Development of New Model EMIA-Pro and EMIA-Expert Carbon/Sulfur Analyzers

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In recent years, analysis of the gases (oxygen, nitrogen, and hydrogen/carbon and sulfur) included in various materials has become very important in material development for things such as composite materials and improving product quality. Out of these, carbon and sulfur analysis methods are widely used in areas such as iron and steel, non-ferrous metals, and ceramics. A stream of oxygen combustion method is used for this gas analysis, and it is also necessary to do maintenance such as removing the oxide dust generated during the material combustion/oxidation processes. HORIBA developed new easy-to-use Carbon/Sulfur Analyzers that reduce the frequency of this maintenance and achieve fundamental system performance. In this paper, we introduce the mechanisms for achieving this, and the main applications for the features such as the intuitive interface.

Introduction

Along with iron and steel production, which supported Japan's post-war recovery, the gas (oxygen, nitrogen, and hydrogen/carbon and sulfur) analysis method has continued to progress toward more accurate and quicker analysis. It has been 37 years since this carbon/sulfur analyzer was transferred to HORIBA in 1978 from Kokusai Denshi KK, when the use of non-dispersive infrared absorption method began to increase. In materials such as ceramics and metals including iron and steel, depending on the material, these gas components can be impurities or main components, so the concentration range needs to cover a range from parts per million (ppm) to several dozen percent (m/m). Furthermore, gas components are controlled to ensure material quality for the application and objective. No other analysis method exists that can ensure this level of accuracy. In recent years, there are two different directions in these analyzers. One type maintains standard performance while reducing the time spent for maintenance and analysis, and the other type is customized based on the materials that the user uses and pursues high-accuracy.

This time HORIBA developed and commercialized the Carbon/Sulfur Analyzer (EMIA-20). These models meet these requirements. We developed the EMIA-Pro with the main focus on extending the maintenance cycle and intuitive handling. With previous devices, dust was generated along with combustion, so it was necessary to do maintenance at relatively short intervals to prevent gas from adsorbing to the dust. In addition to the functions of the EMIA-Pro, the EMIA-Expert has additional functions for achieving analysis with higher accuracy, and was developed to meet increased future requirements [1, 2] (**Figure 1**).

Figure 1 Device Appearance

Gas Analysis Method Principles and Features

In metal analysis including iron and steel, the role of gas analyzers is to analyze impurities. For various ceramics such as oxides, nitrides, and carbides, gas analyzers analyze main components. Both are important analysis methods from the research and development stage to quality control. In carbon/sulfur analyzers, the mechanisms that generate gases are combustion and oxidation, and in oxygen/nitrogen/hydrogen analyzers, the mechanisms are high temperature and reduction. Both are based on chemical reactions, which is a feature of these analysis methods (**Figure 2**).

The combustion in oxygen stream - infrared absorption method is used to analyze the carbon and sulfur in various materials. The device is composed of a combustion area, detection area, and data processing area. The high-frequency induction heating method is used as the combustion extraction method for various reasons, such as ease of handling, high-temperature combustion, and the stirring effect. A high-frequency induced current is induced on the surface of a sample inside a ceramic crucible, and is heated by the resistance of the sample. When it is heated, the oxygen causes a combustion reaction that generates combustion heat. These 2 interactions bring the sample into a high-temperature state. Along with the material, accelerators such as tungsten, tin, copper, and iron are used to accelerate combustion (**Figure 3** and **Figure 4**, **Table 1**). The carbon and sulfur included in the material gasify *due to the high-temperature combustion, and are* extracted as carbon dioxide (some as carbon monoxide) and sulfur dioxide, respectively. The excess oxygen carries the extracted gases to the non-dispersive infrared detector, and they are converted into their respective gas concentrations. These signals are calculated and totaled, and finally the carbon and sulfur concentrations are obtained by dividing by the sample's mass (**Figure 5**). The detector and optical filter used in the non-dispersive infrared absorption method have been optimized through the accumulation of technology over many years, and help provide sensitive and stable detection.

