Development and Application of an Organic Carbon Detection Device for Sodium Aluminate Solution

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Abstract

The build-up of organic matter in Bayer Process leads to an increase in foam and a decrease in equipment capacity at precipitation stage. It has a great adverse impact on product quality and precipitation yield. Potassium permanganate oxidation method, total organic carbon analyzer and other analytical methods are used in alumina industry to determine the content of organic matter. In this paper, a developed technology for organic carbon detection in process liquor is discussed. First, inorganic carbon in liquor is completely precipitated. Then, the total organic carbon can be detected by an on-line organic carbon oxidation technology. Developed testing equipment and oxidation techniques enable to detect oxalates as well. It has been tested and validated in an alumina plant. It can guide operators to monitor the quality and stable operation of alumina.

Keywords: Bayer Process, Organic matter, Organic carbon, Total organic carbon.

1. Introduction

The organic matter is brought with bauxite and used organic additives into the alumina process. Organic carbon content in liquor accumulates in Bayer cycle. China has been importing large quantity of bauxite due to increased alumina production capacity in recent years. These bauxites have been conveying high content of organic matter into the pure Bayer liquor. Organic matter has a serious impact on production system. It requires comprehensive study and efficient detection of organic carbon in solution. The calculation of organic matter content usually is done from combustion products such as water and carbon dioxide. While the mass of hydrogen is calculated from water, mass of carbon is worked out from carbon dioxide quantity. Considering the oxygen used for oxidation, the mass of oxygen is calculated from both of carbon dioxide and water quantity. Finally, the ratio of carbon, hydrogen and oxygen can be figured out with the simplest formula and molecular weight of organics. In this study, a variety of titration reagents were added to the liquor at different stages to generate CO_2. An external CO_2 detection sensor and integrated mass measurement device were used to analyze and calculate the organic carbon content in the solution[1]. Zhengzhou Non-ferrous Metals Research Institute Co. Ltd of CHALCO has independently developed and produced a fully automatic organic detection device, which comprises an integrated units such as sampling, chemical titration, detection and analysis devices. Titration agents has precisely injected with the plunger pumps. Modern integral algorithms have been applied to get high efficiency and accuracy. This set-up has performed an efficient, accurate and stable detection and analysis of organic matter in the liquor. The set-up has been used on-line for the purpose of getting fast and high detection efficiency, improving working conditions, enhancing product quality, saving energy and reducing pollution.

2. Technological Process

A liquor sample of 100 mL was grabbed from the production process. Then, a 500 mL solution of hydrochloric acid of a certain concentration and 500 mL of catalyst solution containing manganese ions were prepared. A certain concentration of 500 mL NaOH solution was prepared as well.

The liquor to be tested was gradually injected into the reaction tank via a mini peristaltic pump. A precise plunger pump was used to add hydrochloric acid at different times by following the the acidification reaction mechanism. Catalyst solution containing ozone were added to oxidize[3] the organic carbon in liquor and produce CO_2. The carrier gas, N_2 was continuously introduced through the system detected CO_2 produced at different times were recorded. The concentration of organic matter was calculated accordingly. Among them, the precise control of hydrochloric acid reagent is the most important control index in the whole detection process.

At the early stage of test, the Bayer liquor was directly acidified with 1:1 hydrochloric acid. During the acidification reaction, strong acids violently reacted with strong bases. While stirring the solution, most of the inorganic carbon in the original liquor evaporated as carbon dioxide. The solution became free of inorganic carbon when the pH is below 2. CO_2 was continually introduced as a carrier gas to flush out the remaining carbon dioxide in the solution. The rest of the carbon in solution was in the form of organic matter.

