Determination of titanium dioxide in cement by Microwave Digestion-VIS Spectrophotometry

Zheng-gen Huang^{1,2*}, Tao Wang², Xiao-bin Li¹, Bei-jia Li¹

¹. National Quality Supervision and Inspection Test Center of Architecture Ceramic, Leshan 614000.

². College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu 610059.

Abstract: A new method to determine titanium dioxide in cement by Microwave Digestion-DAPM VIS Spectrophotometry which has many advantages such as simple operation, safe and fast, dissolve completely is presented in this paper. The determination conditions and working parameters of the microwave digestion instrument including the species and dosage of digestion reagent, wavelength, reaction time and the dosage of DAPM were optimized. The results show that samples were dissolved by HNO₃-HF-H₂O₂, 395nm as the wavelength and 12mL of DAPM. The method has been validated by determination of titanium dioxide in national standard reference materials of GBW03201, GBW03201c, GBW03207 and GBW03205. The results were in agreement with certified values and the RSD was 1.07%-4.52%. The recovery ratio was ranging from 91.8% to 108.0% and the $|\Delta \lg C|$ was less than 0.018. Comparison with the traditional digestion method that analytical cement samples of Sichuan, there is no significant difference between the two methods by Student's t test. This new method provide a new way for quick and accurate to determine the content of titanium dioxide in cement.

1 Introduction

Cement is the basic product of national economic construction, and it is widely used in real estate, infrastructure and rural construction. At present, my country is the world's largest cement producer and consumer, and its total output accounts for more than half of the world's total. The various physical and chemical components and contents in cement are closely related to the quality of cement products and later construction applications [1]. The titanium dioxide present in cement is usually substituted by bauxite and clay raw materials. Titanium dioxide has an impact on the physical and chemical properties of cement. The improvement has been proven. For example, the decomposition temperature of calcium carbonate can be reduced within the range of 0.1-1.0%, and the strength of the product can be increased by up to 20% during use. Titanium dioxide can form a solid solution with cement clinker minerals, which can increase the maturity Material quality; but if the content is too much, titanium dioxide can react with CaO to produce perovskite without hydraulic properties and replace SiO₂, which consumes CaO and affects the strength of cement. Therefore, the simple, fast and accurate inspection of titanium dioxide in cement has important economic and practical significance for the quality control of the production process and the production of high-quality and stable cement products.

Traditional detection methods for the content of titanium dioxide in silicate materials such as cement

mainly use ICP-AES method [3], atomic absorption method, XRF method, etc. [4], but such equipment is expensive and has high cost and limited popularity. Traditional detection methods sample pretreatment methods mainly include wet decomposition, melting decomposition and sintering decomposition methods [5,6]. The wet decomposition method is simple and fast, but the ability to decompose the silicate sample is poor; the melting decomposition method decomposes the sample completely, but the temperature is too high and time-consuming, the solvent erodes the vessel used for decomposition, and introduces a large amount of alkali metal salts; the temperature of the sintering method Not high, but need to add a lot of flux. Microwave digestion technology is a new digestion method that has developed rapidly in recent years. Its advantages are high efficiency, fast speed, simple operation, safety and reliability. The microwave directly releases energy to the sample, which greatly improves the digestion speed. It is now widely used In the fields of geology, environment, metallurgy, biology, food, etc. [7-13], there are relatively few reports on the direct use of microwave digestion of cement to determine the content of titanium dioxide at home and abroad. This article uses microwave digestion to quickly process cement samples, and spectrophotometric determination of titanium dioxide content. The results prove that the method is simple, fast, accurate and precise, and is suitable for rapid determination of titanium dioxide.

