

REAL-TIME SPECIATION OF ETHYLBENZENE FROM THE XYLENES USING SIFT-MS

Direct mass spectrometry (DMS) techniques invariably struggle to speciate ethylbenzene from the xylene isomers, yet increasingly regulators are imposing different emission and exposure limits for these compounds. This application note describes a significant breakthrough for DMS, because selected ion flow tube mass spectrometry (SIFT-MS) can readily achieve direct, realtime speciation of the xylenes from ethylbenzene.

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INTRODUCTION

Direct mass spectrometry (DMS) techniques traditionally have struggled to distinguish ethylbenzene from the xylene isomers, so measurement has been reported as a total concentration of “ethylbenzene plus xylenes”. Conventional wisdom prevailed: speciation requires chromatographic separation, and therefore off-line analysis due to the chromatography. In the European Union — unlike the United States — chromatography would have been essential because regulators have imposed different occupational exposure limits (OELs) for ethylbenzene and the xylenes¹ (time-weighted averages (TWAs) of 100 and 50 ppm, respectively). Likewise, recent vehicle interior air quality (VIAQ) regulations from Japan and Korea impose quite different permissible emission limits on these compounds — albeit the inverse of the EU workplace regulations (Table 1).

COMPOUND	Maximum permissible concentrations ($\mu\text{g m}^{-3}$)		
	CHINA	JAPAN	KOREA
Ethylbenzene	1000	3800	1600
Xylenes (total)	1000	870	870

Table 1. Vehicle interior air quality (VIAQ) regulations for ethylbenzene and the xylenes. Japan and Korea now have significantly different thresholds for the ethyl versus dimethyl isomers. Different thresholds for the ethyl versus dimethyl isomers.

But there is an increasing need in industry for rapid speciation — whether in the lab or in-process. This is where DMS analysis is required, rather than chromatography. Clearly, higher resolution MS is not a solution, because the elemental composition is the same (C_8H_{10}). The need is to utilize an ionization approach that yield different products. With a portfolio of eight rapidly switchable

reagent ions, selected ion flow tube mass spectrometry (SIFT-MS) is the ideal technique with which to seek a real-time solution to problem.

This application note describes a ground-breaking approach to resolving the ethylbenzene from the xylene isomers using different reactivities with the O_2 + reagent ion of SIFT-MS. Based on calibration, it enables the SIFT-MS technique to achieve direct, real-time speciation of the xylenes from ethylbenzene.

METHOD

The data summarized in this application note were obtained using a Syft Technologies Voice200ultra SIFT-MS instrument (see syft.com/SIFT-MS for more information on the SIFT-MS technique²). Air was sampled through the instrument’s high-performance inlet at a flow rate of approximately 25 sccm.

Parameters for detection of ethylbenzene and the xylenes using the standard positively charged reagent ions of SIFT-MS are summarized in Table 1.³ Rate coefficients are not shown, but occur at near collision rate for all ions and between compound variability is less than 10% (i.e. within experimental uncertainty), so that for H_3O^+ and NO^+ they provide a valid sum of all C_8H_{10} isomers.

Table 2. Detection parameters for the xylenes and ethylbenzene using the positively charged SIFT-MS reagent ions.³

SIFT-MS Reagent Ion	Ethylbenzene products Product formula (m/z); branching ratio as a percentage	Xylenes* Product formula (m/z); branching ratio as a percentage
H_3O^+	$\text{C}_8\text{H}_{10}\cdot\text{H}^+$ (107); 100%	$\text{C}_8\text{H}_{10}\cdot\text{H}^+$ (107); 100%
NO^+	$\text{C}_8\text{H}_{10}^+$ (106); 100%	$\text{C}_8\text{H}_{10}^+$ (106); 100%
O_2^+	C_7H_7^+ (91); 70% $\text{C}_8\text{H}_{10}\text{H}^+$ (106); 30%	C_7H_7^+ (91); 20% $\text{C}_8\text{H}_{10}^+$ (106); 80%

* The three xylene isomers (m-, o-, and p-) all react similarly with these reagent ions within 5% relative product abundance.

In this study, the NO^+ reagent ion was utilized to quantify the total concentration of ethylbenzene and the three xylene isomers. To differentiate ethylbenzene from the total xylene isomers, the O_2^+ reagent ion was utilized because of the different branching product ion branching behaviors. Separation of the isomers was achieved through calibration of the 91 to 106 ratios using 20/80, 50/50 and 80/20 ethylbenzene/xylene mixtures carried out at two nominal concentrations (150 ppbv and 10 ppmv). The calibration results are summarized in Figure 1, where the two points for a given ratio arise

from ratio determinations at the two concentrations, showing excellent agreement. Notice the linear response and the y-axis intercepts for 0% and 100% agree very well with the branching ratios shown in Table 1 for xylene and ethylbenzene, respectively.²

RESULTS AND DISCUSSION

The effectiveness of the calibration approach employing the product ions of O_2^+ is illustrated here by some demonstration experiments conducted in the Anatune Limited laboratory. This is an active demonstration and application development lab for chromatography as well as SIFT-MS, so the air is a relatively complex matrix (typical concentrations in the 10s to 100s of ppbv). We only present the results for xylene and ethylbenzene below, but an additional 11 species were monitored concurrently — all with a temporal resolution of just over three seconds.

