Review

Development of Infrared Gas Analyzer

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The non-dispersive infrared (NDIR) absorption measurement technique, which has been developed as the second pillar of HORIBA after pH measurement, has grown into a mainstay of the company. It has been applied in various fields such as measurement in the automobile industry and environmental measurement. Technological development of NDIR has gone through many changes, problems, countermeasures, and epochs. They are discussed here along with my personal experiences.

Introduction

In 1954, soon after the establishment of HORIBA, Dr. Masao Horiba (president at that time, and current supreme counsel) started to consider industrial gas analyzers as a core of the business following pH meters. At the time of early gas analyzer development, it seemed that heated debates took place in the company regarding which method of measurement should be employed. Whether to use the gas chromatography or non-dispersive infrared (NDIR) absorptiometry. At that time, gas chromatography had been the focus of attention because various gases could be easily separated and measured. However, as heavy and chemical industry developed in Japan, there was an increased need for analyzers that would allow real time measurement for process control in chemical plants. The NDIR analyzer had the potential to respond to such needs.

President Masao Horiba decided to develop NDIR as the next business mainstay. He argued that because NDIR was based on physical phenomena only, its measurement principle was extremely clear compared to gas chromatography. Though FTIR and mass spectrometry (MS) for simultaneous measurement of several components in real time have been realized more recently due to the availability of sophisticated computers, he is admired for his decision to select NDIR in that time.

The first infrared gas analyzer called the GA-1 was an analyzer for measuring cyanide gas in acetylene, and was ordered by Osaka University. It seems that the analyzer was extremely large and heavy (Figure 1). The analyzer was filled with gas via a glass cock attached to a stainless detector. From what I've heard, the analyzer was troublesome in that often the gas had already leaked away by the time it was delivered to the customer and so it required re-filling with gas on-site. This instrument used an optical zero-method. A light shield known as a comb was adjusted to achieve light intensity balance between the sample cell and reference cell, and gas concentration was calculated from the displacement of the comb. The comb was manually nonlinearly shaped according to the characteristics of each analyzer so that the output showed linearity. It is still attractive in terms of its artistic quality. Afterwards, it was judged that the comb-based zero-method had substantial drawbacks in that the

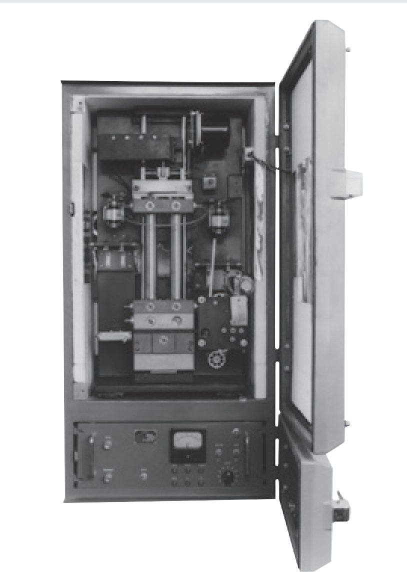

Figure 1 Early Infrared Gas Analyzer GA-2A
(Model change from the GA-1 Japan's first infrared gas analyzer (1957))
Dimensions : 482(W)×408(D)×950(H) mm
Mass : Approx. 100 kg

measurement response time was not satisfactory and the instrument was complex. As a result, the NDIR based on a direct current type deflection method was developed, which is still in use today.

HORIBA's NDIR gas analyzers started in this way and have become prosperous as a result of the accumulation of the original ideas of numerous people.

Next I will discuss the history of NDIR gas analyzer development focusing on the period when I was directly involved as a young engineer.

Countermeasures for Gas Leakage

For some time, NDIR was developed and sold, targeting heavy and chemical industry, in particular, industrial gas analyzers used in environments where explosive gases exist. Later, the method evolved into the development of scentometers taking advantage of fast response and then the "MEXA series" engine emission gas analyzer. With regard to vehicle emission regulations in Japan, the regulation value for CO gas was approximately 26 g/km in the beginning, and at present, it has been decreased up to 0.84 g/km or below. This means that the sensitivity of the analyzer must be heightened by at least 30 times.

