

## Automated Multi-component Detection Methods for Sodium Aluminate Solution

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### Abstract

The determination of sodium aluminate solution composition is very important in alumina production. The traditional manual determination method has high cost, low efficiency and the detection results are greatly affected by subjective judgment. In this paper, a step-by-step potentiometric titration method conforming to the automatic detection logic was proposed based on the traditional detection method, a multi-component automatic analysis equipment for sodium aluminate solution with the functions of automatic recall of different concentration curves and automatic discrimination and dilution of samples was developed, which could directly measure the content of Nc, Nk and AO simultaneously, and then obtain the Nt,  $\alpha k$  and RP values, aiming to achieve efficient, accurate and low-cost intelligent detection. During the research process, the actual sodium aluminate samples from different processes in actual industrial production were used as the experimental objects, and multi-curve fit was performed based on the reference of manual detection results, and performance tests under different sampling conditions, storage conditions and temperature conditions were carried out. The results show that the relative deviation of the device is less than 1.5 % and has good operational stability. This study can be maturely applied to industrial production, which can significantly improve the detection efficiency and accuracy of sodium aluminate slurry, reduce the detection cost, ensure the safety of personnel, and provide strong technical support for the intelligent development of alumina production.

**Keywords:** Sodium aluminate solution, Component determination, Intelligent detection, Potentiometric titration.

### 1. Preface

Sodium aluminate solution runs through almost the entire alumina production process, which is an important intermediate product, and clarifying its composition and content is an important basis for guiding alumina production. For example, the concentration of caustic alkali (Nk) and alumina (AO) directly affects the control of liquid-solid ratio, dissolution rate, decomposition rate and other process indicators in the preparation, dissolution, decomposition and evaporation of raw ore pulp [1]. The concentration of carbonate alkali (Nc) plays an important role in controlling the dissolution rate, decomposition rate, inhibiting the expansion of red mud, and improving the settlement performance of red mud. Therefore, it also determines the importance of sodium aluminate solution composition analysis and is a high frequency multi-indicator. Some automated analysis methods have also been proposed at China and abroad, among which the most studied methods are potentiometric titration [2], flow injection analysis [3], conductivity determination [4], etc.

Based on the previous work, this paper optimizes the traditional manual determination standard method and develops an automatic sodium aluminate solution analyser based on the detection principle of potentiometric titration. The automatic and rapid determination of AO, Nk and Nc in sodium aluminate solution has been achieved. This instrument is simultaneously equipped with an upper computer software, which can then calculate the corresponding values of total alkali (Nt) and caustic ratio ( $\alpha_k$ ). After extensive experimental verification, this equipment is truly capable of being put into production application, replacing traditional manual analysis.

## 2. Measurement Theory

The traditional manual measurement method involves determining Nk, AO and Nt respectively from two samples, which is rather complex and not suitable for the development of automated measurement equipment. This study optimized the method, enabling the sequential determination of Nk, AO and Nc with just one sample.

First, the free hydroxide in the sample was titrated with a standard hydrochloric acid solution until the first endpoint. Then an excess of aluminium complexing agent was added to form an aluminium complex and release the bound hydroxyl group into hydroxide ions. Continue to titrate the released hydroxide ions with the standard hydrochloric acid solution to the second endpoint. At this point, the concentration of AO in the sample can be determined based on the stoichiometric relationship between alumina and bonded hydroxide ions. Meanwhile, the sum of the concentrations of free and released hydroxide ions is the Nk. Continue to titrate with hydrochloric acid until the third titration endpoint, when carbon alkali in the sample is titrated from carbonate to bicarbonate and obtain the concentration of Nc. The sum of Nk and Nc is the content of Nt, and the ratio of Nk to AO coefficient is the value of  $\alpha_k$ . In this process, the pH electrode was used as the detector, and the extremum point of potential change was used to determine the endpoint of titration.

