THE DEVELOPMENT OF "PORTABLE INTELLIGENT EXPRESS IODINE-MEASURING INSTRUMENT"

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INTRODUCTION

Iodine is one of essential trace elements for human. WHO Bulletin that, so far iodine deficiency, as one of the major reasons that damage human intelligence, has become the crucial factor of impact on people health. China is one of the most severe iodine deficiency disorders areas in the world, which accounts for 40 percent of the world's sickness population. As the work of eliminating iodine deficiency disorders and the level of national scientific and technological knowledge is gradually improving, the broad masses of the people pay special attention to the prevention and elimination of iodine deficiency disorders. Practice has proved that, consumption of iodized salt is the most secure, most economical, easiest and most effective measure of prevention of iodine deficiency disorders. Therefore, our government decides that all salt should be iodized, since 1996, the production of edible iodized salt has been fully realized in our country.

The quality of edible iodized salt is directly related to the effect of prevention of iodine deficiency disorders, because of the differences of the production, storage and transportation conditions in all enterprises, the quality of iodized salt is not unified. The supervision and management of the product quality is a key factor of ensuring the consumption of qualified iodized salt of the masses. In order to guarantee the quality of iodized salt, the State Ministry of Health and the National Development and Reform Commission has issued the document for several times and taken corresponding measures to supervise and manage the quality of iodized salt. The salt enterprises also pay great attention to the quality of iodized salt. In order to ensure the quality of iodized salt, it is essential to test the iodine content of salt during the production process; marketing and sales departments should also test the iodine content of salt due to the instability of iodized salt caused by the storage and transportation.

At present, about the methods for testing the iodine content of iodized salt in the national standards, "capacity titration" accounts for a large. However, "capacity titration" has a lot of defects, for example, strict for detecting staff, longer detection time, big drug consumption, strict requirement of environmental, only suitable to use in the laboratory not at the scene, more difficult to achieve the using of portable analytical instrument. In addition, the drug is toxicity, and will cause environmental pollution and impact on the health of analysis staff. Since the national standard "the Main Product sample methods of GQ/T8618-2001 salt Industry" is implemented and" capacity titration " has a lot of inconvenience, in order to master the quality of iodized salt as soon as possible, there is an urgent need of a analysis method that is simple, accurate, rapid and easy to master, non-toxic, non-environmental pollution and un-harm to human body at the scene of the production, storage, transportation and sale of warehouses, Therefore, it is very essential to research and

develop a full-featured "portable intelligent iodine- measuring instrument", It is believed that the successful development of the product will have broad market space and bring better economic and social benefits.

DETERMINING TECHNICAL PROGRAMS

According to the survey, the users all look forward to the successful development of the "iodine-measuring instrument" with a lot of advantages such as simple operation, rapid reaction, stable and accurate measuring, portable, affordable, it also is able to directly show the data indicators according to the National standards "GQ/T8618-2001 Salt Industry Main Products sampling methods". Therefore, the technical program, which we have determined, is available to take into account both the functionality and the economic practicality of the instrument.

(a) Determining the testing method

Nowadays there are many methods for testing the iodine ions. According to it, initially we took all factors into consideration and decided several testing plans:

(i)consider from the aspect of simple operation: because solid samples will produce chroma changes after the chemical action as the change of iodine content, which can reflect the iodine content of samples according to the light refraction and reflection theory. However, the experiment proves that the program is infeasible due to the instability of salt particle size, the differences of tightness, un-uniform of solid colors and so on. All these will cause the instability of testing results and poor accuracy.

(ii) capacity titration: Due to the strict demands of environmental factors and operators, and complex operations, this method only applies to the laboratory not the scene. It's also not able to be used in portable instruments.

(iii) ion-selective electrode method. Ion-selective electrode is not easy to carry, easily broken and polluted. It also has a short life. Soak and clean before using it is needed. Thus it doesn't easily adopt in portable instrument.

(iv) the Spectrophotometry method. According to Lambert - Beer law, when the monochromatic light pass though the homogeneous solution, the solution should absorb the light. Simultaneously, absorbance strictly meets the following relationship:

$$A=\lg(I_0/I) = k\ c\ b$$

Where, A——absorbance
K——proportional coefficient
I_0——intensity of incidence light
I ——intensity of transmitted light
C ——concentration of solution
B ——liquid layer thickness

From above equation it can be seen that, when a bouquet of monochromatic light passes through the homogeneous solution, the absorbance is proportional to the product of concentration and thickness of the solution; when the liquid layer thickness (optical path) remains unchanged, the absorbance is directly proportional to the solution concentration. In other words, when the intensity of incident light and optical path remain the same, the solution concentration changes in logarithms with the transmitted light intensity; if the transmitted light intensity can be detected in a certain way, then the solution concentration will be calculated.

