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Quantitative assessment on soil concentration of heavy metal–contaminated soil with various sample pretreatment techniques and detection methods

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Abstract Detection and quantification of heavy metals in soil samples are significant in terms of environmental monitoring and risk assessment for metals. In order to improve the accuracy and precision to detect heavy metal, in this study, four standard samples (NASS-4, NASS-5, NASS-9, and NASS-16) were analyzed by evolving heating (electric heating plate, water bath, and microwave) and acidic systems (includes HCl, HNO_3, HF, and $HClO_4$). The result shows that different pretreatment methods have different effects on the extraction of heavy metal elements and five heavy metal elements (Cu, Zn, Pb, Ni, and Cr) were selected for optimization through pretreatment methods. Although the contents of heavy metals were same but we found diversity in the results. Under optimal conditions, the selected standard samples were analyzed by inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), and atomic absorption spectroscopy (AAS), and the results were compared. The results show that different elements have their own most suitable detection methods, such as for Pb, the most suitable method is ICP-MS; and for Zn, the most suitable method is AAS. Pretreatment methods and detection techniques are combined to find and improve accuracy of results for certain elements. This study provides a reliable detection method for the accurate detection of heavy metals in the environment.

Keywords Heavy metal · Sample pretreatment · Determination method · Contamination assessment · Soil · Environmental pollution

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Introduction

On the path to socio-economy development where human beings have acquired so much benefits, there emerged serious environmental adversaries and impacts as well (Duan et al. 2016), such as soil heavy metal pollution, which may impose severe consequences to people's healthy. Heavy metal pollution in farmland has been receiving widespread attention from the

governments, scientists, and researchers in various countries for few years (Zhao et al. 2015; Li et al. 2014a, b; Tang et al. 2019). National Soil Pollution Survey of the Ministry of Land and Resources of China quoted in a bulletin on April 17, 2014, that the overall state of the soil environment in the country is not optimistic. Certain areas are seriously contaminated which is primarily the cause of concern for cultivated land. The national soil pollution exceedance rate is 16.1%. Other harmful substances such as cadmium (Cd), copper (Cu), lead (Pb), chromium (Cr), zinc (Zn), and nickel (Ni) (ref: US Environmental Protection Agency) also have exceedance rate of 7.0%, 2.1%, 1.5%, 1.1%, 0.9%, and 4.8%, respectively (State Environmental Protection Administration of China, 2014; Michael et al. 2010). Luo pointed out that China's farmland soil is heavily polluted by heavy metals, especially in the Yangtze River Delta and the Pearl River Delta (Zhao and Luo 2015); Li also demonstrated that the heavy metal pollution is spreading gradually in farmland area across the country (Li et al. 2014a, b). Before 2006, the ministry of environmental protection sampled 3.6×104 hm^2 heavy metals in the soil of 30×104 hm^2 basic farmland protection areas, and the excess rate of heavy metals reached 12.1% (Fu 2012). Wei conducted statistical analysis on the concentrations of Cr, Cu, Pb, Zn, Ni, and other elements in farmland soil of 8 cities in China, and found that most cities had higher soil background values than China (Wei and Yang 2010; Pu et al. 2018). In recent years, the soil pollution problem has enhanced to a certain extent; however, it cannot be overlooked (Zhang et al. 2015; Eshetu 2018).

To minimize the harm caused by pollution, precise sample testing methods are vital. The soil composition is extremely complicated, and it is very difficult to precisely determine the content of heavy metal elements in such a complex matrix (Ahmad et al. 2009). Each country has its own relevant testing standards. For example, foreign standards are mainly based on EPA standards, while the UK and Germany have ISO standards and formulate relevant national standards to follow. Each standard involves a lot of sample pretreatment methods (Tatiana et al. 2018; Lin et al. 2001; Yi et al. 2018; Alumaa et al. 2002; Bradl 2004; Chen et al. 2007; Huo et al. 2010; Hoang et al. 2020), such as heating methods (including water bath heating, electric hot plate heating, and microwave digestion) and digestion systems (including nitric acid, nitric acid-hydrofluoric acid, aqua regia). Elements of the identical content also display significant deviations in utilizing different detection methods. At present, the main methods used for the detection of heavy metal elements include ICP-MS (inductively coupled plasma mass spectrometry) (Lin et al. 2016; Rui et al. 2007; Wang et al. 2018), ICP-AES (inductively coupled plasma atomic emission spectroscopy) (Yu et al. 2020; Tangen et al. 2002), and AAS (atomic absorption spectroscopy) (Lin et al. 2017; Taghipour and Jalali 2020). Moreover, different pretreatment methods and detection methods may have some deviations even in the detection of standard soil samples. Therefore, to determine the content of heavy metals more accurately, this study aims to attempt three heating methods and eight digestion mentioned in some relevant standards. This work primarily comprises of three parts. First, four representative standard soil samples are selected. Secondly, pretreatment methods and detection methods are optimized to select the best pretreatment methods and detection methods for different elements. Finally, the optimized method was used to accurately determine the five heavy metal elements (Pb, Cr, Ni, Cu, Zn) and detect real samples (Fig. 1).

