

Stability test and improvement of hydrogen analyzer with trace reduction detector

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Abstract

We previously developed an analyzer able to detect hydrogen concentrations of less than $50 \text{ cm}^3/1000 \text{ m}^3$. The analyzer uses a carrier gas purifier and a low temperature separation column to remove impurities preventing measurement of low concentrations from the carrier and sample gases. It uses a trace reduction detector with a mercuric oxide bed to detect the concentration of hydrogen based on the reduction reaction of mercuric oxide with hydrogen. We have now evaluated the performance of the analyzer by carrying out a series of tests that measured the spectrum peak and the retention time. We used three sample gases with hydrogen concentrations of 5, 20, and $50 \text{ cm}^3/1000 \text{ m}^3$ in nitrogen dilution gas. The measured peak was stable (it was within a relative standard deviation of less than 10%), and there was a linear relationship between the peak and hydrogen concentration. However, the retention time gradually shortened as the measurements were repeated. The shortening was reduced by warming the low temperature separation column used in the analyzer; it was not observed when we used a hydrogen sample gas diluted by helium instead of nitrogen. Using nitrogen as a dilution gas apparently shortens the retention time. We thus added an MS-5A separation column and a thermal conductivity detector. The nitrogen and hydrogen in the sample/carrier gas are separated, and the nitrogen is efficiently removed by switching the pass line to a release line after the hydrogen has been sent to the low temperature separation column. An analyzer using this “after-cut method” was able to stably measure infinitesimal hydrogen concentrations and was not affected by nitrogen in the sample gas.

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1. Introduction

Although hydrogen is the most abundant element in the universe, the concentration of hydrogen in air is minute: about $500 \text{ cm}^3/1000 \text{ m}^3$ (ppb: parts per billion) [1]. Hydrogen has become a hugely promising energy resource that may replace petroleum as a source of energy in the future. When hydrogen energy does become practical and widely used as a main energy source, for example, as fuel for cars, its abundance in air will increase. It will thus become important to monitor the hydrogen concentration in air from the viewpoint of environmental assessment. We previously developed an analyzer that can detect hydrogen

concentrations of less than $50 \text{ cm}^3/1000 \text{ m}^3$, corresponding to one-tenth the natural abundance of hydrogen in air [2].

Gas chromatographs and atomic absorption spectrophotometers are often used in chemical analysis. These instruments are based on different analysis principles and have distinctive features [3–6]. A gas chromatograph contains a carrier gas flow controller, a sample gas injector, and a gas components separation column. It is excellent for controlling the composition of the gas. An atomic absorption spectrophotometer contains a sample gasifier, a photo multiplier, and a source lamp. It is very sensitive to specific elements, like mercury vapor. Our hydrogen analyzer utilizes functions from both types of instruments.

Each device alone is not capable of measuring hydrogen concentrations below $50 \text{ cm}^3/1000 \text{ m}^3$. A conventional gas chromatograph with a thermal conductivity detector can

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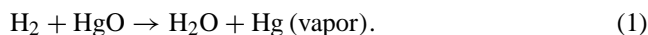
detect hydrogen concentrations of a few hundred parts per million (cm^3/m^3), while a conventional atomic absorption spectrophotometer usually cannot detect hydrogen because it lacks the source lamp needed for detecting hydrogen, and hydrogen gas is often used to make a source-flame to gasify a sample in the apparatus. However, a hydrogen analyzer that combined the composition controlling function of a gas chromatograph with the highly sensitive detector of an atomic absorption spectrophotometer would have sufficient sensitivity. Our analyzer is basically part gas chromatograph and part atomic absorption spectrophotometer. The former functions as a gas flow controller, a sample gas injector, and carrier and sample gas purifier, while the latter functions as a highly sensitive hydrogen detector based on the reduction reaction of mercuric oxide with hydrogen in the sample gas. The detector is called a “trace reduction detector” (Round Science, Uji, Japan). In practical measurement of hydrogen using this analyzer, we obtain the chromatogram monitored at a single ray emitted from mercury based on an atomic absorption, from which we can derive the hydrogen concentration. For simplicity, we call the chromatogram obtained based on the atomic absorption of mercury the “spectrum,” and the usual gas chromatograph obtained by the thermal conductivity detector, the “chromatogram.”