Because of the stable characteristics of monochromatic light source and photosensitive element, plus longer service life, the spectrophotometer method is more suitable for this kind of equipment. Therefore spectrophotometer method is determined to use.

(b) Determining detection conditions

After chemical treatment, samples of iodized salt become stable, homogeneous blue solution, then the samples with the specific monochromatic light selected and its reflected light intensity are detected by using Photoelectric sensor, the computer automatically processes the iodine content and directly display in figure.

(i) Determining the conditions of the sample treatment. After samples being treated, we have also done experiments with respect to the selection of the types of acid and acid dosage, reagent dosage, color time and solution quality in order to achieve the effect of great selection and small interference and high sensitivity during the detection, finally, the best experiment conditions are determined. Experimental data is shown in Table 1, Table II, Schedule 1 and Schedule V (attached):

Table 1: test data table of the election of the types of acid

absorbance acid (A) / acid content	HCl	H_2SO_4	H_3PO_4
2.0 (ml)	0.656	0.669	0.667
2.5 (ml)	0.652	0.666	0.674
3.0 (ml)	0.662	0.670	0.672

Table II: test data table of the election of acid dosage

$C(1/2H_2SO_4)$= 1mol/L sulfate Absorbance (A) Iodide content	3d	0.5 (ml)	1.0 (ml)	1.5 (ml)	2.0 (ml)	2.5 (ml)	3.0 (ml)	3.5 (ml)	4.0 (ml)	4.5(ml)
10(mg/kg)	0.038	0.043	0.112	0.124	0.127	0.134	0.131	0.130	0.136	0.126
50(mg/kg)	0.209	0.238	0.680	0.697	0.707	0.725	0.716	0.710	0.700	0.729

The data of Table 1, Table II and Schedule 1 shows that:

(A) Three types of acid including Hydrochloric acid, Sulfuric acid, and Phosphoric acid are used for testing the standard samples, result shows that the types of acid have little effect on the test results.

(B) When the adding of acid reaches 2.5ml, its absorbance will reach the maximum, so this quantity is more suitable for this analysis.

(C) Within 25min samples tested, its result has little deviation.

(D) After the experiment tests, it is showed that different types of water quality (distilled water, tap water, mineral water) have little effect on the test, the test data is not listed (data table omitted).

(ii) Selecting of the maximum absorption wavelength. In order to select the maximum absorption wavelength of the iodized salt treatment samples, standard iodized salt solution samples with different concentration are prepared. Then 722-type spectrophotometer is used to test samples after chemical action, the maximum absorption wavelength will be selected according to the absorption of samples under different conditions. And Schedule II has showed the test data.

The Schedule II data shows that, the sample absorbance reaches the maximum when single-wavelength chooses 585nm, so monochromatic light of 585nm can be selected as the test source of iodine-measuring instrument.

(c) Selecting a sensor.

It is the key of the research to select a sensor that is able to fast and accurately reflect the changes of the iodine content. A lot of information had been collected throughout the country, photodiodes, optical pressure sensors, optical frequency sensors, photoelectric sensors, Darlington composite pipe

components and so on also were selected for a large number of experiments. After that, relative electric circuit was designed for testing and selecting. Finally a sensitive and stable sensor was determined to use as one of the instrument.

