

# Direct Thermal Extraction Analysis of Solid and Liquid Samples using the GERSTEL MPS Robotic Sampler, Thermal Desorption Unit (TDU 2) and Cooled Inlet System (CIS)

Laurel A. Vernarelli, Jacqueline A. Whitecavage, and John R. Stuff

GERSTEL, Inc., 701 Digital Drive, Suite J, Linthicum, MD, 21090, USA

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## KEYWORDS

Direct Thermal Extraction (DTE), Thermal Desorption, Gas Chromatography, Mass Spectrometry, Volatiles, VOCs

## ABSTRACT

Direct thermal extraction (DTE) is a thermal desorption technique in which a small amount of sample, typically 10-50 mg, is placed in an empty fritted thermal desorption tube or into a small vial ( $\mu$ -vial) within an empty thermal desorption tube. The sample is then heated in a thermal desorption unit under a flow of inert gas, in order to release volatile and semi-volatile compounds. The analytes are trapped and finally determined by GC/MS. DTE requires little sample preparation and can be used for trace analysis of volatile and semivolatile organic compounds in solid or liquid samples. Exhaustive extraction conditions can be developed for an analyte by optimizing temperature, flow rate and extraction time. Calibration and quantification can be performed by externally spiking standards onto Tenax-TA<sup>®</sup> filled sorbent tubes. This study describes the use of the GERSTEL MPS with CIS, and TDU for the analysis of volatile and semivolatile compounds in solid and liquid samples.

## INTRODUCTION

In this study, direct thermal extraction and air sampling with Tenax TA filled sorbent tubes are used to extract aroma compounds from three brands of pumpkin spice scented wax candles purchased from a local store. Direct thermal extraction (DTE) was performed on samples of scented wax with minimal sample preparation. The scented wax candles were lit in a 9' x 13' room with a 10' ceiling, and fragrance compound concentrations were then monitored in the room air.

Quantitative results were generated for limonene, linalool and eugenol, three fragrance compounds common to all three brands of scented wax candles. This type of experiment can be used to show the rate at which scented wax compound concentrations change as a function of time, and to identify the compounds that are important contributors to the perceived odor in the room. Monitoring of key aroma compounds is important for quality control. Identification of off notes can help in pinpointing and solving product defects and thereby increasing consumer acceptance.

## EXPERIMENTAL

### Instrumentation

Agilent 7890A GC / 5977B MSD  
GERSTEL MPS robotic, TDU 2 & CIS 4

### Analysis conditions

TDU: thermal extraction: splitless  
40°C (0.5 min); 720°C/min;  
100°C (10 min)  
Tenax TA: splitless  
40°C (0.5 min); 720°C/min;  
280°C (3 min)

CIS: solvent vent (50 mL/min)  
-120°C; 12°C/sec; 280°C (3 min)

Pneumatics: He, constant flow, 1 mL/min

Column: 30 m Rxi-5Sil MS (Restek)  
 $d_i = 0.25 \text{ mm}$   $d_f = 0.25 \text{ }\mu\text{m}$

Oven: 50°C (2 min); 10°C/min; 280°C (5 min)  
Tenax TA:  
40°C (1 min); 15°C/min; 280°C (3 min)

*Sampling Setup and Conditions.* Air samples were obtained using twelve conditioned TDU sorbent tubes packed with Tenax TA. A 1.0-meter piece of 1/4" Teflon tubing was connected to the back of an air sampling pump using 1 1/4" to 1/8" Swagelok reducing union. The open end of the Teflon tubing was held at the height of the breathing zone of a seated person using a ring stand and three finger clamp. The candle was lit. The tubes were then sampled at a flow rate of 25 mL/min for 20 minutes for a total sample volume of 0.50 L. The total time interval for sampling was 4 hours.

*Sample Preparation.* For quantification of limonene, linalool and eugenol, three solutions of the compounds in the concentration range of 0.3 - 30 mg/L were made in methanol and used to construct an external calibration curve and calculate the average response factor. Three microliters of each standard were spiked onto the fritted end of a clean Tenax-TA tube. A flow of 50 mL/min of dry nitrogen was passed through the tube for 3 minutes.

*Direct Thermal Extraction of Wax Samples.* An 11 mg sample of scented candle wax was weighed, placed into a micro-vial and transferred to an empty TDU tube, which was capped with a transport adapter.

