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Air Sampling of Fragrance Compounds using the Automated GERSTEL Gas Sampling System (GSS)

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KEYWORDS

Air sampling, thermal desorption, gas chromatography, mass spectrometry

ABSTRACT

Air fresheners contained in spray cans are commonly used in households to mask unpleasant odors. Many types of fragrances are commercially available. The fragrance can be a complex mix of many components. The effectiveness of the freshener to mask the off odors over time can be directly related to the concentration of the fragrance components in the air. Therefore, an important aspect in product development is to monitor the airborne concentration of the fragrance components.

This study describes the use of the Field Portable GERSTEL Gas Sampling System (GSS²⁸) for the collection of fragrance compounds in air. The GSS²⁸ is a 28 position sampling system designed to perform active i.e. pumped sampling of air onto sorbent tubes. The sampler can collect multiple samples on a pre-programmed schedule or on demand from the user interface.

Air fresheners were released into the air and dispersed across a room and air samples were collected using the GSS²⁸. The sorbent tubes were subsequently analyzed by thermal desorption GC/MS. Several fragrance components contained in the dispersed products were monitored and quantified over time. The study also included validation of an air sampling method for the compounds.

This type of experiment can be used to show the rate at which compound concentrations decay in the room air as a function of time as well as identifying which compounds are important contributors to the perceived odor in the room.

INTRODUCTION

This AppNote describes the use of the Field Portable GERSTEL Gas Sampling System (GSS²⁸) for air sampling onto sorbent tubes followed by Thermal Desorption (TD)-GC/MS determination of the collected fragrance compounds. Three types of spray air fresheners were purchased from a local store. The fresheners were sprayed in a 9' x 13' office space with 10' high ceiling. Fragrance compound concentrations were then monitored in the room air based on samples taken using the GERSTEL GSS²⁸.

Quantitative results were generated for linalool and limonene, two fragrance compounds common to all three air fresheners used. The GSS²⁸ allows for automated sampling using up to 28 tubes, which can be used to cover a sampling event. This type of experiment can be used to show the rate at which air freshener compound concentrations decrease in the room air as a function of time and to identify those compounds that are important contributors to the perceived odor in the room.

EXPERIMENTAL

Instrumentation. GERSTEL MPS robotic sampler with TDU option, GERSTEL CIS 4 Cooled Inlet System with LN₂ option, GERSTEL GSS²⁸ Air Sampler, Agilent 7890B GC/5977A MSD

Analysis conditions.

TDU:	splitless 40°C, 720°C/min, 280°C (3 min)
PTV:	solvent vent (50 mL/min); split 10:1 -120°C, 12°C/sec, 275°C (3 min)
Column:	30 m Rxi [®] -5 MS (Restek), d _i = 0.25 mm d _f = 0.25 μm
Pneumatics:	He, constant flow (1.0 mL/min)
Oven:	40°C (1 min), 8°C/min, 200°C, 20°C/min, 280°C (3 min)
MSD:	Full Scan, 35-450 amu

Sampling setup and conditions. The GERSTEL GSS²⁸ (Figure 1) was loaded with 12 conditioned TDU sorbent tubes packed with Tenax TA. A 1.0 meter piece of ¼" Teflon tubing was connected to the back of the sampler using a ¼" to 1/8" Swagelock 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 air freshener was sprayed in the room at a height of approximately 7 feet and deployed for a total of 10 seconds while sweeping around the room. A one minute time interval was used prior to sampling. The tubes were 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.



Figure 1. GERSTEL GSS²⁸ Air Sampler.

Combined standards of linalool and limonene were prepared from neat starting material at concentrations of approximately 0.30, 3.0, and 30 μg/mL. 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.

Three spray air freshener products were purchased at a local store. In order to examine the composition of the air fresheners, a static headspace sorptive extraction (HSSE) analysis was performed on each product by spraying a small amount into a 40 mL vial and suspending a GERSTEL Twister[®] above the liquid sample inside the sealed vial for 5 minutes. The Twisters were removed and analyzed with a 50:1 split transfer from the CIS inlet to the column.

