

Determination of BTEX in Cigarette Filter Fibers Using GC-MS with Automated Calibration

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Introduction

Benzene and its alkyl derivatives toluene, ethylbenzene, and xylene (BTEX) have been classified by the World Health Organization (WHO) as a strong carcinogens causing cancer affecting human skin, lungs, and the nervous system.^[1]

Quality control in the cigarette filter manufacturing process is a critical procedure for the tobacco industry. The reagents, accessories and raw filter material used in the production process may be a source of residual BTEX contamination, and hence require quality control. Therefore, the BTEX monitoring of cigarette filters in the tobacco industry has a significant impact on the choice and quality of filter materials.

China is by far the largest tobacco producing country today, followed from a distance by Europe, North America and Latin America.^[2] In China, the directive YC/T 373-2010 for the control of propylene and C-fiber filter material requires the analysis of BTEX residue contaminations by gas chromatography-mass spectrometry (GC-MS).^[3] The YC/T 373-2010 standard has high sensitivity requirements for the detection of BTEX. In this application note, we employ the method used in YC/T 373-2010 with the Thermo Scientific™ ISQ™ GC-MS for detection of BTEX compounds in propylene fiber cigarette filters.



Figure 1. TriPlus RSH robotic sample handler with automated calibration dilution cycle.

Sample Preparation

Calibration

Preparing calibration solutions for BTEX analysis is typically a manual procedure. The low boiling point of the BTEX compounds makes precise low volume pipetting and diluting of a BTEX stock solution into vials particularly critical due to their volatility. In addition, handling such volatile carcinogenic compounds presents a serious health risk for the operators.

The procedure described in this application note utilizes the Thermo Scientific™ TriPlus™ RSH autosampler platform to prepare the BTEX calibration standard series and then to seamlessly perform the injection into the GC-MS system. The autosampler allows fully automated calibration and sample measurement with minimal contact between the analyst and potentially hazardous materials.

Experimental Conditions

Carry out BTEX analyses using an ISQ single quadrupole system, equipped with the Thermo Scientific™ TRACE™ 1310 GC and a TriPlus RSH autosampler with an automated tool changer and vortexing unit as described in Figure 1. Use the detailed configuration provided in Table 1. Figure 2 illustrates the preparation of the calibration dilution levels using dedicated syringes, which are automatically changed by the TriPlus RSH as required by the liquid handling cycle. Use the analytical conditions provided in Tables 2 and 3.

Table 1. TriPlus RSH autosampler configuration used for automated BTEX analysis.

Automatic tool changer
Syringe tool D7 (10 μ L used for dilutions)
Syringe tool D7 (10 μ L dedicated for GC injection)
Syringe tool D8 (1000 μ L used for dilutions)
Vortexer (for vial mixing before injections)
Large washing station (2 \times 100 mL solvent)
Standard washing station (2 \times 10 mL)
Tray holder
Vial tray VT54 (3 pcs, for 2 mL vials)
Cooled tray recommended if the lab temperature goes above 25 $^{\circ}$ C

Preparation of Standard Solutions

The reagents and reference standards mix comprised of benzene, toluene, ethylbenzene, o-xylene, m-xylene, and p-xylene was purchased locally from Sinopharm Chemical Reagent Co. Ltd. 2-hexanone was purchased from Beijing J&K Technology Co. Ltd. n-Pentane, extra pure, from Fisher Scientific was also used.

As required by the Chinese method, use 2-hexanone as the internal standard. Dilute 50 mg of 2-hexanone with n-pentane to 50.0 mL for an initial 1000 ppm internal standard solution. Dilute this solution to a concentration of 0.1 ppm 2-hexanone internal standard work solution, and use for standards preparation and sample extraction.