Materials and methods

Reagents and standards

Ultrapure water ($\rho = 18.25$ MΩ cm) was collected from a Millipore water purification system (Port Washington, NY, USA). The glass ware used in the experiment were washed with detergent, using a 1:1 excellently soaked in grade pure nitric acid for more than 24 h, followed by washing with ultrapure water. HCl, HNO_3, H_2SO_4, $HClO_4$, and HF were purchased from Sinopharm Chemical Reagent Co, Ltd. (Beijing, China). All other reagents were of analytical grade and used without further purification unless otherwise stated.

Standard samples GBW07404 (GSS-4), GBW07405 (GSS-5), GBW07423 (GSS-9), and GBW07430 (GSS-16) were purchased from Wuhan Zhongchang Guodian Bid Material Technology Co. Ltd. (Hubei, China).

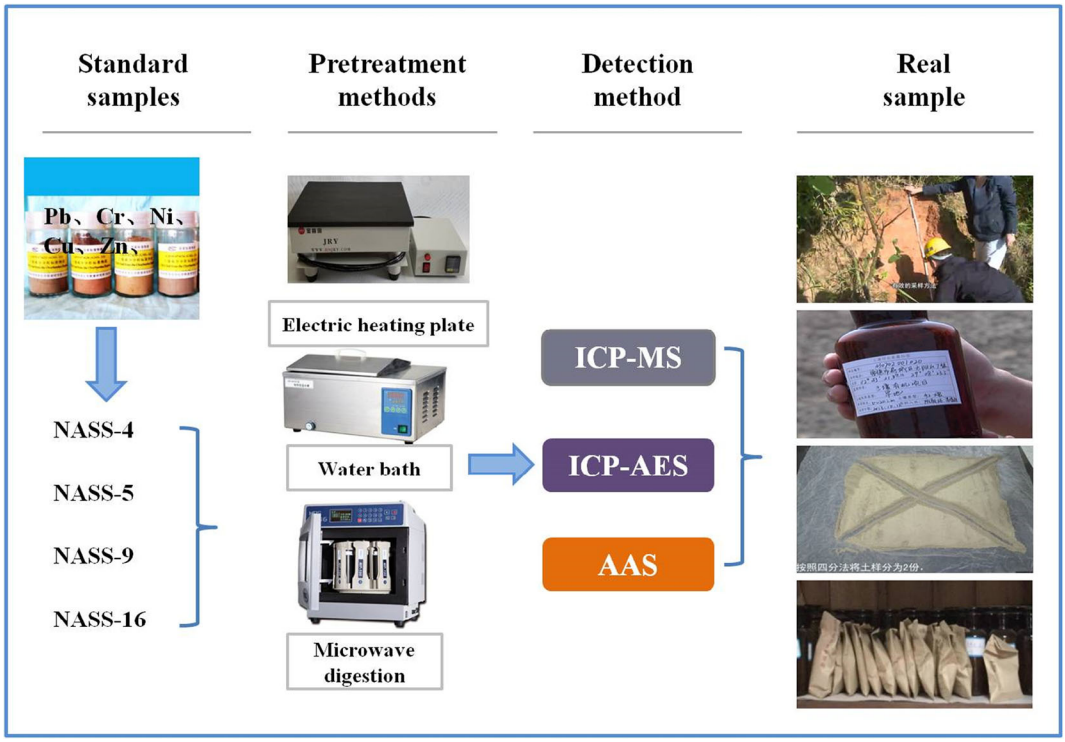

Fig. 1 The process diagram showing the process of analysis of different heavy metals

Instruments

ICP-MS (Type X-II, Thermo Fisher Scientific, USA); ICP-AES (Type 5100, Agilent technology co., Ltd., USA); AAS (Type Varian 240, Varian technologies (China) Co., Ltd., China); automatic microwave digestion instrument (ETHOS1, Maxton co., USA); temperature-controlled electric heating plate (JCY-X350, Hunan Jinrong garden Instrument equipment co., Ltd., China).