Sample introduction to the GC/MS. Twisters and/or Tenax-TA tubes were loaded onto the MultiPurpose Sampler (MPS) VT-98t tray. Samples were desorbed in the TDU in splitless mode under a 50 ml/min helium flow @ 280°C for 3 min. 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 the split mode (10:1) by heating the CIS inlet rapidly to 275°C with a hold time of three minutes.

RESULTS AND DISCUSSION.

Headspace sorptive extraction (HSSE) analysis of the three air freshener products resulted in the chromatograms shown in Figure 2. Several fragrance compounds are identified in the chromatograms. Linalool and limonene are common to all three products, with the Hawaiian scent having a high concentration of limonene. In the other two products, limonene is a minor peak. Linalool is a significant component of all three products. The chromatogram for the magnolia/cherry blossom scent has the fewest peaks with a series of ionones eluting late in the chromatogram.

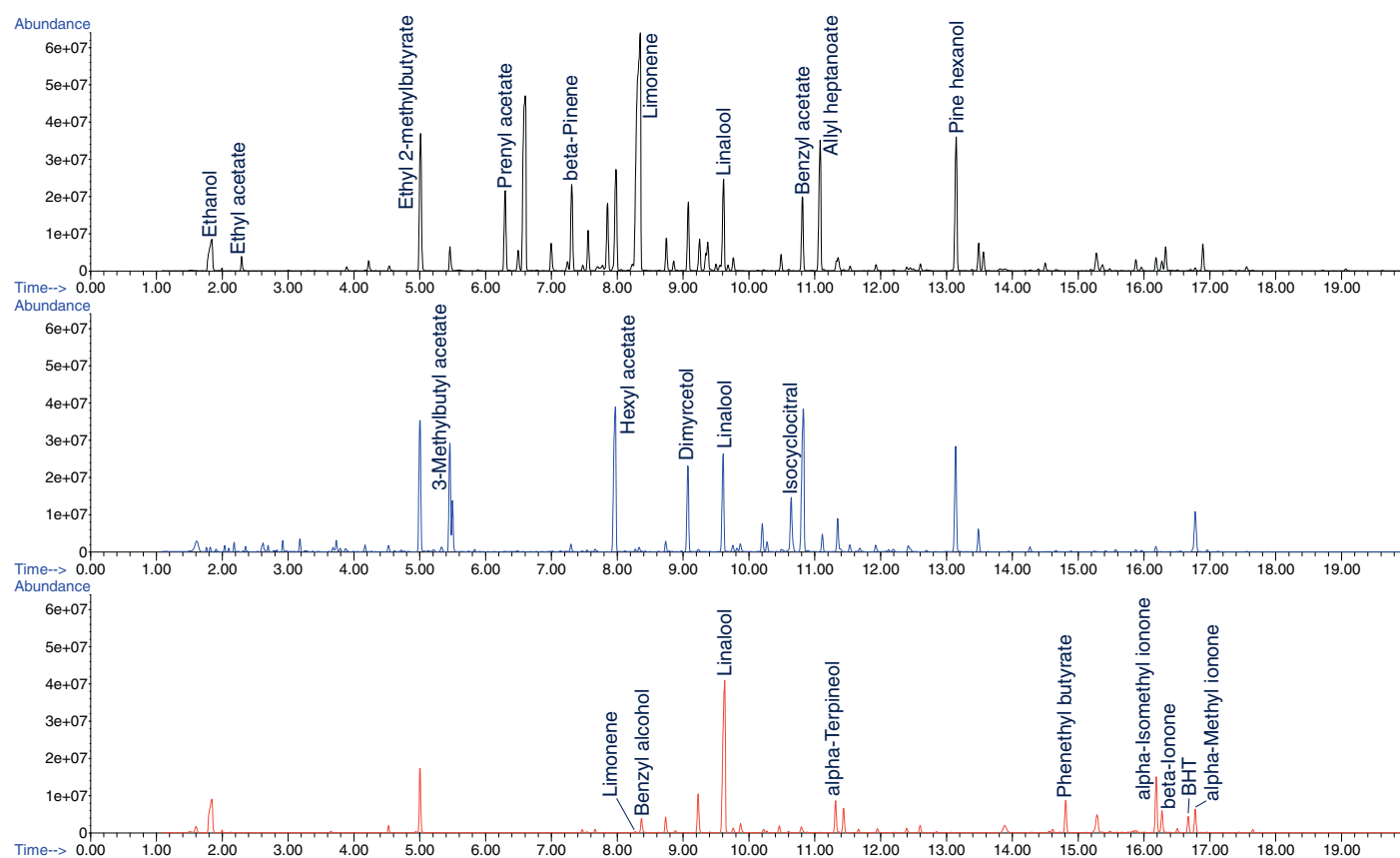


Figure 2. Stacked view of total ion chromatograms for HSSE analysis of air fresheners. Hawaiian scent (black), red honeysuckle (blue), and magnolia/cherry blossom (red).

Standards of linalool and limonene were available in the lab and were common to all three products, so these compounds were chosen for air sampling method development. A flow rate of 25 mL/min and a sampling time of 20 minutes were chosen providing a total volume of 0.50 L per sample tube. The sampling conditions were verified for recovery and precision by spiking $n=3$ tubes with three different levels of the compounds and sampling through each tube for the specified time and flow rate. Quantification was performed by spiking the same amount onto the fritted end of a Tenax-TA tube and purging it onto the tube with dry nitrogen at a flow of 50 mL/min for 3 minutes. All tubes were analyzed with the same thermal desorption and GC/MSD parameters.

Table 1 shows the results for the three spike levels.

Table 1. Spike levels, peak areas and recoveries for limonene and linalool.