Ozone is a strong oxidizing agent. It oxidizes organic carbon into CO_2. In sodium aluminate liquor, CO_2 reacts with NaOH to produce sodium carbonate. Therefore, when organic matter is oxidized, the sodium carbonate content in the liquor increases.

$$C + O_3 = CO_2\uparrow + \tfrac{1}{2}O_2\uparrow \tag{1}$$

$$CO_2 + 2NaOH = Na_2CO_3 + H_2O \tag{2}$$

Ozone generators produce ozone by breaking apart oxygen (O_2) molecules into single atoms, which then attach to other oxygen molecules in the air to form ozone (O_3).. Since ozone decays more easily to give off oxygen, the higher the temperature and the shorter the decay period. Therefore, the reaction temperature is set at room temperature. The whole testing process is shown in Figure 1:

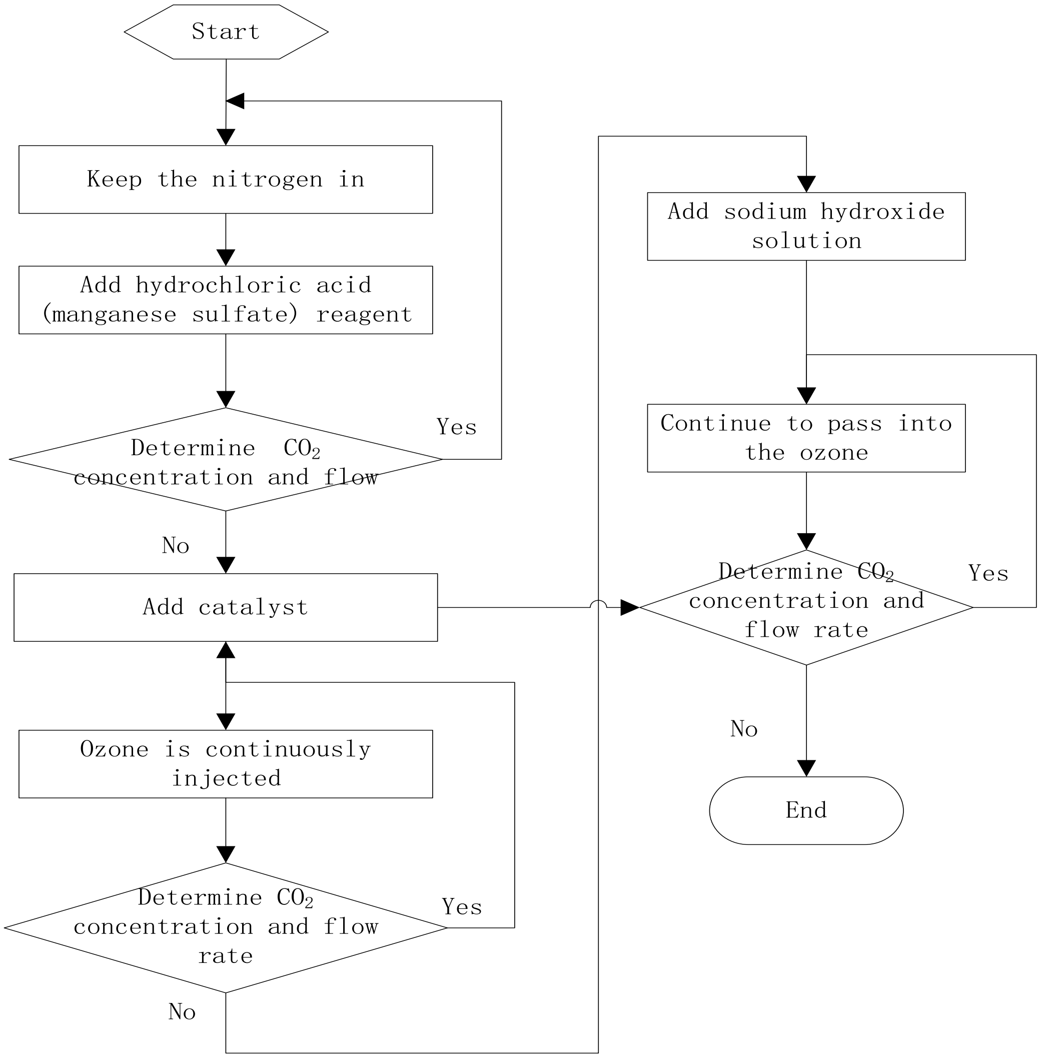

Figure 1. Flow chart of detection device

2.1 Composition of Process Equipment

This testing device consists of logic control unit, solution addition metering unit, reactor, measurement and detection unit, ozone generator, peripheral auxiliary equipment, etc.
The logic control unit consists of a Siemens SMART controller, human-machine interface, I/O module, and switching power supply. It is used for signal acquisition, analysis operation, logic control and human-computer interaction in the working process of the device. It displays the current measurement, test data and the working status of the devices, including driving and controlling the micro peristaltic pump, plunger pump, solenoid valve, ozone generator and other actuators. The control system is equipped with Ethernet interface, which is easy to download and debug programs and network communication of data from the upper computer.