*Corresponding author's e-mail: lszs2102660@aliyun.com

2 Materials and methods

2.1 Reagents and instruments

Titanium standard stock solution 1000mg/L (National Nonferrous Metals and Electronic Materials Analysis Center), concentrated sulfuric acid, concentrated nitric acid, concentrated hydrochloric acid, ascorbic acid, hydrogen peroxide, diantipyrene methane, etc. are all analytically pure (Chengdu Kelong Chemical Co., Ltd. Company), ultra-pure water; GBW03201, GBW03201c, GBW03207 and GBW03205 Portland cement national standard materials (Institute of Geology, National Building Materials Industry Bureau)

Titanium working solution: take 5mL standard solution, constant volume of 2% H₂SO₄ in a 100 mL volumetric flask;

Visible light spectrophotometer (Tianjin Prius Instrument Co., Ltd. 721 spectrophotometer), microwave digestion apparatus (Shanghai New Instrument Microwave Chemical Technology Co., Ltd. MDS-6), box-type resistance furnace (Hunan Xiangtan Instrument Co., Ltd.), electric heating plate (Beijing Zhongxing Weiye

Instrument Co., Ltd.), analytical balance (Mettler-Toledo ME104E).

2.2 Test method

2.2.1 . Sample preparation method

Accurately weigh 0.2g (accurate to 0.0001g), dry the constant weight sample at 105°C, and place it in a polytetrafluoroethylene digestion tank. Add a few drops of water to wet the sample. One group adds 6.0mLHNO₃+2mLHF, and the second group 6.0mLHNO₃+2mLHF+1mLH₂O₂, add8mL HNO₃ for the third group, 6mLHCl+2mLHNO₃ for the fourth group and 6mL HNO₃-2mLH₂SO₄ for the fifth group. After soaking until the reaction is stable and the foam is basically eliminated, tighten the lid and put it in the microwave digestion apparatus, as shown in Table 1. Conditions are resolved. After the digestion is completed, drive the acid at 140°C in the electric heating plate until the smoke is exhausted, add water to a constant volume in a 100mL volumetric flask, and add a blank test at the same time

Table1. Microwave digestion conditions

step	P/W	t/min	°C	t/min
1	400	5	120	1
2	800	5	160	4
3	1000	5	200	15

2.2.2 Sample determination

Pipette 0, 0.2, 0.5, 1.0, 2.0 mL of titanium working solution into a 50 mL volumetric flask, respectively, add 5 mL of 2% ascorbic acid solution, 10 mL (1+1) hydrochloric acid, and 12 mL of diantipyrene methane solution (30 g/L). Dilute with water to the mark, shake well, and measure after standing for 20 minutes. The concentration of titanium in this standard working fluid series is 0, 0.2, 0.5, 1.0, 2.0 µg/mL. Take the developed blank solution as a reference, use a 1cm cuvette at a wavelength of 395nm, measure the absorbance of the standard working solution with a spectrophotometer and draw a standard curve. Pipette an appropriate amount of the liquid to another set of 50mL volumetric flasks, add 5mL 2% ascorbic acid solution, 10mL (1+1) hydrochloric

acid, 12mL diantipyryl methane solution, dilute to the mark with water, shake well, After standing for 10 minutes, measure, check the concentration on the standard curve and calculate the content of titanium dioxide in the sample.

3 Results and discussion

3.1 Measuring wavelength

The test uses a 721 spectrophotometer. Titanium reacts with diantipyrene methane in a 1.2 mol/L HCl medium to form a yellow complex. Pipette 50.00 µg/mL titanium working solution 2.0 mL into Add 10mL HCl, 12mL of ascorbic acid solution and diantipyrene methane solution to a 50mL volumetric flask, develop color for 20 minutes, measure absorbance at different wavelengths (300-500nm), and the results are shown in Figure 1.

Fig 1. Absorption curve

Fig 2. Working curve

It can be seen from the figure that in the hydrochloric acid medium, the maximum absorption wavelength of the complex formed by titanium and diantipyrylmethane is between 385-400nm. In order to obtain high sensitivity and reduce the test error, 395nm is selected as the absorption wavelength for subsequent experiments.