Spike Level [ng]		Sampling Volume [L]	Peak Area	
Limonene	Linalool		Limonene	Linalool
0.885	1.14	0.0	27715	12103
0.885	1.14	0.5	31163	14185
0.885	1.14	0.5	28467	15350
0.885	1.14	0.5	25626	15137
		Avg Recovery	103	123
		%RSD	9.7	4.2
8.85	11.4	0.0	158598	146166
8.85	11.4	0.5	162660	160225
8.85	11.4	0.5	160338	155010
8.85	11.4	0.5	154925	154588
		Avg Recovery	100	107
		%RSD	2.5	2.0
88.5	114	0.0	1525006	1650329
88.5	114	0.5	1502139	1662115
88.5	114	0.5	1529394	1685681
88.5	114	0.5	1474831	1623210
		Avg Recovery	98	100
		%RSD	1.8	1.9

The recovery was calculated by dividing the peak area for the sampled tube by that for the tube onto which nothing was sampled, essentially determining the percentage of the spiked standard compounds retained on the tube during air sampling. The data shows good recoveries and precision for the three spike levels. Linear regression of the three point calibration curves for limonene and linalool shows R^2 values of 1.000 for both compounds.

For air sampling of the actual product, a 9' x 13' office with 10' ceiling was used. The deployment of the air freshener product is described above. The air fresheners were deployed at the end of the work day and the door to the room closed. A large fan was used to ventilate the room between samples. After sampling was complete, the Tenax-TA tubes were removed from the sampler and placed in the VT98t tray on the MPS sampler.

Figure 3 shows the decay curves for limonene, linalool, and alpha-isomethyl ionone for the magnolia/cherry blossom sample air freshener. The area count is plotted against time. The linalool shows an increase in concentration after the first twenty minutes, then a steady decay over the four hour period. The alpha-isomethyl ionone, a higher molecular weight compound with a woody violet floral odor [1], was not

detected on the first tube, reaches a maximum level at 60 minutes, then decays in a similar fashion to the linalool. The limonene, a minor component of this product, shows a very slow decrease in concentration over the sampling time period.