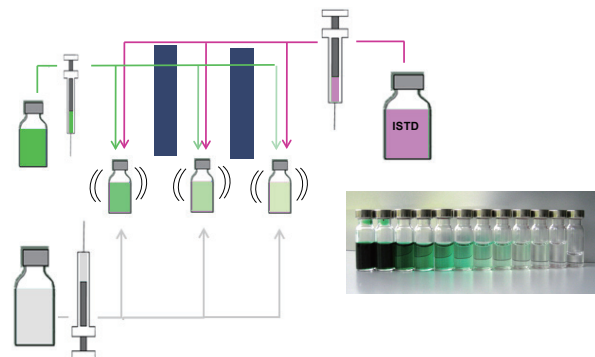


Figure 2. Schematics of the calibration dilution cycle. Dedicated syringes are used for standards, solvent and injection.

Automated Calibration Dilution Cycle

Use the built-in automatic dilution liquid handling cycle of the TriPlus RSH autosampler to prepare the calibration. This function automatically prepares the required calibration level solutions in 2 mL vials (VT54 sample tray type) and adds the internal standard. Inject the prepared calibration standard dilutions before analyzing the samples controlled by the acquisition sequence. Prepare up to three replicates of the calibration samples. See the available vial positions in Figure 3.

Program the TriPlus RSH automatic calibration dilution cycle to prepare seven additional vials with the concentration levels of 1.0 ppb, 2.0 ppb, 5.0 ppb, 10.0 ppb, 20.0 ppb, 50.0 ppb and 100.0 ppb using the BTEX standard mix. Use the initial 100.0 ppb (0.1 ppm) stock solution as a seventh calibration point. Clean the syringe using the large volume solvent station three times after each use.

Place the following solutions and vials into the dedicated TriPlus RSH autosampler tray positions:

- Place empty 2mL vials, capped with septum, on the sample tray, as the target vials receive the calibration dilutions for 100 ppb Pos. 1, 50 ppb Pos. 2, 20 ppb Pos. 3, 10 ppb Pos. 4, 5 ppb Pos. 5, 2 ppb Pos. 6, 1 ppb Pos. 7
- Place the BTEX stock solution with the standard mix with six compounds, 5 mL, 0.1 ppm, in Pos. 4 of the solvent tray
- Place blank solvent in Pos. 12



Figure 3. TriPlus RSH VT54 sample tray positions for calibration dilution.

- Pos. 1–10 first calibration series
- Pos. 19–28 second calibration series
- Pos. 37–46 third calibration replicate
- Pos. 11, 29, 47–solvent with internal standard
- Pos. 12, 30, 48–solvent blank
- Pos. 54–internal standard
- Other positions not used

Table 3. ISQ MS Conditions.

Ionization	EI, 70 eV
Filament current	50 μ A
Scan mode	SIM, see Table 3
Acquisition rate	0.1 s
Ion source temperature	280 °C

Table 2. TRACE 1310 GC conditions.

Column type	Thermo Scientific™ TraceGOLD™ TG-WaxMS
Column dimensions	length 30 m, ID 0.25 mm, film thickness 0.25 μ m (p/n 26088-1420)
Injector, temperature	Instant connect split/splitless injector 240 °C
Injection mode, volume	split injection, 3 μ L
Split flow	10 mL/min (ratio 10:1)
Solvent vent	open until 0.17 min closed until 4.17 min open until end of run
Carrier gas, flow	helium, constant flow 1 mL/min
Oven program	35 °C, 2 min 15 °C/min to 100 °C 20 °C/min to 220 °C 220 °C, 3 min
Transfer line temperature	250 °C

