

Hot Spring Gas Analysis for Earthquake Surveillance Using the Agilent 990 Micro GC

Author

Sheng Geng Agilent Technologies (Shanghai) Co. Ltd. Shanghai 200131 P. R. China

Abstract

An Agilent 990 Micro GC was used to quickly and accurately analyze hot spring gases associated with seismic activity. The 990 Micro GC was equipped with an Agilent J&W CP-Molsieve 5Å backflush channel and an Agilent J&W PoraPLOT U straight channel. All gases analyzed gave good retention time and peak area repeatability.

Introduction

Great earthquakes are usually linked with geochemical changes in the hot spring gases present in active fault zones.

These changes come from the gases in the lithosphere expelled to the surface during the seismogenic process, which can be observed as bubbling gas and dissolved gas in hot springs. The gas composition varies in concentration and ratio and typically contains helium, hydrogen, oxygen, nitrogen, methane, carbon dioxide, and hydrogen sulfide, all of which are critical indicators for checking seismic activity.

The 990 Micro GC can quickly and accurately analyze gas samples, which makes it a suitable platform for checking spring gas compositions. The primary component of the bubbling gas is carbon dioxide at greater than 85%. A focus of this application is to better test the permanent gases in this carbon dioxide matrix, especially early-eluting helium, neon, and hydrogen. A 20 m J&W CP-Molsieve 5Å backflush column with a 3 m precolumn was used to backflush out the carbon dioxide and to obtain good resolution of helium, neon, and hydrogen. Among these gases, helium, hydrogen, and hydrogen sulfide are frequently required to be tested at the low ppm level. These requirements can be met by the 990 Micro GC.

Experimental

The 990 Micro GC was equipped with a 3 m + 20 m J&W CP-Molsieve 5Å backflush channel, and a 10 m J&W PoraPLOT U straight channel. Table 1 shows the experimental conditions of this application. The composition of the spring gas standard is listed in Table 2.

Table 1. Test conditions for the hot spring gas analysis.

Channel	1	2		
Column Type	3 m + 20 m Agilent J&W CP-Molsieve 5Å, backflush, RTS*	10 m Agilent J&W PoraPLOT U, straight		
Carrier Gas	Argon	Helium		
Column Pressure	200 kPa	150 kPa		
Injector Temperature	60 °C	50 °C		
Column Temperature	60 °C	50 °C		
Injection Time	150 ms	100 ms		
Backflush Time**	31 s	NA		
Sampling Time	60 s			
Run Time	400 s			

^{*} The retention time stability (RTS) filters were used to prevent the water and carbon dioxide in the carrier gas from entering the CP-Molsieve 5Å column.

Table 2. Composition of the hot spring gas standard.

Compound	Concentration			
Helium	5.4 ppm			
Neon	5.0 ppm			
Hydrogen	5.0 ppm			
Oxygen	504 ppm			
Nitrogen	0.998%			
Methane	0.201%			
Hydrogen Sulfide	10 ppm			
Carbonyl Sulfide	10 ppm			
Carbon Dioxide	Balance			

Results and discussion

The experimental data are listed in Table 3. Repeatability for retention time (RT) and peak area were measured as the percentage of the relative standard deviation (RSD) compared to the mean of 10 runs. The lower detection limits (LDLs) were calculated as two times the four-sigma noise.

 Table 3. Retention time, peak area repeatability, and LDL of 10 runs of the standard gas.

Compound	Channel	RT (min)	RT RSD	Area (mV × s)	Area RSD	LDL (ppm)
Helium	1	1.631	0.010%	0.0340	3.47%	0.752
Neon	1	1.678	0.012%	0.0122	3.64%	1.44
Hydrogen	1	1.783	0.011%	0.0583	3.57%	0.460
Oxygen	1	2.576	0.019%	0.377	2.49%	8.88
Nitrogen	1	4.002	0.046%	8.93	0.402%	13.8
Methane	1	5.730	0.040%	4.48	2.02%	10.2
	2	0.394	0.006%	5.74	0.503%	0.174
Carbon Dioxide	2	0.448	0.005%	3994	0.0158%	1.27
Hydrogen Sulfide	2	1.145	0.024%	0.0186	5.22%	1.33
Carbonyl Sulfide	2	1.444	0.020%	0.0451	3.27%	0.604

^{**} The backflush time should be tuned for each new channel.

