Determination of Pb in Geological Materials by Heat Extraction Slurry Sampling ET-AAS

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ABSTRACT: Lead (Pb) is a non-essential but extremely noxious metallic element, which is important for the assessment of environmental pollution. A simple and high throughput method involving fast heat extraction slurry sampling electrothermal atomic absorption spectrometry (HESS-GFAAS) was developed to detect trace Pb content in geological standard reference materials (SRMs). Compared with the traditional digestion method, the HESS-GFAAS method greatly reduces the time of sample pretreatment. The HESS-GFAAS technique improved Pb recovery and precision compared to conventional slurry sampling techniques. This optimized HESS-GFAAS procedure was performed as follows: first, the sample was added into 1 mL HNO₃, 1 mL HCl and 1 mL HF, followed by heating for 30 min at 120 °C on a heating block; Next, dilute the solution with 50 mL water, and finally, the solution was introduced into a graphite tube with Pd(NO₃)₂-NH₄H₂PO₄ as the mixed matrix modifier and analyzed by the GFAAS with a Pb electrodeless discharge lamp (EDL). To eliminate the interface of the geological sample matrix, the method of additions calibrate was used for Pb determination in geological samples. The results for 20 of these materials were in good agreement with the reference values. The characteristic mass and limit of detection for Pb based on the integrated absorbance for a 0.2% (m/v) sample were 14.8 ± 0.8 pg and 0.035 mg kg⁻¹, respectively. The accuracy (96.05–102.4% recovery) and precision (0.13–2.07%) of this procedure are illustrate by the results obtained for the 20 geological reference materials. The proposed method shows great potential for the determination of trace Pb in geological samples.

INTRODUCTION

Lead (Pb) is toxic to humans even at low levels, and the most important sources are due to industrial emission, soil, and automobile exhaust.¹⁻⁴ Thus, determining whether the soil needs remediation or not is important for appropriate evaluation of Pb risk to humans. The amount of Pb in soil is usually 2-200 mg kg⁻¹,^{5,6} which is difficult to determine accurately by available analytical methods because of the low content and interference effects. Therefore, a rapid and accurate analytical method is needed to monitor Pb in solid environmental samples.

At present, electrothermal atomic absorption spectrometry

(ETAAS) and inductively coupled plasma mass spectrometry (ICP-MS) are the two main methods for determining trace Pb in soils, sediments, and rocks in geological analysis laboratories.⁷⁻¹¹ Although the ICP-MS method has the advantages of low detection limits and simultaneous multi-element analysis, the ETAAS method remains the preferred method for Pb determination in most laboratories because of its low cost, relative simplicity, and the ability for the direct determination of Pb in complex matrices.¹²

Sample preparation is the most time-consuming step. The conventional methods used for geological sample pretreatment involve wet digestion, high-pressure closed acid digestion and

microwave-assisted acid digestion. Wet digestion can be used for the simultaneous digestion of multiple samples, the equipment used is simple, but the reagent blank may be high because of a contaminated reagent or container, and the digestion time is long, at least 5 h. In addition, the digestion needs to be checked regularly to prevent acid sputtering.

High-pressure closed acid digestion and microwave-assisted acid digestion are widely used because they can avoid analyte loss and contamination.^{13,14} The main drawbacks are the high cost of the vessels and ovens, occasional explosions, low sample throughput, and a long cooling step. In order to reduce the pretreatment time of samples and effectively avoid sample contamination, direct solid sampling GFAAS (DSS-GFAAS) and slurry sampling GFAAS have attracted much attention in recent years.¹⁵⁻¹⁹ However, the DSS-ETAAS method was not widely accepted until recently, owing to the difficulty in handling and introducing small sample masses, the high imprecision of the results due to the heterogeneity of some natural samples, the difficulty in calibration due to the requirement of solid standards with similar matrix composition and structure, the limited linear working range of AAS, and the difficulty in diluting solid samples.^{20,21} Another attractive alternative is the use of slurry sample introduction in ETAAS, which combines the advantages of liquid and solid sampling and avoids many problems associated with direct solid sampling. Here, simple aqueous standards are used instead of solid sample matrix calibration, the sample concentration can easily be changed by dilution, it can avoid weighing errors, inhomogeneity problems are eliminated, and the analyte concentration falls within the linear range²²⁻²⁷. However, past research has shown that for a better recovery rate, the particle size of the sample should be less than 32 μm .²⁸⁻³² At conventional laboratories, special grinding tools need to be prepared, leading to a time-consuming grinding process, and easily leads to contamination.

In this study, a simple heating step was added prior to the slurry sampling procedure to improve the accuracy and precision of Pb determination in geological samples. Compared to the microwave acid digestion and slurry sampling procedures, it has a higher sample throughput and lower analytical costs. The proposed fast heat extraction slurry sampling electrothermal atomic absorption spectrometry (HESS-ET-GFAAS) method was evaluated by analysis of various geological standard reference materials (SRMs).

EXPERIMENTAL

Instrumental. All measurements were carried out with a PinAAcle™ 900T atomic absorption spectrometer (PerkinElmer, Inc., Shelton, CT, USA), equipped with a longitudinal AC Zeeman background correction system, a transversely heated graphite atomizer (THGA), PerkinElmer Pb electrodeless

discharge lamps (EDLs), and an AS 900 autosampler. The standard THGA tubes with integrated platforms and end caps were used, including a TubeView™ color furnace camera to monitor the process of the sample in the graphite tube and to assist the optimization of the heating procedure of the graphite furnace.