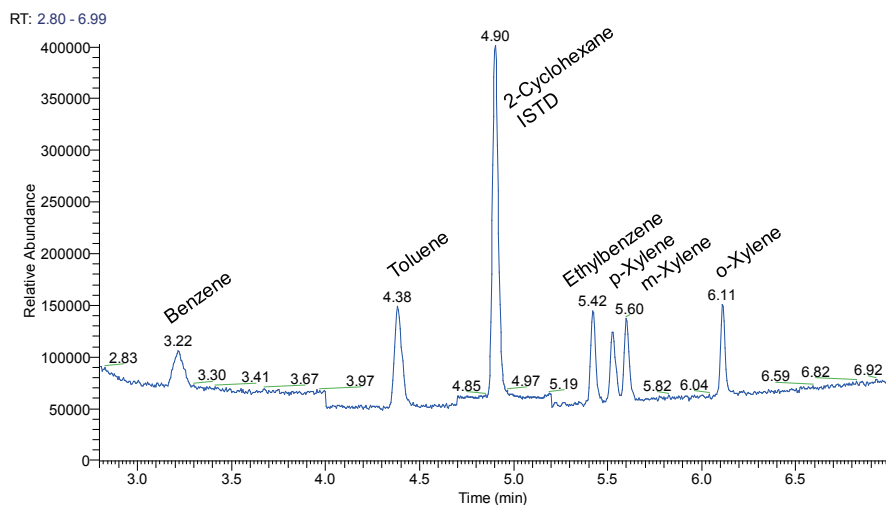


Figure 4. BTEX chromatogram of the standard mix, 5 ppb, ISQ GC-MS SIM.

Sample Measurements

For preparation of the samples, weigh about 3.0 g of the C-fiber filter rod (length of about 1 cm) into 60 mL bottles, adding 50.0 mL of the 2-hexanone internal standard stock solution at a concentration of 0.1 ppm.

Close the bottle and shake at 200 rpm for 1 hour. Take the supernatant and filter over a 0.45 μ m membrane and prepare in 2 mL vials for GC-MS analysis.

Table 4. BTEX ISQ SIM method-instrument and method detection limits (MDL) (* internal standard).

Compound name	CAS#	Retention time	Quantitation Ion	Qualifier Ion	Detection limit	MDL
		[min]	[m/z]	[m/z]	[ppb]	[ppb]
Benzene	71432	3.21	78	51	6	17
Toluene	108883	4.39	91	65	2	17
2-Cyclohexanone*	591786	4.90	58	100	-	-
Ethylbenzene	100414	5.42	91	106	2.2	17
p-Xylene	95476	5.53	91	106	3.8	17
m-Xylene	108383	5.60	91	106	2.5	17
o-Xylene	106423	6.11	91	106	2.5	17

Results

Figure 4 shows the ISQ GC-MS chromatogram of the six BTEX compounds at the standard mix concentration of 5 ppb. It shows that all components in the BTEX analysis were well resolved. The meta-, para-, and ortho-xylene isomers were baseline resolved in only 7 minutes. Each substance showed symmetrical peak shape and a solid base for reliable peak integration and determination, even at very low concentration levels.

$MDL = \frac{50 \times C}{M}$ The method detection limit (MDL) of the described method for the six BTEX compounds was calculated based on the equation shown to the left in which M is the sample weight and C is the lowest calibration point. It is based on the assumption of a similar response for the six BTEX compounds and the use of 50 mL of extraction solvent. See Table 4.