The 3 m + 20 m CP-Molsieve 5Å backflush channel was equipped to separate helium, neon, hydrogen, oxygen, nitrogen, and methane. The separation and detection of the first three peaks - helium, neon, and hydrogen - were critical to this application. Argon was used as carrier gas for this channel to obtain better sensitivity. In the standard gas, the concentrations of helium, neon, and hydrogen were as low as 5 ppm, therefore a long injection time (150 ms) was used. If the concentration of these gases was higher in the actual sample, a shorter injection time should be used for better separation. Similarly, if peaks were found flat-topped or deformed, a shorter injection time should be used. The 3 m precolumn was used to completely backflush out the carbon dioxide. The backflush time should be carefully tuned to prevent carbon dioxide from entering the CP-Molsieve 5Å analytical column, which might lead to baseline bumps and column efficiency decrease. Figure 1 shows the chromatogram of this channel.

The 10 m PoraPLOT U straight channel was equipped to separate methane, carbon dioxide, and hydrogen sulfide. The injection time of 100 ms was set to obtain a better detection limit of hydrogen sulfide. If the separation of methane and carbon dioxide was more important, the injection time could be set lower. Methane had a much better LDL on this channel compared to channel 1. However, if the concentration of air or methane is high, the separation might be a challenge. Note that in this test, the calibration was set using the standard gas with carbon dioxide as the matrix. If in actual samples, the matrix is air (nitrogen) or other gas types, the standard gas matrix should be changed accordingly to obtain more accurate quantitative results. Figures 2 and 3 show the chromatogram of this channel.

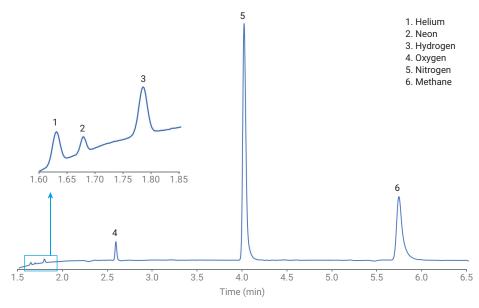
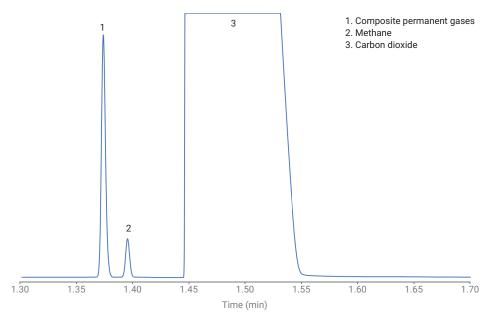


Figure 1. Chromatogram of helium, neon, hydrogen, oxygen, nitrogen, and methane on the 3 m + 20 m Agilent J&W CP-Molsieve 5Å backflush channel.



 $\textbf{Figure 2.} \ \, \text{Chromatogram of methane and carbon dioxide on the 10 m Agilent J\&W PoraPLOT U straight channel.}$

Conclusion

This application note shows the analysis of hot spring gas using the Agilent 990 Micro GC. The permanent gases and hydrogen sulfide in carbon dioxide matrix can be analyzed with good retention time and peak area repeatability. The fast and accurate results of the 990 Micro GC can improve hot spring gas checking and allow a better correlation between gas geochemistry and seismic activity.

References

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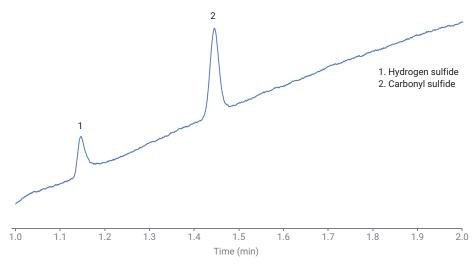


Figure 3. Chromatogram of hydrogen sulfide and carbonyl sulfide on the 10 m Agilent J&W PoraPLOT U straight channel.

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