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Application

TDTS 15

On-line process control of speciated organic chemicals in industrial gases at sub-ppb levels

Summary

This Application Note describes validation of an on-line thermal desorption–mass spectrometry (TD–MS) system for rapid measurement of sub-ppb levels of VOCs in industrial carbon dioxide.

Introduction

Conventional concentration and analysis technologies – based on thermal desorption with gas chromatography (GC) or GC/MS (GC/MS) – offer compatibility with a very wide range of VOCs. Samples are typically collected in bags or on sorbent tubes, allowing simultaneous measurement of hundreds of compounds.

However, TD–GC/MS is invariably limited to off-line laboratory operation, which requires skilled technicians and has restricted sample throughput due to extended analysis times and data processing requirements.

In contrast, TD–MS systems work on-line, pulling sample gas through a focusing trap before desorption and simultaneous analysis of diagnostic ions for 10 or more compounds using MS. For relatively well-characterised matrices, such as industrial gases, where the number and nature of possible interferents is known, the contributions of each analyte to the selected mass ion(s) of another can be calculated and corrected for.

Markes' TD systems are particularly suitable for TD–MS because of the efficiency of operation. The electrically-cooled focusing trap allows selective concentration of target VOCs, while the subsequent rapid heating (~100 °C/s) transfers analytes to the detector in a narrow band of vapour (< 500 µL).

When the focusing trap has returned to its original temperature, collection of the next sample can begin. Using Markes' Air Server™, a choice of three or eight separate inlets is available, offering automatic interchange between multiple gas streams or between sample, zero and calibrant gas streams. Total sampling–analysis cycle times of 3–4 minutes (Figure 1) facilitate both rapid feedback for process stream monitoring and efficient spot-checking of gas deliveries.

Experimental

The TD–MS system was evaluated by running a conventional laboratory GC system in parallel with the integrated process MS. Samples desorbed from the focusing trap of the on-line concentrator were split between the two measurement systems.

Standard solutions containing low levels of benzene, toluene, *m*-xylene, furan and diethyl ether were prepared in methanol. Small aliquots of each solution were then loaded onto ¼″ stainless steel tubes containing 200 mg of Tenax® sorbent under a flow of nitrogen (flow rate 80 mL/min). The methanol was then purged off over 6–7 min to leave only the compounds of interest. Masses of benzene ranged from 0.2 to 6 ng with corresponding ranges for the masses of other analytes.

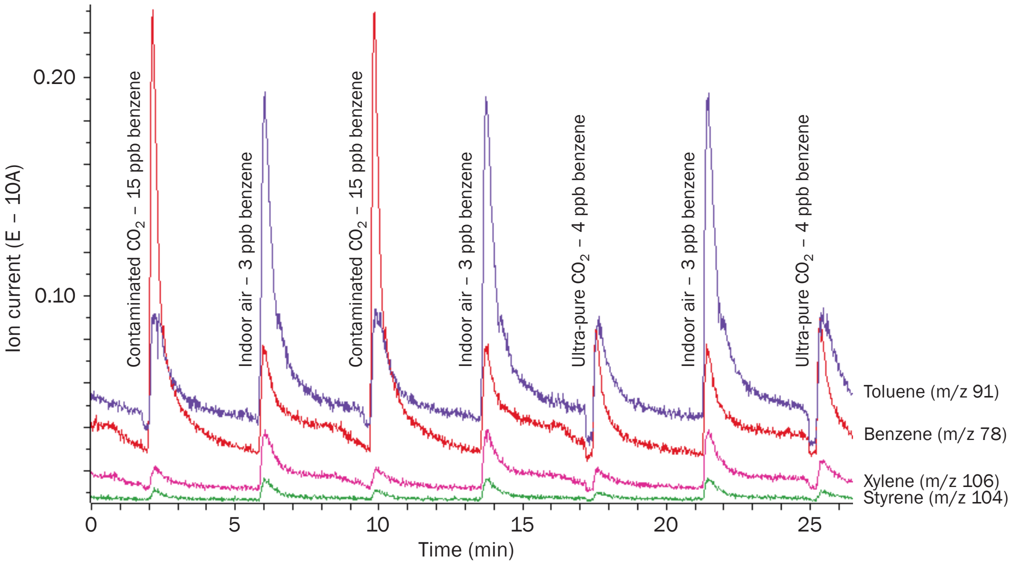

Figure 1: Process measurement of trace-level benzene and other organics in carbon dioxide for the carbonated drinks industry, with a cycle time of *ca.* 4 min.

