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**DETERMINATION OF TITANIUM DIOXIDE IN LIMESTONE BY  
DIANTIPYRINE METHANE PHOTOMETRIC METHOD**

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**ABSTRACT**

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<p>Iron ore contains useless gangue (useless rock or tailings containing useful metals or minerals) in iron-making, the main component of gangue is silica dioxide. In the process of ironmaking, iron is changed into liquid state at high temperature. Because the melting point of silica is very high, this particle impurity is mixed in molten iron. In order to remove this impurity, limestone is chosen as the agent of fusion. The reason for choosing limestone as flux is that limestone will decompose into calcium oxide and carbon dioxide at high temperature. Calcium oxide reacts with silica at high temperature to form calcium silicate with lower melting point than that of molten iron. Because the density of liquid calcium silicate is smaller than that of molten iron, and molten iron and liquid calcium silicate are insoluble. Liquid calcium silicate floats on the molten iron.</p> <p>Because micro alloyed steel and pure steel (steel with few non-metallic inclusions and gases, or steel with few harmful elements such as oxygen, sulfur, phosphorus, hydrogen and nitrogen) have higher requirements for non-metallic inclusion control (in the process of steelmaking, a small amount of slag, refractories and reaction products are formed by entering the molten steel) of steel. Titanium is one of the important alloy elements. In addition to its strong deoxidizing ability, it can also denature non-metallic inclusions in steel, thus improving the mechanical properties of steel. Therefore, adding proper amount of titanium into steel has an important influence on the quality of steel, what kind of inclusions are formed and the shape of inclusions. Therefore, the accurate determination of titanium dioxide in limestone is of great significance to the control of inclusions in steel.</p> <p>The spectrophotometer is a common device. This method does not have high requirements on the laboratory. The diantipyryl methane (DAPM) photometric method is a color reagent with less interference and has strong adaptability. In this experiment, the DAPM photometric method will be used to measure titanium dioxide in limestone.</p>		

<p><b>Key words</b> Ascorbic acid, Diantipyryl methane, Limestone, Silicon dioxide, Spectrophotometer</p>
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## CONCEPT DEFINITIONS

### List of abbreviations

$\text{Al}_2\text{O}_3$	Aluminum oxide
$\text{CaCO}_3$	Calcium carbonate
$\text{CaO}$	Calcium oxide
DAPM	Diantipyril methane
EDTA	Ethylene Diamine Tetraacetic Acid
$\text{Fe}_2\text{O}_3$	Iron oxide
$\text{Fe}^{2+}$	Ferrous iron
$\text{HClO}_4$	Perchloric acid
$\text{HNO}_3$	Nitric acid
$\text{H}_2\text{O}_2$	Hydrogen peroxide
$\text{H}_2\text{SO}_4$	Sulfuric acid
$\text{H}_3\text{PO}_4$	Phosphoric acid
HF	Hydrofluoric acid
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
MgO	Magnesium oxide
$\text{SiO}_2$	Silicon dioxide
$\text{TiO}_2$	Titanium dioxide
$\text{TiO}^{2+}$	Titanium oxide ion
$\text{Ti}^{3+}$	Titanium ion
UV-vis	Ultraviolet visible
XRF	X-ray fluorescence

**ABSTRACT**  
**CONCEPT DEFINITIONS**  
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## 1 INTRODUCTION

Calcium carbonate ( $\text{CaCO}_3$ ) is the main component of limestone, which is the main raw material for glass production. In addition to the main component  $\text{CaCO}_3$  in limestone, limestone also contains a small amount of silicon dioxide ( $\text{SiO}_2$ ), aluminum oxide ( $\text{Al}_2\text{O}_3$ ), iron oxide ( $\text{Fe}_2\text{O}_3$ ), magnesium oxide ( $\text{MgO}$ ) and titanium dioxide ( $\text{TiO}_2$ ). Lime and limestone are widely used as building materials and important raw materials for many industries.  $\text{CaCO}_3$  can be directly processed into stone stock and burnt into quicklime. Lime has quicklime and hydrated lime. The main component of quicklime is calcium oxide ( $\text{CaO}$ ), which is generally lumpy, pure white, light gray or light yellow when containing impurities. In the chemical industry, limestone is mainly used to fabricate alkali, calcium carbide,  $\text{CaCO}_3$ , potassium carbonate, nitrogen fertilizer, phosphate fertilizer and other raw materials. Limestone is used as agent of fusion in ironmaking to remove gangue. (Qingling 2009, 179-180). Quicklime is used as slagging material in steelmaking to remove harmful impurities such as sulfur and phosphorus. Titanium is one of the important alloy elements. In addition to its strong deoxidizing ability, it can also denature non-metallic inclusions in steel, thus improving the mechanical properties of steel. Therefore, adding proper amount of titanium into steel has an important influence on the quality of steel and the formation of nonmetallic inclusions. The determination of  $\text{TiO}_2$  content in limestone is of great significance to the improvement of steel quality and the control of non-metallic inclusions in steelmaking and ironmaking. (Junhua 2016, 37).

There are many methods of measuring  $\text{TiO}_2$ , and there are several determination methods: titration analysis (ammonium ferric sulfate volumetric method, hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) coordination-bismuth salt solution titration method), spectrophotometry  $\text{H}_2\text{O}_2$  photometric method, ferro-titanium reagent photometry), large-scale instrumental analysis (inductively coupled plasma-atomic emission spectrometry (ICP-AES) and X-ray fluorescence (XRF) spectrometry). For the determination of  $\text{TiO}_2$  content in the sample by titration analysis. This method has poor sensitivity and selectivity. In chemical analysis, the sensitivity is expressed by the molar absorption coefficient  $\epsilon$ . It refers to the absorption capacity of matter to light of a certain wavelength. The value of  $\epsilon$  reflects the degree of light absorption of the absorption medium. For the medium with selective absorption in the visible light area, it indicates the sensitivity of a certain color reaction. For the same measured element, the greater the value of  $\epsilon$ , the more sensitive the color reaction is. For the same color reaction, the value of  $\epsilon$  is related to the measured concentration. The higher the molar absorption coefficient, the higher the sensitivity. Selectivity refers to the ability to avoid interference of other coexisting components in the sample when a certain analytical method is used to determine a certain component. Other elements, such as vanadium, tin, molybdenum, tungsten,

copper and arsenic can interfere experimental determination. Together with titanium oxide ion ( $\text{TiO}^{2+}$ ), these elements are completely or partially reduced to a low valence state and oxidized, leading to high experimental results. Although the titration analysis method does not have high requirements for instruments and equipment, the accuracy of the measurement results is poor and the scope of use is narrow. In  $\text{H}_2\text{O}_2$  photometry, the experimental operation is simple and fast but the stability of hydrogen is poor. For the determination of  $\text{TiO}_2$  samples by ICP-AES, the ICP-AES was used to determine the content of  $\text{TiO}_2$  in the experiment. The method is fast, accurate, highly sensitive, and has good reproducibility and stability. But the instrument is expensive, and this method is difficult to widely promote and apply. (Juan 2019, 46).

Using diantipyryl methane (DAPM) photometry method for determining  $\text{TiO}_2$  is easy to operate and it has high sensitivity, good reproducibility and stability. This thesis introduces the method of determining the content of  $\text{TiO}_2$  in limestone sample A (mass fraction of  $\text{TiO}_2$  content is 0.041 %), sample B (mass fraction of  $\text{TiO}_2$  content is 0.074 %) and sample C (mass fraction of  $\text{TiO}_2$  content is 0.130 %) by using DAPM photometry. In the end, influence of different factors for the determination of  $\text{TiO}_2$ , such as dosage of ascorbic acid, dosage of DAPM spectrophotometry chromogenic reagent, influence of acid concentration and elimination method will be discussed.

