- Figure 6. Samples collected at the gate of a chemical plant just before and just after passage of three diesel trucks.

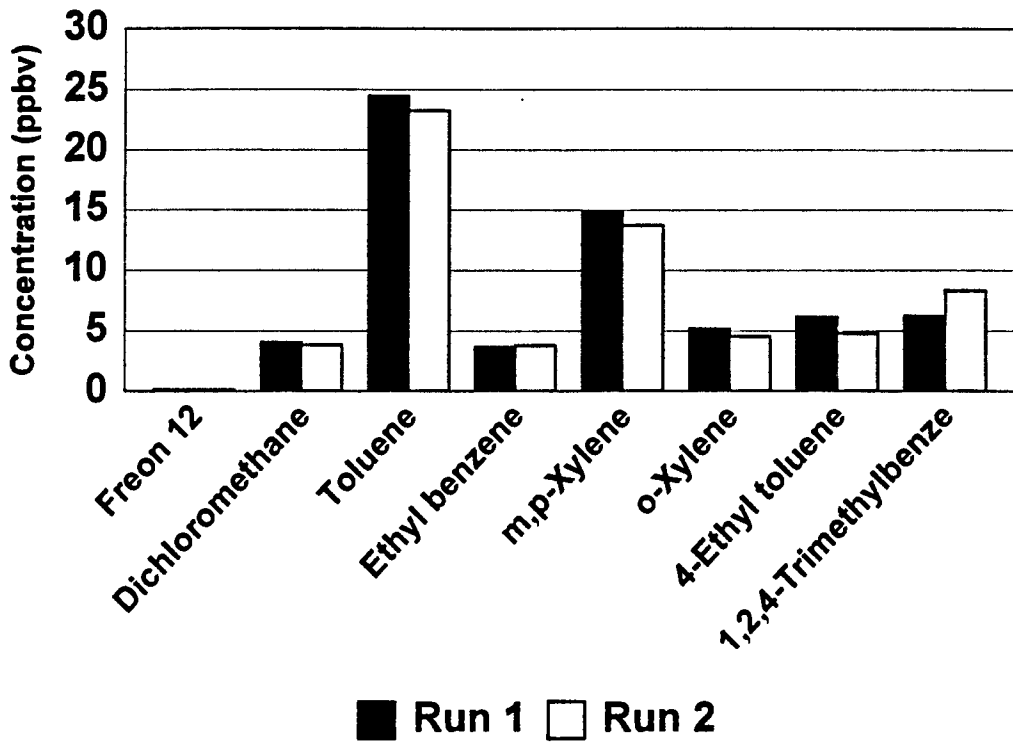
Sample 1 In Parking Lot of Auto Repair Shop