Material	Objective	
Iron and steel	Process control Quality control Research and development	Impurities
Non-ferrous metals		Main component
Ceramics		Impurities
Coke		Impurities

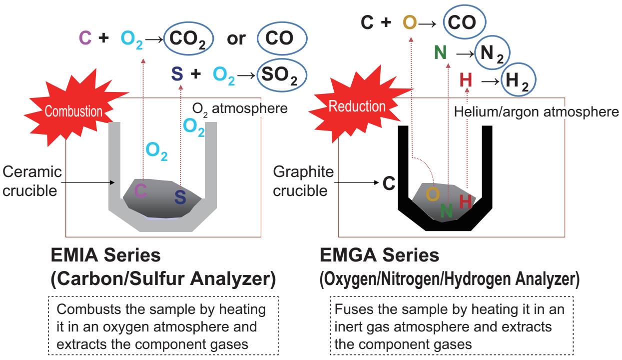


Figure 2 EMIA and EMGA Applications and Differences

Table 1 Heat capacity of metal accelerators

Metal	Metal oxide	Heat capacity ΔHf (kJ/mol)	Viscosity when melted μ x 103 (Pa.s)	Role
W	W_3O_8/ WO_3	2274/842	—	A large amount of heat is generated at the beginning the ignition agent, but it is easy for the temperature to drop quickly
Sn	SnO_2	580	0.8 (1000°C)	Decreases viscosity, increases fluidity, and stirs the sample
Cu	CuO	155	3.2 (1150°C)	Retains heat for a long time for gentle combustion
Fe	Fe_2O_3	821	5.6 (1700°C)	Is often used with tungsten when measuring samples that are difficult to melt that retain heat for a long time

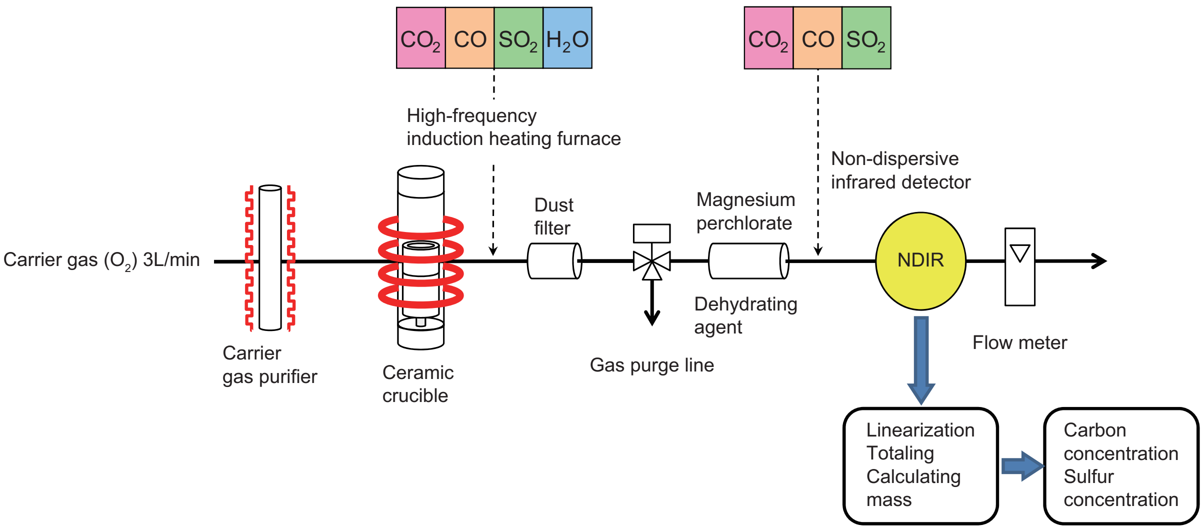


Figure 3 Principles

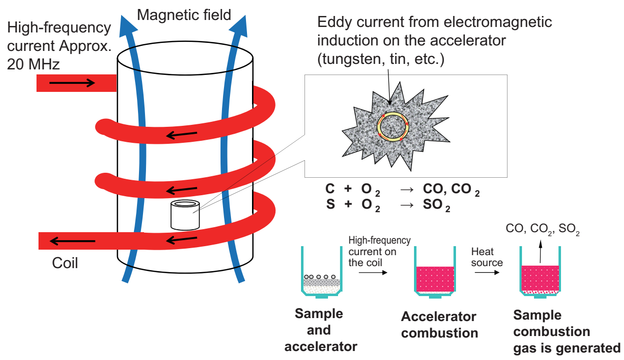
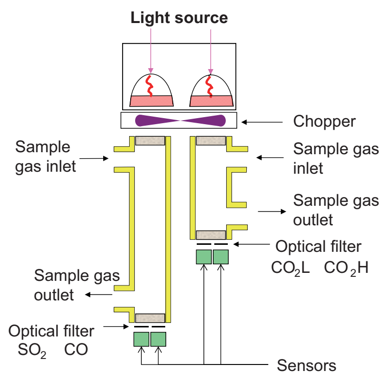