Table III: test data table of photoelectric sensor performance

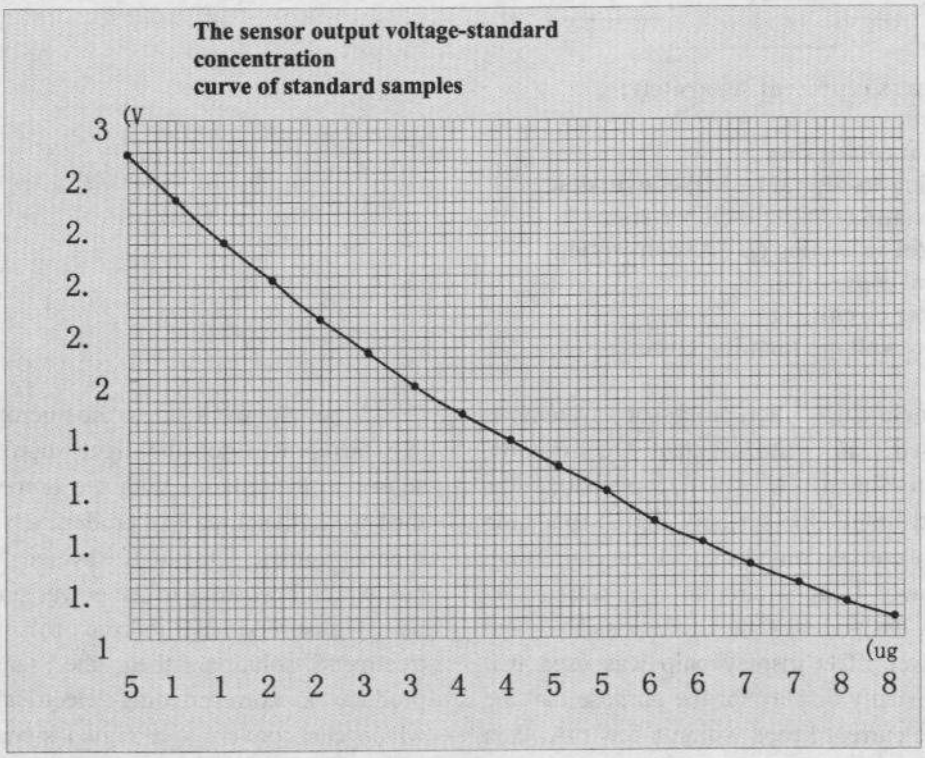
Sample iodine content	Output signal of photoelectric sensor (volts) (testing time)			
	10:00	10:30	11:00	11:30
Distilling water		2.658	2.653	2.651
Tap water		2.686	2.682	2.668
10 (ug)	2.427	2.427	2.429	2.426
20 (ug)	2.172	2.158	2.163	2.165
30 (ug)	1.916	1.926	1.38	1.937
40 (ug)	1.700	1.710	1.720	1.719
50 (ug)	1.483	1.482	1.490	1.498
60 (ug)	1.334	1.346	1.352	1.359
70 (ug)	1.207	1.213	1.225	1.227
80 (ug)	1.094	1.100	1.108	1.113

Table III data shows that, the photoelectric sensor will obviously change the output signal with the different concentration of iodine solution, but the signal values keeps stable at different time. Therefore photoelectric sensor was finally selected as the sensing element of "Measurement of iodine Miriam".

(d) Determining the mathematical model of Iodine content

It is the technical key of the study to find the mathematical model that could really and accurately reflect the change of iodine content.

(i) The solution samples with different iodine content were prepared. By trial and error, the sensor output voltage-standard concentration was finally found out. The curve is similar to a logarithmic curve.