*Sample Introduction to the GC/MS.* TDU tubes containing micro-vials and/or Tenax TA sorbent were loaded onto the MultiPurpose Sampler (MPS robotic) VT-40t tray.

*Direct Thermal Extraction of Wax Samples.* TDU tubes with micro-vials were desorbed in the TDU in splitless mode under a 50 mL/min helium flow at 100°C for 10 minutes. Analytes were cryogenically trapped in the CIS 4 inlet at -120°C on a liner packed with glass wool. When the desorption step was completed, analytes were transferred to the GC column in split mode (100:1) by heating the CIS inlet rapidly to 275°C with a hold time of 3 minutes.

*Air Sampling of Lit Scented Wax Candle.* Tenax-TA tubes were desorbed in the TDU in splitless mode under a 50 mL/min helium flow at 280°C for 3 minutes. Analytes were cryogenically trapped in the CIS 4 inlet at -120°C on a liner packed with glass wool. When desorption was complete, analytes were transferred to the GC column in splitless mode by heating the CIS inlet rapidly to 275°C with a hold time of 3 minutes.

## RESULTS AND DISCUSSION

*Direct Thermal Extraction of Scented Wax Samples.* Direct thermal extraction was applied to three brands of scented candle wax. Figure 1 shows a stacked view of the resulting chromatograms from the direct thermal extraction analyses. Several fragrance compounds are identified in the chromatograms. Limonene, linalool and eugenol were common to all three products, with brand B having the highest concentration of limonene and eugenol. In the other two products, limonene is a minor peak. Linalool is a significant component of brands A and C, but a minor peak in brand B. The chromatogram for the brand C had the fewest peaks with a series of benzene derivatives eluting from 7.5 – 9 minutes.