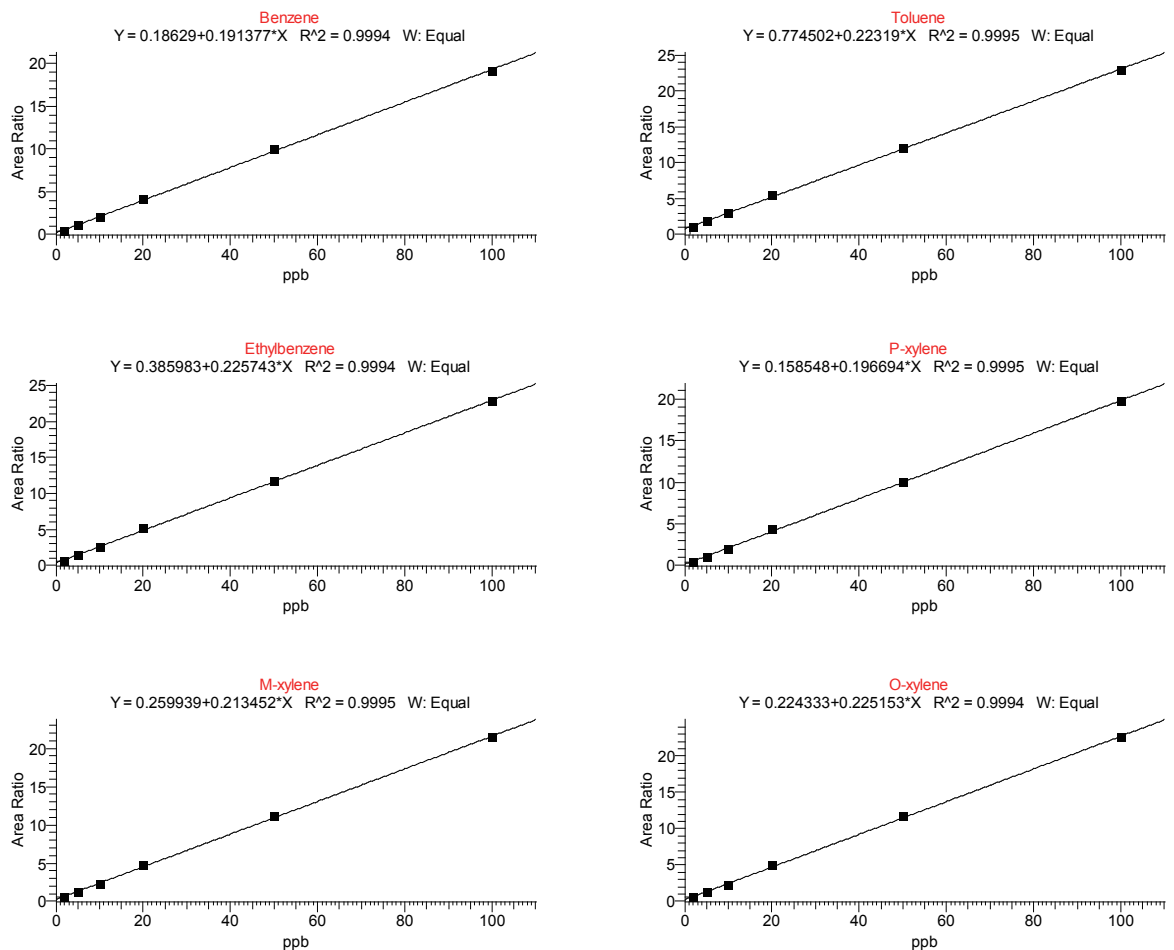


Figure 5. BTEX calibration curves in the range of 1.0 to 100 ppb with R2 better than 0.999 for all compounds.

C-fiber filter rods provided by the tobacco industry were analyzed using the method described above. A recovery test was carried out using the prepared standard solution with a spiked amount of 5 ng/mL (5 ppb) in order to examine the reliability of the method. Due to a lack of confirmed blank fiber material, a previously determined low level sample was spiked. The recovery results of the spiked sample experiment are shown in Table 5. The results show that at the 5 ppb level the recoveries range between 82.0% and 90.8% and are in line with values for daily analysis and detection requirements.

The selected ion chromatograms of the spiked sample and a contaminated fiber rod sample are shown in Figure 6. The experimentally determined concentrations of the C-fiber filter rod had been calculated as:

Benzene	n.d.
Toluene	n.d.
Ethylbenzene	42.0 ng/g
p-Xylene	16.8 ng/g
m-Xylene	52.2 ng/g
o-Xylene	28.5 ng/g

Benzene and toluene were not detected (n.d.) with levels below the limit of quantification.

Table 5. Recovery results from a spiked sample.