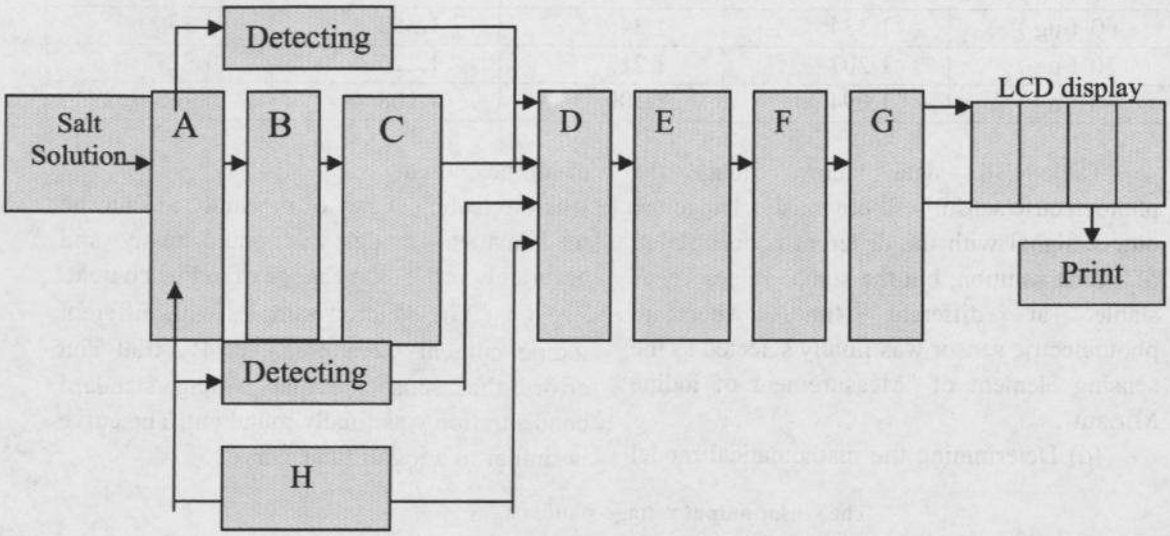


(ii) The instrument requires being portable; therefore, the portable single-chip

microprocessor that has small size and fast response is selected as the apparatus of control components. However, because of the limited memory of single-chip microprocessor, it's difficult to complete the complex operation. Then the mathematical model of depicting the concentration curve does not exists very large data computing and should satisfy the requirements of instrument precision was considered. So a logarithmic expansion method, least square method and so on were selected in order to compute and compare, finally least square method was chose for the curve linearization handling and identify the mathematical model. Through substantial testing on the curve of the high, low-end compensation for deviation correction, finally the ideal mathematical model was obtained.

(e) Hardware design and working principle of iodine analyzer

Iodine analyzer uses a single-chip microprocessor as the system control component. Taking into account the requirements of data collection, computation, signal transmission process, displaying results, high stability, high reliability, self-diagnosis and self-test function of equipment, the structure principle form for machine designing as follows was considered.



The letters represent separately:
A- sensor
B- signal conversion
C- analog-to-digital (A / D) conversion
D- the standard single-chip systems
E- digital-to-analog (D / A) conversion
F- signal conversion
G- driver circuit
H- photo voltage forming circuit

Single-chip microprocessor system is composed of the signal conversion, analog-to-digital (A / D) conversion, the standard single-chip systems, digital-to-analog (D / A) conversion, displaying and printing. Low-power CMOS circuits was selected in circuit design as far as possible and low-power LCD display chip was used that could visually display for the purpose that the machine current keeps within a few mA, then supply power with a battery of 9 V, the system can also work normally.

When the work starts, the microprocessor supplies power for the light source on the sensor in accordance with the procedure set, then the light source will produce a bouquet of monochromatic light of a wavelength of 586 nm, which exposures to the power sensor after being absorbed by iodized salt chemical treatment solution, then the sensor will produce a corresponding electrical signal, which can convert to a digital signal by the analog-to-digital converter (A / D) conversion circuit and can be sent to the microprocessor.

Then the microprocessor will output the corresponding signal of the iodine content after computing and processing according to the pre-set mathematical model, which can be convert to analog circuits, then the signal converts to the standard signal by the signal transform circuit and directly display the iodine content of the measured iodized salt (in mg / kg for units) by the driver circuit in liquid crystal display (LCD), or can be directly printed out by the printer.

(f) Designing the control program of Iodine-measuring instrument and the program flow chart

According to the functions of the instrument such as collecting data, computing, controlling, display and the characteristics of single-chip microcomputer system, the system software design is mainly composed of the main program and several subroutines. The main program concludes initialized modules, self-diagnosis module, optical voltage control module, key scan module, computing modules, etc., while the subroutines conclude calibration modules, measurement modules, data acquisition modules, computing modules, display management module.

And the program flow chart is shown as follows (see Figure 1).

EQUIPMENT TESTING AND THE RESULTS

(a) test the standard samples

First of all, absorb different amounts of potassium iodate standard solution into 50ml colorimetric tubes, add 5mL, 200g / l sodium chloride solution and 2ml reagent (preparation methods: self-developed) and shake; then add 2ml ($1/2H_2SO_4$) = 1mol / L sulfate and shake; finally add water until the scale and shake fully. After measuring the sample solution with "iodine-measuring instrument", then the reading will be the iodine content (in mg / kg as a unit) of the standard salt sample, finally compare its reading with the standard value. Data is listed in Schedule Three (attached).

(b) Testing samples of iodized salt

In the test, the current national standard is adopted to measure the iodine content of the salt sample by "the capacity of the direct titration method" and iodine-measuring equipment, then those two types of data are compared. And the reflected deviation is shown in Schedule IV (attached) by the two different methods regarding to the same sample.

(c) Results and discussion

(i) According to the data of Schedule III it is can be seen that, the maximum deviation value is (+1.5) mg/kg and the smallest deviation is 0.0mg/kg. It shows that, the data measured by "iodine-measuring instrument" fully satisfies the scope of permissible deviation of the national standards regarding to iodide test.