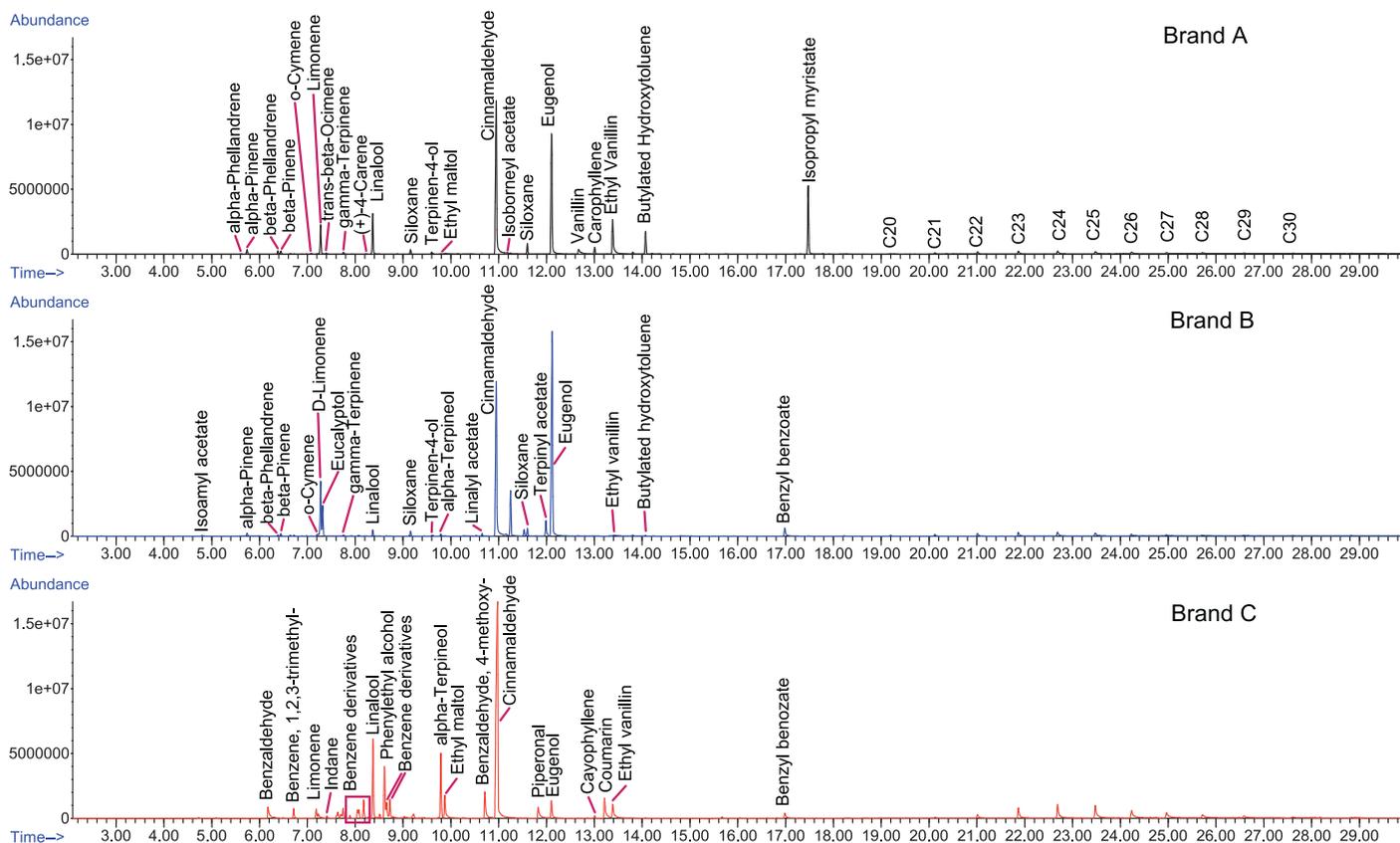


Figure 1. Stacked view of chromatograms for brand A (top), brand B (middle) and brand C (bottom) pumpkin pie scented candles by direct thermal extraction.

Brand A shows the highest level of extractable compounds. Compounds which could potentially derive from the fragrance added to the candle wax include alpha-phellandrene, alpha-pinene, beta-phellandrene, beta-pinene, o-cymene, limonene, trans-beta-ocimene, gamma-terpinene, (+)-4-carene, linalool, terpinen-4-ol, ethyl maltol, cinnamaldehyde, isoborneyl acetate, eugenol, vanillin, carophyllene and ethyl vanillin. The brand A scented candle wax also included butylated hydroxytoluene, an antioxidant, and isopropyl myristate, a diluent for candle fragrances. In addition, a series of n-alkanes from C20 to C30 from the wax eluted late in the brand A chromatogram.

The chromatogram resulting from thermal extraction of the brand B candle shows isoamyl acetate, alpha-pinene, beta-phellandrene, beta-pinene, o-cymene, limonene, eucalyptol, gamma-terpinene, linalool, terpinen-4-ol, alpha-terpineol, linalyl acetate, cinnamaldehyde, terpinyl acetate, eugenol and ethyl vanillin. The brand B scented candle also contained butylated hydroxytoluene and benzyl benzoate, a diluent. As in brand A, a series of n-alkanes from C20 to C30 were present.

Brand C shows the lowest level of extractable aroma compounds. The chromatogram shows benzaldehyde, 1, 2, 3-trimethyl benzene, indane, linalool, phenylethyl alcohol, alpha-terpineol, ethyl maltol, 4-methoxy-benzaldehyde, cinnamaldehyde, piperonal, eugenol, caryophyllene, coumarin and ethyl vanillin. The brand C candle also contained a series of n-alkanes, benzyl benzoate, and several unidentified benzene derivatives.

*Air Sampling in the Presence of a lit Scented Wax Candle.* Standards of limonene, linalool and eugenol were available in the lab and were common to all three products, so these compounds were chosen for the quantification in the collected air samples. Previous studies have verified the air sampling collection method and these results are published elsewhere [1]. Quantification was performed by spiking a standard solution onto the fritted end of a Tenax-TA tube and purging it onto the sorbent with dry nitrogen at a flow of 50 mL/min for 3 minutes. All tubes were analyzed using the same thermal desorption and GC/MSD parameters.

Figure 2 shows an example of a three-point calibration curve for eugenol. A linear trendline, fit to the data, is shown in the figure. Linear regression of the three-point calibration curves for limonene and linalool shows  $R^2$  values of 0.9985 or higher for both compounds. The data show good precision for the three spike levels.