The solution addition metering unit consists of micro peristaltic pump, plunger pump, solenoid valve and so on. It is used for accurate quantitative sampling of test fluid. The various reagents that need to be added in the process are titrated separately. At the same time, solenoid valve switch control is matched.

The reactor is a custom-made glassware. It has 3 solution adding outlets, 3 gas inlet and outlet, 2 detection outlets and 1 drain outlet, placed in a constant temperature box.

The detection unit is composed of a CO_2 detection sensor, a gas flow sensor, a pH meter, a Pt100 thermal resistance, an integrator instrument, etc.

Peripheral auxiliary devices include N_2 bottle, reagent bottle, box, bracket, etc.

3. Function of Detection Device System

Hydrochloric acid reagent containing manganese sulfate was added into organic carbon testing device[2] [4]. According to the composition of sodium aluminate solution, the sampling quantity was calculated and determined. Then different kinds and quantities of titration reagents were added according to the testing process. According to the pH test results of gas and solution produced by reaction, the amount of addition and the type of reagent were controlled. At the same time, the detection device automatically measured and calculated the detection results.

The system mainly contains the following functions:

（1）Measurement of solution addition: The liquor to be tested was quantitatively taken into reactor. Precise addition of titrant was the key factor influencing the success or failure of test. The resulting materials of reaction was quantitatively and rapidly extracted. Accurate control of extraction is an important control index. . It was needed to monitor different stages of the detection process and analyze the response in real time. According to the detection feedback value, the addition amount and control of speed were adjusted.

（2）Detection and tracking of gas process parameter: CO_2 was detected through measuring the quantity and concentration of total process gases. The integral accumulation method was used to accumulate the total gas generation in real time.

（3）Monitoring of solution process parameters: Measurement of temperature and pH value of solution was an important reference control parameter of organic carbon detection device. It was essential to guide for process control. The total pH of inorganic carbon was about 2.

（4）Logic control function of detection device: Linkage control, chain control, data processing and recording of each unit was done under logic control

3.1 Measurement of Solution Addition

The micro peristaltic pump was used for the addition of sodium aluminate solution to be tested, due to the transferring of small amount of solution and high precision requirements. 4-20mA control signal was usedfor Its stability and reliability, resulting anaccuracyas 0.5 %. The effective rate was high and the maximum flow rate reached was 260 mL/min. The reaction reagent was mainly controlled by the plunger pump. The control precision reached as 0.1mL. Titration logic control was shown in Figure 2:

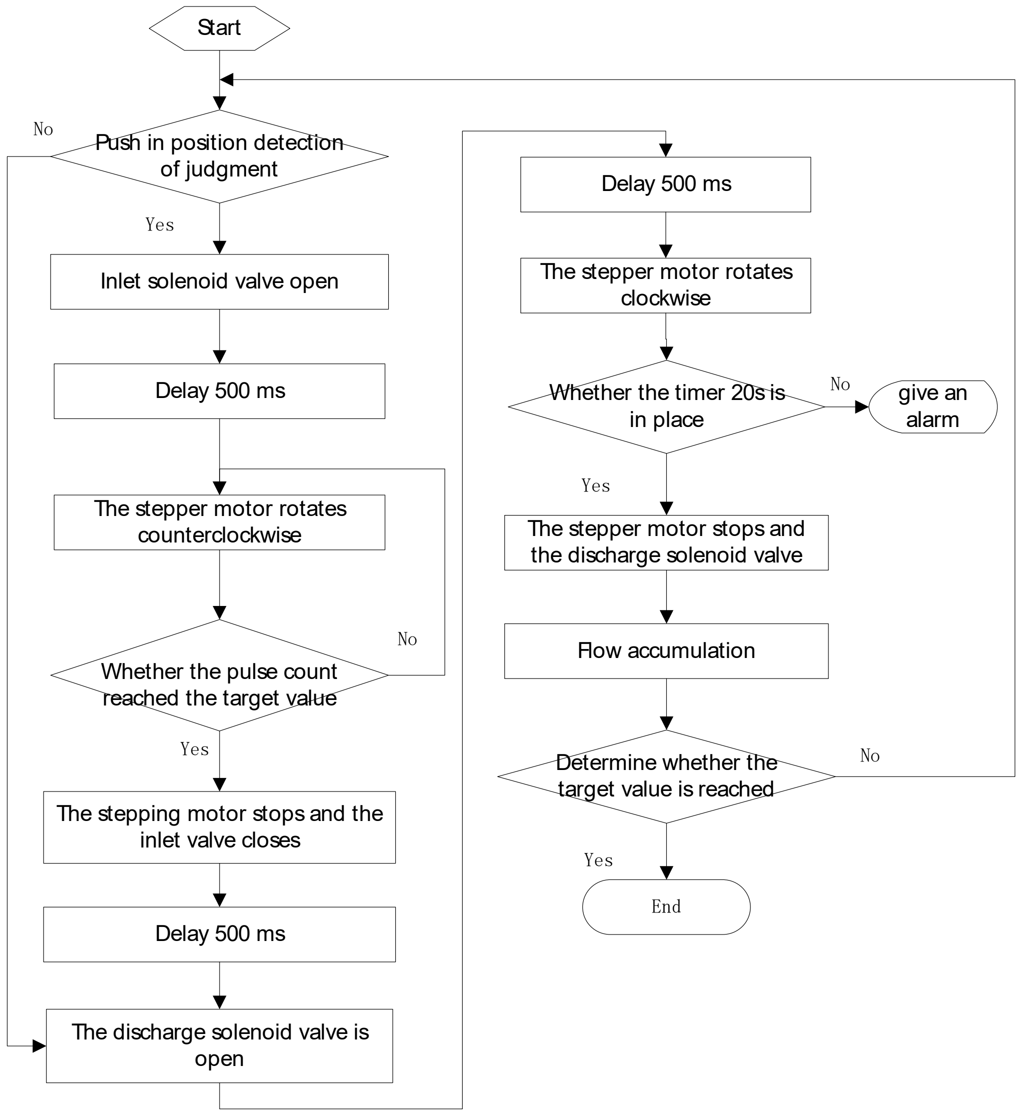

Figure 2. Control logic diagram of plunger pump titration

3.2 Detection, Tracking and Accumulation of Gas Process Parameters

Gas detection included CO_2 concentration and flow measurements. This device was adopted with a gas sensor module of Non-Dispersive Infrared Gas Analyzers (NDIR) principle to detect the concentration value of CO_2. The measurement range is between 0–2000 ppm With a 1 ppm precision and 0.01 % vol (depending on measurement range). In addition, a mass flowmeter was used to detect the mass flow rate of CO_2. An definite integral algorithm was used to accumulate the measurements[5]. Because x was continuously differentiable on the interval [a, b], interval [a, b]$_n$ was divided equally to get a series of points[7].

$$a=x_0,\ \ x_1,\ \ x_2,\ \ x_0+\ldots\ldots,\ \ x_{n-1}, x_n=b \tag{3}$$

And the length between each of these cells was:

$$\triangle\, x = \frac{a-b}{n} \tag{4}$$

Thenthe controller interval was collected:

$$f(x_i) = y_i \tag{5}$$

So:

$$Q=\int_a^b f(x)dx \approx \frac{a-b}{n} * (y_0 + y_1 + \cdots + y_{n-1}) \tag{6}$$

Where:
Q Cumulative mass, g
a Start time, s
b End time, s
x Measurement time, s
y Instantaneous mass flow, g/s
n Acquisition times

The computer approximated the area of the trapezoid by using the area of the narrow rectangle. On the whole, the area of the step was used as the approximate accumulative value of the area of the curved trapezoid, which meant that it was the accumulative value of gas flow.