(ii) From the data of Schedule IV it is can be seen that, the two different testing methods show the maximum difference value (+1.5)mg / kg and the smallest one 0.0 mg / kg. It shows that the data measured by "iodine-measuring equipment" and "the capacity of the direct titration method" satisfies the scope of permissible deviation of the national standards regarding to iodide test.

(iii) Reasons of deviation

(A) Iodine-measuring instrument produces a certain degree of measurement deviation.

(B) Spectrophotometer analysis used by the capacity of the direct titration and iodine-measuring instrument brings about certain measurement deviation.

(C) The differences of operators will also bring about certain measurement deviation.

CONCLUSION

(i) The test results indicate that the technical indicators of "portable intelligent iodine-measuring instrument" have reached the scope of permissible deviation of the national standard GB/T13025.7-1999 test error of permit requirements.

(ii) Because of adopting single-chip microcomputer as control components by "portable Intelligent iodine-measuring instrument" in order to collect data, automatically calculate and treat with the errors, the instrument achieves the functions such as low-power, high stability, high reliability and self-test and self-diagnosis of equipment, which enables it to stand in the domestic leading level of technology in the apparatus of similar instruments

(iii) "portable intelligent express iodine-measuring instrument" has so many unique characteristics regarding to the production, storage and transport of the scene that it can be used in circuit design, software development, and sensor design. For example, portable test probe has replaced the quartz colorimetric plate, which is easy to use and clean and very suitable for the production of the field and storage warehouses, terminal use. So it has broad prospects for the promotion of beneficial use.

(iv) "Portable intelligent iodine-measuring instrument" has excellent performances. It has many advantages such as easy to use, cheap, easily applied to light industry, chemical industry, carbon black, water treatment and similar industries with the exception of the salt industry as well at the same time.

