

Application of Flame Atomic Absorption Spectrophotometry to Detect Metal Elements in Land Engineering

Qing Liu^{1,*}, Simin Feng¹

¹Shaanxi Provincial Land Engineering Construction Group Co., Ltd. Institute of Land Engineering and Technology, Shaanxi Provincial Land Engineering Construction Group Co., Ltd. Key Laboratory of Degraded and Unused Land Consolidation Engineering, the Ministry of Natural Resources Shaanxi Provincial Land Consolidation Engineering Technology Research Center, Shaanxi, Xi'an, 710075, China

Abstract

In this paper, the detection limit, precision and accuracy of the method for the determination of potassium, sodium and iron in water by flame atomic absorption Spectrophotometer were verified, the feasibility of determination of potassium, sodium and iron in water by flame atomic absorption spectrophotometer was discussed. The results showed that Flame atomic absorption spectrophotometry for the determination of potassium, sodium and iron in water had a linear relationship in the concentration range of 0~500μg/L, and the correlation coefficients are all above 0.999, and the correlation coefficients were all above 0.999, the detection limits were 0.02 mg/L, 0.01 mg/L, 0.03 mg/L, respectively, and the lower limits were 0.08 mg/L, 0.04mg/L, 0.12 mg/L, respectively, the results of accuracy and precision meet the requirements of water quality, potassium and sodium determination, flame atomic absorption Spectrophotometer (GB 11904-1989) and water quality determination of iron and Manganese, flame atomic absorption Spectrophotometer (GB 11911-1989), therefore, the two methods both meet the requirements of the laboratory.

Keywords

Flame Atomic Absorption spectrophotometer; Method validation; Detection limit.

1. Introduction

The standard method refers to the technical specification document released to the public after evaluation and confirmation by a recognized institution, which is the main basis for the laboratory to implement inspection and testing work [1, 2]. The "Laboratory Qualification Evaluation Criteria" stipulates: "The laboratory should confirm whether the selected new method can be used correctly" [3], that is, the laboratory needs to verify the laboratory's technical ability to use the standard method before using the standard method for testing Whether it meets the requirements of the standard. At present, the use of atomic absorption spectrometer method to measure metal elements has been widely used in laboratory testing [4-9,14-17], Yang Hui [4] the applicability of flame atomic absorption spectrophotometry for the determination of total chromium in water To verify, Wang Dongli et al. [5] used flame atomic absorption spectrometry to determine the content of gold in gold ore. In order to meet the needs of testing work and ensure the accuracy and effectiveness of laboratory testing methods, this article meets the requirements of "Water Quality Determination of Potassium and Sodium by Flame Atomic Absorption Spectrophotometry" (GB 11904- 1989) and the "Water Quality Determination of Iron and Manganese by Flame Atomic Absorption Spectrophotometry" (GB 11911-1989) to verify the technical requirements to ensure the applicability of the method in the analysis work of this laboratory, thereby ensuring the accuracy of the test data.

2. Experimental Method

2.1. Main Instruments and Reagent Consumables

Atomic spectroscopy methods usually include atomic absorption spectrometry (AAS), atomic emission spectrometry (AES), atomic fluorescence analysis (AFS) and atomic mass spectrometry (AMS) [10]. This article uses ZEE nit 700P atomic absorption spectrometer. The spectrometer uses atomic absorption spectrometry in atomic spectroscopy to detect metal elements. The ZEE nit 700P atomic absorption spectrometer is the latest flame-graphite furnace combined atomic absorption spectrometer launched by the German Jena Analytical Instruments Co., Ltd. [11]. This instrument contains almost all the advanced technologies of the existing similar instruments, such as "transverse heating graphite furnace", "Three magnetic field Zeeman and deuterium hollow cathode lamp background", "direct solid injection" and other new technologies, is an instrument that detects the content of corresponding elements based on the analytical method based on the absorption of the characteristic spectral lines of the ground state atoms to be measured [12], about 70 kinds of elements can be measured, and the measurement accuracy can reach 1% RSD [11]. The sample pretreatment is relatively simple, and the operation and data processing of the instrument are also relatively simple. It is widely used in geology, water conservancy, chemical industry, Research and production in medical and environmental protection disciplines [13].

Other auxiliary equipment needed for the experiment: one-ten-thousandth balance BSA224S-CW, one-hundredth balance BSA2202S-CW, Milli-Q ultrapure water treatment system, etc.