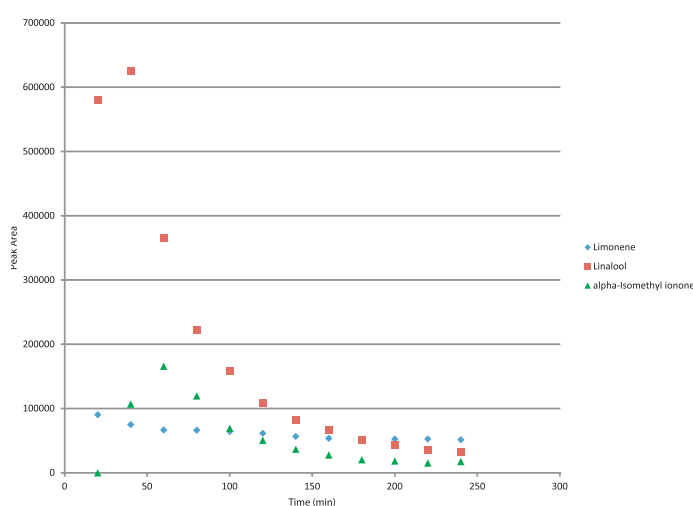


Figure 3. Decay curves for limonene, linalool, and alpha-methyl ionone introduced by spraying the magnolia/cherry blossom fragrance air freshener.

Figure 4 shows the decay curves for hexyl acetate (green, fruity, sweet), linalool, and apple ketal (sweet, fruity, apple) for the red honeysuckle sample. All three compounds show a similar decrease in concentration to a low steady state over the four hour period. The limonene (not shown), a minor component of this product, showed a very slow decrease over the sampling time period. The first tube at time point 20 minutes was unfortunately lost due to an instrument malfunction.

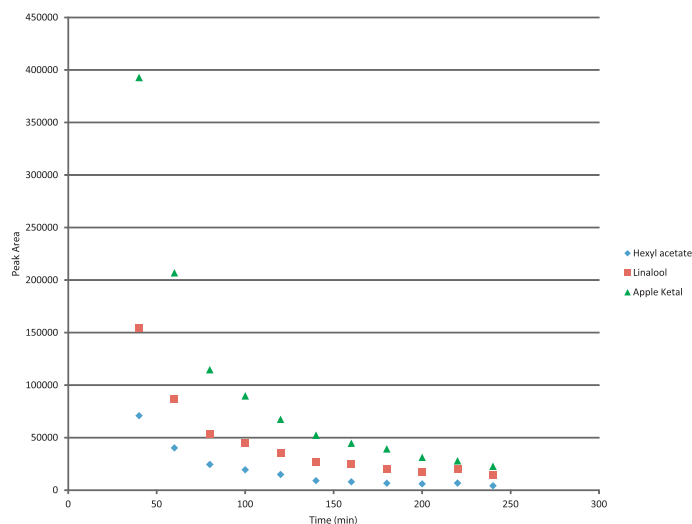


Figure 4. Decay curves for hexyl acetate, linalool, and apple ketal introduced by spraying the red honeysuckle fragrance air freshener.

Figure 5 shows the decay curves for limonene, linalool, and allyl heptanoate (sweet, pineapple, fruity) for the Hawaiian air freshener. The linalool and allyl heptanoate show a similar decrease in concentration to a low steady state over the four hour period. The limonene shows a steady concentration decay with a slight increase in concentration at 160 min. It reaches a steady state after that time. Limonene is a common fragrance ingredient in many commercial products. The increase in concentration at 160 min may be from other sources used by the office night cleaning crew.

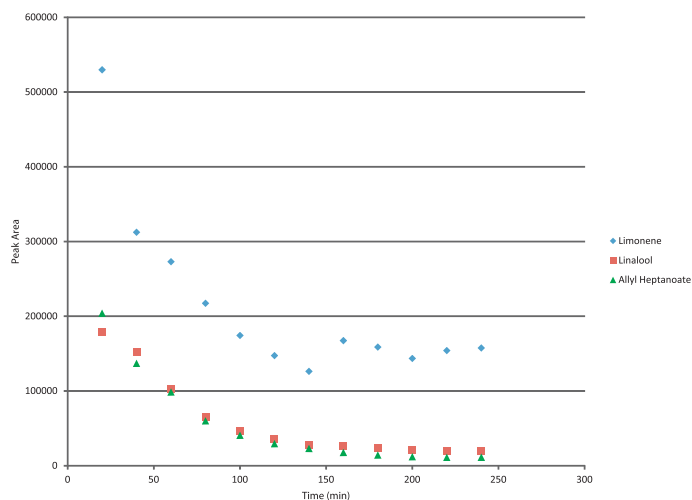


Figure 5. Decay curves for limonene, linalool, and allyl heptanoate introduced by spraying the Hawaiian fragrance air freshener.