## 2 DETERMINATION OF TITANIUM DIOXIDE IN INDUSTRIAL RAW MATERIALS

For the determination of  $\text{TiO}_2$  in alloys, ores or other industrial raw materials, there are several detection methods in the world, such as titration detection method, XRF detection method, ICP-AES detection method and DAPM spectrophotometry. In the experimental for the determination of  $\text{TiO}_2$  by ammonium ferrate volumetric method, the experiment needs to be carried out in hydrochloric acid (HCl) or sulfuric acid medium ( $\text{H}_2\text{SO}_4$ ).  $\text{TiO}^{2+}$  is reduced to titanium ion ( $\text{Ti}^{3+}$ ) by metal aluminum sheet. Potassium thiocyanate is used as indicator and titrated with standard solution of ammonium ferrate sulfate. Vanadium, tin, molybdenum, tungsten, copper, arsenic and other elements will interfere with the experimental results. These elements will be fully or partially reduced to a low valence state together with  $\text{TiO}^{2+}$ , and then oxidized by high iron to produce high results. (Juan 2019, 45).

In the determination of  $\text{TiO}_2$  by  $\text{H}_2\text{O}_2$  coordination-bismuth salt solution back titration method. Firstly, adding appropriate amount of  $\text{H}_2\text{O}_2$  to the solution which containing  $\text{TiO}^{2+}$  will form a yellow complex. And then adding excessive Ethylene Diamine Tetraacetic Acid (EDTA) to make it a more stable ternary complex. The remaining EDTA was titrated with bismuth salt solution to xylenol orange as indicator. This method is often used for samples of high titanium content. Although titrimetric analysis has low requirements for instruments and equipment, its accuracy is poor and its application range is narrow. In the experiment of  $\text{TiO}_2$  sample determination by ICP-AES, the inductively coupled plasma-atomic emission spectrometer was used to determine the content of  $\text{TiO}_2$ . This method is fast, accurate, highly sensitive and has good stability, but the large instruments used are expensive. This method is difficult to widely promote and apply. The advantages of DAPM photometry are as follows: it avoids tedious experimental steps, it can be used as a very practical analysis method in scientific research detection and it can be widely used in the determination of  $\text{TiO}_2$  in steel, alloys and mineral raw materials. Compared with other detection methods, the DAPM spectrophotometry is more simple, the detection speed is faster and the repeatability of the experimental is good. (Juan 2019, 45).

### 2.1 Spectrophotometer

A spectrophotometer is a scientific instrument that breaks light with complex composition into spectral lines. The measurement range generally includes the visible light region with a wavelength range of 380-780 nm and the ultraviolet light region with a wavelength range of 200-380 nm. Different light sources have their own unique emission spectrum, so different luminous bodies can be used as the light source

of the instrument. The emission spectrum of tungsten lamp is formed in this way: After refracting the spectrum light of 380-780 nm wavelength emitted by tungsten lamp light source through a prism, a continuous color spectrum composed of red, orange, yellow, green, blue, indigo and violet can be obtained. The color spectrum can be used as the light source of the visible light spectrophotometer. (Xiaohua 2012, 6).

Ultraviolet spectrophotometer is based on the absorption spectrum of substances to study the composition, structure and interaction of substances. The ultraviolet spectrophotometer can arbitrarily choose different wavelengths of light in the ultraviolet visible region. The absorption spectrum of a substance is that the molecules and atoms in the substance absorb the light energy of certain specific wavelengths in the incident light. The molecular vibrational energy level transition and the electronic energy level transition occur accordingly. All kinds of substances have their own different molecules, atoms and different molecular space structures. Their absorption of light energy is different. Therefore, each substance has its own unique and fixed absorption spectrum curve. The absorbance at certain characteristic wavelengths on the spectrum can be used to distinguish or determine the content of the substance. Ultraviolet spectrophotometry is based on Lambert-Beer law. According to Lambert-Beer law:  $A = \epsilon bc$ , ( $A$  is the absorbance,  $\epsilon$  is the molar absorption coefficient,  $b$  is the thickness of the liquid cell and  $c$  is the concentration of the solution). This law can be used to analyze the solution quantitatively. (Mohamed & Hassan 2015, 4).

There are many types of ultraviolet visible (UV-vis) spectrophotometers, but their basic structures are similar. The UV-vis spectrophotometers are composed of five parts: light source, monochromator, absorption cell, detector and signal display system. The structure of the ultraviolet spectrophotometer is shown in FIGURE 1. The light source is a device to provide the incident light that meets the requirements. The common light source in the visible light area of the UV-vis spectrophotometer is tungsten lamp, and the common light source in the UV-vis light area is hydrogen lamp or deuterium lamp. Tungsten lamp is the most commonly used visible light source. It can emit a continuous spectrum of 325-2500 nm, and the most suitable wavelength range is 320-1000 nm. Therefore, it can also be used as near-infrared light source. Deuterium lamp is the most commonly used ultraviolet light source. It emits light with a wavelength range of 190-400 nm, and the wavelength range is generally 190-360 nm. The second part of the UV-vis spectrophotometer is monochromator, which decomposes the continuous spectrum of the light source into monochromatic light and can accurately and conveniently select the optical device of a certain wavelength needed. It is the heart of the photometer. Monochromator is mainly composed of slit, dispersion element and lens system. The dispersion element is the main part of monochromator. The



most commonly used dispersion elements are prism, grating or a combination of the two. The dispersive element is shown in the FIGURE 1. It is a combination of prism and grating. (Xiaojing 2015, 19-20).

The absorption tank is a vessel used to hold the liquid to be measured and determine the thickness of the transparent liquid layer of the solution to be measured, also known as a cuvette. Generally speaking, the absorption tank is a cuboid, which also has a circle or other shapes. The absorption tank in FIGURE 1 is a cuboid. The bottom and both sides of the absorption tank are ground glass, and the other two sides are optical light transmitting surfaces. According to the material of the light transmitting surface, the absorption tank can be divided into two types: glass absorption tank and quartz absorption tank. The glass absorption cell is used for the determination of visible light area, and the quartz absorption cell is used for the determination of ultraviolet light area. The specification of absorption tank is marked by optical path. The commonly used specifications of absorption cell are 0.5 cm, 1.0 cm, 2.0 cm, 3.0 cm, 5.0 cm. The detector is a device that converts an optical signal into an electrical signal. When measuring the absorbance, it is not to directly measure the light intensity through the absorption cell, but to convert the light intensity into a current for measurement. This photoelectric converter is called a detector. Signal display is a device to amplify and display the output signal of detector. The new spectrophotometer is displayed by digital voltmeter, and the absorbance curve is drawn directly by recorder. The new spectrophotometer is equipped with computer data processor. (Xiaojing 2015, 19-20).