Reagents and consumables: concentrated nitric acid (superior grade pure by Sinopharm Chemical Reagent Co., Ltd.), concentrated hydrochloric acid (superior grade pure by Sinopharm Chemical Reagent Co., Ltd.), cesium nitrate (analytical pure by Hepeng (Shanghai) Biotechnology Co., Ltd.), potassium solution in water Standard material GBW (E) 082776, standard material of sodium solution in water GBW (E) 082775, standard material of iron solution in water GBW (E) 083185.

2.2. Sample Preparation

Potassium and sodium element test solution preparation: if the concentration of potassium and sodium in the sample is generally known, it can be sampled directly, or the concentration range can be obtained by sub-sensitivity line measurement, and then a certain amount (usually 2-10 mL) Add 3.0 mL of cesium nitrate solution to the sample in a 50 mL volumetric flask, dilute to the mark with water, and shake well.

Preparation of the test solution of iron element: Mix the sample into a beaker, add 5 mL of nitric acid for every 100 mL of water sample, place it on a hot plate and steam the sample to near dryness under near boiling state, and then add nitric acid after cooling to repeat the above Step once, until the digestion is complete, add 1 mL of calcium chloride solution, and dilute to the mark with hydrochloric acid solution. At the same time, use pure water to do a blank experiment, and use the same procedure to determine the blank.

2.3. Preparation of the Instrument

Install the element lamp to be tested on the lamp holder, after preheating and stabilizing, perform ignition measurement according to the selected wavelength, lamp current, slit, observation height, air and acetylene flow and other parameters. After ignition, spray nitric acid solution for 5 min before measurement to clean the atomization system.

2.4. Drawing of Calibration Curve

The configuration concentrations are respectively 0, 1.00, 2.00, 3.00, 4.00 mg/L potassium standard curve, 0, 0.20, 0.60, 1.00, 1.50, 2.00 mg/L sodium standard curve, 0, 0.50, 1.00, 2.00,

3.00, 4.00 mg /L iron standard curve, draw the calibration curve of the absorbance of potassium, sodium and iron calibration solution and the corresponding concentration.

3. Result Analysis

3.1. Linear Range of the Method

Draw a standard curve with the measured signal intensity as the ordinate and the concentration (mg/L) as the abscissa. Draw a standard curve for potassium, sodium, and iron, and the correlation coefficients are shown in Table 1.

The correlation coefficients of the standard curve for the determination of potassium, sodium and iron in water quality by flame atomic absorption spectrophotometry are 0.999, 0.999, and 0.999, respectively, which meet the requirements of "Water Quality Determination of Potassium and Sodium by Flame Atomic Absorption Spectrophotometry GB 11904-1989" and "Water Quality Iron, Determination of manganese flame atomic absorption spectrophotometry GB 11911-1989" correlation coefficient greater than or equal to 0.999 requirements.

Table 1. Status of standard curve fitting

element	Standard curve concentration point (mg/L)	Calibration curve equation	Correlation coefficient	The method requirements	Whether it meets the method requirements
K	0,1.0,2.0,3.0,4.0	$y=(0.1222+0.9489x)/(1+0.5873x)$	0.999		
Na	0,0.2,0.6,1.1,5.2	$y=0.0580+1.15560x-0.2421x^2$	0.999	≥ 0.999	Meet the standard requirements
Fe	0,0.5,1.0,2.0,3.0,4.0	$y=-0.0025+0.1627x-0.0075x^2$	0.999		

3.2. The Detection Limit and the Lower Detection Limit of the Method

According to the "Technical Guidelines for the Preparation and Revision of Environmental Monitoring and Analysis Methods Standards" (HJ 168-2010 relevant regulations [18-23]. Measure according to all the steps of sample analysis, and for samples with a concentration content of 2-5 times the detection limit of the estimated method Carry out 7 parallel determinations, calculate the standard deviation of the 7 parallel determinations, and calculate the detection limit according to formula 1. See Table 2 for the summary of data.

$$MDL=t(n-1,0.99)\times S \quad (1)$$

Where: MDL—method detection limit;

n—the number of parallel determinations of the sample;

t—t distribution (one-sided) with a degree of freedom of n-1 and a confidence of 99%;

S—The standard deviation of n parallel determinations.