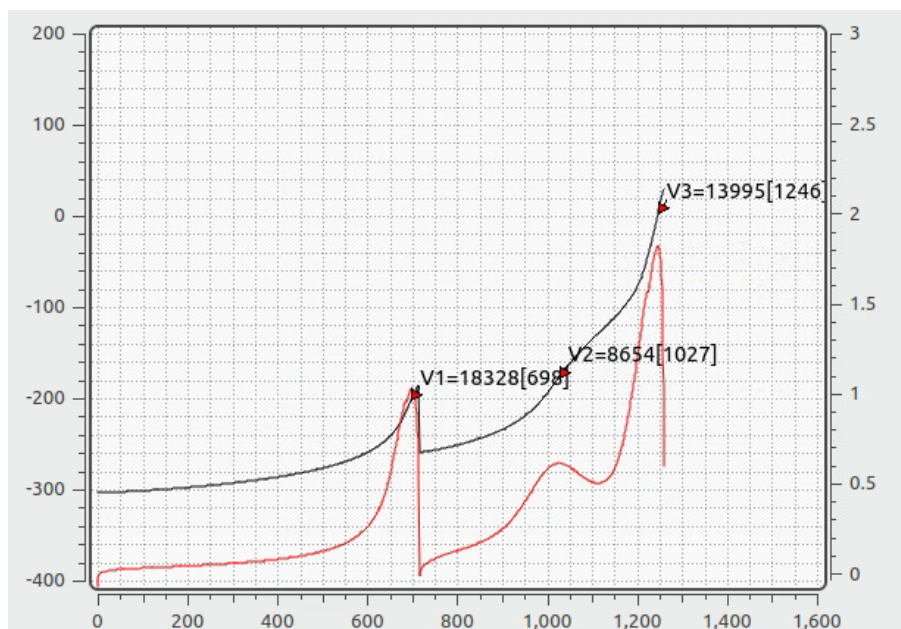


Figure 1. Titration potential variation trend diagram (3 titration endpoints V1/V2/V3).

## 3. Automatic Detection Equipment Development

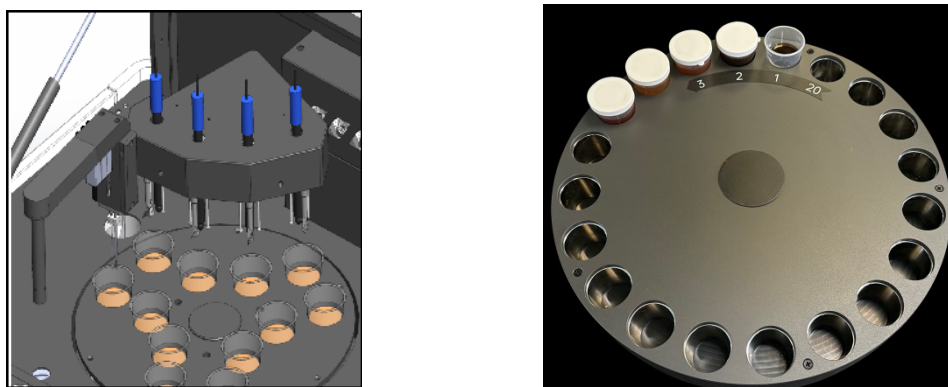
Based on the above measurement theory and following the design logic from the development of split modules to the assembly of the entire machine, the design and development of an automatic

analyser for sodium aluminate solution were carried out. It includes parts such as system workstations, sampling and dilution, analysis and measurement, waste discharge and cleaning, data analysis and processing, etc. The functions and roles of the main parts are as follows:

The host system interactively communicates with each module via the RS485 bus to control their actions, and collects, analyses and displays the data obtained by the electrode module through the RS485 interface.

The sampling dilution part is equipped with a metering module, which contains multiple sets of infrared sensors, and the metering module is driven by the sampling and dilution manipulator to realize the accurate measurement of samples with different measurement volumes.

The analysis and measurement part consists of a sample extraction unit, a titration station, a sample disk, a waste discharge cleaning station and other parts. The sampling unit is set to take samples from all robotic arm and automatically grab/quantitatively transfer the sample cup to drip positioning. The drip positioning independent unit is set, and the single-channel analysis corresponds to the dual-channel liquid adding structure, which is conventionally 4-channel position, supporting unit expansion, equipped with Mettler LE409 PH electrode. The sample tray is set with 20 holes and is equipped with microcomputer temperature control PID regulation to achieve uniform temperature control from room temperature to 45 °C. The sample cup adopts RFID (Radio Frequency Identification) technology, which can intelligently identify sample information from multiple mineral sources and multiple points. The waste discharge and cleaning station can achieve stirring, cleaning, waste liquid discharge, and detection of whether there is liquid in the cup, etc.