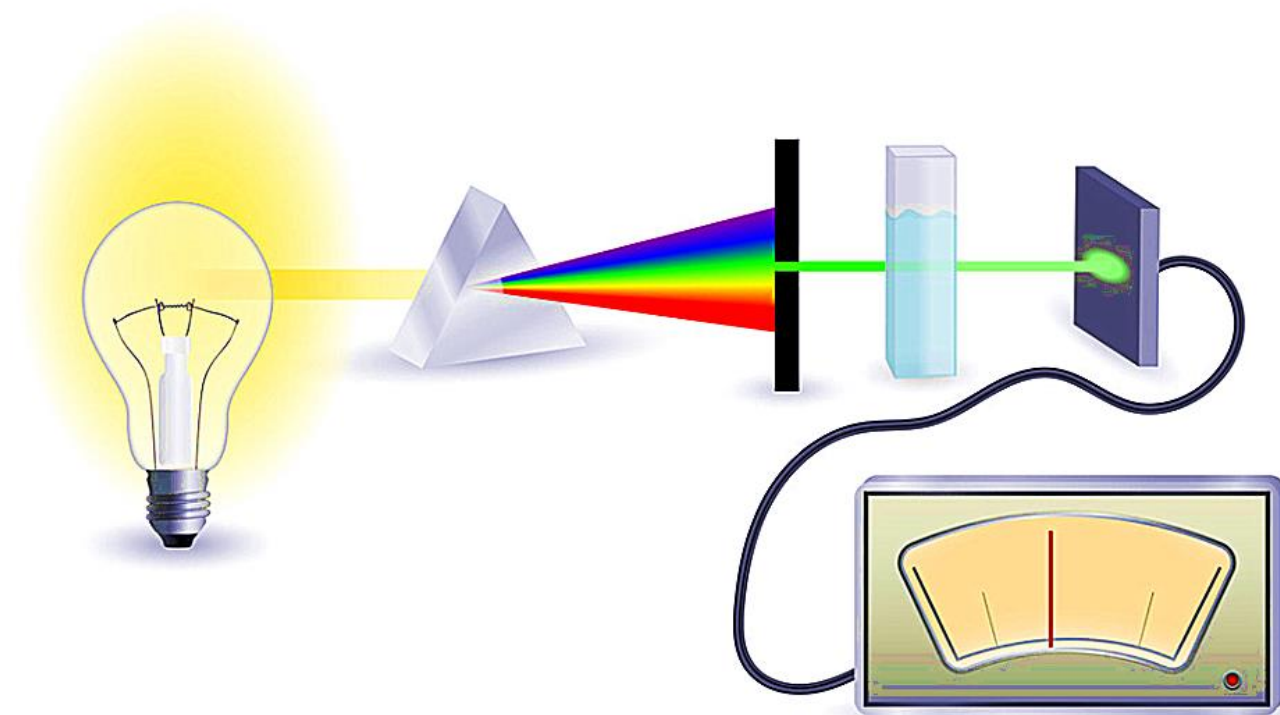


FIGURE 1. The structure of ultraviolet spectrophotometer (adapted from Xiaojing 2015, 19).

## 2.2 Diantipyryl methane spectrophotometry

DAPM is white flake crystals. It is insoluble in water, ether and alkali. But it is soluble in acid, ethanol and chloroform. DAPM is soluble in acids and forms complex organic cations with acids. The solution of DAPM is colorless and it reacts with  $\text{Ti}^{3+}$  to form yellow complexes. DAPM can be used as a sensitive color reagent for the determination of  $\text{Ti}^{3+}$ , iridium, iron, molybdenum, neodymium, uranium, iridium, platinum, rhenium. It can also be used as an extractant for various ions. The molecular formula of DAPM is  $\text{C}_{23}\text{H}_{24}\text{N}_4\text{O}_2 \cdot \text{H}_2\text{O}$ . The molecular structure of DAPM is shown in FIGURE 2.

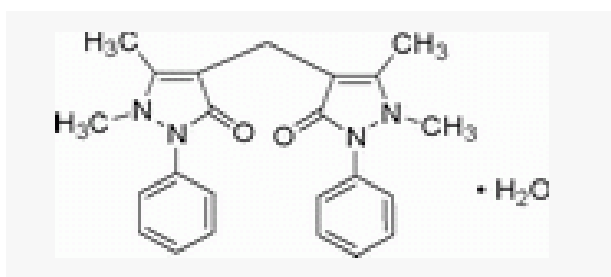


FIGURE 2. The molecular structure of DAPM (adapted from Liu, Zhou & Song 2011, 31).

The UV-vis absorption spectrum of molecules is a common spectral analysis method based on the absorption spectrum generated by the intramolecular electronic transition. When a material is irradiated by light, the material molecules will collide with the light. As a result, the energy of photons is transferred to the molecules. In this way, the stable ground state molecules will jump to the unstable high energy state. This is the absorption of the light. The qualitative analysis of UV-Vis absorption spectrum is based on the fact that the shape of absorption curve of light to the same absorption material is different, the maximum absorption wavelength is the same, but the corresponding absorption rate is different. There are three properties of UV-vis absorption spectrum: the first is that the same concentration of the test solution has different absorbance for different wavelengths of light. The second point is that the higher the concentration of the same test solution, the higher the absorbance. Finally, the smaller the concentration of the same substance, the same wavelength (maximum absorption wavelength  $\lambda_{\text{max}}$ ) corresponding to the maximum absorption peak, and the same curve shape. The absorbance tested results of yellow complex formed by titanium and DAPM by DAPM spectrophotometry are shown in FIGURE 3. The shape of the absorption curve can be seen from FIGURE 3. The abscissa in the chart is the wavelength, the unit of wavelength is nm. The ordinate is the absorbance, and the unit of absorbance is  $\text{L}/(\text{g} \cdot \text{cm})$ . The absorbance reaches the maximum value at the wavelength of 390 nm. In the vicinity of

the maximum wavelength, the closer to the maximum range of the spectrophotometer, the greater the sample absorbance and the smaller the error brought by the photometer itself. (Junhua 2020, 38).

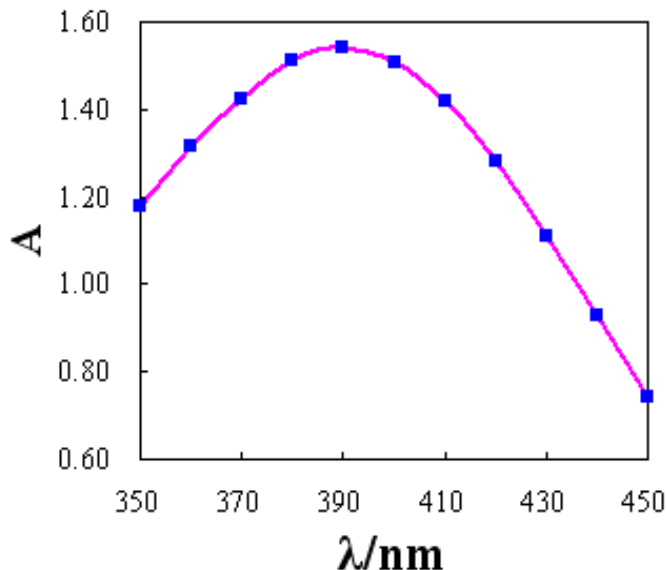


FIGURE 3. Absorbance values at different wavelengths (adapted from Junhua 2020, 38).

After consulting the literatures on the determination of TiO<sub>2</sub> by DAPM Spectrophotometry. It can be founded that the measurement method is essentially similar. The specific method is as follows: Firstly, the sample needs to be decomposed, the sample is placed in a platinum crucible, and mixed flux (limestone samples with accurate TiO<sub>2</sub> content) is added to mix with the sample. Heat the crucible at high temperature (950-1000 °C), take it out and cool it, then add acid to dissolve the sample. After that transfer the solution to a volumetric flask to constant volume and blend well. After transferring the solution, add ascorbic acid, HCl, DAPM solution, put it into the spectrophotometer to measure the absorbance. Finally record the data and calculate the result. (Junhua 2016, 39).

### 2.3 Inductively coupled plasma atomic emission spectrometry

ICP-AES has the advantages of high accuracy and precision, low detection limit, fast determination, wide linear range and simultaneous determination of multiple elements. It has been widely used in determination of dozens of elements in environmental samples and samples of rocks, minerals, metals. Plasma is ionized gas with an ionization degree exceeding 0.1 %. This gas contains not only neutral atoms and molecules, but also a large number of ions and electrons. (Haiyan 2010, 62).

ICP-AES is based on the spectrum emitted by atoms to determine the chemical composition of a substance. Different substances are composed of atoms of different elements, and the atoms all contain a densely structured nucleus. The nucleus is surrounded by moving electrons. Each electron is at a certain energy level and has a certain energy. Atoms are in a stable state under normal circumstances. This state is called the ground state. When the atoms are transformed into gaseous atoms under the action of external energy, the outer electrons of the gaseous atoms are excited to a high energy state. When transitioning from a higher energy level to a lower energy level, the atoms will release excess energy and emit characteristic lines. ICP-AES disperse the generated radiation through the instrument and record it on the photosensitive plate in the order of wavelength, which can show regular spectral lines. The perform quantitative analysis based on the obtained spectrum. ICP-AES is a new type of light source that is developing rapidly and is highly valued in the analysis of emission spectrum. (Haiyan 2010, 62).

ICP-AES consists of sample introduction system, ICP light source, dispersion system and detection system. And equipped with computer control and data processing system, cooling system, gas control system. ICP light source consists of high frequency power supply and ICP torch tube. The ICP torch tube consists of three concentric quartz tubes and a high-frequency induction ring (generally 2-4 rings of hollow copper tubes) surrounded by the upper part of the tube. There are three intake tubes. A 10-20 L/min argon gas is passed between the quartz outer tube and the intermediate tube. Its function is to form plasma as working gas and cool the quartz torch tube, which is called plasma gas or cooling gas. The intermediate tube and the central tube are filled with 0.5-1.5 L/min argon to become auxiliary gas, which is used to assist the formation of plasma. After the plasma torch is formed, it can be turned off. The carrier gas in the central tube is used to introduce the sample aerosol. (Xu, Wang & Xu 2020, 67).

