§7. Improvement of Hydrogen Analyzer with Trace Reduction Detector

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We have developed an analyzer that can measure infinitesimal concentrations of hydrogen that uses functions of a gas chromatograph and an atomic absorption spectrophotometer. The gas chromatograph part acts as a carrier gas purifier, a valve controller, and a gas element separator. The spectrophotometer part acts as a highly sensitive hydrogen detector, that is, a tracer reduction detector composed of a mercuric-oxide bed and a mercury vapor lamp.

We carried out a performance test using three sample gases with 5-, 20-, and 50-ppb hydrogen in nitrogen dilution gas. The nitrogen was used to simulate an air sample. In the test, we repeated the measurements over a period of about 12 hours and obtained more than 30 spectra. Using the data obtained, we examined the change in the peak and the retention time as a function of the elapsed time, which closely corresponded to the number of measurements.

We found that peaks were very stable, with coefficient of variations of less than 7.6, 7.1 and 3.9% for the 5-, 20-, and 50-ppb hydrogen sample gases, respectively. These results demonstrate that the peak was measured independently of the elapsed time, i.e., the number of measurements. However, the performance test showed a shortening in the retention time.

To determine the cause of the retention time shortening, we repeated the measurements using two different approaches. In one, the separation column was extracted from the liquid nitrogen and allowed to warm to room temperature immediately before the start of each measurement. In the other, we used a sample gas of 50-ppb hydrogen diluted by helium instead of nitrogen. These measurements indicated that the retention time was shortened by nitrogen deposited in the separation column immersed in liquid nitrogen.

To verify this, we attached an MS-5A separation column and a thermal conductivity detector (TCD) in front of the separation column (Hydro isopack). The improved analyzer is shown in Fig.1. In the improved analyzer, immediately after the hydrogen has completely passed through the MS-5A column and sent to the hydro isopack column, the pass line is switched to an impurities release line. The carrier gas transporting the hydrogen is drawn into the hydro isopack column, and that transporting the nitrogen is released. We call this the "after-cut method" because the switching occurs after the hydrogen peak appears in the chromatogram.

Using this improved analyzer, we measured the hydrogen concentration over 12 hours and obtained more than 30 spectra again. The peak and retention time data are

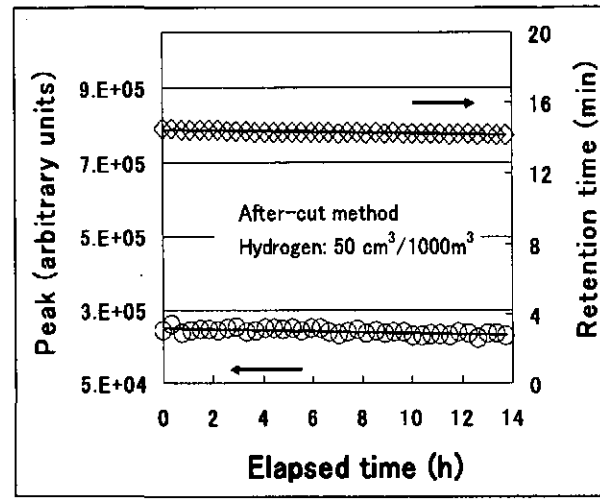

Fig. 2 Elapsed-time dependence of peak and retention time in spectra obtained using improved analyzer.

plotted in Fig. 2 as a function of elapsed time. In Fig.2, the peak was almost constant, and the retention time was constant and independent of the elapsed time, i.e., of the number of measurements. The data for both are distributed closely around the horizontal bold lines obtained by calculation using the least squares method. The relative standard deviations were 4.2 and 0.64%, respectively. These results demonstrate that the after-cut method can effectively eliminate the retention time shortening caused by nitrogen in the sample/carrier gas stream. With this improved analyzer, we can now measure infinitesimal concentrations of hydrogen (less than a few ppb) in air.

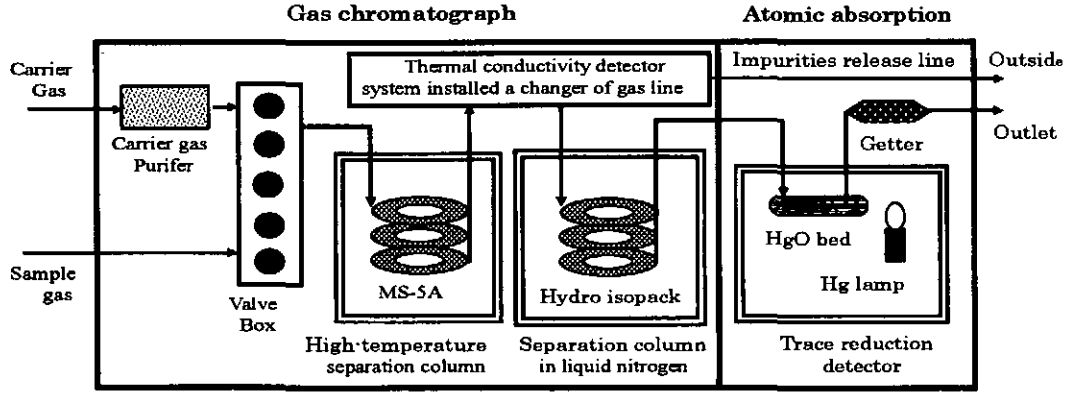

Fig. 1 Configuration of improved analyzer using after-cut method.