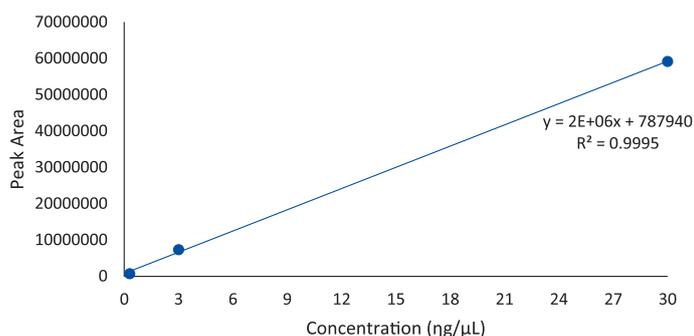


Figure 2. Three-point calibration curve for eugenol at 0.3, 3 and 30 ng/mL.

For air sampling of the product, a 9' x 13' office with a 10' ceiling was used. The candle was lit, and the door to the room was closed during sample collection, described above. A large fan was used to ventilate the room between samples.

Figure 3 shows the concentration of limonene, linalool, eugenol and cinnamaldehyde for the brand A scented wax candle. The area count is plotted against time. The linalool shows a slight increase after eighty minutes, after which no significant increases or decreases in concentration over the four-hour sampling period are observed. The limonene shows an increase in concentration over the sampling time. The eugenol shows a steady decay over the first 160 minutes, likely due to oxidation in air as it is released from the wax. Linalool and cinnamaldehyde remain relatively stable over the 240-minute sampling period.

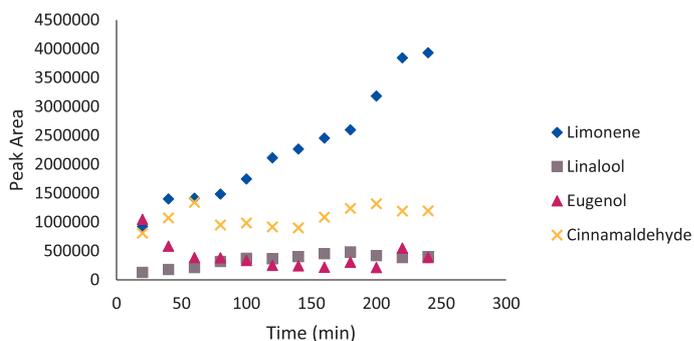


Figure 3. Peak areas for limonene, linalool, eugenol and cinnamaldehyde respectively as a function of time elapsed after lighting a brand A pumpkin spice fragrance scented wax candle in a closed room.

Figure 4 shows the peak areas for limonene, linalool, eugenol and cinnamaldehyde for the brand B pumpkin spice scented wax candle. The cinnamaldehyde and limonene concentrations both increase over the sampling period, with limonene increasing at a higher rate than cinnamaldehyde. Direct thermal extraction of the brand B scented wax candle had the resulted in the largest limonene peak compared with the other brands, as shown in Figure 1. The linalool and eugenol levels remain stable over the air sampling period.

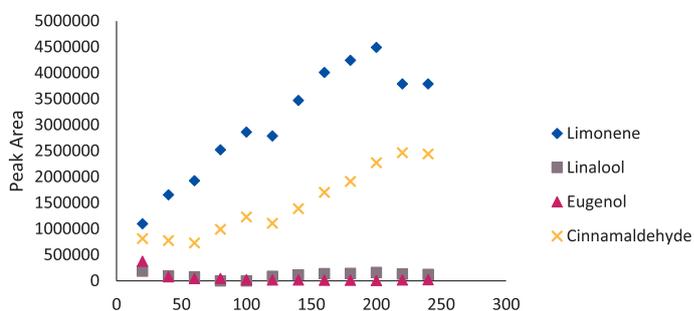


Figure 4. Peak areas for limonene, linalool, eugenol and cinnamaldehyde introduced to room air shown as a function of time expired after lighting the brand B pumpkin spice fragrance scented wax candle in a closed room.

Figure 5 shows the peak area for limonene, linalool, eugenol and cinnamaldehyde for the brand C scented wax candle. The steadily increased cinnamaldehyde concentration in the air from 60 to 240 minutes is likely due to emissions from melting wax. This was to be expected, as cinnamaldehyde was the largest peak found in the chromatogram resulting from direct thermal extraction of the brand C candle wax as seen in Figure 1. For brand C, unlike brands A and B, the linalool level increased steadily over the four-hour sampling window. Eugenol followed the same trend as observed in brands A and B, and limonene remained stable for the duration of sampling.