**Figure 2. Key component configuration schematic diagram. Left: measurement and analysis unit (4 channels), right: original sample tray and cups.**

#### **4. Debugging and Optimization of Industrial Conditions**

The sodium aluminate solution in the industrial production process is extremely complex, and has the characteristics of easy scarring, strong alkali corrosion, etc. to ensure that the automatic sodium aluminate solution analyser can truly replace manual labour and stably guide production, the results determined by the analyser should be as close as possible to those of traditional manual determination. Therefore, Actual samples under different processes such as precipitation, evaporation, digestion and sedimentation were selected to verify the determination conditions and effects of sodium aluminate solution automatic analyser. The determination criteria are shown in Table 1.

**Table 1. Summary of tolerance for determination results.**

Detection of Components	Concentration (g/L)	Tolerance for Automatic Analyzer and Manual Measurements (g/L)	Tolerance for Automatic Analyse Parallel Measurement (g/L)
Nt	≤ 50	2.0	1.5
	50–100	2.0	2.0
	100–200	3.0	2.5
	> 200	3.5	3.0
AO	≤100	2.0	1.5
	>100	3.0	2.5
Nk	≤ 50	2.0	1.5
	50–100	2.0	2.0
	100–200	3.0	2.5
	> 200	3.5	3.0

#### 4.1 Curve Debugging

The method is the following one: First, take samples from a certain point for manual sampling and analysis. At the same time, dilute the original solution to samples of different concentration gradients such as 2, 5, 10, 20, 25, and 40 times. Take 30 mL of each diluted sample and the original sample in a titration cup in sequence and place them on the instrument's sample stage for analysis module testing to obtain the sample analysis results. Conduct parallel analysis on each diluted sample to ensure data stability. Then fit each module curve, each module has three independent AO, Nk, and Nc dilution multiple working curves; finally, 30 mL of the stock solution of each test sample with low, medium and high Concentrations were transferred into the sample cup, and the instrument automatically absorbed 1.0 mL of the stock solution. After automatic dilution and volume setting, the analysis module measured the results are used to correct the dilution multiple of the instrument.

#### 4.2 Temperature Impact Experiment

The sodium aluminate solution in the production pipeline is high temperature. In the measurement, the higher the temperature of the sample, the closer it is to the real state. As the temperature drops, the components of the solution crystallize and precipitate, and the test results will vary significantly. In traditional manual analysis, the temperature of the sample is close to room temperature, At the same time, the temperature resistance of the Ph electrode of the instrument, as well as the operational stability and safety of the heating device of the sample plate, should be taken into consideration. The instrument original sample tray is set to a variable temperature range from room temperature to 45 °C.

##### 4.2.1 Temperature Control Condition Experiment

First, manual and instrumental comparison experiments were carried out under two conditions: original sample tray control 45 °C (controllable maximum temperature condition) and non-temperature control (room temperature condition). Among them, in the non-temperature control conditions, both the instruments and manual analysis were carried out in accordance with the normal procedures, and a total of 557 samples were compared and determined. At a constant temperature of 45 °C, the manual analysis method remained unchanged. All samples analysed by the instrument were kept warm to 45 °C before analysis. Particularly, for samples with higher temperatures such as green liquor and spent liquor, they were first cooled in a water bath for 3

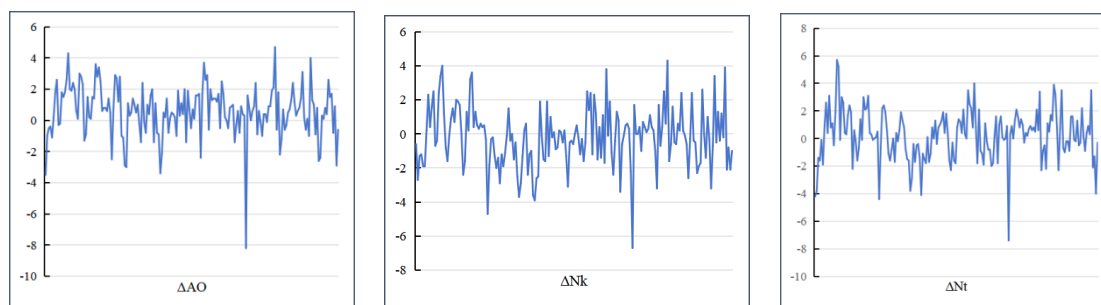
minutes and then kept warm for 5 minutes before analysis. A total of 546 samples were compared and determined.

