



RECOGNITION OF SPECTROPHOTOMETRY

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ABSTRACT

Taking the spectrophotometric determination of manganese in carbon steel, high manganese steel and ferromanganese as an example, a new understandings of spectrophotometry are introduced under the condition of 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": (1) The absorbance of chemical matter is a domain function. "In the domain of incident light, the absorbance change ΔA is proportional to the content change ΔC of the absorbs light matter: $\Delta A = K\Delta C$." We call it the "law of light absorption by chemical matter"; (2) In the domain of incident light, the content C and its absorbance A of all samples must fall on the same line of $\Delta A = K\Delta C$. Therefore, the connecting line of coordinate points of the two standard samples in the upper and lower limits of the domain is the "determination line" of the sample content, and it is not necessary to draw the "calibration curves" with multiple standard samples; (3) Multi-standard the "calibration curve" is only necessary for Lambert-Beer's law; (4) The beam in the absorption band is additive, so the sensitivity of non-monochromatic incident light is higher; (5) The error of spectrophotometric results depends on the degree to which the "precision rule" is followed in its implementation process. It is a function of the sample range R . The maximum error $E_R = 0.65R$, and the measured values exceeding $(\bar{X}' \pm 0.65R)$ are the statistical outliers that should be excluded. (6) The content range given by each method is actually the domain range of the incident light of the method. Samples with different contents can be determined by the original method as long as they are made into samples with absorbance in the domain of incident light; (7) The uncertainty of photometric determination results: $U_{95} = 0.67R/\sqrt{n}$, $k_p=2$, $U_{99} = R/\sqrt{n}$, $k_p=3$ (n is sample capacity, \bar{X}'_{is} sample average), which are simple, clear and realistic; (8) Sample range R is the best index of the quality of the determination. The new understanding has changed the traditional concept of spectrophotometry, simplifies the operation and uncertainty evaluation of spectrophotometry, determines the maximum error of spectrophotometry, expands the content determination range of spectrophotometry to any content, and provides a new idea for the development of spectrophotometer.

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INTRODUCTION

So far, people still believe that, (1) The theoretical basis of spectrophotometry is Lambert-Beer's law. (2) The incident light of "non-monochromaticity" causes the discrepancy between the actual photometric method and Lambert-Beer's law. (3) According to the differential method of Lambert-Beer's law, the relative error $\Delta C/C = 0.4343\Delta T/TLgT$ of the spectrophotometric results is determined, which is 1% in the optimum determination range [1-5]. (4) In order to ensure the reliability of the results, multiplicity standard samples (now use 10 kinds) must be used to draw the "calibration curve" in the actual photometric method [6-10].

(5) The peak value of the absorption band of the colorimetric matter should be selected for the incident light of each method. (6) The content determination range of spectrophotometry should be within the content range given by the method. (7) The uncertainty of determination results should be evaluated by "synthetic method". These traditional concepts make the standard sample series of spectrophotometry hard to equip, complicated operation procedures, high cost and poor efficiency, limited application scope and serious environmental pollution. However, the author has a new understandings under the condition of strictly follows the "precision rule", i.e. "to maintain infection consistency of each factor for each sample in the same measurement series". The determination of manganese in carbon steel, high manganese steel and ferromanganese by permanganic acid

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spectrophotometry is taken as an example to introduce them in detail.

Experiments

Main instruments and Reagents

Spectrophotometer: 721 visible Spectrophotometer, Shanghai Precision Instrument Co., Ltd; HCA Analyzer, Wuxi High Speed Analytical Instrument Factory; Nitric acid solution (1+4); Mixed acid solution : sulfuric acid+ phosphoric acid: + water = 1+1+2; Ammonium persulfate solution : 5% ammonium persulfate solution(available); Silver nitrate solution: 1%. 10 g silver nitrate is dissolved in 1000 mL water with 20 mL concentrated nitric acid is added; Water for experiment: distilled water must be used; The reagents used in the experiment were all analytical pure.

Experimental Conditions

The research shows that “to maintain infection consistency of each factor for each sample in the same measurement series ” is the basic principle to reduce the sample range R and improve the precision of sample measurement. The author calls it the " precision rule". It is also the first condition to ensure a new understanding of spectrophotometry. For a long time, people have not been able to understand the true law of photometry because the rule is not strictly followed in the process of its implementation. There are five main factors affecting the spectrophotometric determination: human, machine, material, method and environment. The details of controlling their consistency are as follows.