3.3 Monitoring the Solution Process Parameters

The temperature of reactor environment and the pH value of reaction solution were important process parameters for the smooth operation of the testing device. The system was adopted with a circulating water bath to provide constant temperature. Heat exchange was carried out by circulating pump. The control logic diagram is shown in Figure 3. The uniformity and stability of temperature in water bath system was ensuredto meet the test requirements[6].

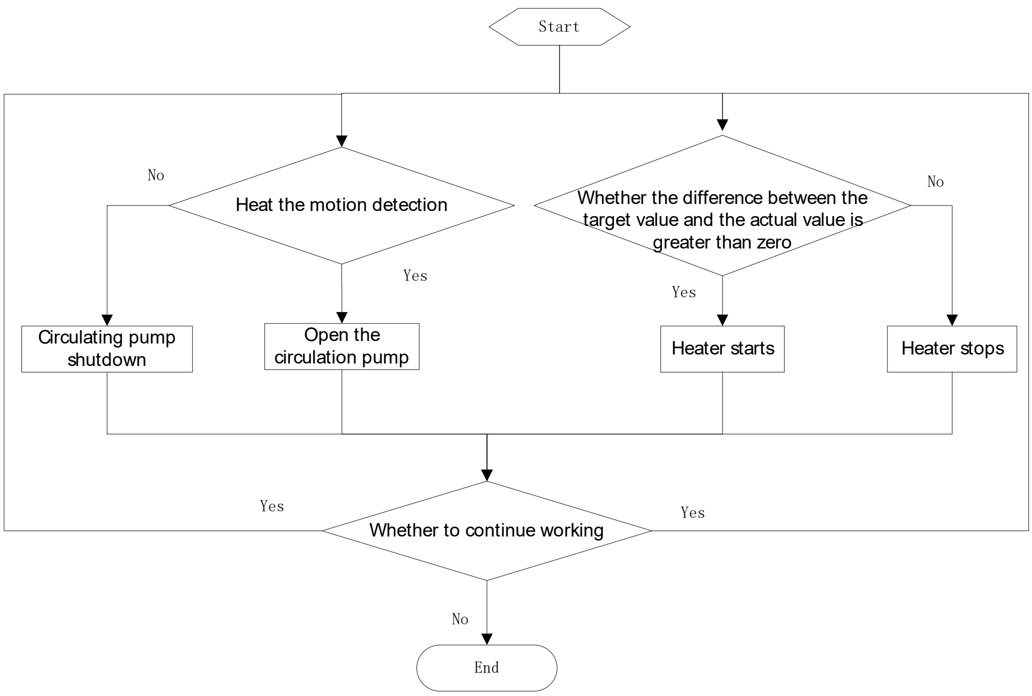

Figure 3. Temperature control unit control logic diagram

3.4 Logic Control Function of Detection Device

The organic carbon testing device included sample collection, titration control of various reagents, oxidation gas generation control, carrier gas switch control, gas detection, reactor cleaning and other operation processes. The whole process was complex and required strict logic control. The device was adopted with a PLC ladder diagram logic language. It was reliable, simple and versatile. The control logic program is shown in Figure 4.