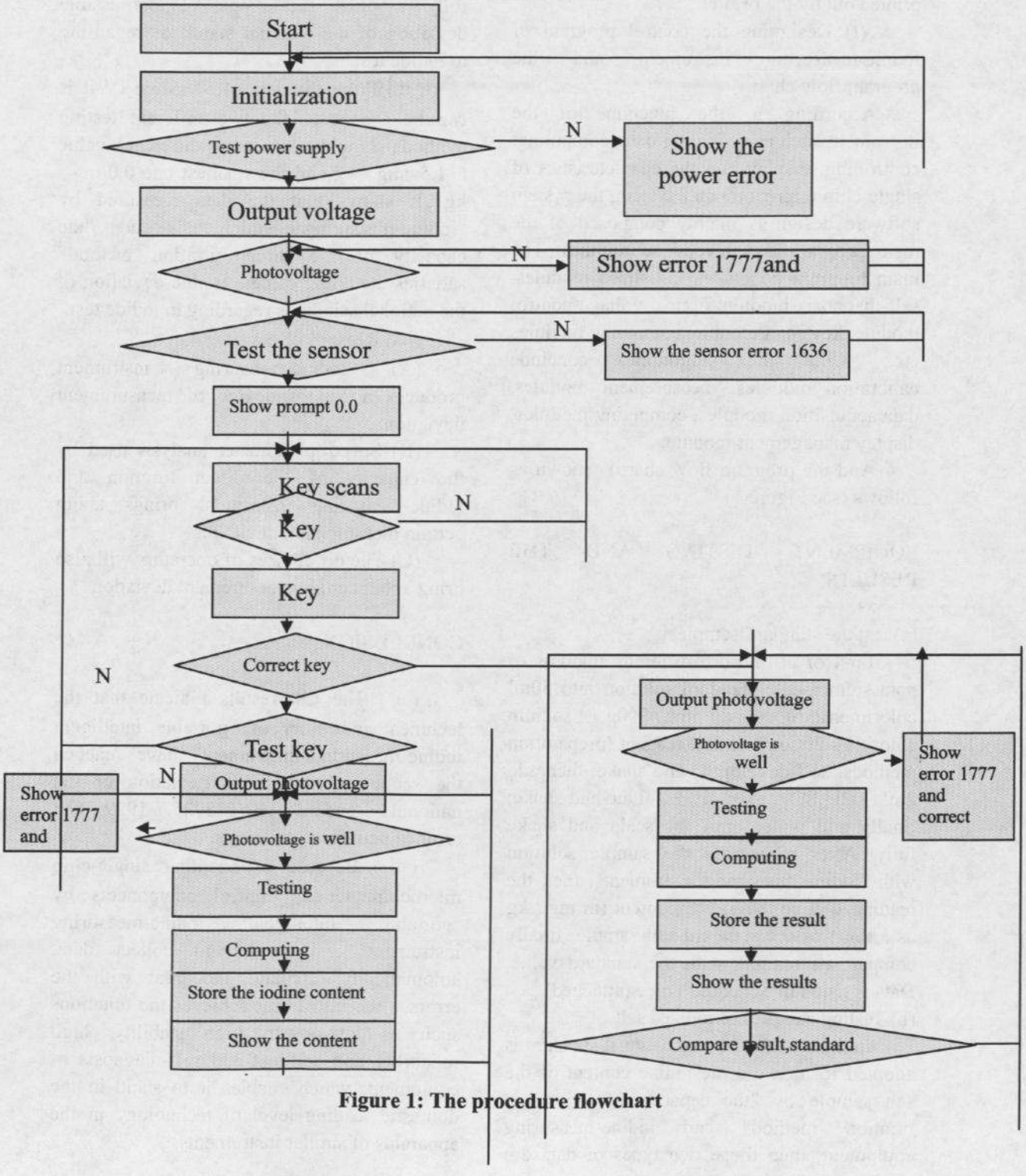


Figure 1: The procedure flowchart

The absorbance I^- (mg)	5	10	15	20	25	30	35	40	45	50	55	60	65	70
Storage times														
Test immediately after preparation	0.056	0.129	0.198	0.270	0.341	0.400	0.471	0.527	0.598	0.646	0.705	0.754	0.795	0.840
After 25min	0.065	0.131	0.205	0.271	0.341	0.402	0.472	0.533	0.595	0.651	0.701	0.752	0.803	0.838

Schedule I : The absorbance table of standard samples in different conditions of storage time

Absorbance Wavelength Iodide content	530	535	540	545	550	555	560	565	570	575	580	585	590
20 (ug)	0.208	0.218	0.229	0.240	0.250	0.258	0.264	0.269	0.271	0.273	0.274	0.273	0.272
40 (ug)	0.443	0.455	0.475	0.449	0.519	0.533	0.548	0.559	0.566	0.569	0.570	0.578	0.574
70 (ug)	0.749	0.790	0.830	0.870	0.907	0.934	0.960	0.979	0.992	1.001	1.006	1.014	1.010
Absorbance Wavelength Iodide content	595	600	605	610	615	620	625	630	635	640	645	650	
20 (ug)	0.270	0.267	0.262	0.257	0.252	0.246	0.240	0.234	0.228	0.221	0.213	0.209	
40 (ug)	0.570	0.563	0.553	0.544	0.533	0.522	0.510	0.499	0.486	0.470	0.459	0.448	
70 (ug)	1.003	0.990	0.970	0.957	0.939	0.915	0.889	0.875	0.853	0.829	0.869	0.785	

Schedule II : The absorbance table of standard samples in different wavelengths

Schedule Ⅲ(i) : The iodine content table of standard samples with iodine-measuring instrument test

Standard I⁻	1#		2#		3#		Remark
(ug)	Actual measurement (mg/kg)	Absolute error (mg/kg)	Actual measurement (mg/kg)	Absolute error (mg/kg)	Actual measurement (mg/kg)	Absolute error (mg/kg)	
10	9.9	-.01	8.8	-1.2	8.8	-1.2	
20	21.5	+1.5	19.8	-0.2	21.5	+1.5	
30	31.6	+1.6	31.2	+1.2	31.3	+1.3	
40	41.6	+1.6	41.3	+1.3	41.1	+1.1	
50	50.0	0.0	50.0	0.0	50.0	0.0	
60	58.9	-1.1	59.3	-0.7	60.7	+0.7	
70	68.3	-1.7	68.8	-1.2	70.5	+0.5	
80	78.9	-1.1	80.0	0.0	80.5	+0.5	

Schedule Ⅲ(ii) : The iodine content table of standard samples with iodine-measuring instrument test