The formation of ICP torch is called ignition. The ignition is divided into three steps: the first step is to introduce plasma and auxiliary gas into the outer tube and the middle tube. At present, the central tube is not connected with gas, and an argon atmosphere is established in the torch tube. The second step is to connect the high-frequency power supply to the induction coil. The general frequency is 7-50 mhz, and the power supply is 1-1.5 kw. At present, there is high-frequency current and high-frequency electromagnetic field generated by the coil. The third step is to ionize the working gas flowing in the middle by means of high frequency spark, and then the ions and electrons produced will interact with the fluctuating magnetic field produced by the induction coil. This interaction causes the ions and electrons in the coil to flow along the closed loop in the figure. Their resistance to this movement causes ohmic

heating. Because of the high temperature generated by the strong current, the gas is heated to form a torch like plasma. (Xu et al. 2020, 67).

Aerosol injection system is a commonly used method at present. The sample introduction system consists of two main parts: sample lifting part and atomization part. The sample lifting part is generally a peristaltic pump, and a self-lifting atomizer can also be used. It is required that the speed of the peristaltic pump is stable and the elasticity of the pump pipe is good, so that the sample solution can be pumped in at a constant speed and the waste liquid can be discharged smoothly. The atomizing part includes atomizer and atomizing chamber. After the sample enters the atomizer by means of pump or self-lifting, small droplets are formed under the action of carrier gas and enter the atomization chamber. The large droplets are eliminated when they touch the wall of the atomization chamber. Only small droplets can enter the plasma source. (Xu et al. 2020, 68). For the optical system, the monochromator of ICP-AES usually adopts the combination of grating or prism and grating. And for the detection system, the detection system of ICP-AES is a photoelectric converter, which uses photoelectric effect to convert the radiation energy of different wavelengths into electrical signals. (Xu et al. 2020, 68).

As a conventional chemical analysis technology, ICP-AES has a wide range of applications in biological samples, materials, geology, environmental protection, metallurgy and other fields. In the field of metallurgical analysis, such as steel, raw materials, and ferroalloys, it is required to measure dozens to hundreds of samples at a time. And each sample must simultaneously analyze dozens of elements such as: Mn, Cu, Al, Cr, Si, P, Ni, Ti, V, Nb, W, Ca, Mg. It can show the absolute advantages of ICP in terms of work efficiency. In the analysis of standard materials, especially the low-value, fixed-value analysis of rare earth elements, the accuracy of ICP data and the simplicity of operation are fully utilized. (Haiyan 2010, 62). The disadvantage of the ICP-AES method is that the equipment and operating costs are relatively high. The sample generally needs to be converted into a solution in advance, and the determination of some elements is not obvious, such as sodium (Na) and potassium (K). (Juan 2019, 46).

## 2.4 Titration analysis

There are generally two types of titration analysis to determine the content of  $\text{TiO}_2$  in the sample: Ammonium ferric sulfate volumetric method and  $\text{H}_2\text{O}_2$  coordination titration. The specific steps of ammonium ferrate sulfate volumetric method are as follows: firstly, reduction of  $\text{TiO}^{2+}$  to  $\text{Ti}^{3+}$  with metal

aluminum tablets in HCl or H<sub>2</sub>SO<sub>4</sub> medium. And then using potassium thiocyanate as an indicator. Finally, titration with standard solution to ammonium ferrate sulfate. The method has poor sensitivity and selectivity. But there are interference elements such as vanadium, tin, molybdenum, tungsten, copper and arsenic that affect the experimental results. These elements and TiO<sub>2</sub> are completely or partially reduced to a low valence state, and these elements are oxidized by ferric ions (Fe<sup>3+</sup>). Leading to errors in the experimental results. (Juan 2019, 46).

The specific steps of H<sub>2</sub>O<sub>2</sub> coordination titration are as follows: firstly, the yellow complex will be formed by adding an appropriate amount of H<sub>2</sub>O<sub>2</sub> to a solution which containing TiO<sup>2+</sup>. Then add excess EDTA to the solution. (EDTA is a good complexing agent in chemistry. It has six coordination atoms. The complex formed is called chelate. EDTA is often used in coordination titration to determine the content of metal ions. In biological application, it is used to exclude most transition metal elements. For example, it is used to exclude the interference of iron ion, nickel ion and manganese ion in the experiment.) Make it form a more stable ternary complex. The remaining EDTA was titrated with xylenol orange as indicator. For the back titration with bismuth salt solution method, when the reaction is slow or the reactant is solid, add a certain amount of titration solution. Normally the reaction cannot be completed immediately. At this time, a certain amount of excess titrating solution can be added first to accelerate the reaction. After the reaction is completed, titrating the remaining titrant with another standard solution. This method is mostly used for samples with high titanium content. Although the titration analysis method does not have high requirements for instruments and equipment, but the accuracy of the measurement results is poor and the scope of use is narrow. (Juan 2019, 46).

## 2.5 X-ray fluorescence spectrometry

People usually irradiate X-rays on substances to produce secondary X-rays called XRF. The X-rays used for irradiation are called primary X-rays, XRF is still X-ray. XRF spectrometer is mainly composed of excitation, dispersion, detection, recording and data unit. The role of the excitation unit is to generate primary X-rays. It consists of high-voltage generator and X-ray tube. The role of the dispersion unit is to separate X-rays of the desired wavelength. It consists of sample chamber, slit, goniometer, analysis crystal and other parts. The role of the detector is to convert X-ray photon energy into electrical energy. The recording unit is composed of an amplifier, a pulse amplitude analyzer and a display part. X-ray tube generates incident X-rays to excite the tested sample. Each element in the excited sample emits

secondary X-rays, and the secondary X-rays emitted by different elements have specific energy characteristics or wavelength characteristics. The detection system measures the energy and quantity of these emitted secondary X-rays. The instrument software converts the information collected by the detection system into the types and contents of various elements in the sample. By using the principle of X-ray fluorescence, every element after beryllium in the periodic table can be measured theoretically. In practical applications, the effective element measurement range is element 9 (F) to element 92 (U) in the periodic table. (Chu, Li & Jiang 2014, 40).

The characteristic X-ray energy and wavelength emitted by different elements are different. Therefore, no matter what kind of element can be detected by measuring the energy or wavelength of X-ray. At the same time, the characteristic X-ray intensity of an element emitted after the sample is excited. It is related to the content of this element in the sample, so the quantitative analysis of the element can be performed by measuring its intensity. There are two basic types of XRF spectrometers: wavelength dispersive spectrometer and energy dispersive spectrometer. The structure of the instrument is shown in FIGURE 4.