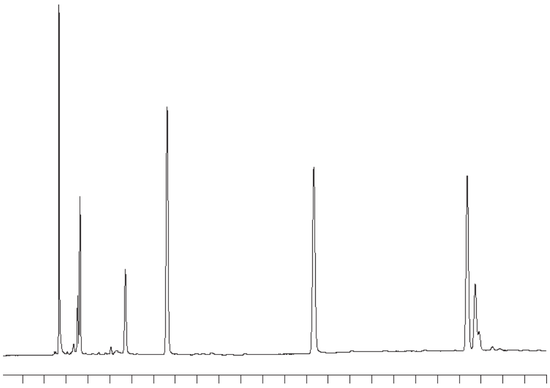

Figure 2: TD–GC/FID chromatogram of standard solution.

Results

Figure 2 shows the TD–GC/FID results for the standard solution, while Figure 3 shows the target ions selected for each component for TD–MS. The ratio of the response from TD–GC/FID to TD–MS remained constant over the concentration range (Figure 4).

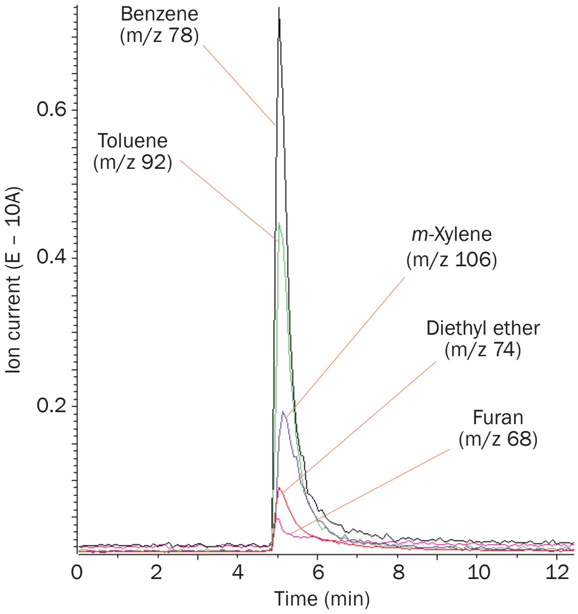

Figure 3: Process MS trace of standard solution.

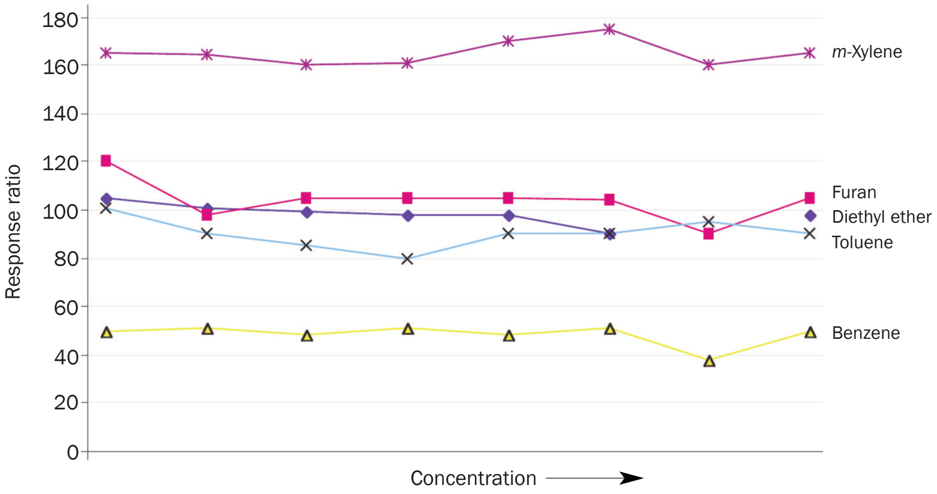

Figure 4: Ratio of response from TD–GC/FID to TD–MS for the standard solution.