**Table 2. Comparison of pass rates between manual and instrument methods under control at 45 °C and non-controlled conditions.**

Temperature	Condition	Number of Analyses	Number of Failures	Pass Rate
Non-Temperature Controlled	Nt	185	99	46.5 %
	AO	185	95	48.7 %
	Nk	187	89	52.4 %
	Total	557	283	49.2 %
Control at 45 °C	Nt	182	27	85.2 %
	AO	182	50	72.5 %
	Nk	182	22	87.9 %
	Total	546	99	81.9 %

As can be seen from the table above, whether or not the temperature of the sample is controlled has a significant impact on the analysis results. After the instrument was set to constant temperature analysis, the pass rate of manual comparison was significantly improved, from the original 49.2 to 81.9 %.

Under the condition of constant temperature of 45 °C, the fluctuation of the difference value of the three indicators is shown in Figure 3 (Unit: g/L).



**Figure 3. Difference range between manual and instrument methods at constant temperature (45 °C).**

#### 4.2.2 Comparative experiment of constant temperature conditions

The lower the temperature setting of the original sample tray is, the better the economy will be. Therefore, the temperature condition of the instrument was adjusted from 45 to 40 °C, and a comparative determination of 174 samples from 59 batches under the insulation condition was conducted.

**Table 3. Pass rate statistics for manual vs. instrument comparison under 40 °C constant temperature.**

Condition	Condition	Number of Analyses	Number of Failures	Pass Rate
Constant 40 °C	Nt	59	25	57.6 %
	AO	59	22	62.7 %
	Nk	56	14	75.0 %
	Total	174	61	64.9 %

The results show that the sample holding temperature has a significant impact on the analysis results. When the instrument was set to a constant temperature of 40 °C, the pass rate compared with manual operation had dropped significantly. Specific results are shown in Table 3.

### 4.3 Conditional Impact Experiment

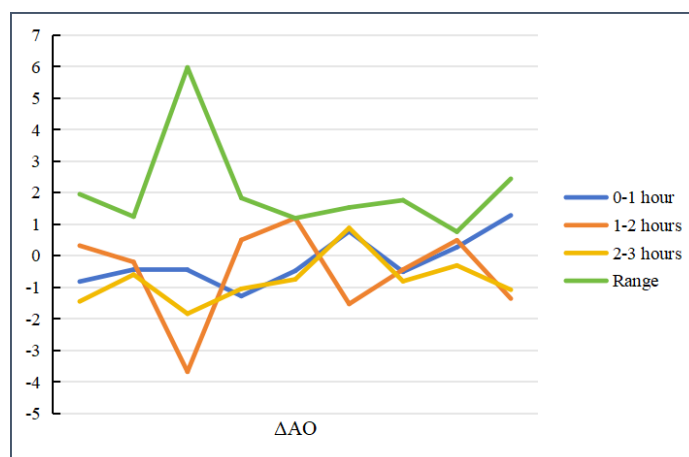
#### 4.3.1 Instrument Stability Experiment

Since the concentration of the test data still changes greatly after the stock solution is placed even under insulation conditions, the main reason is that the sample cup condenses more under the open mouth. Therefore, a group of 9 samples of comparative experiments were set up, the solution was poured into the sample cup and covered with plastic wrap at the mouth of the cup, and the temperature was stabilized, and the instrument analysed the original sample every hour, a total of four times, and the difference between the two adjacent analysis results and the extreme difference of the four analysis results were counted. Results are shown in Table 4.

**Table 4. Pass rate statistics for manual vs. instrument comparison under covered cup condition.**

Condition	Time Sequence	Pass Rate		
		Nt	AO	Nk
Constant 45 °C, Cup Covered	0-1 hour	100 %	100 %	100 %
	1-2 hours	88.9 %	88.9 %	88.9 %
	2-3 hours	100 %	100 %	100 %
	Range	55.6 %	66.7 %	66.7 %

The results show that after covering them with plastic wrap, the stability of the original sample analysis results has been significantly improved. Within one hour, the analysis results were all within the tolerance range. All the out-of-tolerance samples were obtained from the digestion slurry and the circulating spent liquor. The decomposition pregnant liquor, sedimentation pregnant liquor and dilution liquor from the sinter leaching workshop were all completely qualified. The difference floating situation is shown in Figures 4 to 6 (Unit: g/L).