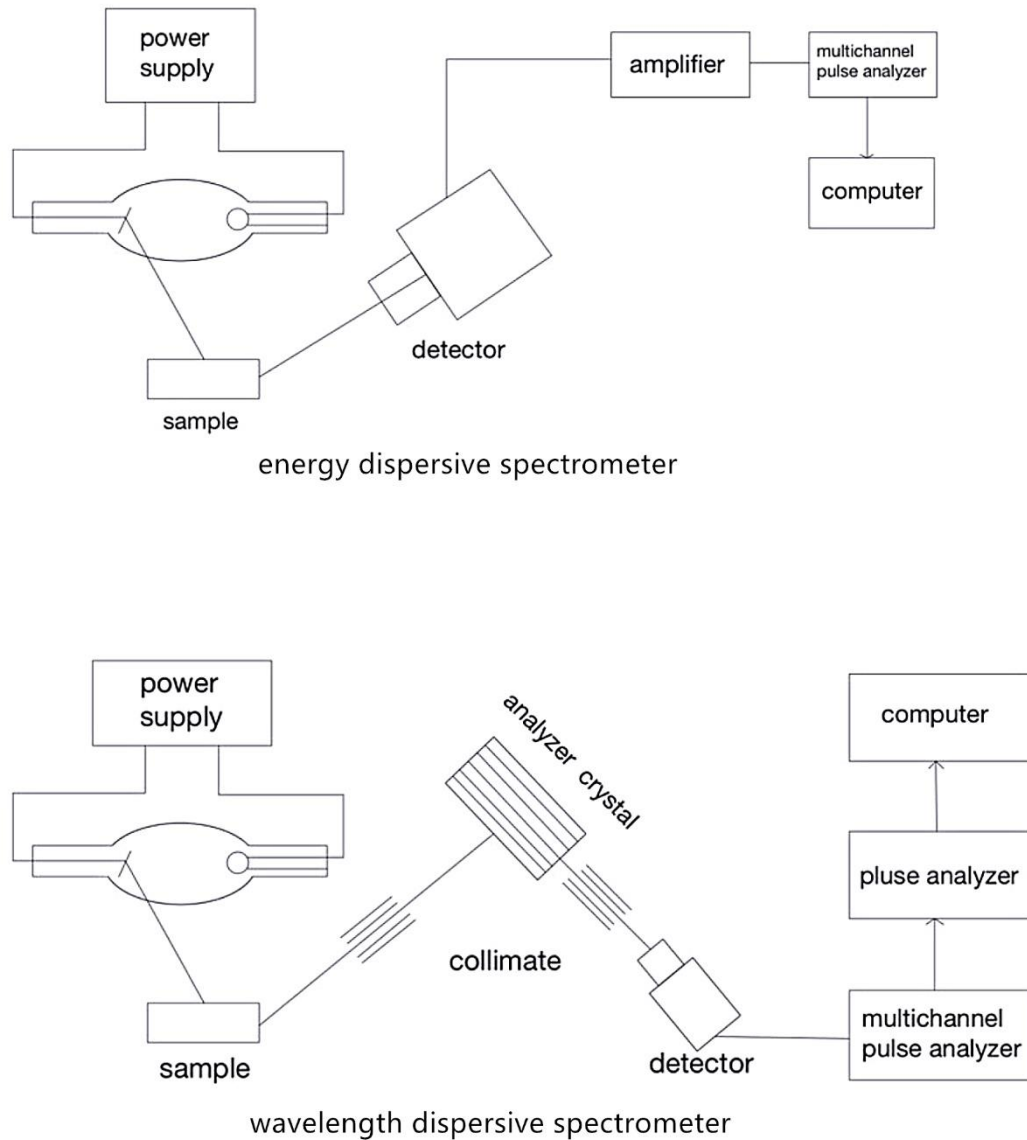


FIGURE 4. Wavelength dispersive spectrometer and energy dispersive spectrometer (adapted from Bo, Xiao & Tao 2015, 1308).

With the development of instrument technology and theoretical methods, the application range of XRF analysis is very widely. In the analysis of the composition of substances, in the metallurgy, geology, chemical industry, machinery, petroleum, building materials and other industrial sectors, agriculture and medicine and health, as well as physics, chemistry, biology, geoscience, environment, astronomy and archaeology and other research departments have been widely applications. (Chu et al. 2014, 37).



## 2.6 Hydrogen peroxide photometry and ferrotitanium spectrophotometry

H<sub>2</sub>O<sub>2</sub> is a colorless, odorless liquid with bitter taste and easy to decompose into water and oxygen. It is a strong oxidant. H<sub>2</sub>O<sub>2</sub> is often used for sterilization in the workplace, starch whitening in the industry, or as a strong oxidant for food or food packaging and liquid fuel propellant. In this method, phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and H<sub>2</sub>SO<sub>4</sub> were used to dissolve the sample. In the medium of 5 % H<sub>2</sub>SO<sub>4</sub> by volume, TiO<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> formed a yellow complex ion in the acidic condition. The stable equilibrium constant of the complex is  $k = 1.0 \times 10^4$  and the maximum absorption wavelength is  $\lambda_{\max} = 405$  nm. H<sub>2</sub>O<sub>2</sub> spectrophotometry is simple and rapid, but its sensitivity and selectivity are poor. Sodium catechol-3,5 sulfonate forms a yellow complex with titanium at pH = 4.7-4.9. Ferrotitanium reagent has high sensitivity and can be used for the continuous determination of trace titanium and iron. (Xinyan 2006, 66).

### 3 EXPERIMENT

There are three main experimental steps: sample decomposition, color rendering and absorbance experiment which are studied and developed extensively in this project. The detail procedures of both topics will be fully displayed. Besides, some important choices of chemical reagents during the experiment will be explained by five variable value optimization experiments: optimal selection of the spectrophotometer's wavelength, the optimal dosage of acidity, the optimal dosage of DAPM, the optimal dosage of ascorbic acid and the interference factors analysis experimental.

#### 3.1 Reagents and reagents preparation

The reagents used in the experiment are as follows: mixed flux grind from anhydrous sodium sulfate and boric acid, potassium pyrosulfate, HCl with a density of 1.19 g/mL, H<sub>2</sub>SO<sub>4</sub> with a density of 1.84 g/mL, HCl (1+1), ((1+1) is the solution which mix 1 ratio of HCl with 1 ratio of water in volume. The molar concentration of HCl (1+1) is 6 mol/L.) H<sub>2</sub>SO<sub>4</sub> (5+95), ((5+95) is the solution which mix 5 ratio of H<sub>2</sub>SO<sub>4</sub> with 95 ratio of water in volume. The molar concentration of H<sub>2</sub>SO<sub>4</sub> (5+95) is 0.9 mol/L), ascorbic acid solution (20 g/L), DAPM solution (50 g/L), TiO<sub>2</sub> stock solution (100 µg/mL) and TiO<sub>2</sub> standard solution (10 µg/mL).

The preparation steps for ascorbic acid solution (20 g/L) are as follows: weigh 20g of ascorbic acid, add 200-300 mL of water to dissolve the sample and stir evenly. After the ascorbic acid is completely dissolved, transfer the solution to a 1 L volumetric flask and make up to volume. The preparation steps of the TiO<sub>2</sub> stock solution (100 µg/mL) are as follows: weigh 0.1 g of TiO<sub>2</sub> and place it in a platinum crucible, and then add 5-7 g of potassium pyrosulfate. Put them into a high-temperature furnace, raise the temperature to 600 ° C to melt. Use 60 mL H<sub>2</sub>SO<sub>4</sub> to dissolve the melt. After it cooling to room temperature, transfer it to a 1000 mL volumetric flask, diluted with H<sub>2</sub>SO<sub>4</sub> to the mark and mixed fully. The preparation of the TiO<sub>2</sub> standard solution (10 µg/mL) are as follows: add 50mL of TiO<sub>2</sub> stock solution to a 500 mL volumetric flask. And then add H<sub>2</sub>SO<sub>4</sub> to constant volume and mix it well.

Three instruments are used in this experiment: platinum crucible (The volume needs to be greater than 30 mL), high temperature furnace (The crucible heating temperature is suitable for 100-1100 °C) and UV-vis spectrophotometer (1000 nm  $\geq$  wavelength  $\geq$  180 nm). Before using the spectrophotometer,

connect the spectrophotometer to the power supply, turn on the instrument switch, lift the lid of the sample chamber and preheat the sample chamber for 10 minutes.

### 3.2 Experimental procedure

Before the experiment, the preparation of reagents and the commissioning of equipment need to be completed. The preparatory work includes preparation of ascorbic acid solution (20 g/L), preparation of DAPM solution (50 g/L), preparation of  $\text{TiO}_2$  stock solution (100  $\mu\text{g}/\text{mL}$ ) and preparation of  $\text{TiO}_2$  standard solution (10  $\mu\text{g}/\text{mL}$ ). After the reagent preparation is completed, proceed to the second step as shown in FIGURE 5. Dissolve the sample after weighing it. Thirdly render the color of the sample solution. The fourth step is measure the absorbance of the developed solution by spectrophotometer. And finally record and process the experimental data.