Figure 4 High-Frequency Heating Method



	Infrared absorption wavelength (μm)
CO	4.7
CO_2L	4.3
CO_2H	4.45
SO_2	7.3

Figure 5 Infrared Detector Structure and Optical Filter

Development Intentions and Opinions From Users

This time, we emphasized the following 3 points in developing the EMIA-Series Carbon/Sulfur Analyzers.

- What kinds of things a gas analyzer can do
- How we want it to be used
- Opinions from existing users

Based on these, we developed the EMIA-Pro, which allows anyone to take professional-level measurements, and further improved the functions to develop the EMIA-Expert, which allows for expert-level measurements. Using these basic common elements, we incorporated 1) revisions to the method for cleaning combustion dust, 2) quick analysis, and 3) operation that is easier to understand into the EMIA-Pro, and added mechanisms to the EMIA-Expert that provide high-accuracy analysis.

Explanation of Features

Combustion Dust Cleaning Mechanism

Combustion is an important element in the high-frequency combustion method, but has problems such as the detected gas adsorbing to the dust after combustion. For that reason, we previously tried many methods for cleaning the inside of the combustion furnace, which affects the accuracy of analysis. We revised the method we had been using previously for scraping off dust from the combustion tube and dust filter using a metal brush, and developed a new cleaning mechanism. Using the new cleaning mechanism makes it possible to efficiently remove dust stuck to the filter area, and reduces the residual dust inside the combustion furnace (**Table 2**). To achieve a device that will allow anyone to take professional-level measurements, it is essential to ensure that anyone can do maintenance quickly, easily, and securely. The effects of the new cleaning mechanism are shown in **Figure 6**. Using the new mechanism made it possible to shorten the time by about 10 seconds compared to conventional devices, which also improved throughput.

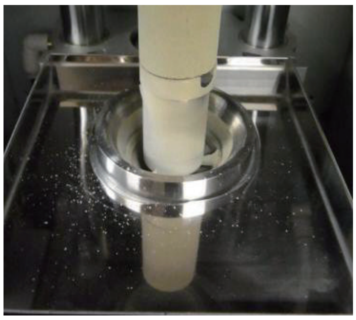
Table 2 Amount of Dust (g) in Each Area After Continuous

	Conventional device	EMIA-Expert
Around dust filter	3.0	0.9
Inside combustion tube	3.1	2.8
Around crucible stand	0.7	0.04
Total	6.8	3.7

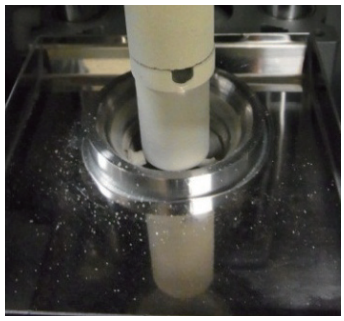
Easy Maintenance

To achieve the EMIA-Pro, where anyone can take professional-level measurements, we needed simple, quick, and reliable maintenance. We designed it to eliminate the issues that conventional devices have, such as 1) the user's hands won't fit in the work area, 2) there are too many operations, and 3) tools are necessary, which shortened the time it takes for maintenance to 1/5 (**Figure 7**).

At the start of measurements



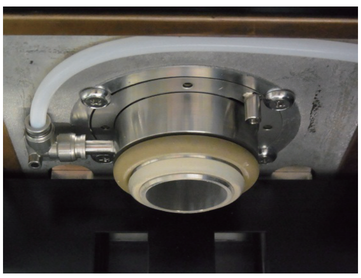
After 100 *measurement cycles*



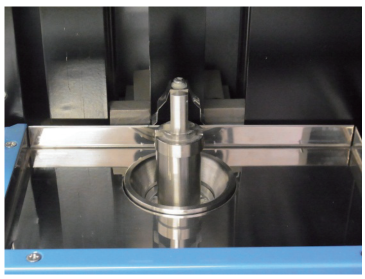
After 200 *measurement cycles*

Figure 6

Top part of the combustion furnace



Bottom part of the combustion furnace



Combustion dust discharge area

Figure 7 Main Locations Requiring Maintenance

Gas Adsorption Measures

We also made revisions to the basic structure for gas adsorption, which affects the accuracy of analysis.