Among them, when the degree of freedom is 6, the t value with a confidence of 99% is 3.143. The detection limits of potassium, sodium, and iron in water by flame atomic absorption spectrophotometry were 0.02 mg/L, 0.01 mg/L, and 0.03 mg/L, respectively, and the lower detection limits were 0.08 mg/L, 0.04 mg/L, 0.12 mg/L, all meet the requirements of "Water Quality Determination of Potassium and Sodium by Flame Atomic Absorption Spectrophotometry GB 11904-1989" (detection limit: potassium 0.05 mg/L, sodium 0.01 mg/L, lower detection limit: potassium 0.20 mg /L, sodium 0.04 mg/L) and "Water Quality-Determination of Iron and Manganese by Flame Atomic Absorption Spectrophotometry GB 11911-1989" (detection limit 0.03 mg/L, determination lower limit 0.12 mg/L) for corresponding element detection The detection limit is required.

Table 2. Test data table of detection limit and determination lower limit

Parallel sample number		Sample		
		K	Na	Fe
The measurement results (mg/L)	1	0.336	0.171	0.334
	2	0.328	0.168	0.333
	3	0.334	0.167	0.338
	4	0.335	0.167	0.352
	5	0.326	0.168	0.344
	6	0.330	0.167	0.334
	7	0.331	0.165	0.336
average value $\bar{x}$ (mg/L)		0.33	0.17	0.34
standard deviations (mg/L)		0.004	0.002	0.007
t		3.143	3.143	3.143
The detection limit (mg/L)		0.02	0.01	0.03
Lower limit of determination (mg/L)		0.08	0.04	0.12

3.3. Verification of Method Precision

The laboratory added the corresponding element standard solutions to the water samples of the 3 content levels, and measured them according to all the steps of the sample analysis. Each sample was measured in parallel 6 times. The data summary table is shown in Table 3. Calculate the average value, standard deviation, relative standard deviation and other parameters of different samples.

Table 3. Precision test data

Parallel sample number	The measurement results (mg/L)						average value (mg/L)	standard deviation (mg/L)	The relative standard deviation RSD (%)	
	1	2	3	4	5	6				
K	1	1.494	1.498	1.502	1.503	1.506	1.51	1.5	0.006	0.38
	2	2.072	2.077	2.089	2.089	2.09	2.101	2.09	0.01	0.50
	3	2.886	2.864	2.866	2.862	2.857	2.884	2.87	0.012	0.42
Sample Na	1	0.251	0.246	0.246	0.25	0.249	0.248	0.25	0.002	0.82
	2	0.939	0.948	0.945	0.93	0.956	0.939	0.94	0.009	0.93
	3	1.772	1.756	1.785	1.741	1.777	1.777	1.77	0.016	0.93
Fe	1	0.763	0.762	0.762	0.764	0.754	0.753	0.76	0.005	0.62
	2	1.522	1.524	1.508	1.513	1.51	1.522	1.52	0.007	0.46
	3	4.868	4.838	4.784	4.822	4.776	4.776	4.81	0.038	0.79

For three actual samples with potassium content levels of 1.50 mg/L, 2.00 mg/L, and 3.00 mg/L, the relative standard deviations were 0.38%, 0.50%, and 0.42%, respectively. For three actual samples with sodium content levels of 0.25 mg/L, 1.00 mg/L, and 2.00 mg/L, the relative standard deviations were 0.82%, 0.93%, and 0.93%, respectively. For three actual samples with iron content levels of 1.00 mg/L, 1.50 mg/L, and 5.00 mg/L, the relative standard deviations were 0.62%, 0.46%, and 0.79%, respectively. y All above meet the requirements of "Water Quality Determination of Potassium and Sodium by Flame Atomic Absorption Spectrophotometry GB 11904-1989" (relative standard deviation of potassium 0.50%, sodium 1.52%) and "Water Quality Determination of Iron and Manganese by Flame Atomic Absorption

Spectrophotometry GB 11904-1989" 11911-1989" (relative standard deviation: 1.00%) requirements for the detection precision of corresponding elements.

3.4. Verification of Method Accuracy

The laboratory uses the actual sample spiked to determine the accuracy of the determination [21, 22]. The actual sample water samples of 3 content levels were spiked and measured, and the measurement was carried out according to all the steps of sample analysis. Each sample was measured in parallel 6 times. The data summary table is shown in Table 4. Calculate the average value of the spiked samples at different concentrations, the spike recovery rate and other parameters.