**Figure 4. Difference range of multiple measurements under covered cup condition (AO).**

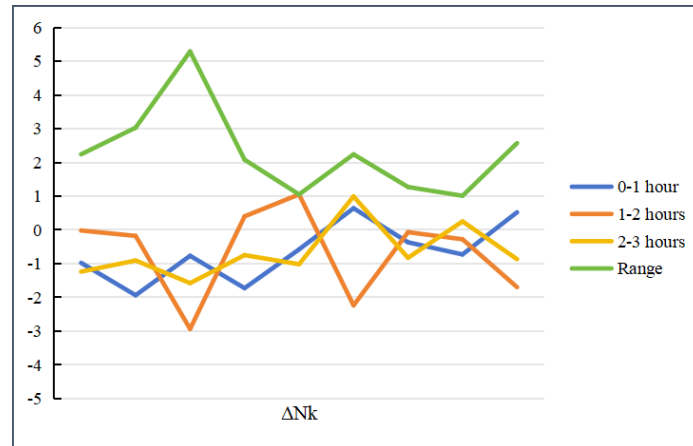


Figure 5. Difference range of multiple measurements under covered cup condition (Nk).

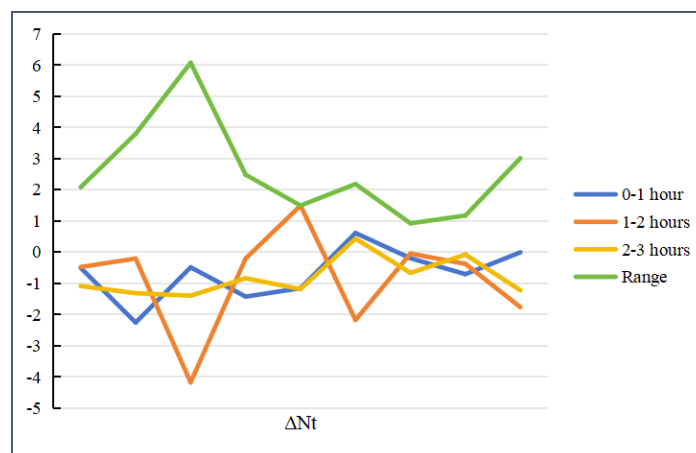


Figure 6. Difference range of multiple measurements under covered cup condition (Nt).

#### 4.3.2 Sampling Condition Experiment

In order to verify the impact of sampling conditions on the analysis results, based on the above-mentioned comparison results under constant temperature of 45 °C, the temperature conditions remain unchanged, the sampling conditions are controlled, and both manual and instruments are used to perform sampling and analysis from the original sample tray. That is, after the sample is kept in the analysis disk for 5 minutes, the laboratory personnel will take samples from the original sample tray for dilute and analysis. At the same time, the instrument began its measurement work. The comparison pass rate is shown in Table 5.

Table 5. Pass rate statistics for manual and instrument sampling from the same original sample tray.

Condition	Condition	Number of Analyses	Number of Failures	Pass Rate
Constant 45 °C, Covered Cup, Same Sampling Point	Nt	144	14	90.3 %
	AO	144	18	87.5 %
	Nk	139	11	92.1 %
	Total	427	43	89.9 %

Compared with the constant temperature 45 °C conditions in Table 1 in Table 5; after unifying the sampling conditions, the pass rates of each analysis item have significantly increased.

### 4.3.3 Artificial Influence Experiment

Considering the impact of operational differences generated by multiple inspectors on test results, based on the above experiments, a total of 414 projects were compared and analysed by 138 batches of sodium aluminate slurry samples. That is, keep the sample covered with cling film and maintain it at 45 °C for 10 minutes on the original sample tray. Then, the same person takes samples from the original sample tray and for dilution and analysis. At the same time, the instrument starts the analysis, eliminating the inconsistencies caused by multiple people analysing simultaneously in the past. The comparison of the pass rate is shown in Table 6.