3.2 Drawing of working curve

According to the test method in 1.2.2, draw a working curve of absorbance value (y) versus the solubility of titanium standard solution (x, μg/mL), and the results are shown in Figure 2. The regression equation of the standard working curve is $y = 0.26903x + 0.00412$, which conforms to the Beer-Lambert law in the range of 0-2.0 μg/mL, the absorbance A has a linear relationship with the standard

solution, and the correlation coefficient $R^2 = 0.9995$.

3.3 The effect of the amount of color developing agent diantipyryne methane

Pipette an appropriate amount of 50 μg/mL titanium working solution, add 10mL HCl, ascorbic acid solution, add different content of the color developing solution diantipyryne methane solution (0-25ml), develop color for 20 minutes, measure the absorbance, the results are shown in Figure 3. It can be seen from the figure that when the added color solution reaches the peak at about 10 mL, the absorbance reaches the highest. In order to ensure that the color solution is sufficient to undergo complexation with all the titanium in it, the dosage of diantipyrylmethane is selected as 12 mL.

Fig 3. Effect of the amount of color developing solution

Fig 4. Effect of color development time

3.4 Influence of color development time

According to the test method of 1.2.2, the absorbance was measured at different color development times. The results

are shown in Figure 4. It can be seen from the figure that as the color development time increases, the absorbance gradually increases, and the color development of diantipyryl methane and titanium The absorbance over 15min reaches the maximum and remains stable. In order

to ensure that the color reaction is completed, the color development time is set to 20min.

3.5 Selection of melting conditions

In view of the characteristics of cement belonging to the silicate system, this paper selects 5 kinds of digestion

systems, including HNO₃-HF、HNO₃-HF-H₂O₂、HNO₃、HNO₃-H₂SO₄ and aqua regia. According to the conditions in Table 1, the four national standard materials of cement GBW03201, GBW03201c, GBW03207 and GBW03205 were subjected to microwave digestion test. The measurement results are shown in Table 2.

Table2. Comparison of determination results of titanium dioxide in different digestion systems

Digestion system	W _{TiO₂} /(%)			
	GBW03201 value (n=4)	GBW03201c value (n=4)	GBW03207 value (n=4)	GBW03205 value (n=4)
HNO ₃ -HF	0.25	0.20	0.48	0.36
HNO ₃ -HF-H ₂ O ₂	0.26	0.21	0.50	0.38
HNO ₃	0.23	0.16	0.45	0.33
HNO ₃ -H ₂ SO ₄	0.24	0.19	0.49	0.35
Aqua regia	0.25	0.19	0.48	0.36
Recommended value	0.27	0.21	0.51	0.39

It can be seen from the table that under the two digestion conditions of HNO₃ and aqua regia, the sample still has a small amount of precipitation. Due to the high content of silicon in the cement and incomplete decomposition, the measured value is low; HNO₃-H₂SO₄ is also the recommended value of the standard material. Some deviations may be due to the high boiling point of H₂SO₄ and incomplete sample digestion. If the temperature of the microwave digestion apparatus is set too high and the pressure is too high, it is not advisable from the aspects of damage to the instrument and experimental safety; The added H₂O₂ can effectively remove the organic matter in the sample. This paper chooses the HNO₃-HF-H₂O₂ mixed acid decomposition system to dissolve ore.

3.6 Accuracy and precision

GBW03201, GBW03201c, GBW03207 and GBW03205 were tested in parallel six times to investigate the accuracy and precision of the method. The results are shown in Table 3. From the results in the table, it can be seen that the measured value of this method is basically consistent with the standard value. The absolute value of the logarithmic error $\Delta \lg C$ between the average and the standard value is within 0.018, and the relative standard deviation (RSD) of the sample analysis is 1.07%-4.52 %, the method has high precision and repeatability, the absolute value of the relative error is less than 4.00%, the method has good accuracy.