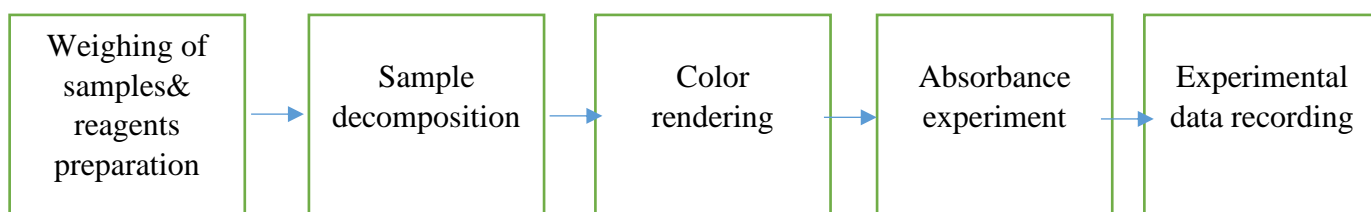


FIGURE 5. The experimental procedure of measuring titanium dioxide content in limestone by diantipyryl methane photometry

### 3.3 Procedure of sample decomposition

In this experiment, the samples selected three limestones with known accurate  $\text{TiO}_2$  content. The  $\text{TiO}_2$  content (mass fraction) of sample A is 0.041 %, the  $\text{TiO}_2$  content (mass fraction) of sample B is 0.074 % and the  $\text{TiO}_2$  content (mass fraction) of sample C is 0.13 %. The purpose of these accurate data is to make a precision comparison with the data measured in this experiment, and verify the accuracy of the experimental method. A total of three sets of experiments were conducted and each set was measured 6 times.

The sample decomposition steps are as follows: take 0.2 g limestone (crumb limestone) sample into a platinum crucible, add 5 g mixed flux (anhydrous sodium carbonate and boric acid). Secondly, place the platinum crucible in a high-temperature furnace and gradually increase the temperature to 950-1000  $^{\circ}\text{C}$ .

After the sample is melted, take it out and cool it to room temperature. Thirdly, put the crucible in the 250 mL beaker together with the sample, and add HCl into the beaker. Finally, heat the beaker at around 75 °C to make the solution transparently. After cooling to room temperature, dilute the solution to 100 mL with water. (Wang, Yan & Zhu 2013, 49). During the experiment, HCl is used to dissolve the sample. The choice of acid type needs to be determined through the phenomenon of sample dissolution in different acid systems. Through experiments of dissolving samples in various acid systems, the results can be obtained the most suitable acid for dissolving limestone.

For the optimal selection of the dosage and the type of acid to dissolve the sample, the experimental procedure is as follows: select 0.25 g of limestone sample B with a TiO<sub>2</sub> content of 0.074 % and place it in 6 polytetrafluoroethylene beakers. Add HCl (1+1), nitric acid (HNO<sub>3</sub>) (1+1), perchloric acid (HClO<sub>4</sub>) (1+1), hydrofluoric acid (HF) (1+1) and H<sub>2</sub>SO<sub>4</sub> (5+95) to dissolve the sample with different acid systems composed of these acids. Put 20 mL HCl into the first beaker. By observing the solution in the beaker, the solution is cloudy with residue. For the second beaker, add HCl of the same volume as the first beaker and 5 mL HNO<sub>3</sub>. The phenomenon of the solution is cloudy with residue. For the third beaker, add HCl and HNO<sub>3</sub> of the same volume as the second beaker and 10 mL HClO<sub>4</sub> into the beaker. By observing the phenomenon of the reaction, the solution is cloudy with residue. For the fourth beaker, put 20 mL HCl, 10 mL HClO<sub>4</sub>, 5 mL HF into the beaker. The limestone sample is completely dissolved. And then put add HCl, HNO<sub>3</sub> and HClO<sub>4</sub> of the same volume as the third beaker and 5 mL HF into the fifth beaker, the limestone sample is completely dissolved. For the last beaker, choose 20 mL HCl, 10 mL HClO<sub>4</sub>, 5 mL HF and 5 mL H<sub>2</sub>SO<sub>4</sub> to dissolve the sample. The solution is turbid.

### 3.4 Procedure of color rendering

Whether the color rendering reaction can meet the requirements of the photometric method, in addition to mainly related to the nature of the chromogenic reagent, it is also very important to control the conditions of the color reaction. The color rendering conditions mainly included the dosage of the chromogenic reagent and the acidity of the solution. In order to make the color reaction as complete as possible, it is necessary to add an appropriate dosage of the chromogenic reagent. If an excessive dosage of chromogenic reagent is added, it will cause side reactions which are not conducive to the measurement. In the experiment, the appropriate dosage of the chromogenic reagent is obtained through related experiments. Most chromogenic reagents are organic weak acids. The acidity of the solution affects the disso-

ciation of the chromogenic reagent and the completeness of the color rendering reaction. Many chromogenic reagents are acid-base indicators. The acidity of the solution will change the initial color of the chromogenic reagent. The acidity of the solution also has an effect on the composition and stability of the colored complex.

Three solutions need to be added in the color rendering experiment. Firstly, HCl needs to be added to control the acidity of the solution. Secondly, ascorbic acid solution needs to be added to reduce  $\text{Fe}^{3+}$  to ferrous iron ( $\text{Fe}^{2+}$ ) in the solution. Because of the main interference element of this experiment is iron. So it is necessary to eliminate this interference by adding ascorbic acid solution. Finally, add DAPM for color rendering reaction. So before rendering colors, the optimal dosage of these three solutions needs to be found.

The acidity of the solution affects the dissociation of the chromogenic reagent and the completeness of the color rendering reaction. Therefore, maintaining the acidity of the solution is a prerequisite for starting the color rendering experiment. Determine the experiment steps of optimum dosage of HCl are as follows: take 10 mL of the test solution in 50 mL volumetric flask. And then add 5 mL of ascorbic acid solution and mix it well. Place it for about 5 minutes. Add 2 mL, 4 mL, 6 mL, 8 mL, 10 mL, 12 mL, 16 mL, 20 mL HCl to 8 flasks respectively, then add 7 mL of DAPM solution into each flask. Dilute the solution to the mark with water and mix it well. Leave it for about half an hour at room temperature. Then put the chromogenic reagent into the spectrophotometer to measure the absorbance (detection wavelength is 385 nm). It can be realized from TABLE 1 that the acidity in HCl medium has minimal effect on the color rendering reaction. During the analysis, add 6 mL of 6 mol/L HCl to control the normal concentration of about 1.13 N. Normality (N) is defined as the number of equivalents per liter of solution, where definition of an equivalent depends on the reaction taking place in the solution. For an acid-base reaction, the equivalent is the mass of acid or base that can furnish or accept exactly 1 mole of proton ( $\text{H}^+$  ions). And this is based on the HCl concentration. It can be seen from the absorbance value in the last row of TABLE 1 that the acidity has little effect on the color rendering reaction in HCl medium. In the analysis process, add 6 mL 6 mol/L HCl solution to control the normal concentration at 1.13 N.

TABLE 1. Effect of acidity in HCl medium on color reaction

	Flask1	Flask 2	Flask 3	Flask 4	Flask 5	Flask 6	Flask 7	Flask 8
HCl (1+1) mL	2	4	6	8	10	12	16	20
Normal concentration (N)	0.65	0.89	1.13	1.37	1.61	1.85	2.33	2.90
Absorbance L/(g·cm)	0.185	0.185	0.185	0.185	0.185	0.185	0.185	0.180

After determining the acidity of the solution, the second problem to be determined is the optimal dosage of ascorbic acid reagent. Take several copies of 10 mL sample B solution with 0.074 % TiO<sub>2</sub> content, add different amounts of ascorbic acid solution. Then add 6 mL of HCl and 7 mL of DAPM for color development, and measure the absorbance by spectrophotometer (detection wavelength is 385 nm). The absorbance values of different ascorbic acid dosages are shown in TABLE 2. The effect of adding different volume of ascorbic acid on absorbance is shown in TABLE 2. The experimental results show that when the dosage of ascorbic acid is between 3 mL and 15 mL, the absorbance remains stable. In order to facilitate the operation and ensure complete reduction reaction, we chose the dosage of ascorbic acid to be 5 mL.