Sample pretreatment

The real samples were taken from Chenzhou and Zhuzhou, respectively, and sampling points may vary between surface samples or soil profiles. Generally, the topsoil is collected at a sampling depth of 0–20 cm. If necessary, it is better to select a profile sample. The specific sample pretreatment steps are as follows: firstly, the soil samples collected from the fields were transferred to the laboratory. Later, these samples were dried in dark place and filtered to remove stones, plant rhizomes, and any other substances. The samples were then crushed until passed through a 2-mm sieve and stored in polymer to avoid any contamination after being thoroughly mixed on the Teflon film. Finally, samples were discarded and weighed by the quartering method following their division into two parts after passing through a 1.00-mm nylon sieve. One part was set aside, and the other part was ground to pass through a nylon sieve with a pore size of 0.25 mm (60 meshes), which were discarded by the quartering method, and equipped with a bottle for next experiment (Table 1).

Table 1 Basic sample information

No.	Sample	Type	Source
1	GSS-4	Standard sample	Guang xi
2	GSS-5	Standard sample	Hu nan
3	GSS-9	Standard sample	Hongze lake
4	GSS-16	Standard sample	Zhujiang River
5	Sample 1	Real sample	Hu nan
6	Sample 2	Real sample	Hu nan
7	Sample 3	Real sample	Hu nan
8	Sample 4	Real sample	Hu nan

Table 2 Sample pretreatment method

Pretreatment method	Digestion system	Heating method	Pretreatment method	Digestion system	Heating method
Ea	HNO_3-HF	Electric heating plate	Ma	HNO_3-HF	Microwave
Eb	HNO_3	Electric heating plate	Mb	HNO_3	Microwave
Ec	HNO_3-HF-H_2O_2	Electric heating plate	Mc	HNO_3-HF-H_2O_2	Microwave
W	Aqua regia	Water bath			
Ef	HNO_3-HF-HCl	Electric heating plate	Mf	HNO_3-HF-HCl	Microwave
Eg	HNO_3-HF-$HClO_4$	Electric heating plate	Mg	HNO_3-HF-$HClO_4$	Microwave
Eh	HNO_3-HCl-$HClO_4$	Electric heating plate	Mh	HNO_3-HCl-$HClO_4$	Microwave
Ei	HNO_3-HF-HCl-$HClO_4$	Electric heating plate	Mi	HNO_3-HF-HCl-$HClO_4$	Microwave