Standard I⁻	1#		2#		3#		Remark
(ug)	Actual measurement (mg/kg)	Absolute error (mg/kg)	Actual measurement (mg/kg)	Absolute error (mg/kg)	Actual measurement (mg/kg)	Absolute error (mg/kg)	
10	10.3	+0.3	10.5	+0.5	10.2	+0.2	
20	20.2	+0.2	19.9	-0.1	20.7	+0.7	
30	30.3	+0.3	30.8	+0.8	29.8	-0.2	
40	41.5	+1.5	39.6	-0.4	41.1	+1.1	
50	50.0	0.0	50.0	0.0	50.0	0.0	
60	59.8	-0.2	59.8	-0.2	59.3	-0.7	
70	70.2	+0.2	69.8	-0.2	68.3	-1.7	
80	80.3	+0.3	80.0	0.0	79.3	-0.7	

Schedule Ⅲ(iii) : The iodine content table of standard samples with iodine-measuring instrument test

Standard I⁻	1#		2#		3#		Remark
(ug)	Actual measurement (mg/kg)	Absolute error (mg/kg)	Actual measurement (mg/kg)	Absolute error (mg/kg)	Actual measurement (mg/kg)	Absolute error (mg/kg)	
10	9.2	-0.8	9.4	-0.6	9.2	-0.8	
20	20.3	+0.3	19.2	-0.8	18.5	-1.5	
30	30.8	+0.8	29.5	-0.5	29.6	-0.4	
40	41.0	+1.0	40.0	0.0	40.0	0.0	
50	50.0	0.0	50.0	0.0	50.0	0.0	
60	59.9	-0.1	59.9	-0.1	59.5	-0.5	
70	70.0	0.0	70.5	+0.5	69.6	-0.4	
80	79.6	-0.4	80.3	+0.3	79.4	-0.6	

Schedule Ⅳ(i): The iodine content table of standard samples with iodine-measuring instrument and capacity titration

Salt Samples No.	capacity titration	iodine-measuring instrument					
		1#		2#		3#	
	Iodine content (mg/kg)	Iodine content (mg/kg)	Deviation	Iodine content (mg/kg)	Deviation	Iodine content (mg/kg)	Deviation
10#	5.2	6.3	+1.1	4.4	-0.8	3.9	-1.3
15#	11.1	11.9	+0.8	10.9	-0.2	9.8	-1.3
25#	21.4	22.9	+1.5	22.1	+0.7	21.8	+0.4
40#	38.0	38.5	+0.5	37.5	-0.5	37.4	-0.6
50#	48.3	48.9	+0.6	48.6	+0.3	49.0	+0.7
60#	58.4	57.9	-0.5	58.2	-0.2	58.6	+0.2
70#	71.4	72.5	+1.1	72.0	+0.6	69.9	-1.4
80#	81.4	80.0	-1.4	81.1	-0.3	81.5	+0.1

Schedule Ⅳ(ii) : The iodine content table of standard samples with iodine-measuring instrument and capacity titration

Salt Samples No.	capacity titration	iodine-measuring instrument							
		1#		2#		3#		4#	
	Iodine content (mg/kg)	Iodine content (mg/kg)	Deviation	Iodine content (mg/kg)	Deviation	Iodine content (mg/kg)	Deviation	Iodine content (mg/kg)	Deviation
1#	30.2	30.0	-0.2	30.6	+.4	29.0	-1.2	30.0	-0.2
3#	28.4	28.3	-0.1	27.6	-0.8	27.9	-0.5	28.4	0.0
4#	33.8	33.5	-0.3	33.1	-0.7	33.9	+0.1	35.1	+1.3
6#	36.1	36.4	+0.3	35.1	-1.0	36.6	+0.5	37.3	+1.2
7#	15.3	14.6	-0.7	13.6	-1.7	14.4	-0.9	14.0	-1.3
8#	43.0	41.9	-1.1	43.5	+0.5	44.3	+1.3	43.0	0.0
9#	37.5	38.5	+1.0	36.7	-0.8	38.7	+1.2	36.5	-1.0

Schedule(v) : data table under the different reagent amount in 18℃

Sample content （ug）	20			30			40			60			70		
Reagent amount (ml)	2.0	2.5	3.0	2.0	2.5	3.0	2.0	2.5	3.0	2.0	2.5	3.0	2.0	2.5	3.0
Transmittance	54.60	55.30	55.35	39.90	39.80	39.90	28.8	28.50	28.80	15.70	15.20	17.50	11.20	11.20	11.50
Absorbance	0.259	0.254	0.254	.395	0.395	0.395	0.534	0.538	0.534	0.801	0.810	0.749	0.940	0.940	0.930