Control of Human Factors

The measurement of the same measurement series can be coordinated by many people. However, the same procedure (such as weighing or dissolving samples) for the same series of measurements must be completed by the same qualified personnel in the same way.

Control of Mechanical Factors

The main machines affecting photometric measurement are balance, containers and photometers. In the use of the balance, we should achieve "the same measurement series, weighing with the same weighing state of the balance"; In the use of containers, we should achieve “the same procedure and reagent of the same measuring series are completed in the same container”; In the use of photometers,“ the same measuring series, using the same colorimetric cell and measuring in the same state of the photometer should be achieved”.

Control of Material Factor

The main materials of photometric method are samples, chemical reagents and solvents. Samples and reagents of the same measuring series must be in the same original package, and solvents must be solutions prepared in the same batch.

Control of Method Condition

Ensure that the operation of each sample (including standard sample) in the same determination series is performed in the same way as specified in the method.

Control of Environmental Factors

The main environmental factors affecting spectrophotometric determination are temperature and time. High temperature can

improve the color rendering speed, but also reduce the stability of the chromogenic matter. The color of this experiment is to shake heating for a certain time in a water bath with a certain temperature range. Then the flowing water is cooled to room temperature, and fixed volume, and the absorbance measurement is completed within a certain time.

Experimental Method

Determination of Manganese in Carbon Steel

Sample 0.2000g was weighed and placed in a 200 mL conical bottle, 30 mL nitric acid solution was added, and dissolved by heating to remove nitrogen oxides. After the sample is dissolved, the flowing water is cooled to room temperature. In a 100mL volumetric bottle, add water to 100 ml as the sample "mother liquor". 10 mL of the“ mother liquor” was absorbed by 10mL calibrated pipette, and placed in 200 mL conical bottle. Using 5ml measuring pipet, silver nitrate solution and ammonium persulfate solution were added 5 ml respectively. shake heating for 40 seconds in a water bath at 80-100 °C. Take out and the flowing water is cooled to room temperature. Within 30 minutes, the absorbance of MnO_4^{-1} was determined at 520nm (or 540nm) using 1cm colorimetric cell and water as reference.

Determination of Manganese in high Manganese steel

Sample 0.2000g was weighed and placed in a 200 mL conical bottle. The “mother liquor” was prepared by 2.3.1 method. 10 mL of the“mother liquor” was absorbed by 10mL calibrated pipette, place in 100mL volumetric bottle, add 30 mL nitric acid solution, and add water to constant volume, as the sample “liquid to be measured”. 10 mL of the “liquid to be measured” was absorbed by 10mL calibrated pipette, and placed in 200 mL conical bottle. Color rendering according to 2.3.1 method, and the absorbance of MnO_4^{-1} was determined.

Determination of Manganese in Ferromanganese

Sample 0.2000g was weighed and placed in a 200 mL conical bottle, and adding 20 mL of the sulfur-phosphoric acid. Dissolve by heating and destroy carbides by dropping nitric acid. After the sample is dissolved, the flowing water is cooled to room temperature. In a 100 mL volumetric bottle, add water to 100 ml as the sample "mother liquor". Use a 2mL calibrated pipette to absorb "mother liquor" 2mL and place it in 100mL volumetric bottle, and add 30 mL the nitric acid solution, and add water to 100 mL as the sample "liquid to be measured". Using a 10mL calibrated pipette to absorb the "liquid to be measured" 10 mL and place it in a 200 mL conical bottle. Color rendering according to 2.3.1 method, and the absorbance of MnO_4^{-1} was determined.

RESULTS AND DISCUSSION

The “light Absorption law of Chemical Matter”

Seven carbon steel standard samples were selected(we don't have 10 kinds.). Their manganese contents (%) were 0.19, 0.48, 0.77, 0.96, 1.40, 1.78 and 2.02, respectively. They was determined by the 1.3.1 method under the condition of strictly following the "precision rule". The results are listed in Table 1.