Figure 6 shows the decay curve for ethanol as a function of time for the Hawaiian fragrance. The ethanol shows a pattern similar to the fragrance compounds in the sample. The ethanol is most likely used in this type of product to help solubilize the fragrance compounds. The graph demonstrates that with the proper selection of sorbent tube and sampling conditions, even very volatile compounds can be monitored successfully.

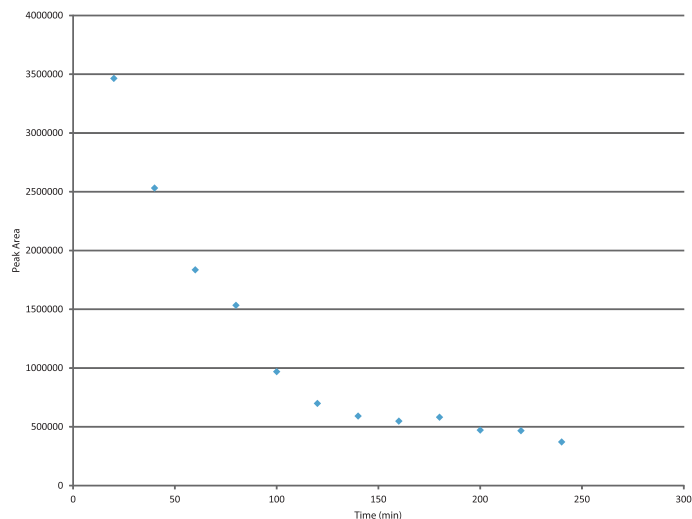


Figure 6. Decay curve for ethanol introduced by spraying the Hawaiian fragrance air freshener.

Figure 7 shows the decay curve for Linalool for the Hawaiian fragrance. 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). This provides a convenient way to look at the data and see how the actual airborne concentration changes as a function of time. For the purposes of this figure, an additional time point was taken at 23 hours (1380 minutes) using a GERSTEL GSS handheld sampler. A clean Tenax-TA tube was attached to one channel of the sampler and placed in the office area. The tube was sampled at 25 mL/min for 20 minutes. A power curve, fit to the data, is shown in the figure. The red line denotes the odor threshold, 4.5 ng/L (0.8 ppbV), for R-linalool [1]. The level of the linalool falls below the odor threshold at 180 minutes. Under the sampling conditions used for these experiments, quantification below the odor threshold is easily accomplished for this analyte.

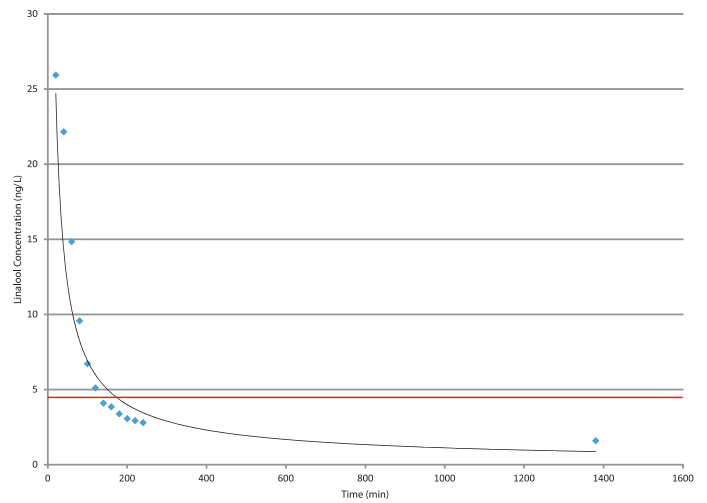


Figure 7. Decay curve for linalool introduced by spraying the Hawaiian fragrance expressed as air concentration.