TABLE 2. The absorbance values of different ascorbic acid dosages

	Flask 1	Flask2	Flask3	Flask4	Flask5	Flask6
Ascorbic acid (mL)	1	3	5	6	10	15
Absorbance L/(g·cm)	0.509	0.514	0.515	0.515	0.515	0.515

After determining the dosage of the HCl and the ascorbic acid, the third question is the optimal dosage of DAPM. Firstly, take several copies of 5 mL sample B solution which content about 0.074 % of TiO<sub>2</sub> and put the each solution into a 50 mL volumetric flask. Secondly, add 6 mL of HCl, 5 mL of ascorbic acid and different amounts of DAPM for color rendering reaction. Finally, measure the absorbance value

at 385 nm wavelength, the experimental results are shown in the TABLE 3. From the experimental data, it can be seen that the absorbance of the DAPM chromogenic reagent is basically constant when it is above 5 mL. So the optimum dosage of the DAPM chromogenic reagent is 7 mL.

TABLE 3. The dosage of DAPM experiment

	Flask1	Flask2	Flask3	Flask4	Flask5	Flask6	Flask7	Flask8	Flask9
The dosage of DAPM (mL)	2	3	4	5	6	7	8	9	10
Absorbance L/(g·cm)	0.226	0.259	0.282	0.299	0.231	0.232	0.232	0.234	0.233

Through the above three experiments (determine the optimal dosage of HCl, ascorbic acid and DAPM), the exact dosage of the three reagents in the color rendering experiment was determined. The order and steps of adding the three reagents are as follows: firstly, take 10 mL of TiO<sub>2</sub> standard solution and put it in a 50 mL volumetric flask. Secondly, add 5 mL of ascorbic acid solution, mix it well. Place the solution for 5 minutes in the room temperature. Then add 6 ml hydrochloric acid to mix the reagent evenly. Finally, add 7 mL of DAPM into the solution. Dilute the solution to the mark with water and mix it well. Leave it for 30 minutes in the room temperature and prepare to measure the absorbance.

### 3.5 Procedure of the absorbance measuring

After the color rendering reaction is completed, the test solution needs to be placed in a cuvette for absorbance testing. By changing the test wavelength, the optimal wavelength is determined according to the absorbance corresponding to each wavelength. The absorbance at different wavelengths after color development is shown in TABLE 4. It can be seen from the data that the wavelength has a maximum value at 380-390 nm. To ensure the best sensitivity, the test wavelength is selected at 385 nm. Under the test of the maximum absorption wavelength, the response of the instrument is more sensitive and the measurement data is more accurate.

TABLE 4. Optimal wavelength test data

	Flask1	Flask2	Flask3	Flask1	Flask4	Flask5	Flask6	Flask7
Wavelength (nm)	360	370	380	385	390	400	410	420
Absorbance L/(g·cm)	0.499	0.533	0.547	0.554	0.543	0.533	0.502	0.461

After determining the optimal wavelength, use the spectrophotometer to analyze the content of TiO<sub>2</sub> in the sample: firstly, prepare the spectrophotometer and open the sample chamber cover. Turn on the power and the indicator lights up, let the instrument warm up for 20 minutes. Set the selector switch to the "T" knob to display the number as "00.0". Secondly, turn the wavelength knob to the 385 nm wavelength, and align the scale line. Transfer the color rendering solution into a 3 cm cuvette, and place it on the colorimetric shelves. And then close the sample chamber cover and adjust the light transmittance "100% T" knob to make the number display as "100.0 T". Turn the selector switch to the A zero adjustment knob, the digital display should be ".000". Then pull out the lever to put the solution to be measured into the optical path, and the digital display value is the absorbance A of the sample. According to the absorbance data, it can be easily get the mass of TiO<sub>2</sub> in the test solution. After the measurement is completed, open the sample chamber cover and turn off the power switch.

### 3.6 Interference test of calcium and magnesium ions

The main components of limestone are CaO and magnesium oxide (MgO). In order to determine whether CaO or MgO has an effect on the determination of TiO<sub>2</sub>. Firstly, prepare two standard solutions: CaO standard solution and MgO standard solution. The content of CaO in the CaO standard solution is 10 mg/L. And the content of MgO in the MgO standard solution is 10 mg/L. Extract several parts from the two prepared solutions, and add a certain amount of TiO<sub>2</sub> standard solution 4 mL (The amount of TiO<sub>2</sub> added is 40 ug) to each part. According to the method of 3.4 for color rendering, the interference experiment results of calcium ion and magnesium ion are as shown in TABLE 5. It can be seen from the absorbance value in TABLE 5 that CaO and MgO have no effect on the determination of TiO<sub>2</sub>. There was no difference in absorbance before and after adding CaO and MgO.



TABLE 5. The interference experiment results of calcium ion and magnesium ion

	Flask 1	Flask 2	Flask 3	Flask 4
The amount of TiO <sub>2</sub> added	40 ug	40 ug	40 ug	40 ug
The amount of CaO added (no MgO)	10 mg	20 mg	30 mg	40 mg
Absorbance L/(g·cm)	0.551	0.548	0.550	0.551
	Flask 5	Flask 6	Flask 7	Flask 8
The amount of TiO <sub>2</sub> added	40 ug	40 ug	40 ug	40 ug
The amount of MgO added (no CaO)	10 mg	15 mg	20 mg	25 mg
Absorbance L/(g·cm)	0.551	0.550	0.548	0.551

## 4 RESULTS AND DISCUSSIONS

Through the acid system selection experiment, the optimal selection of the spectrophotometer's wavelength experiment, the optimal dosage of acidity selection experiment, the optimal dosage of DAPM selection experiment, the optimal dosage of ascorbic acid selection experiment and the interference factors analysis experimental, the accurate dosage of reagents was determined by these experiments. According to the reaction phenomena or absorbance results of each experiment, the corresponding experimental results were obtained.

In the acid system selection experiment, the following conclusions can be drawn from the observation of six experimental phenomena. In the system of HF and HClO<sub>4</sub>, the sample is completely dissolved (the precipitation is precipitated by adding H<sub>2</sub>SO<sub>4</sub>, the solution is turbid), but HClO<sub>4</sub> and HF have a effect on the determination of titanium, and the fluoride ion is easy to complex with titanium. And this combination is likely to lead to the results on the low performance. The presence of HClO<sub>4</sub> can combine with DAPM to produce white flocculent precipitate, which led to the failure of the experiment. In order to eliminate the influence of insoluble residue to the analysis, and ensure the sample is completely dissolved. The experiment uses the usual method which is anhydrous sodium carbonate and boric acid system solvent mixed together for melting. This method is simple and fast, and the melting is complete. The acid system is relatively simple, without introducing HClO<sub>4</sub> acid, HF acid and other kinds of acid. HCl is used to dissolve the sample, and the sample dissolves quickly.

In the optimal dosage of acidity selection experiment. By observing the results of absorbance under different acidity. The best color acidity can be obtained: add 6 mL of 6 mol/L HCl to control the color acidity of solution. In the optimal dosage of DAPM selection experiment, through the absorbance test results of solutions with different DAPM dosage. It can be concluded from the data that the best dosage of DAPM solution is 7 mL. In the the optimal selection of the spectrophotometer's wavelength experiment, according to the test results of absorbance of solution at different wavelengths, it can be concluded that the optimal wavelength is 385 nm. In the optimal dosage of ascorbic acid selection experiment, through the absorbance test results of several solutions added with different volume of ascorbic acid, it can be concluded that the optimal dosage of ascorbic acid is 5 mL. In the interference factors analysis experimental, it can be seen from the absorbance value in experiment results that CaO and MgO have no effect on the determination of TiO<sub>2</sub>. By determining the accurate dosage of various reagents, a set of measurement steps with accurate actual dosage is formulated.