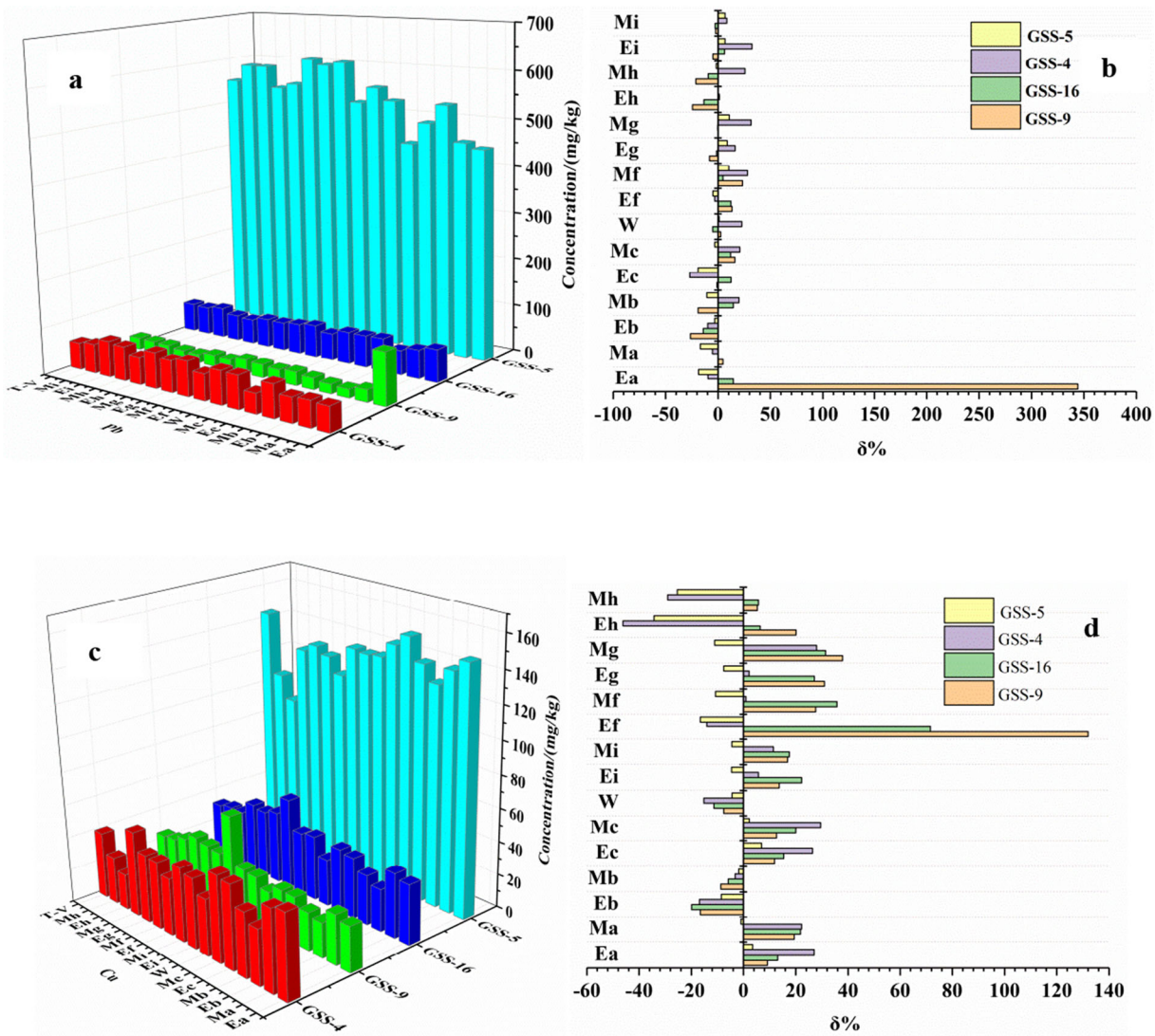

Fig. 2 Fifteen kinds of test results and relative errors of lead and copper (**a** test results of lead; **b** relative error of lead; **c** test results of copper; **d** relative error of copper; T-V: truth value; $n = 6$)

Table 3 Appropriate digestion system

Element	Sample	Appropriate method	Recommended method
Pb	GSS-9	Ea, Ec, W, Ei, Mi, Eg, Mg	Mi
	GSS-16	Ma, Ei, Mi, W, Mf, Eg, Mg, Mh,	
	GSS-4	Ea, Ma, Eb, Mi, Ef, Eh,	
	GSS-5	Eb, Mc, Ei, Mi, W, Ef, Eg, Eh, Mh	
Cr	GSS-9	Ma, Mc, Mi, Mf, Eg, Mg	Mi, Mc
	GSS-16	Ea, Ma, Mb, Ec, Mc, Ei, Mi, Ef, Mf, Eg, Mg, Mh,	
	GSS-4	Ea, Ma, Ec, Mc, Ei, Mi, Eh, Mh,	
	GSS-5	Ea, Ma, Ec, Mc, Ei, Mi, Mf, Eg, Mg, Mh,	
Ni	GSS-9	Ea, Eb, Mb, Ec, Ei, Mi, W, Ef, Mf, Eg, Mg, Eh, Mh,	Ea, Ec, Ei, Eg, Mi
	GSS-16	Ea, Ma, Ec, Mc, Ei, Mi, Mf, Eg, Mg, Mh,	
	GSS-4	Ea, Ma, Mb, Ec, Mc, Ei, Mi, Eg,	
	GSS-5	Ea, Ma, Mb, Ec, Mc, Ei, Mi, Eg,	
Cu	GSS-9	Ea, Mb, W, Mh	Mb
	GSS-16	Mb, Eh, Mh	
	GSS-4	Mb, Ei, Mf, Eg	
	GSS-5	Ea, Ma, Eb, Mb, Ec, Mc, Ei, Mi, W	
Zn	GSS-9	Ea, Ma, Eb, Mb, W, Eh, Mh	Ea
	GSS-16	Ea, Ma, Eb, W, Mi, Mg, Mh	
	GSS-4	Ea, Mc, Mi, Eh	
	GSS-5	Ea, Ma, Eb, Ec, Ei, Mi, W, Mf, Eg, Mg, Eh, Mh,	