However, gas leakage from the detector became an issue before increasing sensitivity. This was a difficult problem that always annoyed us from the beginning of NDIR analyzer development. Many senior engineers repeatedly tried many ways including O-rings, lead packing, and araldite adhesion. In my early days after entering the company, gas leakage had occurred very frequently. Adhesion bonds had been used at most junctions such as the cell window and detector, from which most leaks originated. At that time, President Masao Horiba thundered at us saying things like "What's going on? You are using adhesive bonds pointlessly like a fool with a single idea!" not once or twice. In those days, a large gas leakage problem occurred in a detector made from brass for the small MEXA that was exported to the United States. As a consequence, the current president Atsushi Horiba, who had belonged to HORIBA Instruments Inc. (HII), a corporate body in USA, had to run about to settle the trouble. It is a still a bitter memory.

After this trouble, we started to concentrate on our long-cherished wish, improvement of the detector. The simple gas leakage was resolved mostly by employing a ConFlat Flange and hermetic sealing and changing the structure through direct adhesion of the CaF_2 window. Furthermore, we thoroughly reviewed the structure and materials of the detector by changing the titanium film forming the capacitor to a press fitting type making use of the difference of thermal expansion coefficient or changing the material of the fixed electrode to ceramic. Figure 2 shows the internal structure of the improved detector (schematic illustration). In addition, we renewed the manufacturing facilities including the ultrasonic cleaning equipment, 10^{-7} Torr gas filler, and clean room. As a result of such accumulation of developments and improvements, it seemed that the fundamental technology for a pneumatic detector[*1] was established at last.

*1: A gas filling type infrared detector is called a pneumatic detector because the pressure change of the filler gas is utilized.

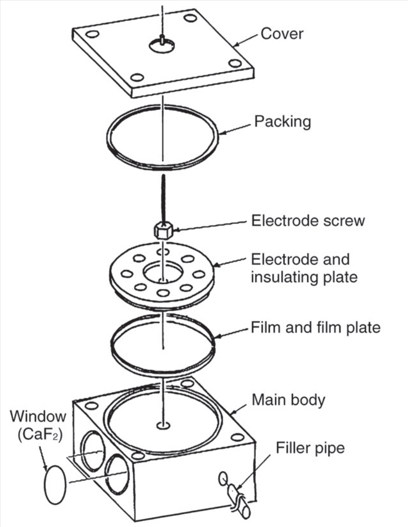

Figure 2 Internal Structure of Detector (Schematic Illustration)

In-House Production for Key Components

Simultaneously with the improvement of the detector features, we also developed peripheral technologies. One of them was the development of an infrared multilayer interference filter. In the latter half of the 1960s, NDIR was recognized in the automobile emission measurement field, and there was a growing demand for analyzers with higher precision. In the case of automobile emissions, especially, it is necessary to measure a minute amount of specified gases selectively from among an extremely large amount of interfering constituents. For instance, when CO of the ppm level is measured within CO_2 of the percent level using NDIR, CO_2 interference due to overlapping of the both absorption spectra becomes an issue.

Though narrowing down the wavelength range to be used for measurement can reduce the influence of the interference, this requires a multilayer interference filter. From 1962, soon after HORIBA started the development of NDIR analyzers, we had started "research of high-performance infrared filters" under a grant from the Ministry of International Trade and Industry. However, a good filter was not made easily. In or around 1970, at last we tried to mount the filter in the actual detector; however, it was a "flimsy filter". When you blew, the multilayer separated in pieces, and the filter was sometimes transparent. That's why we had to run around the customer's sites. As an aside, this filter had been referred to as a "solid filter" at that time in spite of its weakness.

In those days, excellent US-made filters were already commercially available, but they were extremely expensive. Nevertheless, introduction of high-priced facilities was required in order to manufacture similar products. After repeated episodes of consideration and frustration at the problem, by using the government subsidies we prepared vacuum deposition apparatus that could evaporate Ge and SiO and obtained a minicomputer for designing multilayer.

In this way, the 1970s was the period for preparing the in-house production system for key components such as the detector and filter. Such investments became possible thanks to the tail wind of the huge hit from sales of the small MEXA which came as a result of emission regulation against in-use cars enforced in 1974, and more than that, HORIBA's spirit of challenge. We treated such a rare chance aggressively and desired to realize our dream while sometimes creating chance. We would like to hand down such positive corporate culture to the next generation to expand further.