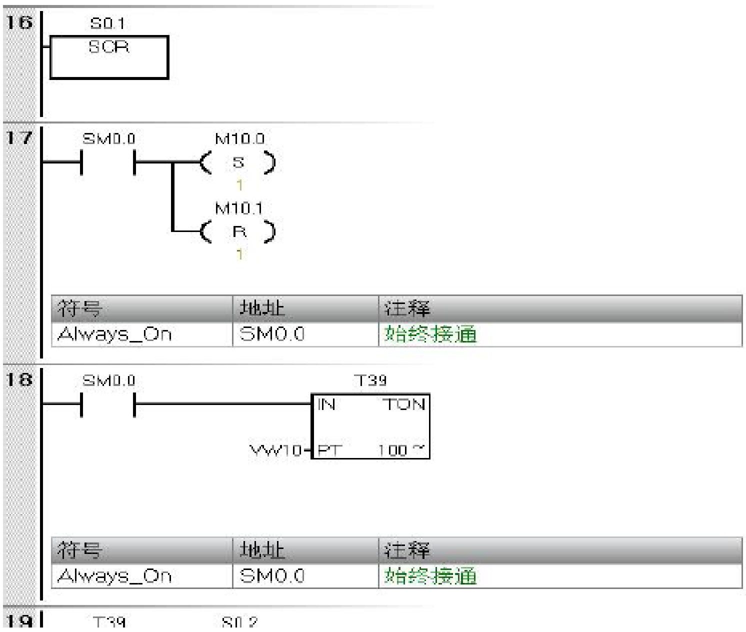

Figure 4. Logic control program

4. Results

4.1 Trend of CO_2 Concentration Detection

100 mL of the solution to be tested was put into the reactor. Hydrochloric acid reagent was added. For a while, there was an obvious correspondence between the added test dose and the measured CO_2 concentration. After a certain of time, the concentration measurement still decreased despite adding a larger trial dose. The results indicated that the reaction was completed at this stage. The reagent addition could be reduced appropriately until the CO_2 concentration value tended to zero. It could be used for the next phase of testing. Then, gradually add the solution containing manganese ion and ozone to continuously precipitate carbon dioxide until it is zero, so as to detect the content of oxalate. In addition, take 100 ml of solution, add sodium hydroxide solution, pass ozone, continuously precipitate carbon dioxide until it is zero, and detect the organic carbon content. CO2 concentration trend was shown in Figure 5

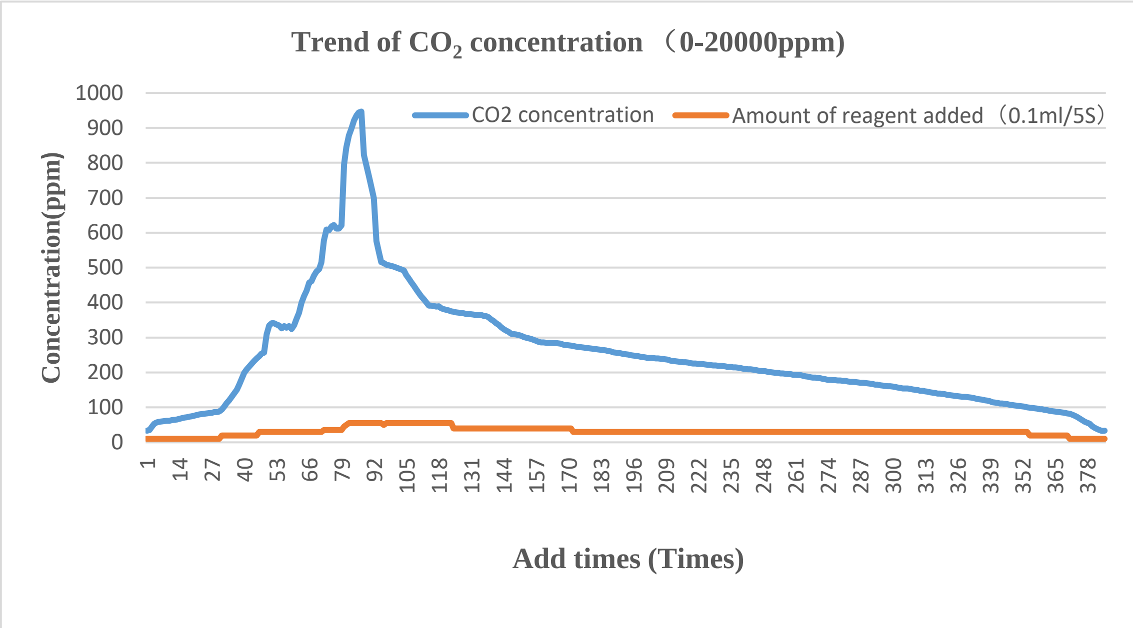

Figure 5. CO_2 concentration trend

4.2 Test Results

The project team took 9 groups of samples from the production site for testing. It was respectively in accordance with the inorganic carbon (instrument), inorganic carbon (artificial), organic carbon (instrument), organic carbon (artificial), $Na_2C_2O_4$ (instrument), $Na_2C_2O_4$ (artificial) data comparison. The specific results were shown in Figure 6. Artificial means that the data is measured by man, and instrument means that the data is measured by instrument.