Table3. Method accuracy and precision

Number	W _{TiO₂} /(%)		Recommended value (%)	Relative error (%)	RSD%	$\Delta \lg C$
	measured value (n=6)	average value				
GBW03201	0.26 0.27 0.25 0.24 0.27 0.26	0.26	0.27	-3.70	4.52	-0.018
GBW03201c	0.21 0.20 0.22 0.21 0.20 0.20	0.21	0.21	0.00	3.95	-0.016
GBW03207	0.50 0.50 0.52 0.50 0.50 0.50	0.50	0.51	-1.96	1.62	-0.0036
GBW03205	0.38 0.38 0.39 0.38 0.38 0.38	0.38	0.39	-2.56	1.07	-0.011

3.7 Method plus standard recovery test

The ordinary Portland cement national standard materials GBW03201, GBW03201c, GBW03207 and GBW03205 were quickly dissolved by microwave digestion with HNO₃-HF-H₂O₂ according to 1.2.1 sample pretreatment method. Each standard substance was treated with three solutions (each 0.2g in a 100ml volumetric flask), one of which was used to measure the original background value,

and the other two were added with an appropriate amount of titanium dioxide standard solution according to the gradient before dissolving the sample, according to 1.2. The test method of 2 develops color, determines the absorbance, calculates the titanium content according to the working curve, and then obtains the corresponding titanium dioxide content, and calculates the recovery rate. The results are shown in Table 4. The results of the standard addition recovery test show that the standard addition recovery rate of the test sample is between

91.8%-108.0%, indicating that the method has good accuracy.

Table4. Standard recovery test

Number	W _{TiO2} /(μg)			Recovery rate %	W _{TiO2} /(μg)		Recovery rate %
	Background value	Scalar	measured value		Scalar	measured value	
GBW03201	520.0	250.0	790.1	108.0	500.0	1030.2	102.0
GBW03201c	420.0	250.0	660.2	96.1	500.0	956.2	107.2
GBW03207	1000.0	250.0	1232.4	93.0	500.0	1538.5	107.7
GBW03205	760.1	250.0	1026.2	106.4	500.0	1219.2	91.8

3.8 Sample analysis

Use the established method-microwave digestion spectrophotometry to analyze the titanium dioxide content of cement samples produced in a certain place in Sichuan, and compare it with the national standard method GB/T176-2017[14] that uses conventional digestion, and use the t-test method[15] to determine the two Whether there are significant differences between these methods, the results are shown in Table 5. It can be seen from the table that the relative standard deviation RSD of the two

methods of microwave digestion spectrophotometry and the national standard conventional digestion method to determine the content of titanium dioxide (μg.g⁻¹) are less than 1.54% and 3.65%, respectively, with good repeatability and Precision: The t-test method judges the two sets of data obtained by two methods for each sample. After calculation, all $t < t_{0.05,6} = 2.45$ (confidence is 95%, degree of freedom $f = 6$) [15] It shows that there is no significant difference between the newly established microwave digestion method and the conventional digestion national standard method, and the measurement results of the two methods are in good agreement.

Table5. Comparison of the results of microwave digestion and conventional digestion methods

Number	Microwave digestion W _{TiO2} /(μg.g ⁻¹)			National standard conventional digestion method W _{TiO2} /(μg.g ⁻¹)			t value
	Sub-measured value	average value	RSD%	Sub-measured value	average value	RSD%	
2020LSTY001	10345 10287 10321 10322	10318.8	0.23	10235 10487 10421 10122	10316.2	1.63	0.03
2020LSTY002	2093 2056 2105 2047	2075.2	1.35	2176 2089 2054 2049	2092.0	2.81	0.51
2020LSTY003	5234 5300 5268 5200	5250.5	0.82	5134 5323 5234 5229	5230.0	1.48	0.46
2020LSTY004	4560 4457 4565 4509	4522.8	1.12	4456 4628 4657 4530	4567.8	2.02	0.85
2020LSTY005	760 746 762 770	759.5	1.31	756 780 749 768	763.2	1.79	0.44
2020LSTY006	562 556 560 550	557.0	0.95	545 556 550 552	550.8	0.83	1.79
2020LSTY007	15200 15300 15668 15200	15342.0	1.45	14734 15023 15234 15029	15005	1.37	2.22