Flexible Minds that Produced AS Detector and Sector Motor

Thanks to the strengthening of production systems, we could realize a strong filter that was not stripped even if immersed in water or cut by a diamond cutter. However, the concentration range of the analyzer had been reduced up to the extent that gases could not be separated sufficiently using only the interference filter. In around 1975, our target was to control the interference of CO_2 with 5% concentration within 2% of the full scale in a CO meter whose full-scale concentration is 100ppm, i.e. achieve a discrimination ratio of 1:25,000.

In the beginning, we could not clear this target easily even though we refined the filler gas for the detector and narrowed down the half bandwidth of the filter in a straightforward manner. As a result of some hard thinking, we came up with an idea of eliminating the influence of interference by arranging two detectors in series. The details of the principle are omitted here; however, in short, the interfering components of CO_2 are removed selectively by using subtraction between the two detector signals. This technology called AS detector is still used effectively. Figure 3 shows an NDIR setup in which an AS detector is incorporated.

Then, we coped with one of the trouble-causing components in the rotating sector to make chopping light at a constant frequency. Realization of a stable and easy-to-handle rotating sector was one of our large tasks since the start of the NDIR development. Though various type sectors including employment of a phonograph turntable motor were tried, no satisfactory result was achieved easily.

In 1969, a sector motor (Figure 4) was developed, which advanced the system dramatically. The sector motor was produced from an idea that irregular rotations will be reduced and the life will be extended if the rotor of the synchronous motor itself serves as a light shield.

In the above mentioned AS detector, a basic principle thought out to prevent noise by vibration of a capacitor microphone detector was applied expansively for the purpose of eliminating the influence of interference. As in the idea of the sector motor, I think that flexible minds are the principal reason that HORIBA has taken the No. 1 position for NDIR.

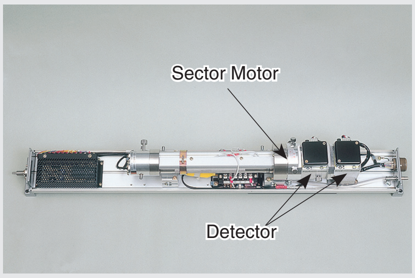

Figure 3 NDIR Bench Setup in which an AS Detector was Incorporated
AIA-23<AS>
Dimensions : 100(W)×165(D)×856(H) mm
(Including cover)

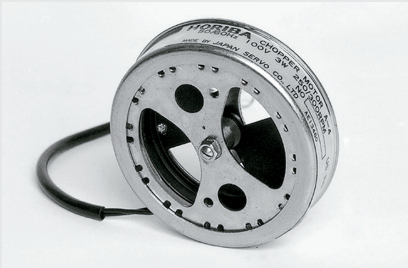

Figure 4 Sector Motor

Realization of Substantial Drift-free through Cross Flow

Since 1978 or around, when CO meters and HC meters for in-use automobile emissions regulation reached saturation, new markets such as the SO_2 analyzer and NO_X analyzer for flue gases started to appear. In such markets, long-term stability was important in addition to sensitivity and the influences of interference, and thus, the drift of NDIR was brought under the spotlight.

Because a direct current type deflection method is used for the present NDIR and a certain bias is applied optically, a drift of the indicated value is inevitable. At the beginning, we sometimes could not ship the products due to drift or we experienced customer complaints about the drift. Drift sometimes occurred immediately after the delivery of the product to the customer and the product was sent back.

In order to overcome this problem, we invented the cross flow[*2] technology. In cross flow, light is not modulated as in the previous NDIR system. The gas itself is modulated. In other words, a drift-free optical system was realized by using a reference zero gas and sample gas alternately in two cells and completely removing the optical offset.

Though this method was based on a deceptively easy idea, it was highly rated worldwide including the U.S. I think that this technology allows us to maintain the high market share of our flue gas analyzer.

The cross flow technology developed further. Dual cross flow is one such development. My junior colleagues who were in charge of the AP (air pollution monitoring system) so as to expand the features of the cross flow technology, thought it out. Two types of gasses are fed into a single-unit analyzer by switching the lines in different cycles, and the complex signals obtained are separated according to frequencies and concentrations of different components, which are calculated respectively. I think that this is also an excellent technology, which makes an epoch together with cross flow in the NDIR history of HORIBA.