Compound name	Sample measured [ppb]	Standard addition [ppb]	Spiked calculated [ppb]	Spiked measured [ppb]	Recovery %
Benzene	0	5.00	5.00	4.54	90.8
Toluene	0.21	5.00	5.21	4.43	84.4
Ethylbenzene	2.52	5.00	7.52	6.62	82.0
p-Xylene	1.01	5.00	6.01	5.49	89.6
m-Xylene	3.13	5.00	8.13	7.19	81.2
o-Xylene	1.71	5.00	6.71	5.9	83.8

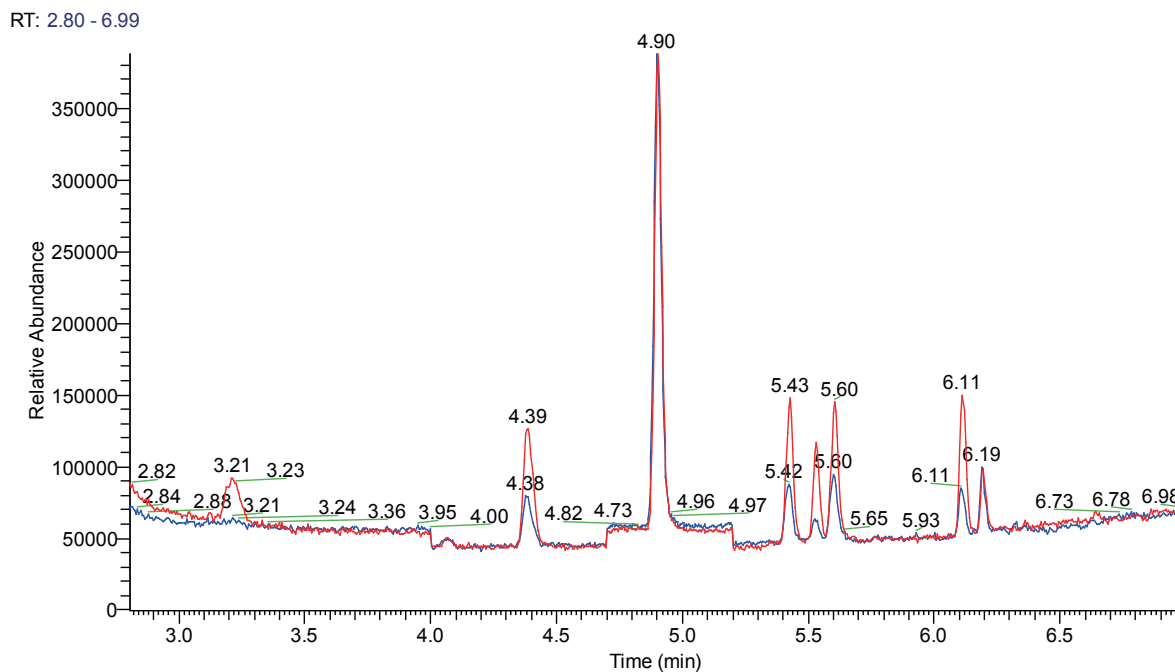


Figure 6. Chromatograms of a sample (blue) and sample spike (red) (overlay, 5 ppb run with high peaks).

Conclusions

This application note describes an easy-to-handle n-pentane solvent extraction method for the quality control of BTEX compounds in cigarette fiber filters using the TriPlus RSH autosampler and the TRACE 1310 ISQ single quadrupole GC-MS system. This analytical method can also be applied to similar sample types.

Very precise, correct, and freshly prepared calibration solutions for each batch of samples are provided by the automated calibration dilution function of the TriPlus RSH autosampler. This fully automated and optimized method provides short analysis cycle times for a more economical sample throughput. The need for fewer manual pipetting steps improves the method precision significantly for such highly volatile compounds. In addition, human contact with hazardous and carcinogenic compounds is minimized.

This analytical method provides high BTEX compound recovery with a wide method linearity and high sensitivity. The linear concentrations cover seven concentration levels in the automatic preparation of samples in the 1-100 ppb range, with precision greater than 0.999 for all compounds. The detection limits of BTEX compounds are 2.0-6.0 ppb (ng/g) with quantification limit of the method at 17 ppb (ng/g). Recoveries were determined to be 82.0-90.8%. The described analytical ISQ GC-MS method and its resulting performance data readily meet the high routine analytical testing requirements of the tobacco industry.

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