2020LSTY008	10211 9987 10123 10068	10097.2	0.93	10867 10278 10189 10297	10407.8	2.98	1.92
2020LSTY009	444 459 448 456	451.8	1.54	430 432 458 421	435.2	3.65	1.90
2020LSTY010	844 829 818 826	829.2	1.31	810 850 801 802	815.8	2.84	1.05

4 Conclusion

Microwave digestion and dissolution technology is used to pre-treat ordinary Portland cement to provide work efficiency. The established method test results are accurate, fast, and precise. Compared with the traditional electric heating plate digestion method, the two methods have no significant difference. The established method provides a new way for the rapid and accurate detection of TiO₂ in cement.

References

1. Dai Jinhui, Ge Zhaoming. The concept of inorganic non-metallic materials [M]. Harbin: Harbin Institute of Technology Press, 2004.
2. Xia Hui, Dang Xianmin, et al. Determination of titanium dioxide in wheat flour by microwave digestion-ultraviolet spectrophotometry[J]. Cereals and Food Industries, 2015, 22(6): 88-90.
3. Luo Haiying, Guo Xindong, Ye Jiarong, et al. Determination of titanium in food by microwave digestion-inductively coupled plasma atomic emission spectrometry[J]. Food Science, 2008, 29(3): 409-412.
4. Sun Baolian, Zhang Xiaoyan, Li Bo. Determination of trace titanium in alloy steel, copper alloy and aluminum alloy by graphite furnace atomic absorption method[J]. Rare Metal Materials and Engineering, 2003, 32(01): 76-79.
5. Wang Mohui, Lang Chunyan. Analysis of complex matter[M]. Chengdu: University of Electronic Science and Technology Press, 2002.
6. Compilation Group of Rock and Mineral Analysis. Rock and Mineral Analysis (Volume 1) [M]. Beijing: Geological Publishing House, 1991.
7. Li Zhiwei, Tai Zi'an, Ren Wenyan, Gao Zhijun, Li Yanhua. Determination of rare rare earth elements in black shale by microwave digestion inductively coupled plasma mass spectrometry[J]. Rock and Mineral Testing, 2010, 29(3): 259-262.
8. Yang Fucheng, Pei Wen. Microwave Digestion-Dual Channel Atomic Fluorescence Spectrometry Simultaneous Determination of Mercury and Arsenic in Blood[J]. Chinese Journal of Industrial Medicine, 2008, 21(3): 196-198.
9. Ma Li, Si Han. Simultaneous determination of heavy metal elements and rare earth elements in soil by microwave digestion of samples-inductively coupled plasma mass spectrometry[J]. Guide to Environmental Science, 2016, 35(02): 88-91.
10. Chen Yan, Nie Jihua, Zheng Shuanglai. Microwave digestion of diluted nitric acid assisted analysis of 5 elements in soil[J]. Chinese Journal of Health Inspection, 2016, 26(11): 1548-1551.
11. Baogui Rong, Zhao Yuying, Zheng Qingfu, Song Juanjuan, Zhou Hong. Simultaneous determination of 13 elements in tartary buckwheat leaves by microwave digestion-inductively coupled plasma atomic emission spectrometry[J]. Chinese Inorganic Analytical Chemistry, 2015, 5(04) : 88-90.
12. Zeng Y B, Xu H P, Liu H T, et al. Application of artificial neural networks in multifactor optimization of an on-line microwave FIA system for catalytic kinetic determination of Ruthenium (III) [J]. Talanta, 2001, 54(4): 603— 609.
13. Djingova R, Heidenreich H , Kovacheva P, et al . On the determination of platinum group elements in environmental materials by Inductively Coupled Plasma Mass Spectrometry and microwave digestion[J]. Anal. Chim. Acta, 2003, 489(2): 245-251.
14. GB/T 176-2017 Cement chemical analysis method [S]
15. Wuhan University. Analytical Chemistry [M]. Beijing: Higher Education Press, 2006.