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TWO STANDAARD PHOTOMETRIC METHOD FOR THE DETERMINATION OF Mn,Si, P IN STEEL AND IRON

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Abstract

At present, the photometric method uses multiple standard samples to draw "calibration curves" to determine the results of sample measurement. However, the difficulty of preparing multiple standard samples has become a major obstacle to the popularization and application of spectrophotometry. The results show that if the spectrophotometric determination process strictly follows the "precision rule", i.e. “to maintain infection consistency of each factor for each sample(including standard sample) in the same measurement series ”, then in the "calibration curve" , that is, in the domain of incident light. the absorbance difference ΔA of chemicals proportional to its content difference ΔC: $\Delta A = K\Delta C$. The coordinate points (C, A) of content and absorbance of all the samples, must in the same $\Delta A = K\Delta C$ article line. Therefore, the line between the upper and lower coordinates of the standard sample is the "proportional determination line" of the sample content. Relative standard deviations of 10 determination results of Mn, Si,P were : 2.26%，3.63%，6.45%， and the uncertainties U_{95} were: 0.04%，0.03%，0.005%（k=2）, respectively. In this paper, the implementation details of the "Precision Rule" in spectrophotometry are introduced, which provides the basic operation technology for the popularization and application of spectrophotometry.

Keywords： photometric method; incident light; domain; steel;Mn;Si;P

Spectrophotometry can be used not only in inorganic field but also in organic field. It can not only determine trace and high content, but also realize multi-component united determination easily[1] . However, the current photometric methods use standard samples to draw "calibration curve" to determine the results of determination, and rely on the "many" of standard samples to ensure the reliability of "calibration curve"[2-5] . It is difficult to equip multi-standard samples (such as ferroalloys), which has become a great obstacle to the application of spectrophotometry. Moreover, even if the "calibration curve" is reliable, it can not guarantee the reliability of the results of sample determination. The author found that under the condition that the operation of spectrophotometry follows the " precision rule", i.e."to maintain infection consistency of each factor for each sample(including standard sample) in the same measurement series ", then in the "calibration curve" , that is, in the domain of incident light. the absorbance difference ΔA of chemicals proportional to its content difference ΔC: ΔA = KΔC. The coordinate points (*C, A*) of content and absorbance of all the samples, must in the same ΔA = KΔC article line. Therefore, the line between the upper and lower coordinates of the standard sample is the "proportional determination line" of the sample content. There is no need to use a large number of standard samples to draw "calibration curve". The stricter the "precision rule" is followed, the more reliable the "proportional measuring line" is. the higher the accuracy of the results is. Taking the joint determination of manganese, silicon and phosphorus in iron and steel as an example, this paper introduces the implementation details of "Precision rule" in photometric determination.It provides the basic technology for the popularization and application of spectrophotometry.

1. Experiments

1.1 Main instruments and reagents

Spectrophotometer:721 visible Spectrophotometer, Shanghai Precision Instruments Co., Ltd; Sample dissolution system: 0.4 g silver nitrate is dissolved in 1000 mL nitric acid (1+4);Ammonium persulfate solution: 5% ammonium persulfate solution (available);Hydrogen peroxide solution: 1 mL hydrogen peroxide dissolved in 5 mL water (available);Silver nitrate solution: 1%. 10 g silver nitrate dissolved in 1000 mL distilled water with 20 mL concentrated nitric acid； Ammonium molybdate solution: 1%. 1 g ammonium molybdate dissolved in 100 mL water；Silicon chromogenic solution: 4g oxalic acid dissolves in 100 mL water and 1g ascorbic acid is added (available);Phosphorus chromogenic solution: (1) 8 g bismuth nitrate is dissolved in 1+5 nitric acid of 1000 mL; (2) 30 g ammonium molybdate and 45 g potassium sodium tartrate are dissolved in 1000 mL water. Mix (1), (2) two solutions evenly;Ascorbic acid solution: 1%. 1 g ascorbic acid dissolved in 100 mL water (available);

The experimental water is distilled water, and the reagents are analytical pure.