Into this complex lab matrix, a small volume (1 mL) of each of m-xylene, ethylbenzene, and a mixture of the two was introduced via 20 mL headspace vials. They are shaken and then uncapped and recapped after a few minutes. The lab windows were then opened to ventilate the room before the next sample was opened. Figure 2 shows the total ethylbenzene + xylene concentration measured continuously over the 140-minute duration of the experiment using the NO^+ reagent ion of SIFT-MS.

Figure 3(a) shows the O_2^+ data acquired (via the m/z 91 and 106 product ions) simultaneously with the NO^+ data (Figure 2). These data do not match each other nor the NO^+ data in Figure 2 because of the different relative sensitivities of the O_2^+ 91 and 106 ions for the isomers. This is illustrated in Figure 3(b) where the relative proportions of the 91 and 106 ions to the total O_2^+ signal are shown.

Using the 91/106 ratios and the above calibration, it is possible to separate the ethylbenzene from the xylenes at very low ppbv concentrations and in a relatively complex matrix, as shown in Figure 4. The first exposure was xylenes, followed by ethylbenzene and then a 50/50 mixture of the two.

CONCLUSIONS

Excellent speciation of ethylbenzene from the xylenes in real time can be achieved by using the O_2^+ reagent ion of SIFT-MS together with simple calibration derived from mixtures of different proportions of the isomers. This approach can be applied to both real-time and high-throughput applications, providing benefits in testing and contract research laboratories through to continuous and process monitoring applications.

REFERENCES

1. See the NIOSH International Chemical Safety Cards (cdc.gov/niosh/ipcsneng/nengnameA.html); accessed on December 5, 2017), which list several international OELs.
2. B.J. Prince, D.B. Milligan, M.J. McEwan (2010), "Application of [SIFTMS] to real-time atmospheric monitoring", *Rapid Commun. Mass Spectrom.* 24, 1763; V.S. Langford, I. Graves, M.J. McEwan (2014), "Rapid monitoring of volatile organic compounds: a comparison between gas chromatography/mass spectrometry and [SIFT-MS]", *Rapid Commun. Mass Spectrom.*, 28, 10.
3. P. Spänel, D. Smith (1998), "[SIFT] studies of the reactions of H_3O^+ , NO^+ , and O_2^+ with several aromatic and aliphatic hydrocarbons", *Int. J. Mass Spectrom.*, 181, 1.

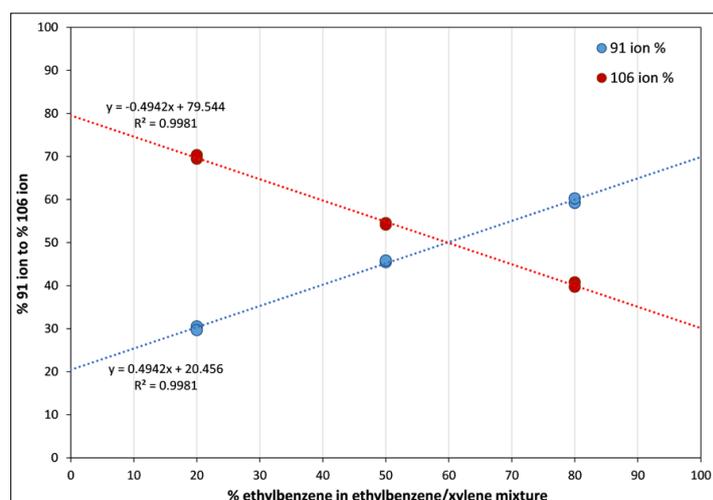


Figure 1. Calibration of relative abundance ratios (expressed as percentages) for the m/z 91 and 106 product ions formed when O_2^+ reacts with different mixtures of ethylbenzene and the xylenes. More details are given in the text.