We have now carried out a series of performance tests to evaluate the stability of the analyzer as measured by the peak and the retention time in the spectrum. A previous study demonstrated that this hydrogen analyzer can detect a hydrogen concentration as low as $5 \text{ cm}^3/1000 \text{ m}^3$ in nitrogen gas [2]. The present study goes beyond the previous in its use of a longer measurement period. The performance tests showed a shortening in the retention time and that the shortening might be caused by nitrogen in the sample gas. To confirm this, we improved the analyzer to efficiently remove the nitrogen gas. Using the improved analyzer we were able to stably measure infinitesimal hydrogen concentrations, confirming that nitrogen shortened the retention time.

2. Construction of initial hydrogen analyzer

The initial hydrogen analyzer utilizing the functions of a gas chromatograph and an atomic absorption spectrophotometer is illustrated in Fig. 1. The chromatograph part consists of a carrier gas purifier, a valve box, and a separation column (Hydro Isopack, GTR TEC, Uji, Japan). The separation column is immersed in liquid nitrogen in a vacuum bottle. The other components of the chromatograph part, like the circler pump, are omitted in Fig. 1 for simplicity. The atomic absorption part contains a trace reduction detector composed of a mercuric oxide (HgO) bed and a mercury vapor lamp and with an attached getter tube. The other components of the atomic absorption part, like the photometer, are again omitted for simplicity.

The trace reduction detector is able to detect hydrogen with very high sensitivity based on a chemical reduction reaction:



This reduction reaction of hydrogen with mercury generates mercury vapor, and the vapor is measured, in place of the target hydrogen, using the vapor’s spectral absorption. The measured concentration of mercury exactly reflects the hydrogen concentration in the sample, because a hydrogen molecule generates a mercury atom and the number of the atom thus generated corresponds to strength of atomic absorption. Since the generated mercury vapor is very dangerous, a getter tube packed with activated carbon is attached to the outlet of the mercury oxide bed. The carbon immediately absorbs the mercury vapor, preventing its release into the atmosphere. Using a trace reduction detector with a getter tube is a distinctive feature of the analyzer.

Another distinctive feature is the use of a carrier gas purifier and a low temperature separation column to remove impurities in the sample/carrier gas in the gas chromatograph part. The first purifier is used because impurities in the carrier gas create a noise signal larger than one of hydrogen we intend to measure, making it difficult to measure low

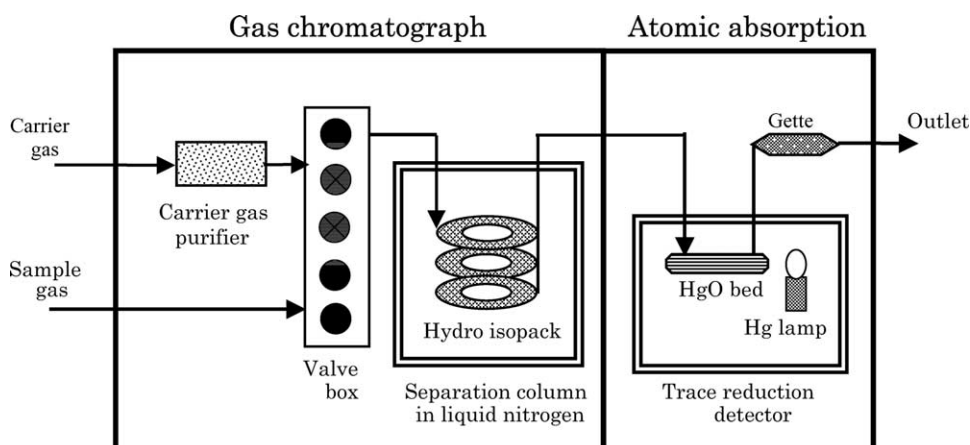


Fig. 1. Initial hydrogen analyzer utilizing functions of gas chromatograph and atomic absorption spectrophotometer.

concentrations of hydrogen, particularly when there are less than a few cubic centimeter per cubic meter (cm^3/m^3) of hydrogen to be measured in the sample gas. We used neon (Sumitomo Seika Chemicals, Osaka, Japan) as the carrier gas, and it can originally contain up to $2 \text{ cm}^3/\text{m}^3$ of hydrogen, much higher than the concentration of hydrogen we wanted to measure. We thus used an inert gas purifier (Gate Keeper, Aeronex, San Diego, CA, USA) to remove such impurities as hydrogen before the carrier gas was drawn into the valve box. The purified carrier gas and the sample gas were separately drawn into the valve box of the gas chromatograph part and then mixed there, making a carrier/sample gas.