1.2 Experimental condition

1.2.1 "Precision rule"

Following the "precision rule", i.e. “to maintain infection consistency of each factor for each sample(including standard sample) in the same measurement series ”, is the necessary condition to ensure that the changeΔA of absorbance is proportional to the changeΔC of absorbant content in the range of incident light. The factors affecting the results of spectrophotometric determination are man, machine, material, method and ring. The details of controlling their consistency are as follows.

1.2.2 Human factor control

Among the factors affecting the results of photometric measurement, the human factor is the most important one. In particular, this study emphasizes that all samples of the same measurement series, from the beginning of weighing to each independent procedure of reporting the results, must be completed by the same qualified personnel in accordance with the measurement operation mode.

1.2.3 Environmental control

Temperature and time are the most important environmental factors affecting photometric measurement. High temperature can accelerate the color reaction, but high temperature can reduce the stability of the colorimetric system. In order to improve the color rendering efficiency, this method uses timing heating, and then uses flowing water cooling to place at room temperature. The absorbance of each color solution must be determined within 30 minutes.

1.2.4 Mechanical condition control

The main mechanical factors affecting photometric measurement are balance, capacity vessel and photometer. In the use of the balance, it should be "the same measurement series, weighed by the same weighing state of the same balance"; In the use of volumetric containers, the same procedure and reagent in the same measuring series should be applied to the same containers. In the use of photometer, it should be "the same measurement series, the same colorimetric dish and the photometer in the same state to carry out the measurement";

1.2.5 Material condition control

The main materials used in spectrophotometry are samples, chemical reagents and various solvents. Samples and reagents used in the same measurement series must be in the same original package, and solvents must be in the same batch of prepared solutions.

1.3 Experimental method

1.3.1 Sample mother liquor preparation

The contents of manganese, silicon and phosphorus were selected as the upper and lower limits of the sample content range (the manganese content was 0.19% and 2.02%, the silicon content was 0.11% and 0.58%, and the phosphorus content was 0.012% and 0.094%, respectively). Samples of 0.2000g (pig iron 0.1000g) were weighed and placed in a 150 mL conical flask. The solution system was added to 30 mL. After the sample was dissolved, ammonium persulfate solution was added to 30 mL. The sample was heated until red appeared and kept for 1 minute, so that P in the sample was completely converted to P (V). Drop "hydrogen peroxide solution" until red disappears, boil for 5 to 10 seconds，then uses flowing water cooling to place at room temperature. In 100 mL measuring cylinder (if graphite carbon can be filtered with degreased cotton), add water to 100 mL and return to the original conical bottle. This solution is "sample mother liquor" for the joint determination of manganese, silicon and phosphorus in the sample. The whole process is completed by the same person using the same equipment and measuring tool in the same way.

1.3.2 Determination of manganese content

10 mL of the “sample mother liquor” was removed by 10 mL measuring pipet to in 100 mL conical bottle (several copies may be removed according to need). Using 5ml measuring pipet add "silver nitrate solution, ammonium persulfate solution" 5 ml each. Shake and heat for 30s in a water bath at 80-100°C. Remove and cool to room temperature with flowing water. The absorbance of MnO_4^- was determined at 540nm within 30min using 1cm color cell and water as reference. On the coordinate paper, the C and A coordinate points of the two standard samples are determined, and the manganese content corresponding to the absorbance of the MnO_4^- is found on connecting lines of the coordinate points.

1.3.3 Determination of silicon content

5 mL of the "sample mother liquor" was removed by 5 mL measuring pipet and place it in 100 mL conical bottle (several copies may be removed according to need). Using 10ml measuring pipet add 10 mL the “ammonium molybdate solution ”. In a water bath at 50-80°C, shake and heat for 30s, remove and immediately add the "silicon developer" 10 mL, shake well, and flow water is cooled to room temperature. The absorbance of the "silicon molybdenum blue" was determined at 780nm within 30 minutes with 1cm color cell and water as reference. On the coordinate paper, the C and A coordinate points of the two standard samples are determined, and the silicon content corresponding to the absorbance of

the "silicon molybdenum blue" is found on connecting lines of the coordinate points.