Table 4. Labeled test data of real samples

sample number			K			Na			Fe		
			1	2	3	1	2	3	1	2	3
The measurement results (mg/kg)	1	Before	0.328	0.505	1.538	0.168	0.251	0.843	1.522	2.786	4.65
		After	0.708	0.81	2.106	0.985	1.384	1.645	1.97	3.732	5.602
	2	Before	0.334	0.507	1.529	0.167	0.246	0.839	1.524	2.788	4.644
		After	0.714	0.806	2.09	0.99	1.37	1.674	1.961	3.7	5.636
	3	Before	0.335	0.496	1.503	0.167	0.246	0.83	1.508	2.782	4.62
		After	0.711	0.811	2.077	0.972	1.355	1.663	1.959	3.72	5.674
	4	Before	0.326	0.502	1.494	0.168	0.25	0.839	1.513	2.788	4.552
		After	0.709	0.805	2.101	0.978	1.342	1.665	1.997	3.676	5.652
	5	Before	0.33	0.499	1.472	0.167	0.249	0.831	1.51	2.83	4.586
		After	0.685	0.8	2.067	0.99	1.366	1.667	1.981	3.682	5.546
	6	Before	0.331	0.503	1.444	0.165	0.248	0.831	1.522	2.812	4.598
		After	0.703	0.802	2.036	1.001	1.362	1.643	1.967	3.678	5.512
	average value	Before	Before	0.5	1.5	0.17	0.25	0.84	1.52	2.8	4.61
		After	After	0.81	2.08	0.99	1.36	1.66	1.97	3.7	5.6
	Detection spike		0.0146	0.019	0.027	0.042	0.0695	0.043	4.25	8.2	10.58
	Target scalar		0.015	0.02	0.026	0.04	0.07	0.045	4.20	8.0	11.0
	Standard recovery rate (%)		97.47	94.81	102.81	104.84	99.32	95.24	101.2	102.5	96.2

Three actual samples with concentration levels of 0.33mg/L, 0.50mg/L, and 1.50mg/L were spiked with flame atomic absorption spectrophotometry. The spiked amounts were 0.015mg, 0.020mg, and 0.026mg, respectively. The standard recovery rates were 97.47%, 94.81%, and 102.81%. Three actual samples with concentration levels of 0.17mg/L, 0.25mg/L, 0.84mg/L were spiked with flame atomic absorption spectrophotometry. The spiked amounts were 0.040mg, 0.070mg, and 0.045mg, respectively. The standard recovery rates were 104.84%, 99.32%, and 95.24%. The recovery rate of standard addition meets "Determination of potassium and sodium in water quality by flame atomic absorption spectrophotometry GB 11904-1989" (recovery rate of addition: potassium 99.60% ± 5.36%; sodium 100.13% ± 5.08%) and "Water quality iron and manganese The accuracy requirements in the determination of flame atomic absorption spectrophotometry GB 11911-1989 (with standard addition recovery rate of 93.3%-102.5%).

4. Conclusion

The laboratory verifies the linear relationship, detection limit, precision, and accuracy of the flame atomic absorption spectrophotometric method for determining potassium, sodium, and iron in water quality. Among them, the linear relationship of potassium, sodium, and iron is

good and relevant. The coefficients are all > 0.999 , the detection limits are 0.02mg/L, 0.01mg/L, 0.03mg/L, and the lower determination limits are 0.08mg/L, 0.04mg/L, 0.12mg/L, respectively for 3 content levels. The samples were tested for precision, and the relative standard deviations all met the precision requirements of the standard method. The actual sample water samples with 3 content levels were spiked and determined, and the spiked recovery rates all met the accuracy requirements of the standard method. As mentioned, the laboratory verifies the determination of potassium, sodium, and iron in water by flame atomic absorption spectrophotometry, and its linear relationship, detection limit, accuracy and precision are in compliance with the "Determination of Potassium and Sodium in Water Quality by Flame Atomic Absorption" Spectrophotometric method GB 11904-1989" and "Water quality-Determination of iron and manganese, flame atomic absorption spectrophotometry GB 11911-1989" method requirements. Therefore, it is feasible in our laboratory to detect potassium, sodium, and iron in water by atomic absorption flame spectrometer.

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