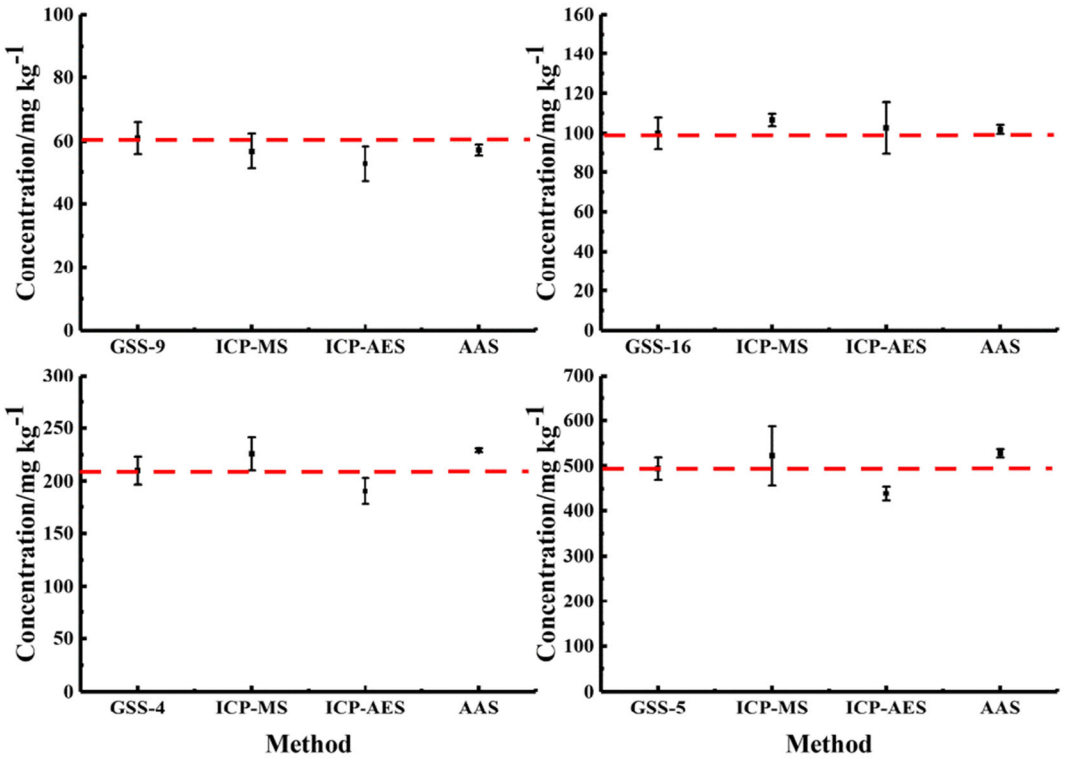

Fig. 3 Test results of different detection methods for zinc

Table 4 The suitable pretreatment methods and detection methods

Element	Pretreatment	Detection method
Pb	Mi	ICP-MS
Cr	Mi	ICP-MS
Ni	Mi	ICP-MS/AAS
Cu	Mb	ICP-MS/AAS
Zn	Ea	AAS

In order to systematically compare the effects of different digestion heating methods and acid systems on the determination of heavy metal content in soil, three heating methods and eight digestion systems were used. The heating methods include electric heating plate (E), water bath (W), and microwave (M). Whereas, the digestion systems include nitric acid-hydrofluoric acid (a), nitric acid (b), nitric acid-hydrofluoric acid-hydrogen peroxide (c), aqua regia (w), nitric acid-hydrofluoric acid-hydrochloric acid (f), nitric acid-hydrofluoric acid-perchloric acid (g), nitric acid-hydrochloric acid-perchloric acid (h), and nitric acid-hydrofluoric acid-hydrochloric acid-perchloric acid (i). The details are shown in the following table (Table 2).