1.3.4 Determination of phosphorus content

10 mL of the “sample mother liquor” was removed by 10 mL measuring pipet to in 100 mL special conical bottle for phosphorus measurement (several copies may be removed according to need). Add the "phosphorus chromogenic solution and ascorbic acid solution" 10 mL respectively, shake and heat for 30s in a water bath at 50-80°C , take out and cool to room temperature with flowing water. The absorbance of the "phosphomolybdenum blue" was determined at 690nm in 30min with 2cm color cell and water as reference. On the coordinate paper, the C and A coordinate points of the two standard samples are determined, and the phosphorus content corresponding to the absorbance of the " phosphomolybdenum blue" is found on connecting lines of the coordinate points.

2. Results and discuss

2.1 Selection of standard samples

The content range of each photometric method is the sample content of upper and lower limits of the calibration curve of the method, that is, the domain range of the incident light of the method. Using the original method, the standard samples whose content is close to the upper and lower limits of the original method should be selected, and their coordinate point connection lines are close to the "calibration curve" of the original method.

2.2 Elimination of interference ions

Experiments show that the absorption of Cr(VI) is less than 480nm and does not interfere with the determination of MnO_4^- at 540nm. Artaric acid in the“ phosphorus chromogenic solution” can mask the interference of Cr (III) and Ni (II) on the determination of phosphorus. Oxalic acid in the "silicon chromogenic solution" can mask the interference of Fe (II), Cr (III) and Ni (II) on the determination of silicon.

2.3 Discovery of the“light absorption law of chemical matter”

Strictly following the "precision rule", the determination of spectrophotometry must be "in the domain of incident light, the absorbance difference ΔA of chemicals proportional to its content difference ΔC: ΔA = KΔC. ", which we call the“light absorption law of chemical matter”. The existence of this law determines that the coordinate points of the content and absorbance of all samples must fall on the same ΔA = KΔC line. It shows that for spectrophotometry, it is more reliable to strictly follow the "precision rule" than to adopt the "multi-standard calibration curve". Because "multi-standard calibration curve" can improve the reliability of the "calibration curve" falling on the line ofΔA = KΔC , but it can not guarantee that the results of the determination of samples will also fall on the same line of ΔA = KΔC , while strictly following the "precision rule", it can ensure that the coordinate points of all samples will inevitably fall on the same line of ΔA = KΔC .

2.4 Uncertainty evaluation of photometric results

According to the requirement of uncertainty for laboratory measurement results [6], according to JJF 1059.1-2012 "Evaluation and Representation of Uncertainty in Measurement" [7], we have carried out the pre-evaluation of uncertainty in the photometric measurement of each element.

Following the "precision rule", the measured values of sample of the same valueμ are "like a mold". The central limit theorem shows that the "large sample (n→∞) of the same valueμ obeys the normal distribution [8-12], and the larger the capacity of the small sample, the closer it approximates the normal distribution [13]. JJF 1059.1-2012 points out: class A standard uncertainty of the mean value $\overline{X}'$ of the "small sample" with capacity n is indicated :

$$.\ u(\overline{X}')=S/\sqrt{n} \qquad (1)$$

Statistics show that $S/\sqrt{n}$ is the experimental standard deviation of the mean of the "small sample". It shows that the $\overline{X}'$ probability of falling into the two intervals of$\mu\pm2\ S/\sqrt{n}$ and$\mu\pm3\ S/\sqrt{n}$ is 0.9545% and 0.9973 [11,13], respectively. The half widths of these two intervals are the extended uncertainties U_p of mean values $\overline{X}'$ respectively:

$$U_{95}=2S/\sqrt{n}, \qquad k_p=2 \qquad (2)$$

$$U_{99}=3S/\sqrt{n}, \qquad k_p=3 \qquad (3)$$

S is the experimental standard deviation of each measured value of the "small sample". The "small sample" approximates the normal distribution, so S can be evaluated according to the “range method” $S = R/C$. According to the JJF1059.1-2012 the capacity of the "small sample" should be 10 , then $C \approx 3$, $S = R/3$ [7,13]. By substituting $S = R/3$ into formulas (2) and (3), we can obtain expanded uncertainty of mean value $\overline{X}'$ of the "small sample":

$$U_{95} = 0.67R/\sqrt{n}, \quad k_p=2 \qquad (4)$$

$$U_{99} = R/\sqrt{n}, \quad k_p=3 \qquad (5)$$

Formulas (4) and (5) show that the uncertainty of mean value $\overline{X}'$ is directly proportional to the range R of the "small sample" and inversely proportional to the square root of the capacity n of the "small sample", which accords with objective reality and has universal applicability [14-16].

