KI-MIBK extraction flame atomic absorption spectrophotometry for determination of cadmium in soil of Jining area

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Abstract. The collected soil samples of Jining area were subjected to microwave digestion (HNO₃ + HF + H₂O₂), and the absorbance of the organic phase MIBK was determined by flame atomic absorption spectrophotometry after extraction with KI-MIBK. Results According to the measured results, within 20 meters, the content of cadmium increased gradually with increasing distance, and gradually decreased with increasing distance after 20 meters. The content of cadmium in the soil shows a clear change trend due to the distance from the source of pollution. Based on this change, favorable conditions suitable for crop growth can be created.

1. Introduction
It can provide some references for the determination of total flavonoids in other fruits. As we all know, soil is both a precious resource of nature and a constituent element of the natural environment [1]. When the natural environment is contaminated by cadmium, cadmium enrichment will occur in the body, and then enter the human body through the food chain, causing chronic human poisoning. Therefore, the pollution of soil by heavy metal cadmium poses a serious threat to human health to a certain extent. Common methods for detecting cadmium in soil at home and abroad include graphite furnace atomic absorption spectrophotometry [2], hydride generation-atomic fluorescence spectrometry [3], inductively coupled plasma spectrometry [4], and so on. Flame atomic absorption spectrophotometry has high sensitivity to cadmium, has the advantages of simple operation and good reproducibility, so it is widely used.

2. Experimental

2.1. Reagents
HNO₃, HCl, HF, H₂O₂, methyl isobutyl ketone water saturated solution, cadmium standard solution(1.000mg / ml, Tianjin Guangfu Fine Chemical Industry Research Institute), ionized water.

2.2. Instruments and equipment
Atomic absorption spectrophotometer (TAS-990 Beijing General Analysis General Instrument Co., Ltd.); microwave digestion instrument (XH-800C Beijing Xiangye Technology Development Co., Ltd.); 50ml colorimetric tube, 50ml separation funnel (the above are all Tianjin glass Instrument Factory).
2.3. Operation method

Sample preparation: Pass the collected soil sample through a 40pm nylon sieve. Carefully reduce the sieve to about 100g by the quarter method, carefully grind it until it all passes through the 100pm nylon sieve, mix well and place it in a cool place for later use [5]. Samples are numbered 1, 2, 3, 4, 5, 6, and 7, respectively. Accurately weigh 0.25g of the sample in a microwave digestion tank, wet it with a little water, add 2.5ml HNO₃, 1.5ml HF, 0.5ml H₂O₂, and perform microwave digestion according to the heating program (see Table 1). Wait for the digestion to complete and transfer to 50ml Cool in the colorimetric tube. After cooling, perform constant volume operation, place it in a cool place after shaking evenly. First add 1.0ml ascorbic acid aqueous solution and 1.25ml KI solution to the colorimetric tube and shake well. Then add 2.5ml methyl isobutyl ketone water saturated solution accurately, shake for 1 minute, and let the organic phase stand for layering.

Standard curve: First add the standard cadmium use solution to the 50ml colorimetric tube, then add 0.5ml hydrochloric acid solution (1 + 1), add water to 25ml and measure the standards in order from low to high concentration solution absorbance. After the measurement, a standard curve was drawn by subtracting the absorbance of the blank and the corresponding cadmium content.

Stability test: Take a 25mL colorimetric tube, measure 0.1mL of the treated soil sample and place it in it, and then measure the absorbance values for 10, 20, 30, 40, and 60 minutes in order, and calculate the absorbance.

3. Results and discussion

3.1. Optimization of conditions

Selection of HNO₃, HF and H₂O₂ dosage: The purpose of using concentrated nitric acid is to acidify the digested substances; hydrofluoric acid has a strong complexing effect; hydrogen peroxide in it mainly plays the role of oxidative decolorization. Select the darkest soil sample for testing. According to the experimental results, it can be seen that the digested sample is incompletely digested before the maximum absorbance value appears. The test solution is yellow and has residue. Under the condition of No. 6 (HNO₃ 2.5ml, HF 1.5ml, H₂O₂ 0.5ml), It was seen that the test solution was clear and transparent, and the absorbance value reached the maximum. It can be seen from Fig. 1 that with the gradual increase in the amount of HNO₃, HF, and H₂O₂, the measured absorbance of cadmium also gradually increases. Therefore, the amount of HNO₃, HF and H₂O₂ under this condition was selected for the determination of other samples.

| Table 1. HNO₃, HF and H₂O₂ dosage |
|-----------------------------------|
|                                   | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   |
| HNO₃/ml                           | 1.5 | 1.5 | 2.0 | 2.0 | 2.5 | 2.5 | 3.0 | 3.0 |
| HF/ml                             | 0.5 | 0.5 | 1.0 | 1.0 | 1.5 | 1.5 | 2.0 | 2.0 |
| H₂O₂/ml                           | 0.0 | 0.5 | 0.0 | 0.5 | 0.0 | 0.5 | 0.0 | 0.5 |
| A                                 | 0.103 | 0.157 | 0.173 | 0.216 | 0.221 | 0.243 | 0.223 | 0.242 |

Figure 1. Absorbance at different HNO₃, HF and H₂O₂ dosages
Selection of ascorbic acid and KI dosage: Ascorbic acid can play a reducing role, while KI plays a complexing role. The amount of the two will determine the degree of reduction of cadmium, so it will affect the accuracy of the measurement results. One of the samples was randomly selected and tested under different dosage Element's absorbance value. It can be seen from Figure 2 that with the changes in the amount of ascorbic acid and KI added, the absorbance value of this element is gradually increasing, and it reaches the maximum under condition 6 (ascorbic acid 2ml, KI 2.5ml). Therefore, the amount used under this condition is selected for the determination of other samples.