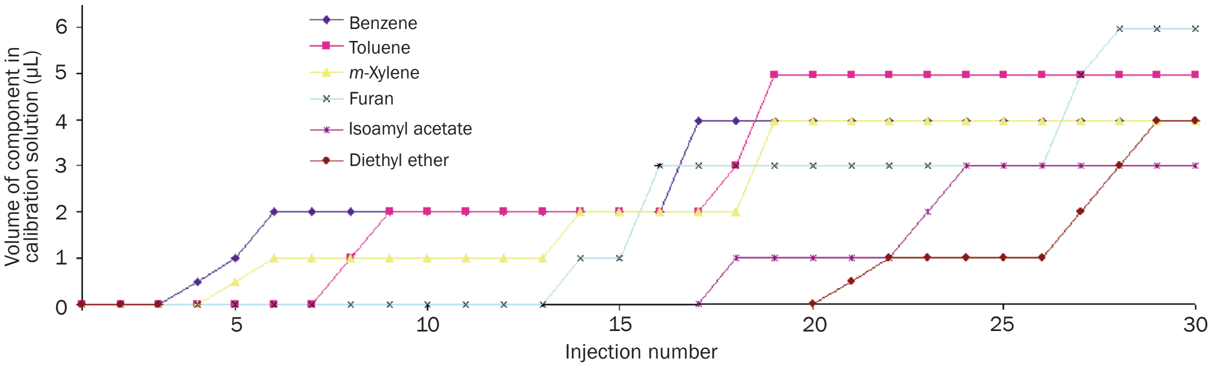

Figure 5: Relative concentration of each component in the standard solution, used to carry out the linearity experiments shown in Figure 6.

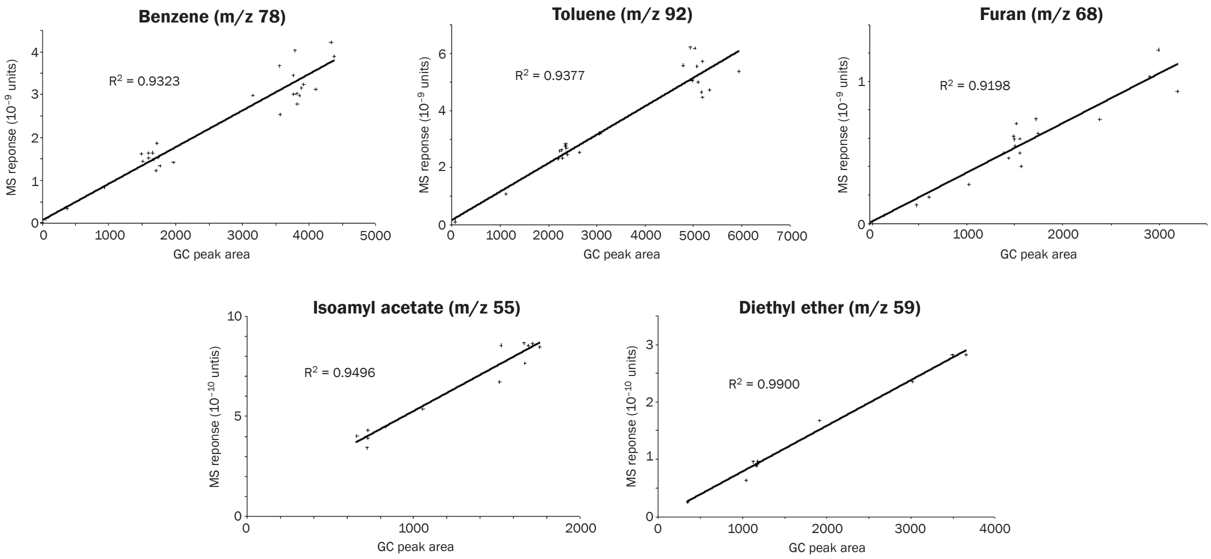

Figure 6: MS response for five components as a function of GC peak area. Each data point corresponds to the result from an individual injection, containing one or more other compounds, as shown in Figure 5.

Subsequent tests were carried out to assess data stability for each analyte while the concentration of one or more of the other components was varied. These tests were performed by loading different volumes of a dynamically prepared solution containing the same five compounds as before plus isoamyl acetate. The concentrations of each of the components in the solution are shown as a function of injection number in Figure 5. The good data stability obtained (Figure 6) demonstrates that contributions from other ions can be adequately compensated for.

The TD–MS systems are available in 19″ rack format (Figure 7) with all control and data processing software combined into one simple user interface. One button is required for system activation, and high-concentration readings automatically signal the action required.

Systems also feature desorption of sorbent tube or canister standards for routine quality assurance. Cost-effective certified reference standard (CRS) tubes loaded with up to six analytes at ng or µg levels can be obtained from Markes International for laboratory quality control.

Figure 7: A 19″ rack-mounted TD–MS system.

Conclusions

We have shown in this Application Note that combining on-line TD with process MS allows the high-throughput, near-real-time measurement of trace-level VOCs in carbon dioxide. Such an approach could be valuable for the the detection of hydrocarbon contaminants and volatile fermentation byproducts in streams of industrial gases.

Trademarks

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