Table 1 Absorption of manganese standard sample at 520 nm

Manganese content C (%)	0.19	0.48	0.77	0.96	1.40	1.78	2.02
520nm absorbance A	0.114	0.235	0.350	0.428	0.608	0.760	0.860

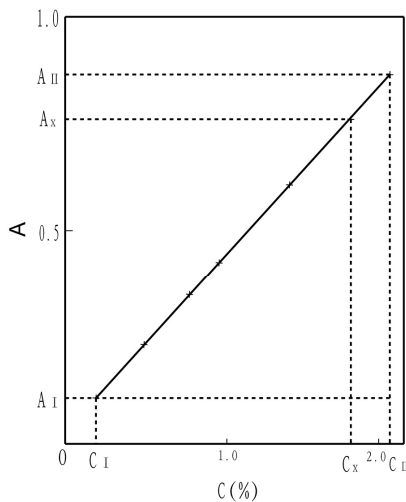


Figure 1. The "calibration curve" of Mn

Draw the "calibration curve" according to the data in Table 1 (Fig.1). As can be seen from figure 1, the interval of "calibration curve" is actually the interval of the domain of incident light (0.11-0.86). The coordinate points (C, A) of all samples are strictly on the same line, and its equation is "two-point formula":

$$(A_x - A_I) / (A_{II} - A_I) = (C_x - C_I) / (C_{II} - C_I) \quad (1)$$

According to Fig.1, the line equation can also be in the following form:

$$A_{II} - A_I = k (C_{II} - C_I) \quad (2)$$

Replacing $A_{II} - A_I$ and $C_{II} - C_I$ with ΔA and ΔC respectively, formula (2) can be simplified as follows:

$$\Delta A = k \Delta C \quad (3)$$

Formula (3) shows that if the spectrophotometric determination process strictly follow the "precision rule", "in the domain of incident light, the absorbance change ΔA of chemical matter proportional to its content change ΔC : $\Delta A = k \Delta C$ ", which we call the "light absorption law of chemical matter".

Establishment of the "two- Standard Spectrophotometry"

The "light absorption law of chemical matter" determines that in the domain of incident light, the coordinate points (C, A) of all samples must fall on the same $\Delta A = k \Delta C$ line. Therefore, the line between the upper and lower coordinates of the two standard samples is the "determination line" of the sample content, which we call the "two- standard spectrophotometry". Sample content C_x can be found on the "determination line" according to the absorbance A_x . It can also be directly displayed by an instrument according to the following formula, which is determined by the "light absorption law of chemical matter":

$$C_x = [(A_x - A_I) (C_{II} - C_I) / (A_{II} - A_I)] + C_I \quad (4)$$

For example, the absorbance $A_x = 0.428$ corresponding manganese content C_x .

The manganese content corresponding to 0.428 is 0.96% on the "determination line". According to formula (4), $A_x = 0.428, A_I = 0.114, C_{II} = 2.02\%, C_I = 0.19\%, A_{II} = 0.860$, input formula (4) directly shows the manganese content: $C_x =$

0.96%. The results show that the "determination line", the formula (4) and the "light absorption law of chemical matter", which all conform to the reality of spectrophotometry.

The "calibration curve" is only necessary for Lambert-Beer's Law

We have already seen the "two-standard spectrophotometry", but because Lambert-Beer's law does not conform to the reality of spectrophotometry, and it must use "calibration curve" to obtain the sample content. For example, for the sample with 520 nm absorbance $A_x = 0.428$. If according to standard $C_I = 0.19\%, A_I = 0.114$, and $A = kC$, the corresponding sample content $C_x = 0.71\%$; If according to standard $C_{II} = 2.02\%, A_{II} = 0.860$, then $C_x = 1.01\%$. Both results were discrepancy with the actual content of 0.96%. To get 0.96% of the content, the multi-standard "calibration curve" must be used. Therefore, multi-standard "calibration curve" is only necessary for Lambert-Beer's Law. Even so, it does not guarantee that the absorbance A_x of the sample must fall on the corresponding position of "calibration curve", and guarantee the reliability of the sample content.