Results and discussion

The influence of different pretreatment methods on the detection results

In order to ensure the consistency in detection of results, the experiment used fifteen digestion methods to examine four soil standard samples, and analyzed accuracy comparing different digestion methods for same elements. Taking Pb and Cu as examples (other elements can be seen in the supporting information), it is given in Fig. 2a and b that for Pb elements, when using different sample pretreatment methods (as shown in Table 2), the detection results deviate from the true value to some extent. For the GSS-9 standard sample, the detection deviation after treatment with fifteen different pretreatment methods ranged between −0.1 and 344.1%; for the GSS-16 standard sample, the detection deviation after treatment is between −14.2 and 14.5%; for GSS-4 standard samples −26.9 and 32.4%; for GSS-5 standard samples −19.1 and 10.7%. It can be seen from Fig. 2c and d that there was a certain deviation from the true value for the Cu element when different sample pretreatment methods were used. For GSS-9 standard samples, the detection deviation after fifteen different digestion methods was between −16.6 and 132%; for GSS-16 standard samples −19.9 and 71.6%; for GSS-4 standard samples −46.2 and 29.5%; for GSS-5 standard samples −34.3 and 6.9%. (For other elements and detailed data, please refer to supporting information Fig. S1 to Fig. S10 and Table S1 to Table S10.). It is evident from the above data that different pretreatment methods have certain variation in the detection of standard samples. Therefore, different pretreatment methods were selected for different elements by analyzing the experimental results.

Optimization of pretreatment methods

According to the above data, we sorted out the pretreatment methods corresponding to different elements with deviation less than 10%. The results are shown in the Table 3. Many pretreatment methods for Pb element had a good treatment effect for a certain standard sample; they were not applicable to all standard samples. However, it was only Mi that can measure four standard samples at the same time and the relative error is within 10%. Therefore, it is recommended to use Mi as the sample pretreatment method when doing soil sample

Table 5 Real sample detect results (mg/kg)

	Pb (ICP-MS)	Cr (ICP-MS)	Ni (ICP-MS)	Cu (ICP-MS)	Zn (AAS)
Sample 1	22,815 ± 661	1274 ± 43.32	26.5 ± 0.69	53.2 ± 3.83	22,188 ± 288
Sample 2	25,283 ± 1870	1967 ± 118.02	25.1 ± 0.75	47.1 ± 3.39	25,075 ± 401
Sample 3	26,460 ± 1640	1791 ± 134.33	24.3 ± 1.48	44.8 ± 4.48	25,265 ± 278
Sample 4	169 ± 7.61	92 ± 2.77	32.4 ± 0.65	33.2 ± 3.65	640 ± 31.36

analysis. Similarly, for the other four elements, Mi and Mc are recommended for Cr; Ea, Ec, Ei, Eg, and Mi for Ni; Mb for Cu; and Ea for Zn.

Optimization of detection methods

After determining the pretreatment methods of different elements, in order to further improve the accuracy and precision of detection, we choose the best pretreatment method applicable to each element. In the following experiments, ICP-MS, ICP-AES, and AAS were used to test the standard samples, and the best detection method corresponding to each element was determined. Taking zinc as an example (the other elements are shown in the supporting information), the detection method is shown in Fig. 3. Although the best sample pretreatment method was used, there were still some deviations (from 0.8 to 12.4%, as shown in Table S10) in the detection of results using different instruments. Compared with ICP-MS and AAS, the ICP-AES detection results for Zn are slightly larger, but the accuracy of ICP-MS is relatively inadequate. Therefore, the pretreatment method of Ea combined with AAs can possibly more accurate detection results. ICP-MS is a well-recognized detection method, but sometimes this method may deviate in the detection of some elements, such as Fe and Hg. Therefore, other elements may also play a role in the detection process in different substrates. Best detection methods for the other four heavy metal elements are shown in Table 4. Pb, Cr, and Ni use ICP-MS to obtain good results, and Cu use ICP-MS and AAS to obtain similar results.

Real samples

After optimizing the pretreatment and detection methods, we used the best experimental design to examine real samples. The samples were taken from Hunan province, which used to have heavy metal, so it is of great significance to survey this place. The test data is shown in Table 5.