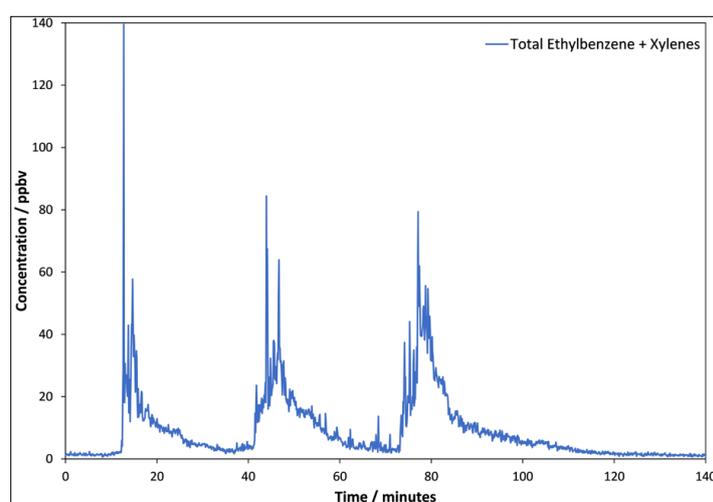


Figure 2. Exposure of laboratory air to m-xylene and ethylbenzene; total measured using NO^+ .

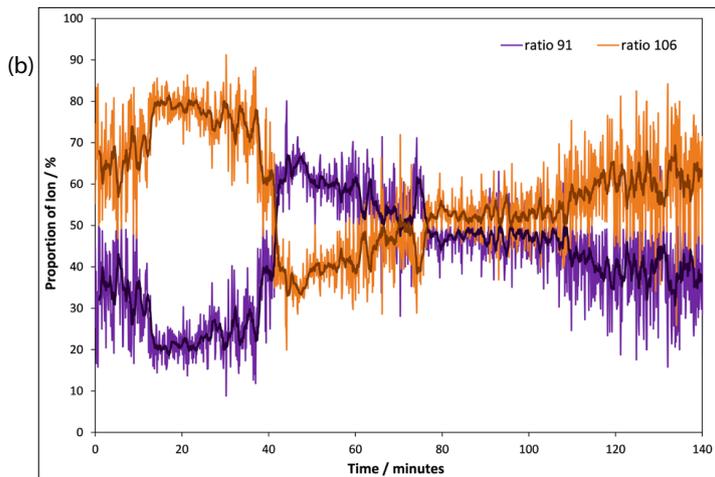
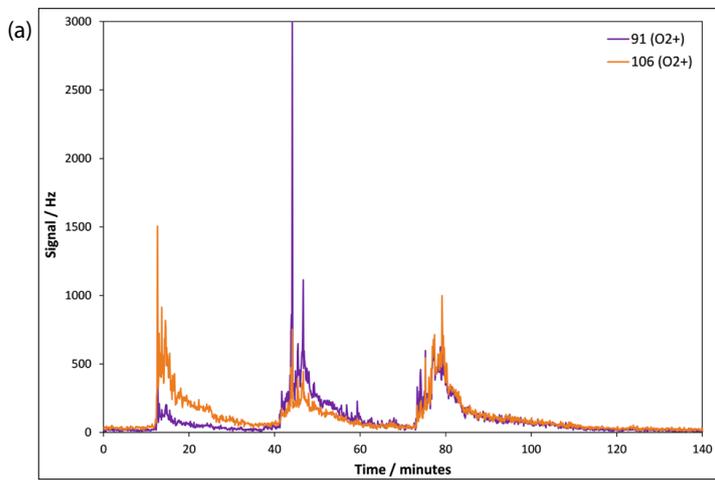


Figure 3. O₂⁺ product ions 91 and 106: (a) the ion counts (in Hz or counts per second) and (b) the simple proportions of these in the total O₂⁺ signal.

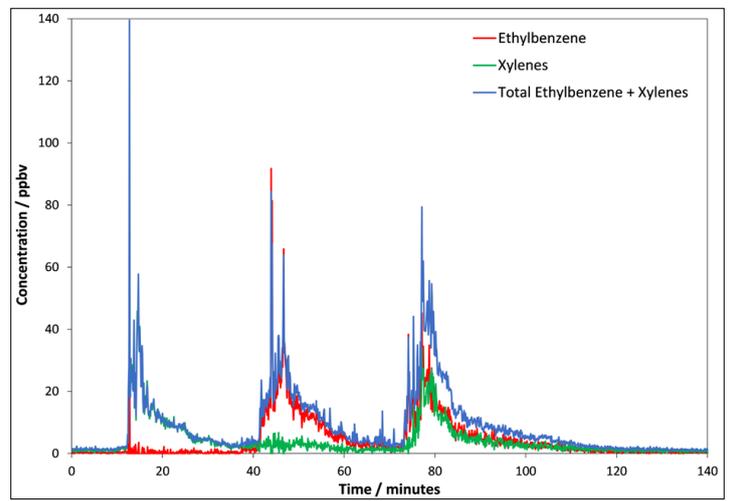


Figure 4. Separation of ethylbenzene and xylenes concentrations using O₂⁺ with the total concentration (ethylbenzene + xylenes) superimposed.