The low temperature separation column is used as the second purifier because the sample gas, like air, contains such impurities as carbon monoxide and oxygen and these impurities may react with the mercuric oxides in the mercuric-oxide bed of the trace reduction detector or with the generated mercuric vapor. This would make it difficult to generate mercury vapor in an amount proportional to the hydrogen concentration. We thus used a liquid nitrogen cooling method (77 K) that utilizes a low temperature separation column (Hydro Isopack) in the gas chromatograph part. The sample/carrier gas is passed through the column, and all impurities with a boiling point higher than the 77 K of liquid nitrogen are deposited and removed from the streaming gas. The oxygen and carbon monoxide, which are the components of air and are strong reducing agents for mercuric oxides, have boiling points of 90 and 81.5 K, respectively [7]. Thus, as the sample/carrier gas pass through the low temperature separation column, all impurities that degrade the measurement are completely removed before the gas is sent to the trace reduction detector in the atomic absorption part.

3. Experiment and results

We tested the analyzer in a series of measurements using three sample gases with different hydrogen concentrations (5, 20, and $50 \text{ cm}^3/1000 \text{ m}^3$) in neon carrier gas. Nitrogen was used to dilute the hydrogen to simulate air when we made a sample gas. The sample gases were prepared using our own gas mixer [2], a commercially available standard hydrogen gas of a known concentration ($2 \text{ cm}^3/\text{m}^3$), and pure nitrogen gas. The mixer consisted of three mass flow controllers with maximum controllable flow rates of 2, 100, and $1000 \text{ cm}^3/\text{min}$ (STEC, Kyoto, Japan). The sample gas being tested was continuously provided to the analyzer from the mixer.

For each sample gas, we carried out three performance tests: one to test the hydrogen detection limit and two to test the stability of spectrum measurement. For all three tests, we repeatedly measured the hydrogen concentration for about 12 h, obtaining more than 30 spectra for each gas.

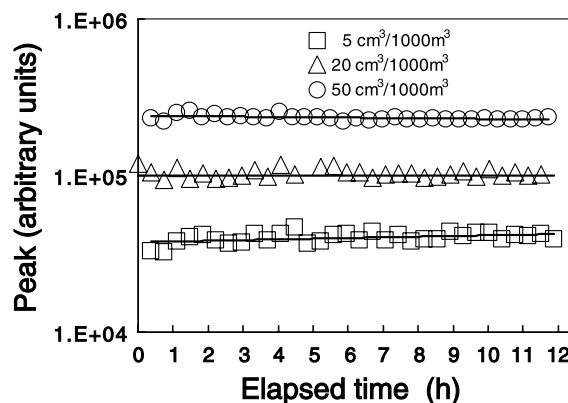


Fig. 2. Peaks in spectra obtained by repeated measurements over 12 h.

3.1. Detection limit and linearity between hydrogen concentration and peak

Using the data spectra obtained for the three sample gases, we calculated the average hydrogen peak in the spectra and its standard deviation. Then, the straight line was derived by calculation using the least squares method and the average peak data and standard deviations for the three sample gases as the following equation: $Y = 4314.6X + 18124$ (X : hydrogen concentration, Y : peak). The coefficient of determination (R^2 value) was 1.00, indicating a definite linear relationship between the peak and the hydrogen concentration. These results strongly support our previous findings [2].

3.2. Stability of measurement: peak

The changes in the peaks in the spectrum obtained for the test gases are shown in Fig. 2. Each measurement took about 20 min, so more than 30 measurements were completed in the 12 h. The lines were derived using the least squares method. They are almost horizontal, and the relative standard deviation derived for the 5, 20, and $50 \text{ cm}^3/1000 \text{ m}^3$ samples were about 7.6, 7.1, and 3.9%, respectively. That is, the deviation increased as the concentration was reduced. These results demonstrate that the peak was independent of the elapsed time and the number of measurements. Fig. 2 also shows that the peaks were stable; they were not affected by the number of measurements.

3.3. Stability of measurement: retention time

The retention time corresponds to the position of the peak, as represented in elapsed time, in a spectrum. The retention times for the three samples and the line derived by calculation using the least squares method and data for the $5 \text{ cm}^3/1000 \text{ m}^3$ sample are put in Fig. 3. As shown in Fig. 3, the data for the 20 and $50 \text{ cm}^3/1000 \text{ m}^3$ samples were distributed closely along the line for the $5 \text{ cm}^3/1000 \text{ m}^3$ sample. The curves are virtually indistinguishable. This clearly shows that the retention time shortened as time elapsed,