*2: It was called cross flow because gasses were switched using a rotary valve at that time. At present, the term "flow modulation" is generally used.

Troubles Nurture Technologies and People

From what I have explained so far, it may appear that the NDIR-based system has grown smoothly. However, I think that the accumulation of bitter failures and difficult, troubled experiences has lead to today's honorable evaluations such as "You can't think of infrared analyzers without thinking of HORIBA, no matter what anyone says."

One of the unforgettable complete failures was a die casting detector for the small MEXA. In 1968, the Muskie Act was enforced in the U.S., and subsequently, automobile emission regulations were consequentially reinforced in Japan. Though HORIBA developed a portable CO gas analyzer, MEXA-200 (Figure 5) for maintenance shops in 1969. This was estimated to be a giant market reaching hundreds of thousand of units, the manufacturing method for detectors was changed from conventional aluminum forging to die casting because mass production was easy and the cost was low. However, some time after the shipment, a large problem occurred - loss of sensitivity. Of course, we thought we had sufficiently examined the situation of whether or not the filler gases leaked before introducing die casting. As a result of strenuous examinations, it turned out that the cause was a slow leak from the dividing wall of the CO gas detector (die cast material). From this bitter experience, we went back to forging materials and so the present situation was reached. This is a good example that taught us the lesson that materials must be selected with due caution.

Figure 5 Portable CO Gas Analyzer for Maintenance Shops MEXA-200
Dimensions : 200(W)×363(D)×214(H) mm
Mass : Approx. 7.2 kg

Further, the "whiskers problem" was also unforgettable. In 1969, "Environmental criteria for sulfur oxide (SO_2)" were decided in cabinet, and HORIBA rushed a flue gas analyzer ESDA-200 (Figure 6) into production. This analyzer had a smart design in the shape of a mailbox. However, this product also had big problems. A complaint that the indicator showed a whisker-like noise was received one after another. Even if our service engineer replaced the detector repeatedly, this problem was not solved. As an anecdote, a service engineer was scolded with the words "Come back when you've shaved!" and was prohibited from entering the customer's site.

Figure 6 ESDA-200 under Examination
Dimensions : 400(W)×550(D)×1200(H) mm
Mass : Approx. 60 kg

After all that, it was found that the trouble was caused by impurities remaining on the electrode surface, and it was resolved by thoroughly polishing and cleaning the electrode. At that time, HORIBA's educational policy was "Solve your mistakes by yourself." As a matter of course, even a freshman had to supply the replacement parts free of charge while sitting up all night - even for 3 or 4 days. The young corporate members should always keep the fact in mind that the HORIBA we see today was made by the continuous efforts of such senior members.

Analyzers also Need to be Matured

"CO disappears?" was also an interesting episode. This is a phenomenon where the sensitivity of the CO detector is lost and then recovered. I guess that sensitivity is decreased because the CO filling the detector adhered to the inner wall surface or ceramic electrode selectively, and then recovered by coming out of the gas if heated. However, the reason for the dip is not known yet.

The most effective way to prevent this is aging, though it is very illogical. In this method, the detector and light source heated are stored for several months. Similar processing is implemented for delicate parts in other sensors and electronic devices. As in whisky, the products yield a good taste after being aged and matured. NDIR seems to be a technology in such a field. However, aging means that the stock increases and expenses pile up. I cannot ask young engineers in future generations to act in such a manner. I believe that your flexible minds will surely realize devices that do not require this step.

Conclusion

It is really difficult to explain NDIR system development, nurtured by hundreds of people including the supreme counsel of HORIBA since its establishment, within the scope of such a restricted number of characters. This is like feelings of a TV director who summarizes the global history of 4.6 billion years as a 30 minute nonfiction drama. While feeling like this, I would like to introduce what I become strongly aware of : “Persistence is power”.

An excellent technology is surely accepted by the market and evolves continually. A technology matching needs awakens new needs, which promote the further advancement of the technology. Also, individual technologies do not exist independently. They evolve together with surrounding technologies over changing times. I pause to realize what is important is that fundamental technologies will stay for eternity as one business useful for people if they are nurtured with patience.

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