1)Reduced the surface area in places that come into contact with dust
 •Reduced the metal filter area by 25%
 •Extended the quartz glass tube

2)Filter heating mechanism: EMIA-Expert exclusive function

We checked the effects on sulfur analysis, from the state after the inside of the furnace has been cleaned. As shown in **Table 3**, adsorption at the 1-ppm level is allowed, but has been reduced to 1/3 of conventional devices. Also, when the filter heating mechanism is used, adsorption is at a level that can be ignored within variations.

Advanced Operation Software

When we developed the software, our objectives were 1) to have icons that can be intuitively understood and 2) to minimize the amount of information on the screen to make it easy to understand. The basic screen is shown in **Figure 8**. The tabs can be switched based on the usage situation. We also installed navigation functions for analysis, maintenance, and troubleshooting to make it possible for anyone to take professional-level measurements.

Table 3 Gas Adsorption Improvement Effect

EMIA-Pro (Leave for 30 minutes between first and second cycle)

Unit: ppm	First cycle	Unit: ppm	Second cycle
1	11.64	1	11.93
2	12.16	2	12.31
3	12.42	3	12.13
4	11.49	4	12.42
5	11.92	5	12.06
6	12.74	6	12.31
7	12.28	7	12.23
8	12.07	8	12.20
9	12.38	9	12.06
10	12.25	10	12.00
$X_{N6\text{-}10}$	12.34	$X_{N6\text{-}10}$	12.16
X_S	0.71	X_S	0.23

EMIA-Expert (Leave for 30 minutes between first and second cycle)

Unit: ppm	First cycle	Unit: ppm	Second cycle
1	12.02	1	12.48
2	12.16	2	12.21
3	12.56	3	12.36
4	12.57	4	11.87
5	12.78	5	12.21
6	12.41	6	12.21
7	12.53	7	12.22
8	12.11	8	12.79
9	12.59	9	11.94
10	12.66	10	12.56
$X_{N6\text{-}10}$	12.4	$X_{N6\text{-}10}$	12.36
X_S	0.44	X_S	-0.12

The amount of adsorbed sulfur(X_S) is calculated using the following formula.