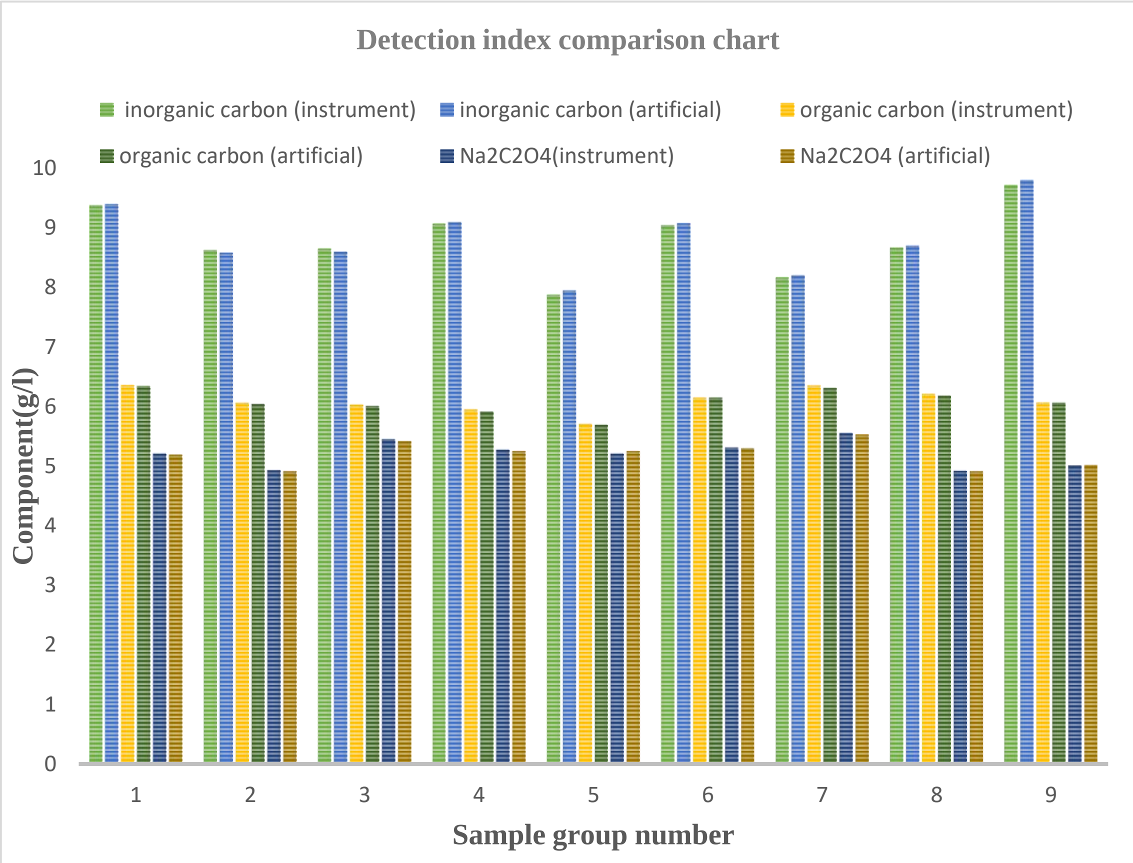

Figure 6. Detection index comparison chart

5. Conclusion

According to the principle of NDIR infrared absorption method, an analysis device of organic carbon in sodium aluminate solution was researched and realized. The sampling unit, reagent addition unit and an analytical unit were designed. PLC based control system was adopted to coordinate the overall monitoring of the machine. At the same time, a man-machine interface of the system was developed. Complete the test of one sample in 50 minutes. According to the test results, the measuring range of organic carbon in this device was determined as 0–50 g/L where, the measurement range CO_2 concentration was between 0–2000 ppm with 1 ppm precision and ≤ 2 % FS(Full-scale), lower limit of measurement:. The measurement range of gas mass flowmeter was 0–10 L/min. The operating temperature was between -10~50 °C. Signal output for Modbus communication was enabled.

The application of this device has solved the problem of rapid analysis of organic carbon in sodium aluminate solution in alumina process. It is convenient for operators to adjust production control parameters in time and ensure high production quality in alumina. The device has friendly interface, simple design and reliable operation. It fills the gap of this kind of testing device in domestic aluminum industry with its low-cost high-performance value.

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