§ 4. Infinitesimal Concentration Hydrogen Analyzer Using TRD

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By combining the functions of a gas chromatograph and an atomic absorption spectrophotometer, we have developed an infinitesimal concentration hydrogen analyzer capable of analyzing hydrogen concentrations of from a hundred ppb down to a few ppb. The analyzer comprises a gas chromatograph and atomic absorption parts as shown in Fig.1. The gas chromatograph part consists of a carrier gas purifier, a valve box and a separation column (Hydro isopack), which is immersed in liquid nitrogen in a vacuum bottle vessel. The atomic absorption part contains a tracer reduction detector (TRD, Round Science Inc.) and a getter tube. The TRD is composed of a mercuric-oxide bed and a mercury vapor lamp.

Using the gas chromatograph functions, a sample gas is drawn into the analyzer, where it mixes with purified carrier gas and goes through a separation column (its role is shown later) before being sent to the atomic absorption part. The atomic absorption spectrophotometer analyzes the hydrogen concentration through a reduction reaction of mercuric-oxide with hydrogen.

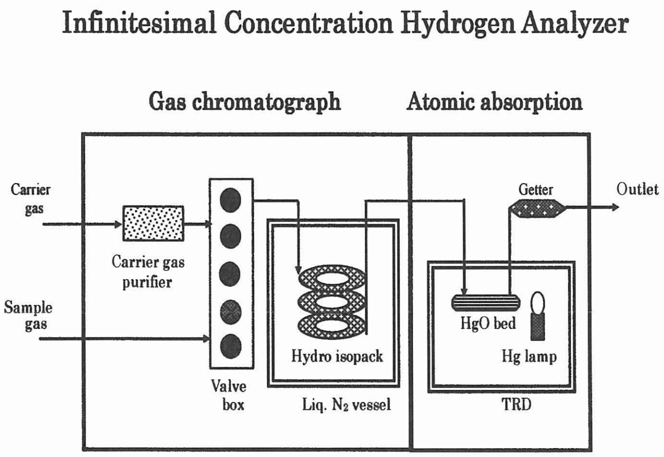

Fig. 1 Configuration of analyzer developed for measurement of infinitesimal concentrations of hydrogen gas.

Regarding the measurement of a very low hydrogen concentration (ppb level), we have to consider several problems. The first is the impurities contained in the carrier gas, because one of the impurities is often hydrogen. In our case, neon gas was used as the carrier gas and a commercially available "pure" neon gas may contain up to 2 ppm of hydrogen, which is far lager than the hydrogen concentration we intend to measure. Therefore, we had to ensure that such impurities had been removed from the carrier gas before the measurement. For this purpose, we employed a gas purifier, which is marketed under the brand name "Gate Keeper (Inert Gas Purifier)" (Aeronex Inc.). Purified carrier gas is sent into a valve box, which injects the sample gas into the carrier gas stream.

Besides carrier gas, we have to deal with impurities contained in the sample gas because the impurities like oxygen and carbon dioxide react with mercuric oxides in the bed and so disturb the expected reaction of mercuric oxide with hydrogen. Thus, we employed the following liquid nitrogen cooling method. The sample gas is drawn in a low-temperature separation column, immersed in liquid nitrogen, and cooled to the liquid nitrogen's temperature (77 K). Then all impurities with boiling points higher than liquid nitrogen temperature will be deposited and removed from the streaming carrier/sample gas, in particular, oxygen (boiling point 90 K) and carbon dioxide (194.5 K) which are the main components of air and strong reducing agents for mercuric oxides.

Thus, while carrier and sample gases pass through the gas chromatograph part, impurities hindering a high sensitivity measurement are removed, and only hydrogen gas remains in the carrier gas to be transported to the atomic absorption part.

In the atomic absorption part, an atomic absorption spectrophotometer with a high sensitivity to mercury vapor is used to detect hydrogen reacting in the TRD. The TRD detects hydrogen with the following reduction reaction:

$$H_2 + HgO \rightarrow H_2O + Hg\ (vapor)\ . \quad (1)$$

That is, hydrogen is drawn through a bed of mercuric oxides and reacts with the mercury oxides to produce free mercury vapor. The mercury vapor amount is measured by using its spectral absorption, the method usually employed in an atomic absorption spectrophotometer, and the mercury concentration corresponds exactly to that of the hydrogen contained in the sample.

At this stage, we should outline the safety measures regarding use of mercury vapor. The mercury vapor resulting from the mercuric oxide reducing reaction with hydrogen is harmful to humans. Therefore, a getter tube is attached at the outlet of the mercury oxide bed of the TRD. The present getter tube is stuffed with a sufficient amount of activated carbon grains. These getter materials completely absorb the mercury vapor discharged from the bed.

Next, we carried out a corroborative experiment to establish the detection limit for hydrogen. Test sample gases with low concentrations of hydrogen in nitrogen gas (5, 10, 20, 50, and 100 ppb) were prepared. We repeated the hydrogen analyses ten times for each of the test sample gases by using the present analyzer. As a result we concluded that the analyzer combining the functions of a gas chromatograph and atomic absorption spectrophotometer is sufficiently promising for measurement of infinitesimal hydrogen concentrations below 100 ppb.