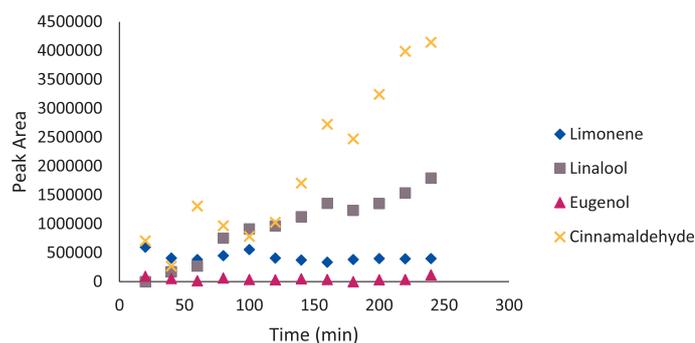


Figure 5. Peak areas for limonene, linalool, eugenol and cinnamaldehyde introduced to indoor air as a function of time expired after lighting a brand C pumpkin spice fragrance scented wax candle in a closed room.

Figure 6 shows the concentration of limonene for the three scented wax candles during their individual sampling periods. The y-axis was converted to air concentration (ng/L) by multiplying the area counts for each time point by the average response factor for the three spike levels and then dividing by the volume of air sample (0.50 L). A linear trendline, fit to the data, is shown in the figure. This provides a convenient way to look at the data and see how the actual concentration in air changes as a function of time. The concentration in air of limonene and linalool corresponds well with the relative concentrations found by direct thermal extraction in all cases, for example, the brand B candle was found to have the highest amount of limonene, and this corresponded well with a higher rate of release into the air. Limonene was a minor peak in the direct thermal extraction chromatogram for the brand C candle, and only a small amount was found to be released into the air resulting in a low concentration that remained constant over the duration of the experiment.

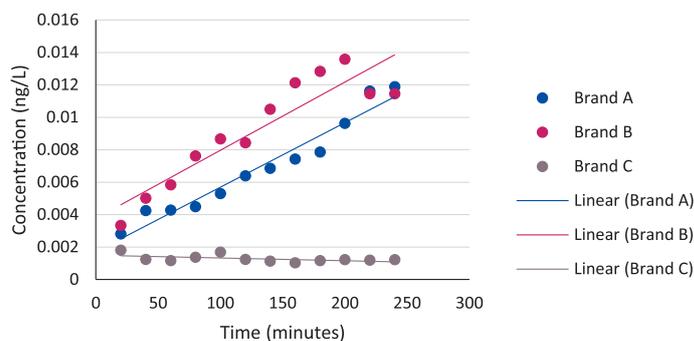


Figure 6. Concentration curves for limonene in air as a function of time elapsed after independently igniting three brands of pumpkin spice scented candles in a closed room.

Figure 7 shows the concentration curves for linalool for the three brands of scented wax candles. Linalool was found in the highest concentration in the brand C candle and this correlates well with the brand C candle producing the highest linalool concentration in air when burning. Direct thermal extraction of the brand B candle resulted in a chromatogram in which linalool was a minor peak and this correlates well with it producing the lowest concentration in air of the three candle types burning. The low concentration of linalool in air remained relatively constant over the monitoring period.

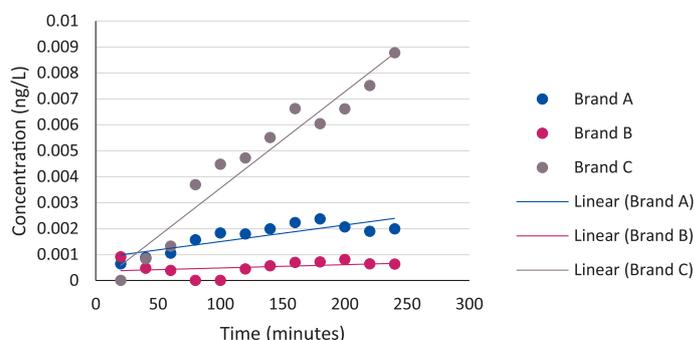
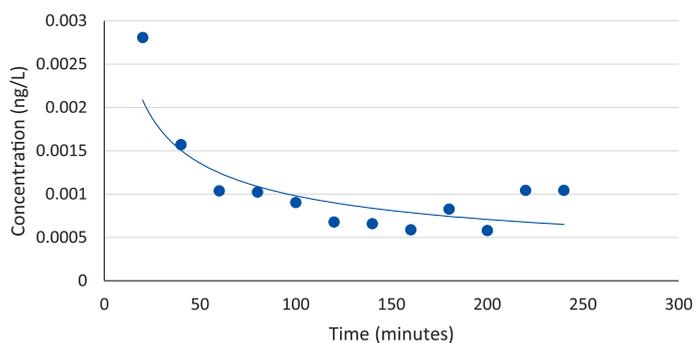


Figure 7. Concentration curve for linalool in air as a function of time elapsed after independently igniting three brands of pumpkin spice scented candles in a closed room.