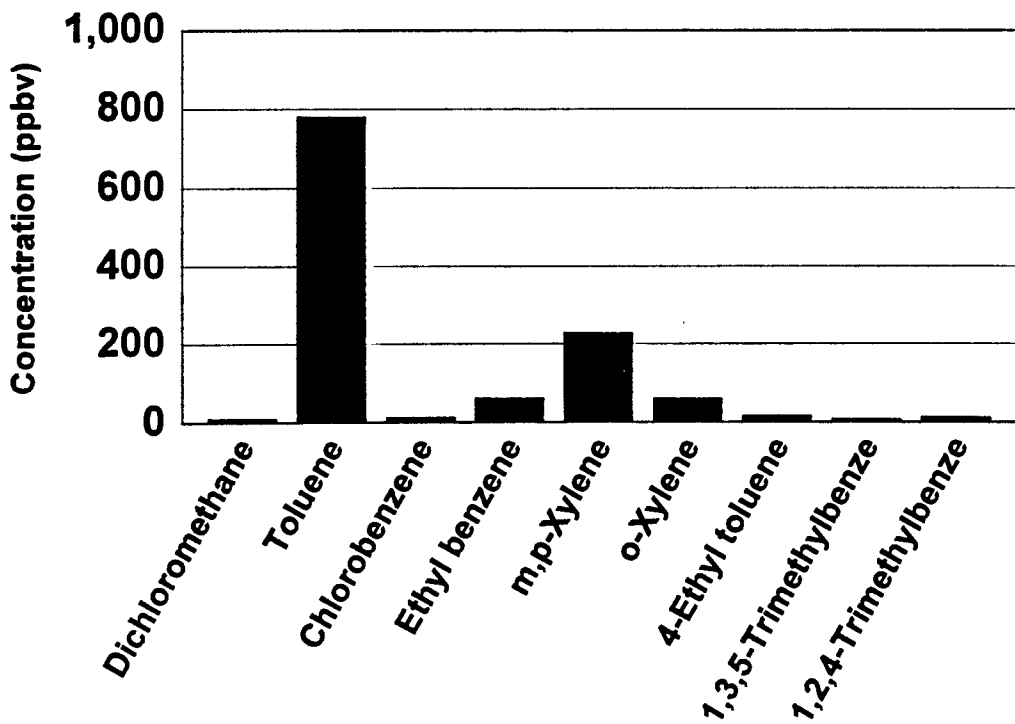
Sample 2 Office of Auto Repair Shop



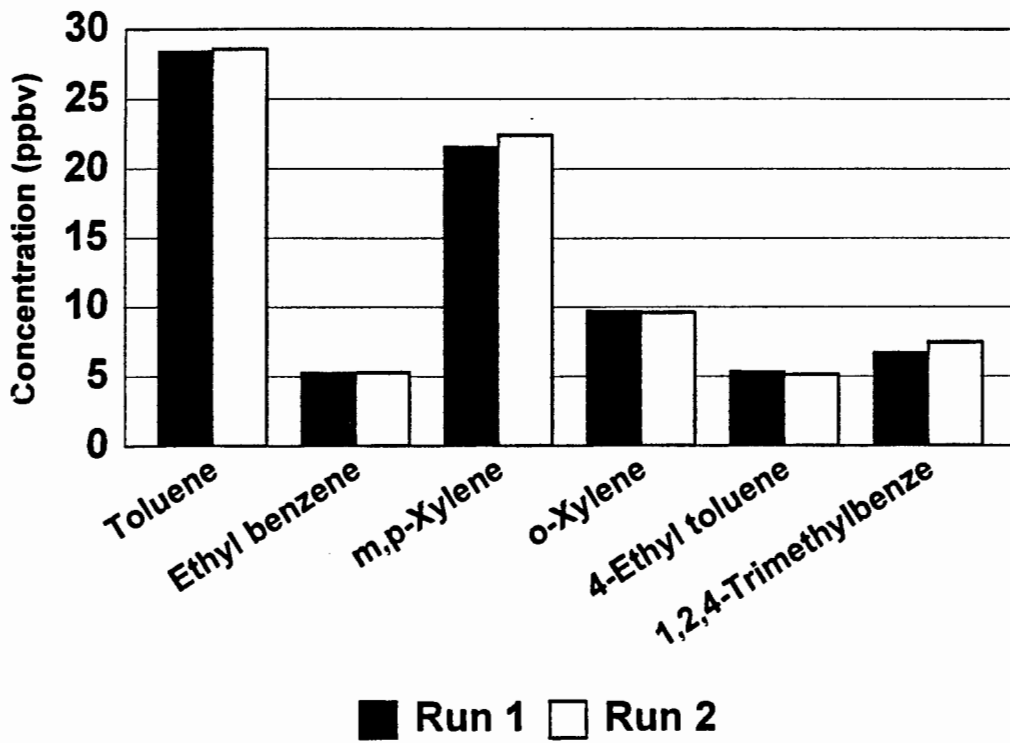
Sample 3 Inside Auto Repair Shop



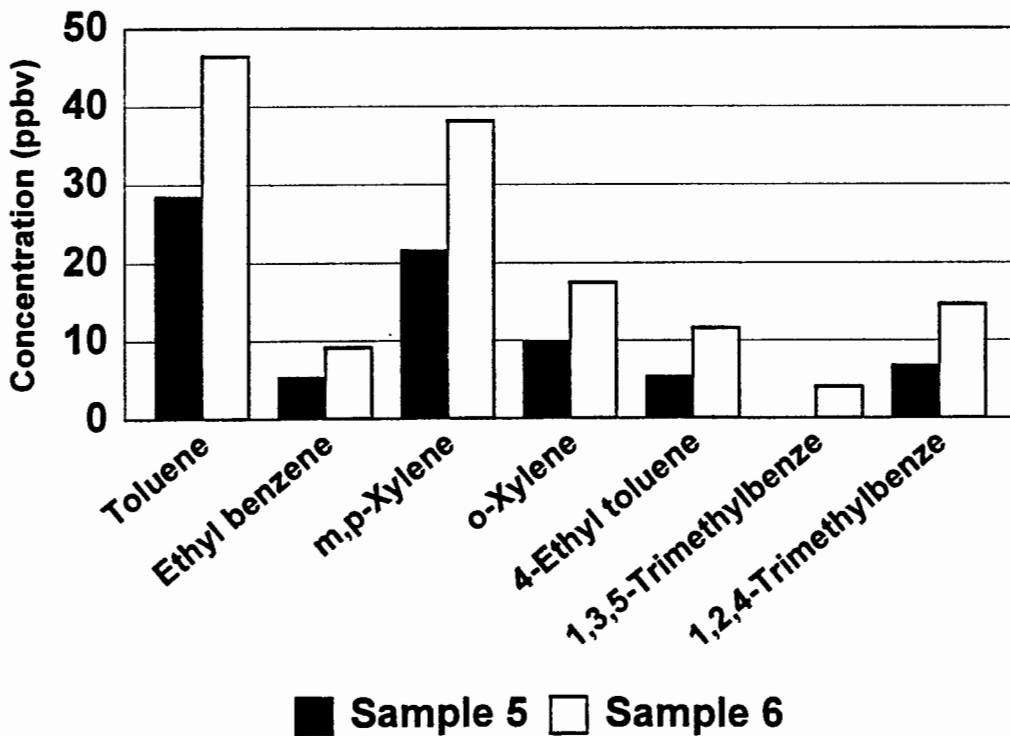
Sample 4 Inside Paint Locker of Auto Body Shop




Sample 5 At Gate of Chemical Plant



Samples 5 & 6 Before and After Trucks



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