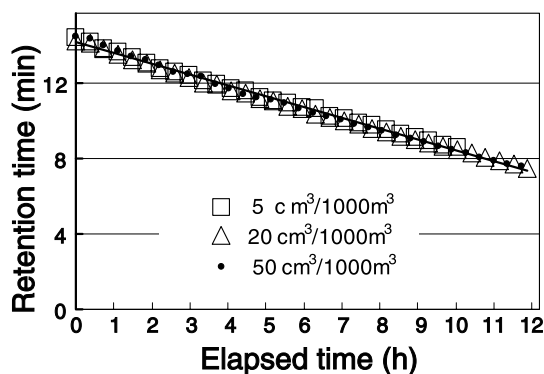


Fig. 3. Time-dependence of retention time in spectra obtained by repeated measurements over 12 h.

independent of the hydrogen concentration, while the peaks did not change much with the elapsed time (Fig. 2).

4. Improved analyzer

To determine the reason for the retention time shortening, we carried out the measurements again using a different approach. Immediately before each measurement, we extracted the separation column from the liquid nitrogen in the vacuum bottle, allowed it to warm for about 20 min under the room temperature and then re-immersed it into the liquid nitrogen. We suspected that the agent causing the retention time shortening would be gasified and removed by this procedure. This is apparently what happened because the retention times for the later measurements were exactly the same as the one for the first measurement. The retention time shortening may be due to nitrogen deposited in the separation column at low temperatures because nitrogen occupied a larger part of the sample gas, and some of it was likely to be deposited, either as a solid or as a liquid, at low temperatures.

To confirm our hypothesis, we prepared another test sample of $50 \text{ cm}^3/1000 \text{ m}^3$ hydrogen diluted by helium instead

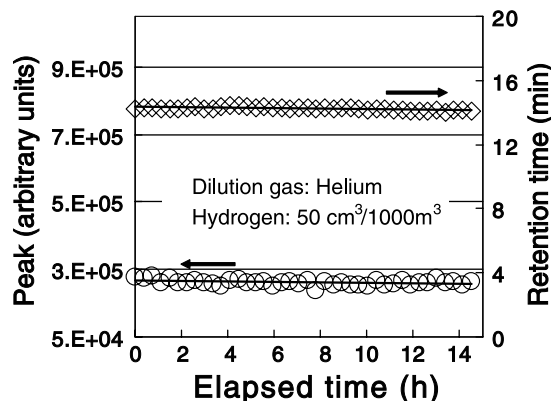


Fig. 4. Elapsed-time dependence of peak and retention time of hydrogen sample diluted by helium instead of nitrogen.

of nitrogen. We measured the hydrogen concentration over 12 h and obtained more than 30 spectra. The peak and retention time data are plotted in Fig. 4 as a function of elapsed time. The relative standard deviations were 3.9 and 0.7%, respectively, indicating that the peak and retention time were stable and independent of the elapsed time. That is, the retention time was not shortened when helium was used to dilute the hydrogen. Therefore, the nitrogen must have shortened the retention time. Since the fraction of nitrogen in air is 0.78, using air as the sample gas is problematic. Although warming the separation column alleviated this problem, this approach is not practical because it takes a great deal of time and makes automatic measurement repetition difficult.

We thus took a different approach to improving the analyzer so that it can detect infinitesimal concentrations of hydrogen in an air sample without being affected by nitrogen in the sample/carrier gas. As illustrated in Fig. 5, we attached an MS-5A separation column and a thermal conductivity detector to the front of the low temperature separation column. In this improved analyzer, the other spectrum measured in advance by the thermal conductivity detector as shown in the next paragraph is used to eliminate the nitrogen