The Beam in the Absorption band is Additivity

Up to now, it is still believed that the "non-monochromaticity" of incident light leads to the discrepancy between the photometric method and Lambert-Beer's law. In fact, the absorption band is the embodiment of quantized absorption of different quantum levels of ground state of chemical matter, each of its beams can be used to determine the content of related matter, only their determine sensitivity is different [11]. But their absorbance is additivity, so the "non-monochromatic" incident light has higher sensitivity. Table 2 shows the absorbance of 530nm measured by 721 spectrophotometer and HCA analyzer in the same series of high manganese steels.

Table 2 Absorption of the same series of high manganese steel at 530 nm of different photometers

Manganese content in standard samples	11.14%	14.42%	17.42%
530nm absorption of 721 spectrophotometer	0.524	0.668	0.803
530nm absorbance of HCA analyzer	0.962	1.233	1.484

The data in Table 2 show that the results of two groups of manganese determination differing from 520nm beam still obey $\Delta A = k \Delta C$. But HCA is a filter photometer. Its 530nm beam is wider than 721's 530nm beam, so its 530nm absorbance is almost double that of 721's 530nm. The results show that the wider the beam in the absorption band, the higher the sensitivity. Therefore, the photometer should not pursue the "monochromaticity" of the incident light, but should adopt the "non-monochromaticity" of the incident light in order to improve the sensitivity.

The Error of Spectrophotometric Results

The result of any physical quantity is a random number. With the differential method of Lambert-Beer law, the mathematical model of the relative error of the result is deduced: $\Delta C/C = 0.4343 \Delta T / T L G T$, it's unscientific.

Using statistical research method and statistical induction for many years, the author determines that the error is a function of the sample range R, the maximum error $E_R = 0.65R$, and the

measured value exceeding ($\bar{X}' \pm 0.65R$) is the statistical outlier that should be eliminated[12,13]. Two samples were selected, one content 0.29% and transmittance 0.695, the other content 1.78% and transmittance 0.174. The absorbance of 520nm was measured on 721 photometer. The results are listed in Table 3.

Table 3 the determination results of samples with different transmittance (%)

Nominal value	Measured value	Average value	Range R	Maximum error E_R	RSD
0.29	0.30 0.28 0.29 0.28 0.29 0.29 0.30 0.29 0.28	0.29	0.020	0.013	2.7
1.78	1.79 1.78 1.77 1.78 1.77 1.78 1.77 1.79 1.78	1.79	0.020	0.013	0.74

According to the mathematical model of relative error $\Delta C/C = 0.4343 \Delta T / TLgT$, the smaller the transmittance, the greater the relative error. In fact, the transmittance of 1.78% is much less than that of 0.29%, but the relative error RSD of 1.78% is only 1/4 of that of 0.29%. This fully proves that the mathematical model of the relative error is not practical.

As can be seen from the data in Table 3: The maximum error between each of the nine measured values and the cognizance value is not greater than each maximum error 0.65R. It is shown that the measurement error of photometric method depends on the degree to the "precision rule" is followed in the determination process, and $E_R = 0.65R$ are all in line with the reality.

Upper and lower limits of Spectrophotometric Determination

Practice has proved that the upper and lower limits of each photometric method are actually the upper and lower limits of their corresponding domain of the incident light. Samples with different contents can be determined by the original method, as long as it is made into a colorimetric sample whose absorbance is in the domain of incident light. For example, permanganate spectrophotometry of manganese, which the corresponding absorbance range is 0.11~0.86. To determine the content of manganese in high manganese steel and ferromanganese, only the colorimetric samples with 520nm absorbance in the range of 0.11~0.86 can be determined by the original method.

The manganese content of the upper and lower limit standard samples of high manganese steel is 17.42% and 11.14%, respectively. Determination according to the determination of manganese in high manganese steel in this paper 1.3.2. The absorbance of the upper and lower limit of standard samples at 520nm is 0.803 and 0.524, respectively, which are within the original absorbance range. The line between the coordinate points (17.42, 0.803) and (11.14, 0.524) of the upper and lower limits of the two standard samples is the "determination line" of 11%-17% samples. The determination results are listed in table 4.

The manganese content of ferromanganese standard samples was 65.67% and 82.09%, respectively. Determination according to the determination of manganese in ferromanganese in this paper 1.3.3. The absorbance of the two standard samples at 520nm is 0.570 and 0.712, respectively, which are within the original absorbance range. The line between the coordinate points (65.67, 0.570) and (82.09, 0.712) of the upper and lower limits of the two standard samples is the "determination line" for 66%-82% ferromanganese samples. The results are listed in table 4.