Figure 8 shows an example chromatogram for the Hawaiian fragrance air freshener for the first tube in the series. Several of the fragrance peaks are labeled in the figure.

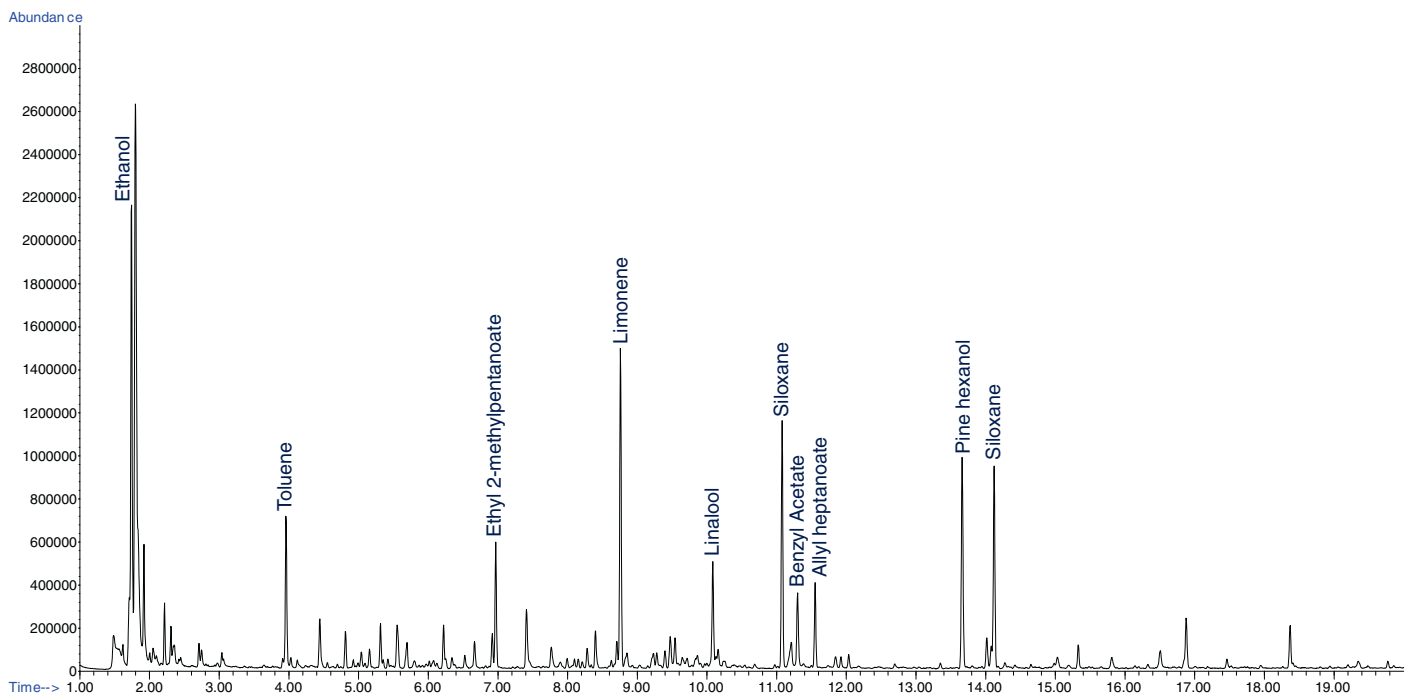


Figure 8. Total ion chromatogram for tube #1 for the Hawaiian fragrance air freshener.

CONCLUSIONS

This study shows the use of the GERSTEL GSS²⁸ for quantitative air sampling for the determination of fragrance compounds released from a spray air freshener. Sampling conditions were optimized for limonene and linalool. For other analytes, sampling conditions, 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. A series of 12 Tenax-TA TDU tubes were used to cover a 4 hour time period. The GSS²⁸ allows for automated sampling onto as many as 28 tubes, which can be used to cover a user defined time period. This type of experiment can be used to determine the rate at which compound concentrations decay in indoor air as a function of time, as well as to identify those compounds, which contribute to the perceived odor in the room.

REFERENCES

- [1] <http://www.thegoodscentcompany.com>



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