$X_S = X_{N6\text{-}10} - X_1$

$X_{N6\text{-}10}$: Average value from N = 6 to N = 10

X_1: N = 1 measurement value

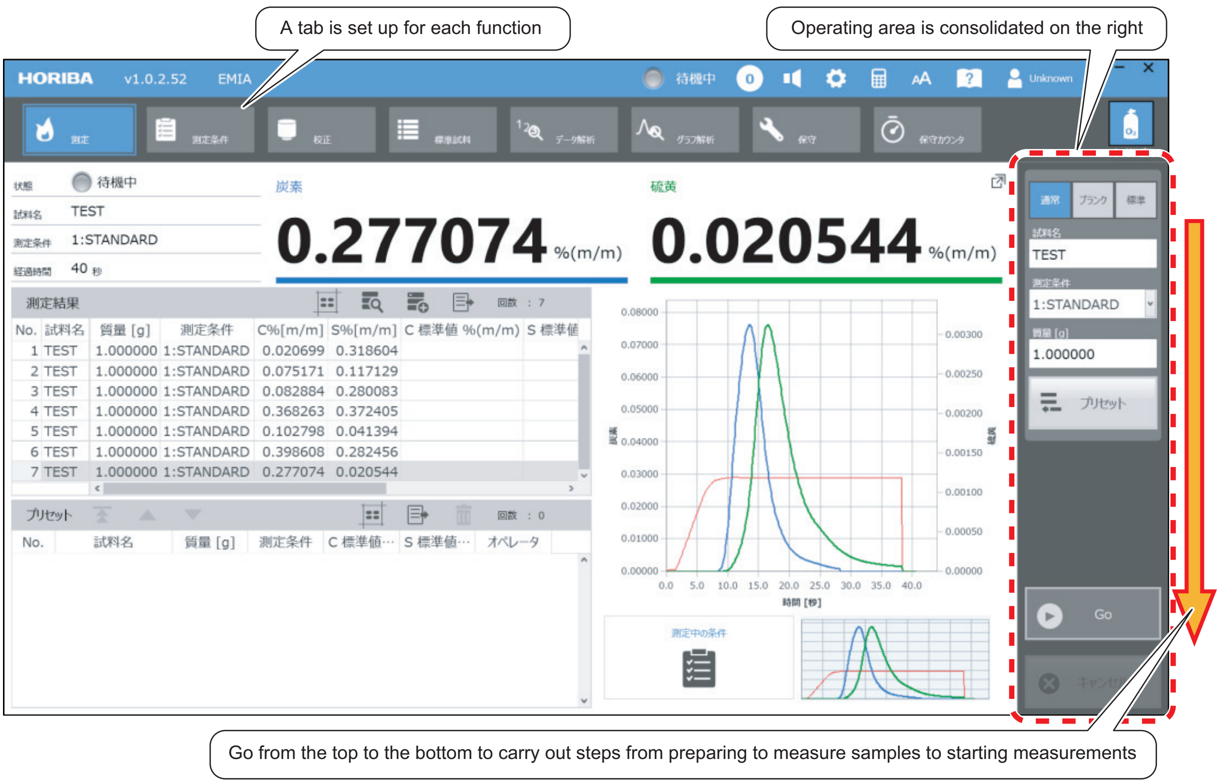


Figure 8 Basic Screen

Unit: ppm	Certification substance	
	Without purifier	With purifier
1	11.20	8.11
2	10.22	7.97
3	10.93	8.07
4	10.92	8.07
5	10.89	8.00
6	10.84	7.94
7	10.84	8.09
8	10.74	8.11
9	10.91	8.05
10	11.00	8.30
AVE.	10.85	8.10
SD.	0.25	0.10

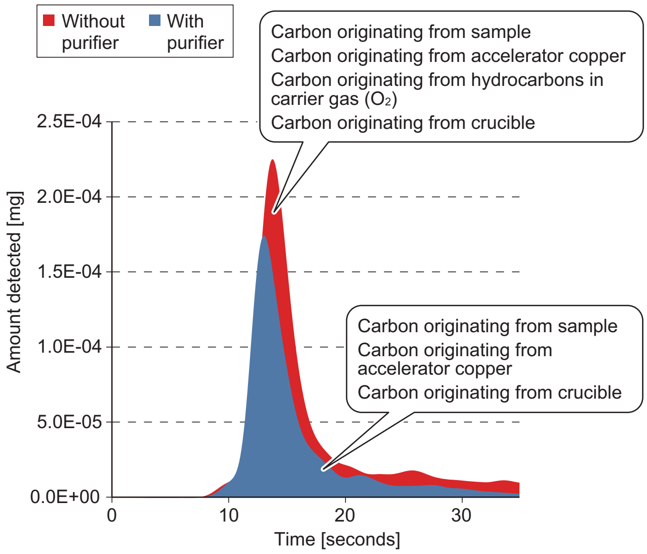


Figure 9 Effect of the purifier on carbon trace analysis

Factors for High-Accuracy Analysis

We developed the EMIA-Pro to increase basic performance, but the oxygen gas used in combustion is an important element for achieving analysis with higher accuracy. Oxygen gas cylinders with a purity of 99-99.9% include about 20-30 ppm of hydrocarbon gas. When the sample combusts, these hydrocarbons also combust, which can appear as an error on the plus side. For this reason, it is desirable to use high-purity gases with a purity of 99.999% or higher in carbon trace analysis, but this affects the running costs.

What is important in high-purity carbon analysis is removing hydrocarbons. The EMIA-Expert, which doesn't need high-purity oxygen, has a gas purifier and filter heating mechanism and achieves high-accuracy analysis of carbon and sulfur traces. The effect of the purifier on carbon trace analysis is shown in **Figure 9**.

Conclusion

HORIBA developed the new EMIA-Pro and EMIA-Expert Carbon/Sulfur Analyzers. This time, our basic development concept was to (1) eliminate time that can't be spent for analysis, (2) improve the ease of use to give users peace of mind, and (3) incorporate opinions from users. We consider that these products are just standing at the starting line. In the future we want to continue to get opinions and extend the line-up, as well as develop applications that can be specialized for customer requirements.

References

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