Table 4 Determination results of high manganese steel and ferromanganese (%)

Nominal value	Measured value	Average value	Range R	Maximum error E_R	RSD
14.25	14.20 14.15 14.20 14.20 14.30 14.30 14.35 14.30 14.35	14.26	0.20	0.13	0.47
73.88	73.60 73.50 73.50 74.10 74.10 74.20 73.80 73.60 73.80	73.80	0.70	0.46	0.62

Table 4 shows that the maximum error between each of their nine measured values and their respective certified values is all smaller than their respective maximum error E_R , which show that the upper and lower limits of each photometric method are actually the upper and lower limits of the domain of the incident light and the maximum error is $E_R = 0.65R$. which are all realistic

Uncertainty Evaluation of Spectrophotometric Results

Following the "precision rule", the measured values of a sample of the same quantity μ are "as if they came from the same mould". The central limit theorem shows that under this condition, the "large sample" ($n \rightarrow \infty$) of the μ is normal distribution, and the "small sample" is that the larger the capacity, the more approximate the normal distribution [14,15]. According to the JJF1059.1-2012 (hereinafter referred to as "specification") the class A standard uncertainty of mean value \bar{X}' of the "small sample" with capacity n [16]:

$$u(\bar{X}') = S / \sqrt{n} \tag{5}$$

Statistics show that S / \sqrt{n} is the experimental standard deviation of mean value \bar{X}' of the "small sample", which shows that the probability of fall on two intervals ($\mu \pm 2 S / \sqrt{n}$)

$$\text{and } (\mu \pm 3 S / \sqrt{n})$$

is 0.9545% and 0.9973, respectively[17]. According to the "specification" the half-width of the two intervals is the two extended uncertainties of mean value \bar{X}' :

$$U_{95} = 2 S / \sqrt{n}, \quad k_p = 2 \tag{6}$$

$$U_{99} = 3 S / \sqrt{n}, \quad k_p = 3 \tag{7}$$

S is the experimental standard deviation of each measured value of the "small sample". According to the "specification" the capacity of the "small sample" should be 10. The "small sample" approximates the normal distribution [15], so S can be evaluated according to the "range method" $S = R / C.n = 10$, then $C \approx 3, S = R/3$. By substituting $S = R/3$ into formulas(6) and (7), we can get extended uncertainties of mean value \bar{X}' of the "small sample":

$$U_{95} = 0.67 R / \sqrt{n}, \quad k_p = 2 \tag{8}$$

$$U_{99} = R / \sqrt{n}, \quad k_p = 3 \tag{9}$$

Formulas (8) and (9) show that the uncertainty of mean value \bar{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 [12,18].

The Sample Range R is the best Index of the Quality of the Measurements

For a long time, people used standard deviation S and relative error RSD to express the quality of measurements. However, the data in tables (3) and (4) show that The sample range R is the best index of the quality of the determination: sample precision, maximum error, statistical outlier, uncertainty, etc. However, relative errors RSD do not give any information about the quality of the measurements. Moreover, the sample range R is more stable and intuitive than the standard deviation S and relative error RSD. So the sample range R actually is the best index of the quality of the measurements.

CONCLUSION

Taking the determination of manganese in carbon steel, high manganese steel and ferromanganese by permanganic acid spectrophotometry as an example, which proves that

1. Strict follow the "precision rule" is a number one condition for new understanding of photometry. Details of the implementation of "precision rule" in spectrophotometric determination in this paper, which are basic technology for the application and popularization of spectrophotometry.
2. The new understanding of spectrophotometry has changed the traditional concept, the operation of photometric method and the evaluation of uncertainty are simplified, the content determination range of spectrophotometry was extended to any content, but also improves the "environmental friendly" effect of spectrophotometry;
3. The sample range R actually is the best index of the quality of the measurements;
4. The beam in the absorption band is additive, the "non-monochromatic" incident light has higher sensitivity. Photometer should not pursue "monochromaticity" of incident light.

This paper can provide reference for the application and research of the industry.

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