Generally, the uncertainty of test results is calculated by formula (4). The results, mean, range, relative error RSD and uncertainty of 10 test samples of manganese, silicon and phosphorus are listed in Table1.

Table 1 Examines the results, precision and uncertainty of the sample /%

element	Nominal value	Measured value	Average value	Range R	RSD	U_{95}
Mn	0.69	0.70，0.67，0.71，0.69，0.68， 0.69，0.71，0.67，0.70，0.71，	0.69	0.04	2.26	0.008
Si	0.26	0.26，0.26，0.26，0.26，0.25， 0.27，0.27，0.28，0.28，0.27，	0.27	0.03	3.63	0.006
P	0.024	0.021，0.025，0.025，0.024，0.024， 0.025，0.024，0.023，0.025，0.027，	0.024	0.006	6.45	0.001

Table 1 shows that the relative standard deviations of manganese, silicon and phosphorus are 2.26%, 3.63% and 6.45% respectively. The uncertainty of the results was 0.008%, 0.006%

and 0.001% respectively. The results of manganese, silicon and phosphorus determination are as follows:

Mn：（0.69±0.008）%，$k_p=2$；

Si：（0.27±0.006）%，$k_p=2$；

P：（0.024±0.001）%，$k_p=2$。

2.5 Sample detection conditions satisfying permissible error △

The daily detection of samples requires that the uncertainty of the results of measurement should not be greater than the permissible error△, so the permissible error△ is the "agreed uncertainty" of the results of sample detection. Because the uncertainty is inversely proportional to the square root of the sample capacity , and the uncertainty U_{95} of the known capacity of 10 is', the sample capacity n of the “agreed uncertainty”△ should be:

$$n = 10\,(U_{95}/\triangle)^2 \qquad (6)$$

The allowable error △ of manganese is 0.04%, and the capacity of manganese is 10 U_{95} = 0.008%. According to formula(6), the sample capacity corresponding to the allowable error △(±0.04%) is n=0.4, that is to say, the allowable error can be satisfied by one measurement.

The allowable error of silicon is 0.03%, and the capacity of silicon is 10 U_{95} = 0.006%. According to formula(6), the sample capacity corresponding to the allowable error △(±0.03%) is n=0.4, that is to say, the allowable error can be satisfied by one measurement.

The allowable error of phosphorus is 0.005%，and the capacity of phosphorus is 10 U_{95} = 0.001%. According to formula(6), the sample capacity corresponding to the allowable error △(±0.001%) is n=0.4, that is to say, the allowable error can be satisfied by one measurement.

In fact, the difference between each of the 10 measured values of manganese, silicon and phosphorus and their respective nominal values is not greater than their respective allowable error△ , which indicates that the formulas (4) and (6) are correct.

3. Conclusion

Manganese, silicon and phosphorus in iron and steel are determined by two standard samples, one weighing and one joint measurement, and the results meet the allowable error requirements of their respective determination, which shows that:

（1）The colorimetric method of manganese, silicon and phosphorus is reliable;

（2）Following the "precision rule" is the necessary condition for the results of spectrophotometric determination to conform to the“light absorption law of chemical matter”. Details of the application of "Precision rule" in spectrophotometric determination are described in this paper, which provides basic technology for the popularization and application of spectrophotometry;

（3）Under the condition of following the "precision rule", the "two-standard spectrophotometry" conforms to the " light absorption law of chemical matter ", and the results are reliable. The "two-standard spectrophotometry" not only simplifies the operation of spectrophotometry and improves its efficiency, but also improves the "environmentally friendly" effect of spectrophotometry, which is of great popularization value.

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