### Table 2. Ascorbic acid and KI dosage

|    | 1   | 2   | 3   | 4   | 5   | 6   | 7   |
|----|-----|-----|-----|-----|-----|-----|-----|
| ascorbic acid /ml | 1   | 1.5 | 1   | 2   | 2.5 | 2   | 3   |
| KI/ml         | 1.5 | 1   | 2   | 1   | 2   | 2.5 | 2.5 |
| A             | 0.135 | 0.158 | 0.196 | 0.207 | 0.218 | 0.229 | 0.203 |

**Figure 2.** Absorbance at different ascorbic acid and KI dosages

#### 3.2. Inspection of sensitivity

According to the standard curve in the figure below, find the regression equation $Y = 1.9891X + 0.171$. The correlation coefficient is 0.9982, and the results show that the method has a good linear relationship. Repeat the determination of the prepared blank solution 11 times. The calculation formula of the detection limit is $LD = 3SA / k$ [6]. The detection limit of cadmium in this experiment is 0.014mg / l. The detection limit is close to that of GB-T-17140-1997 for the determination of lead and cadmium in soil quality. The detection limit measured using the same method has higher sensitivity, but this method is simpler than the national standard method, which explains this method. After improvement, it can be better applied to the determination of trace cadmium content.
Figure 3. Rutin standard curve

Calculate the cadmium content in the soil according to the standard curve. The calculation formula is:

Table 3. Cadmium in soil

| Distance (m) | Cd (mg/l) |
|--------------|-----------|
| 1 (5m)       | 0.0360    |
| 2 (10m)      | 0.1133    |
| 3 (15m)      | 0.1978    |
| 4 (20m)      | 0.2145    |
| 5 (25m)      | 0.1833    |
| 6 (30m)      | 0.1468    |
| 7 (35m)      | 0.0216    |

According to the data in Table 4, it can be seen that in the distance within 20 meters, the cadmium content increases with distance, and gradually decreases after 20 meters. The reason may be that there is a reed sway around the soil collection site, and the reed has a certain absorption and enrichment effect on cadmium [7], so the cadmium content in the soil begins to decrease after 20 meters.

3.3. Stability investigation
The deviation of the absorbance values measured under different standing times is between 0.002 and 0.003, and the relative standard deviation conforms to the range of relative standard deviation specified in the determination of lead and cadmium in soil quality GB-T-17140-1997, which fully explains the stability of this method is good.

4. Conclusion
When using this method to determine cadmium in soil, the regression equation obtained is $Y = 1.9891X + 0.171$, and the correlation coefficient is 0.9982, which has a good linear relationship, good stability, and high sensitivity. This method is relatively simple and fast. The sample can be directly measured after digestion and extraction. Microwave digestion has the advantages of high efficiency, tightness, light pollution, low background, and safety[8]. can be used for the determination of low levels of cadmium in soil. The content of cadmium in the soil measured by this method is within 20 meters, which gradually increases with increasing distance, and after 20 meters, the content of cadmium gradually decreases with increasing distance. The reason may be that there is a reed swing at 17 meters where the sample is collected. The reed has a certain enrichment and absorption of cadmium, so the cadmium content in the soil begins to decrease after 20 meters. To sum up: when carrying out agricultural planting activities, first choose to stay away from factories that have pollutant emissions; secondly, plant plants that absorb cadmium, such as reeds, holly, poplar, and gramineous plants, near the pollution source. This can effectively reduce the pollution of cadmium, and can provide favorable conditions for the growth of crops.
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References
[1] Li Weihao, Han Yonghong, Dong Junxing, etc. Investigation on the content of heavy metals in the soil of five counties in Handan City [J]. Medical Animal Control. 2016.32 (10): 1155-1157.
[2] Liu Xina, Leng Jiafeng, Deng Baojun. Determination of cadmium in soil by graphite furnace atomic absorption spectrophotometry [J]. Chemical Analysis Metrology. 2002.11 (5): 26-27.
[3] Wu Cheng. Determination of cadmium in soil by hydride generation-atomic fluorescence spectrometry [J]. Spectroscopy and Spectral Analysis. 2003.23 (5): 990-992.
[4] Dong Guibin, Wang Yulan, Zhao Shuo. Determination of arsenic and cadmium in soil by aqua regia-inductively coupled plasma mass spectrometry [J]. Chemical Engineer. 2015.3: 39-41.
[5] Xiao Fan, Xu Chongying, Xing Gang, etc. Continuous determination of trace silver, cadmium and thorium in geochemical samples by potassium iodide-methyl isobutyl ketone extraction-flame atomic absorption spectrometry [J]. Rock Test. 2007. 26 (1): 67-70.
[6] Long Gahong, Wu Yinju, Xu Xiongfei, etc. Comparative study of different digestion methods for determination of soil heavy metal content [J]. Changsha Environmental Monitoring Center Station. 2013.29 (1): 123-126.
[7] Wei Benjie, Zeng Xiaoxi, Jiang Huiyun, etc. Accuracy analysis of cadmium detection by flame and graphite furnace atomic absorption spectrophotometry [J]. Journal of Hunan University of Technology. 2013.27 (1): 16-19.
[8] Lin Xiyan, Liu Yuxiang, Hu Gongren. Analysis and pollution assessment of soil cadmium in different functional areas of a city [J]. Non-ferrous Metals. 2010.62 (4): 130-132.