Figure 8 shows a concentration curve for eugenol in air introduced by igniting the brand A pumpkin spice scented candle. A power curve, fit to the data, is shown in the figure. Unlike limonene and linalool, the concentration of eugenol decreases over time, likely due to oxidation of the compound in air after it is released from the melting wax. This example illustrates the importance of this type of experiment, as consumers expect the characteristic note of a fragrance to remain stable over time. It is possible that as the candle is burned, fragrance compounds may be oxidized or otherwise degraded.



*Figure 8. Concentration curve for eugenol in air as a function of time elapsed after igniting a brand A pumpkin spice scented candle.*

## CONCLUSION

This study demonstrates the usefulness of the GERSTEL MultiPurpose Sampler (MPS) combined with a Thermal Desorption Unit (TDU)/CIS system for direct thermal extraction (DTE) of fragrance compounds from pumpkin spice scented wax candles and for quantitative determination by GC/MS of those compounds in air samples collected onto sorbent tubes while the candles were burning in a confined space. The results show that DTE is a very good method for quantification as well as for assessment of quality defects that may arise in scented wax candles. The method requires very little sample preparation. Air sampling conditions were optimized for limonene, linalool and eugenol. For other analytes, sampling conditions, including flow rate, time and sorbent material, may require further optimization. Lower detection limits can be readily achieved using longer sampling times or higher sampling flow rates.

The GERSTEL MPS/TDU/CIS provides a versatile automation platform for quantitative analysis of fragrance. Several techniques can be applied quickly to the same samples, providing the necessary data for quality control, product development troubleshooting or competitive analysis. With appropriate use of standards, any of the techniques can be used for quantitative analysis.

## REFERENCES

- [1] Air Sampling of Fragrance Compounds using the Automated GERSTEL Gas Sampling System (GSS), GERSTEL AppNote 5/2014. <http://www.gerstel.com/pdf/p-gc-an-2014-05.pdf>



**GERSTEL GmbH & Co. KG**

Eberhard-Gerstel-Platz 1  
45473 Mülheim an der Ruhr  
Germany

+49 (0) 208 - 7 65 03-0  
+49 (0) 208 - 7 65 03 33  
gerstel@gerstel.com  
www.gerstel.com

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## GERSTEL Worldwide

**GERSTEL, Inc.**

701 Digital Drive, Suite J  
Linthicum, MD 21090  
USA

+1 (410) 247 5885  
+1 (410) 247 5887  
sales@gerstelus.com  
www.gerstelus.com

**GERSTEL AG**

Wassergrabe 27  
CH-6210 Sursee  
Switzerland

+41 (41) 9 21 97 23  
+41 (41) 9 21 97 25  
swiss@ch.gerstel.com  
www.gerstel.ch

**GERSTEL K.K.**

1-3-1 Nakane, Meguro-ku  
Tokyo 152-0031  
SMBC Toritsudai Ekimae Bldg 4F  
Japan

+81 3 5731 5321  
+81 3 5731 5322  
info@gerstel.co.jp  
www.gerstel.co.jp

**GERSTEL LLP**

10 Science Park Road  
#02-18 The Alpha  
Singapore 117684

+65 6779 0933  
+65 6779 0938  
SEA@gerstel.com  
www.gerstel.com

**GERSTEL (Shanghai) Co. Ltd**

Room 206, 2F, Bldg.56  
No.1000, Jinhai Road,  
Pudong District

Shanghai 201206  
+86 21 50 93 30 57  
china@gerstel.com  
www.gerstel.cn

**GERSTEL Brasil**

Av. Pascoal da Rocha Falcão, 367  
04785-000 São Paulo - SP Brasil

+55 (11)5665-8931  
+55 (11)5666-9084  
gerstel-brasil@gerstel.com  
www.gerstel.com.br

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