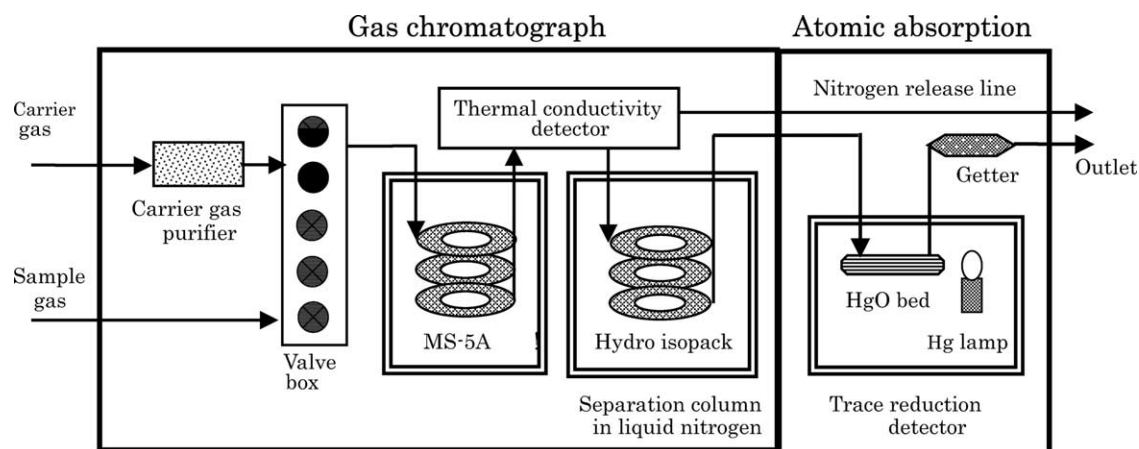


Fig. 5. Configuration of analyzer using after-cut method.

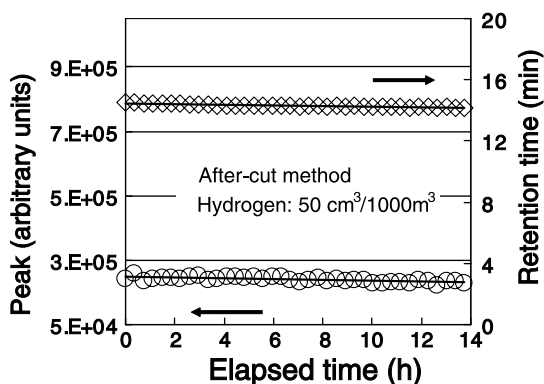


Fig. 6. Elapsed-time dependence of peak and retention time in spectra obtained using improved analyzer.

from the sample/carrier gas when it is in the form of steam. A nitrogen peak generally appears after each hydrogen peak along the retention time axis in a chromatogram measured by the thermal conductivity detector. That is, when a sample/carrier gas with hydrogen and nitrogen passes through the MS-5A column, the two elements are separated based on the principle of gas chromatograph separation. The hydrogen appears first at the outlet of the MS-5A separation column; the nitrogen appears a certain time later. In the improved analyzer, immediately after the hydrogen has completely passed through the MS-5A column, the pass line is switched to a release line. The carrier gas transporting the hydrogen is drawn into the low temperature column (the hydrogen isopack), 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.

The time when the switching has to occur is practically determined beforehand using a sample gas that contains an enough higher concentration of hydrogen (more than $100 \text{ cm}^3/\text{m}^3$) in stead of a hydrogen sample with an infinitesimal concentration to be measured finally, because the thermal conductivity detector has not enough sensitivity to detect an infinitesimal hydrogen concentration below $100 \text{ cm}^3/\text{m}^3$. In this pre-measurement, we can observe the progress of separation by the thermal conductivity detector and know the timing of switching to be occurred. That is, the correct time to switch is determined by the thermal conductivity detector with a large concentration of hydrogen sample and the switch was driven by time alone for the lower concentration. Thus, we could remove nitrogen in a sample gas, where nitrogen gas was used as a dilution gas because we would like to imitate air.

As shown in Fig. 6, with the improved analyzer, 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 are very close to those obtained for the sample of $50 \text{ cm}^3/1000 \text{ m}^3$ hydrogen diluted by helium instead of nitrogen (see Fig. 4), demonstrating that the after-cut method can effectively eliminate the retention time shortening caused by nitrogen in the sample/carrier gas stream.

5. Conclusion

We have developed an analyzer that can measure infinitesimal concentrations of hydrogen that uses functions of a gas chromatograph and an atomic absorption spectrophotometer. To evaluate the analyzer, we carried out three performance tests using three sample gases with 5, 20, and $50 \text{ cm}^3/1000 \text{ m}^3$ hydrogen. As a consequence, we found that peaks in spectra for the three sample gases were very stable. However, the retention time was shortened as time elapsed by nitrogen deposited in the low temperature separation column immersed in liquid nitrogen.

To verify this, we attached an MS-5A separation column and a thermal conductivity detector in front of the separation column. In this improved analyzer, we used the spectrum measured by the thermal conductivity detector to eliminate nitrogen from the sample/carrier gas. Using this improved analyzer, we found that the peak still remained almost constant, while the retention time also became constant and independent of the elapsed time, i.e., the number of measurements. These results demonstrate that the after-cut method used in the improved analyzer effectively eliminates the retention time shortening. With this improved analyzer, we can now measure infinitesimal concentrations of hydrogen (less than a few $\text{cm}^3/1000 \text{ m}^3$) in air.

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