Conclusions

In this study, fifteen different kinds of samples were treated by pretreatment methods and three kinds of detection methods were optimized against four standard substances. Through this method, contents of different heavy metal pretreatment methods and detection techniques are combined to find and improve accuracy of results for certain elements heavy metals are determined accurately and precisely. This study identified the most suitable pretreatment methods for the detection of Pb as Mi, Cr as Mi and Mc, Ni as Ea, Ec, Ei, Eg and Mi, for the measurement of Cu element as Mb, and the most suitable pretreatment method for the measurement of Zn element as Ea. Pb and Cr elements are detected more accurately and precisely by ICP-MS than AAS and ICP-AES. It is also observed that results obtained by ICP-MS and AAS were almost same for Ni and Cu, whereas for Zn, AAS method is more accurate detection than ICP-MS and ICP-AES. This study provides a stable, accurate, easy, and reliable detection method for environmental pollutants such as Pb, Cd, Ni, Cu, and Zn, and poses great significance for future environmental governance.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10661-020-08775-4.

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References

Ahmad, I., Rashid, H., & Rehman, Z. U. (2009). Study of heavy metals in some environmental samples. *Environmental Monitoring and Assessment, 158*, 139–144. https://doi.org/10.1007/s10661-008-0576-z.

Alumaa, P., Kirso, U., Petersell, V., & Steinnes, E. (2002). Sorption of toxic heavy metals to soil. *International Journal of Hygiene and Environmental Health, 204*, 375–376. https://doi.org/10.1078/1438-4639-00114.

Bradl, H. B. (2004). Adsorption of heavy metal ions on soils and soils constituents. *Journal of Colloid and Interface Science, 277*, 1–18. https://doi.org/10.1016/j.jcis.2004.04.005.

Chen, Y., Wang, C., Wang, G., Luo, C., Mao, Y., Shen, Z., & Li, X. (2007). Heating treatment schemes for enhancing chelant-assisted phytoextraction of heavy metals from contaminated soils. *Environmental Toxicology and Chemistry, 27*, 888–896. https://doi.org/10.1897/07-345.1.

Duan, Q. N., Lee, J. C., Liu, Y. S., Chen, H., & Hu, H. Y. (2016). Distribution of heavy metal pollution in surface soil samples in China: a graphical review. *Bulletin of Environmental Contamination and Toxicology, 97*, 303–309. https://doi.org/10.1007/s00128-016-1857-9.

Eshetu, S. (2018). Review of heavy metals pollution in China in agricultural and urban soils. *Journal of Health and Pollution, 8*, 180607. https://doi.org/10.5696/2156-9614-8.18.180607.

Fu, G. (2012). Countermeasures for water and soil heavy metal pollution in China (in Chinese). *China Environmental Science, 32*, 373–376.

Hoang, M. T., Pham, T. D., Pham, T. T., Nguyen, M. K., Nu, D. T. T., Nguyen, T. H., Bartling, S., & Bruggen, B. V. (2020). Esterification of sugarcane bagasse by citric acid for Pb^{2+}adsorption: effect of different chemical pretreatment methods. *Environmental Science and Pollution Research*. https://doi.org/10.1007/s11356-020-07623-9.

Huo, X., Li, H., Sun, D., Zhou, L., & Li, B. (2010). Multi-scale spatial structure of heavy metals in agricultural soils in Beijing. *Environmental Monitoring and Assessment, 164*, 605–616. https://doi.org/10.1007/s10661-009-0916-7.

Li, M., Xi, X. I., Xiao, G., et al. (2014a). National multi-purpose regional geochemical survey in China (in Chinese). *Journal of Geochemical Exploration, 139*, 21–30.

Li, Z., Ma, Z., Der Kuijp, T. J., Yuan, Z., & Huang, L. (2014b). A review of soil heavy metal pollution from mines in China: pollution and health risk assessment. *Science of the Total Environment, 468-469*, 843–853. https://doi.org/10.1016/j.scitotenv.2013.08.090.

Lin, S. H., Lai, S. L., & Leu, H. G. (2001). An improved method for determination of heavy metal bioavailability in contaminated soil. *Environmental Technology, 22*, 731–739. https://doi.org/10.1080/09593332208618249.

Lin, H., Song, B., Zhu, R., et al. (2016). Determination of beryllium in soil and sediment by ICP-MS with a microwave-acid digestion method (in Chinese). *Journal of Analytical Science, 32*, 427–430.