#### 4.1 Measurement results of titanium dioxide content

The content of TiO<sub>2</sub> in three limestone samples was determined six times in parallel. The analysis result is rounded according to the rules of banker's rounding. In order to avoid the phenomenon of big error caused by rounding rules. The specific method of data processing in this rule is as follows: when the mantissa is less than or equal to 4, the mantissa will be directly rounded off. When the mantissa is greater than or equal to 6, round off the mantissa and carry forward one digit. When the mantissa is equal to 5, but the numbers after the mantissa are all 0, the previous digit of the mantissa should be used as a reference. If the previous number is an odd number, move one digit forward. If the previous number is even, the mantissa is discarded. If the mantissa is 5, but there is a number that is not 0 after the mantissa, whether the number before the mantissa is odd or even, the number must move forward one bit.

This experiment is carried out under the specified repeatability conditions: the same experimental researcher carries out the experiment, uses the same instrument to carry out the experimental measurement, carries out the experiment under the same experimental conditions, carries out the same calibration in a short time. TiO<sub>2</sub> content is calculated according to the mass fraction  $W_{TiO_2}$  calculation formula (1):

$$w_{TiO_2} = \frac{m_1 \times 10^{-6}}{m \times V_1 / V} \times 100 \quad (1)$$

V<sub>1</sub>: The volume of the solution obtained separately from the sample solution. The unit is milliliter (mL);

V: Total volume of sample solution. The unit is milliliter (mL);

m<sub>1</sub>: The quality of the titanium dioxide obtained separately from the sample solution. The unit is microgram (μg);

m: The quality of the sample. The unit is gram (g).

The measurement results of the experiment are shown in the TABLE 6. The experimental data compared with the TiO<sub>2</sub> content in three limestone samples are shown in TABLE 7. For sample A, the TiO<sub>2</sub> content obtained from the first and third experiments is basically consistent with the known accurate TiO<sub>2</sub> content of sample A. In addition to the second experimental data, the accuracy of other experimental data is good. Compare with the other five groups of data, the results of the second experiment have relatively large errors. For sample B, the content of TiO<sub>2</sub> obtained in the third experiment is almost the same as the given value. The TiO<sub>2</sub> content measured in the fifth experiment is quite different from the given value compared with the other five groups of data. For sample C, the TiO<sub>2</sub> content obtained from six experiments is almost the same as the given TiO<sub>2</sub> content.

TABLE 6. Experimental measurement data

	Experiment 1	Experiment 2	Experiment 3	Experiment 4	Experiment 5	Experiment 6
Sample A (%)	0.0412	0.0423	0.0409	0.0414	0.0416	0.0415
Sample B (%)	0.0730	0.0750	0.0740	0.0765	0.0780	0.0735
Sample C (%)	0.1250	0.1280	0.1290	0.1310	0.1240	0.1260

#### 4.2 Accuracy of results discussion

From the average value of the data, it can be seen that the accuracy of using the DAPM photometry to determine the TiO<sub>2</sub> content in limestone. TABLE 7 is the average value of TiO<sub>2</sub> content measured in six experiments for each sample from TABLE 6. The second column is the certified value of the three samples. The mass fraction of TiO<sub>2</sub> content in sample A is 0.041 %. The mass fraction of TiO<sub>2</sub> content in sample B is 0.074 %. The mass fraction of TiO<sub>2</sub> content in sample C is 0.13 %. And the third column is the average values which are obtained through experimental measurement and calculation. As can be seen from TABLE 7. The average value of TiO<sub>2</sub> content in several groups of limestone samples measured by this experiment have high accuracy.

TABLE 7. Average mass fraction of TiO<sub>2</sub> content in limestone

	Certified value	Average value
Sample A (%)	0.041	0.0414
Sample B (%)	0.074	0.0750
Sample C (%)	0.130	0.1272

HCl was used to dissolve the sample. If HClO<sub>4</sub> is used in the experiment, it will form white flocculent precipitate with DAPM, which will affect the absorbance test. If HF is used in the experiment, fluorine ions will complexate with titanium to form titanium fluoride complex, which will affect the accuracy of

the experimental results. If only  $\text{HNO}_3$  is used for decomposition, except for incomplete decomposition of the sample,  $\text{HNO}_3$  also destroys DAPM, thus affecting the continuation of the experiment. According to the dissolution treatment experiment and acidification experiment, the HCl system is relatively simple, without the introduction of  $\text{HClO}_4$ , HF and other types of acids. And the sample dissolves quickly by HCl leaching.

In the experiment of determine the optimal dosage of DAPM solution, it can be concluded that the optimal dosage of DAPM is 7mL. When the amount of DAPM is more than 6 mL, the absorbance tends to be stable. If the flux of DAPM does not reach 6 mL, the color reaction will be incomplete, which will affect the whole experiment. For the selection of the amount of ascorbic acid, ascorbic acid is used to reduce  $\text{Fe}^{3+}$  in the solution to  $\text{Fe}^{2+}$ . In order to eliminate the interference, 5 mL ascorbic acid was selected to reduce  $\text{Fe}^{3+}$  in the sample. If the amount of ascorbic acid is less than 5 mL, the remaining unreduced  $\text{Fe}^{3+}$  will affect the accuracy of the whole experiment.

In this experiment, temperature and time have influence on the measurement results. In 15-80 °C, the absorbance value is not affected by temperature. However, if the iron content in the sample is high and the temperature is higher than 60 °C, the solution is easy to be turbid and unable to compare colors. Therefore, this experiment uses 15-30 °C room temperature to render color. The color solution is very stable and can be maintained for several months. When the room temperature is higher than 20 °C, it tends to be stable after 20 minutes of color development. When the room temperature is lower than 20 °C, it needs 40-60 minutes to be stable. In this color rendering experiment, the accuracy of temperature control is particularly important.

When selecting the optimal wavelength of the test absorbance, the wavelength corresponding to the maximum absorbance is selected according to the absorption curve of the test solution. In this experiment, when the wavelength is 385 nm, the absorbance changes with the concentration in the largest range, so the determination is the most sensitive. The absorption curve is an important basis for choosing the wavelength of incident light in quantitative analysis. In the wavelength selection experiment, if the wavelength corresponding to the maximum absorbance is not selected, the accuracy of the experiment will be insufficient.

## 5 CONCLUSION

In this experiment, the DAPM photometric method was used to determine the content of  $\text{TiO}_2$ . The sample is melted by sodium carbonate-boric acid mixed flux and leached with dilute HCl. The experiment used ascorbic acid as a masking agent to reduce  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  in the solution to eliminate interference. In this experiment, DAPM solution was added to render the solution color. In order to ensure the accuracy of the experimental results, the amount of various reagents was optimized. The following five aspects were quantitatively analyzed in the experiment: optimal selection of the spectrophotometer's wavelength, the optimal dosage of acidity, the optimal dosage of DAPM, the optimal dosage of ascorbic acid and the interference factors analysis. The exact dosage of each reagent was determined. The  $\text{TiO}_2$  content measured in the experiment was compared with limestone with known accurate  $\text{TiO}_2$  content. The accuracy of the measurement can be seen in this experiment. This experimental method has a perfect effect on the use of spectrophotometers, and promotes the determination of mineral raw materials containing low  $\text{TiO}_2$  content by spectrophotometer.

For the measurement results of the experiment, there is a certain error between the  $\text{TiO}_2$  content measured in this experiment and the  $\text{TiO}_2$  content given in the limestone sample. Through the interference element analysis experiment, it is determined that the two main components of limestone (MgO and CaO) are not the cause of this error. For several values with slightly poor accuracy, there may be some problems in the operation of the experiment. The most likely reason for the poor accuracy of the data is that after the sample dissolves, the color reaction does not wait until the solution cools to room temperature. Another possibility is that the limestone sample is not well preserved, resulting in a certain error between the actual  $\text{TiO}_2$  value and the given value. In the future experiments, the above two error aspects are further studied to ensure that the measurement method is accurate and the measurement results are more accurate.

Compared to ammonium ferric sulfate volumetric method and  $\text{H}_2\text{O}_2$  coordination titration method, DAPM photometric method has high accuracy and eliminates the interference of vanadium, molybdenum, tungsten, copper, arsenic and other elements to the experiment. Compared to ICP-AES method, DAPM photometric method is simple in operation and suitable for popularization and application. The results of the project provided a technical method for accurately and quickly determining the content of  $\text{TiO}_2$  in limestone.

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