**Table 6. Pass rate statistics for dedicated person vs. instrument analysis.**

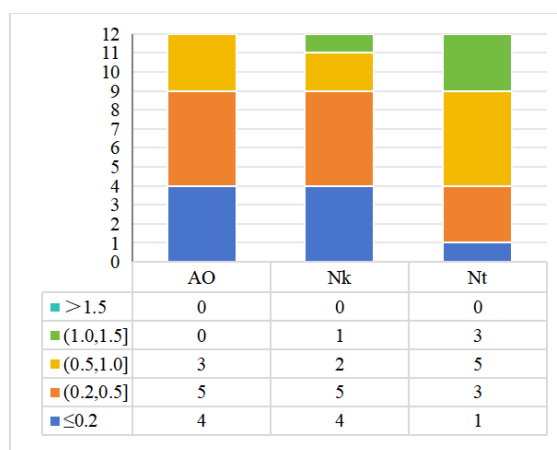
Condition	Condition	Number of Analyses	Number of Failures	Pass Rate
Constant 45 °C, Covered Cup, Same Sampling Point, Dedicated Person	Nt	138	17	87.7 %
	AO	138	13	90.6 %
	Nk	138	4	97.1 %
	Total	414	34	91.8 %

Compare with Table 6 and Table 5, after dedicated measurement, the pass rates of all analysis items except Nt have significantly increased.

### 4.4 Instrument Stability Verification

#### 4.4.1 Accuracy Experiment

Measurement accuracy refers to the degree of consistency between the measurement result and the true value of the measured quantity. According to the control requirements of inspection and testing, the accuracy experiment of the instrument was conducted. Under the above verified optimal conditions, the instrument carried out 12 parallel sample measurements on the sodium aluminate solution samples which had been determined by manual detection for many times. Among them, the AO truth value is 71.2 g/L, the Nk truth value is 149.4 g/L, and the Nt truth value is 165.8 g/L. The pass rate of measurement reached 100%, and the difference was less than 1.5 g/L. The distribution of the difference between each index and the truth value is shown in Figure 7.



**Figure 7. Distribution of differences between indicators and true values.**

#### 4.4.2 Precision Experiment

Measurement precision refers to the proximity between the results obtained by repeated measurement of the same sample, in accordance with the control requirements of inspection and testing, the precision test of the instrument, by the instrument under the optimal conditions after the above verification of 124 batches of sodium aluminate slurry samples a total of 372 items, the overall two rounds of repeated measurement, AO, Nk, Nt determination pass rates were 94.4 %, 100 %, 99.2 %, the total pass rate reached 97.9 %, and the relative deviation (PRD) was less than 1.5 %. The relative deviation distribution of each index is shown in Figure 8.

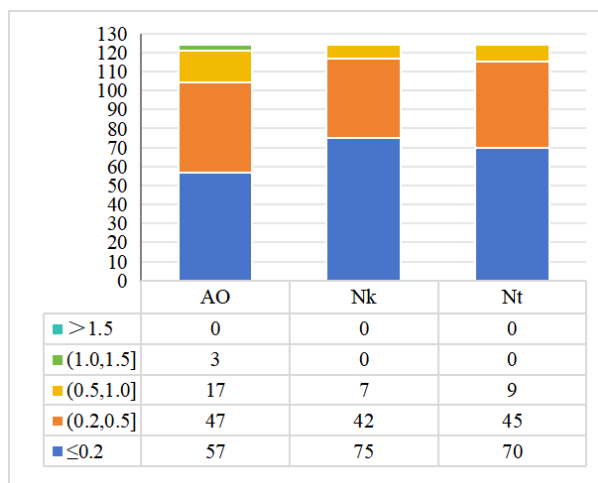


Figure 8. Distribution of PRD for each indicator.

## 5. Conclusion

According to the above experimental results, it can be clear that the sample holding temperature and sample storage conditions have a great impact on the measurement results of the instrument, and after test verification, the optimal condition is determined to be a constant temperature of 45 °C and the original cup is laminated, under this condition, the equipment runs stably, and the measurement accuracy and precision fully meet the requirements of the measurement index.

In addition, when the instrument measurement results are truly applied to guide the production of alumina, they must be compared with the measurement results under the original manual measurement system. This experiment verified through multiple comparisons and analyses between manual and instrument measurements, determining that under the optimal conditions, while ensuring that both manual and instrument sampling conditions are the same, and when multiple people in the inspection team are conducting measurements simultaneously, the comparison pass rate of the measured results is nearly 90%, which can basically meet the needs of guiding production. In particular, if other conditions remain unchanged, the total pass rate of comparison is increased by 1.86 % compared with the instrument measurement, and the pass rate of AO and Nk reaches more than 90 %, which further shows that the reliability of the instrument measurement can be maturely applied to industrial production.

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