Lin, H., Xie, S. W., Zhuo, Q., et al. (2017). Determination of chromium(VI) in soil and solid waste by alkaline digestion-flame atomic absorption spectrometry (in Chinese). *Chinese Journal of Analysis Laboratory, 36*(02), 198–202.

Michael, F., Robert, K., Hal, Z., et al. (2010). The U.S. EPA working group on the future of toxicity testing. The U.S. Environmental Protection Agency Strategic Plan for Evaluating the Toxicity of Chemicals. *Journal of Toxicology and Environmental Health, Part B, 13*, 139–162. https://doi.org/10.1080/10937404.2010.483178.

Pu, H., Luo, K., Zhang, S., Du, Y., & Zhao, C. (2018). Relationship between lifespan indicators and elemental background values: a case study in Guangdong Province, China. *Science of the Total Environment, 624*, 1658–1668. https://doi.org/10.1016/j.scitotenv.2017.10.046.

Rui, Y., Kong, X. B., & Qin, J. (2007). Application of ICP-MS to detection of heavy metals in soil from different cropping systems. *Spectroscopy and Spectral Analysis, 27*, 1201–1203.

State Environmental Protection Administration of China, State Land and Resources Administration of China. (2014). *National bulletin of soil pollution survey* (In Chinese).

Taghipour, M., & Jalali, M. (2020). Effects of some industrial and organic wastes application on growth and heavy metal uptake by tomato (Lycopersicum esculentum) grown in a greenhouse condition. *Environmental Science and Pollution Research, 27*, 5353–5366. https://doi.org/10.1007/s11356-019-07017-6.

Tang, J., Zhang, J., Ren, L., Zhou, Y., Gao, J., Luo, L., & Chen, A. (2019). Diagnosis of soil contamination using microbiological indices: a review on heavy metal pollution. *Journal of Environmental Management, 242*, 121–130. https://doi.org/10.1016/j.jenvman.2019.04.061.

Tangen, G., Wickstrom, T., Lierhagen, S., Vogt, R. D., & Lund, W. (2002). Fractionation and determination of aluminum and iron in soil water samples using SPE cartridges and ICP-AES. *Environmental Science & Technology, 36*, 5421–5425. https://doi.org/10.1021/es020077i.

Tatiana, M., Saglara, S., Marina, V., Tatiana, V., & Svetlana, N. (2018). Method of determining loosely bound compounds of heavy metals in the soil. *MethodsX, 5*, 217–226. https://doi.org/10.1016/j.mex.2018.02.007.

Wang, R., Shafi, M., Ma, J., Zhong, B., Guo, J., Hu, X., & Liu, D. (2018). Effect of amendments on contaminated soil of multiple heavy metals and accumulation of heavy metals in plants. *Environmental Science and Pollution Research, 25*, 28695–28704. https://doi.org/10.1007/s11356-018-2918-x.

Wei, B., & Yang, L. (2010). A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. *Microchemical Journal, 94*, 99–107. https://doi.org/10.1016/j.microc.2009.09.014.

Yi, R., Yang, X., Zhou, R., Li, J., Yu, H., Hao, Z., Guo, L., Li, X., Lu, Y., & Zeng, X. (2018). Determination of trace available heavy metals in soil using laser-induced breakdown spectroscopy assisted with phase transformation method. *Analytical Chemistry, 90*, 7080–7086. https://doi.org/10.1021/acs.analchem.8b01756.

Yu, X., Zhang, L., Chen, K., Xiang, Y., et al. (2020). Comparison of analytical methods of lead in soil (In Chinese). *Chemical Analysis and Meterage, 29*, 103–107.

Zhang, X., Zhong, T., Liu, L., & Ouyang, X. (2015). Impact of soil heavy metal pollution on food safety in China. *PLoS One, 10*, 1–14. https://doi.org/10.1371/journal.pone.0135182.

Zhao, Q., & Luo, Y. (2015). The macro strategy of soil protection in China (in Chinese). *Bulletin of the Chinese Academy of Sciences, 3*, 452–458.

Zhao, F., Ma, Y., Zhu, Y., Tang, Z., & Mcgrath, S. P. (2015). Soil contamination in China: current status and mitigation strategies. *Environmental Science & Technology, 49*, 750–759. https://doi.org/10.1021/es5047099.