Reagents and standards. High purity water was used for the preparation of all blank, standard, and sample solutions, obtained from a water purification system (Merck Millipore, Fontenay-sous-Bois, France). The Pb standard solution (1000 mg L⁻¹) and Triton X-100 (>99%) were purchased from PerkinElmer. Nitric acid (65–70%, w/w, 99.999%), hydrochloric acid and hydrofluoric acid were purchased from Alfa Aesar Ltd. (Tianjin, P.R. China). Twenty geological SRMs (Institute of Geophysical and Geochemical Exploration of China, Langfang, P.R. China) were used to evaluate the accuracy of the proposed method, which includes six soil SRMs, one rock SRM, and 13 stream sediments SRMs.

Heat extraction slurry sampling procedure. Each sample was accurately weighed from 0.1000 g to 0.3000 g and placed into a 50 mL conical polypropylene tube. Subsequently, 1 mL nitric acid, 1 mL hydrochloric acid and 1 mL hydrofluoric acid were added and gently shaken to ensure adequate contact of the acid with the geological sample. At the same time, the same amount of acid was added to another tube as a reagent blank. The tubes were placed on a heating block (120 °C) and heated for 1 h. During the heat-extraction process, the tube needs to be manually shaken slightly every half hour. After cooling, the sample is diluted with high purity water to the mark, the slurries manually shaken before placing them into the autosampler cups. The heat-extraction process will produce yellowish brown color and irritating gas; thus, care should be taken to ensure that the operation takes place in the fume hood. For comparison, a conventional slurry sampling procedure with a mixture of 0.5% (v/v) HNO₃ containing 0.6% (v/v) Triton X-100 was also used. The samples were homogenized in an ultrasonic bath for 30 min before transfer into the autosampler cups.

RESULTS AND DISCUSSION

Optimization of HESS-GFAAS method

Preliminary experiments were carried out to investigate the Pb recovery and precision of the traditional slurry sampling GFAAS techniques. Five geological SRMs, Sichuan basin soil (GSS-4), Saline-alkali soil of Inner Mongolia (GSS-18), Qinghai haiyan county brown desert soil (GSS-19), Limestone soil of Shihezi City, Xinjiang (GSS-21), Tidal flat deposits in the South China Sea, Yangjiang City, and Guangdong province (GSS-24), were selected for analysis. As shown in Fig. 1, the Pb recoveries for five SRMs by slurry sampling GFAAS ranged from 23.5% to 46%. The recovery experiment for the selected SRMs was not

satisfactory, maybe the particle size (75 μm) of the sample did not meet the requirements or the particle size is too large so that the solvent cannot fully contact with the sample. Another reason may be the stable structure of Pb in the SiO_2 matrix and cannot be completely dissolved in the solvent. The poor precision (%RSD) of the slurry sampling GFAAS technique (5.2-8.6%) is not satisfactory for testing. In order to improve the accuracy and precision of the Pb determination in geological samples, a simple method involving a fast heat extraction and different combinations of acids was evaluated.

To obtain accurate results with the fast heat extraction slurry sampling GFAAS techniques, the heat extraction procedures and furnace heating parameters were optimized and are listed in detail. As shown in Fig. 2, the recovery of Pb from five geological SRMs were investigated by changing the composition of the acids, while other parameters, such as the heat extraction temperature (120 $^{\circ}\text{C}$), heat extraction time (60 min), slurry concentration (0.2% m/v), pyrolysis temperature (900 $^{\circ}\text{C}$), and atomization temperature (1900 $^{\circ}\text{C}$), were kept constant. As is evident from the Fig. 2, the combination of 1 mL nitric acid (HNO_3) + 1 mL hydrochloric acid (HCl) could not achieve a very satisfactory recovery rate for the standard substances. It is possible that these combinations did not fully dissolve the Pb of the geological samples. The combination of 1 mL nitric acid (HNO_3) and 1 mL hydrofluoric acid (HF) could achieve the recovery rate for all standard substances except GSS-18, which may be caused by the special composition of the standard substances of the saline-alkali soil. The best recovery and accuracy of Pb was obtained when the combination of 1 mL nitric acid (HNO_3) + 1 mL hydrochloric acid (HCl) + 1 mL hydrofluoric acid (HF) was used. Therefore, this combination was used in further studies as the medium for the heat extraction of Pb from geological samples.

It is important to optimize the heat extracting temperature and time in order to attain quantitative recoveries with the heat extraction procedure. Different heat extracting temperature ranges for GSS-19 with a Pb content of $18.7 \pm 0.9 \text{ mg kg}^{-1}$ were studied. Temperatures of 0 $^{\circ}\text{C}$, 30 $^{\circ}\text{C}$, 60 $^{\circ}\text{C}$, 90 $^{\circ}\text{C}$, and 120 $^{\circ}\text{C}$ were investigated, as shown in Fig. 3a, and quantitative recoveries were obtained for both 90 $^{\circ}\text{C}$ (98.39%) and 120 $^{\circ}\text{C}$ (101.99%). However, at the temperature of 120 $^{\circ}\text{C}$, the sample solution is clearer, indicating that the sample digestion is more thorough, reducing the possibility of the insoluble matter containing Pb, and at the same time reducing the matrix into the graphite furnace. It is important to note that temperatures above 130 $^{\circ}\text{C}$ can damage the conical polypropylene tube. Therefore, we chose 120 $^{\circ}\text{C}$ as the optimal temperature for the heat extraction procedure. Different heat extracting time ranges for GSS-19 were also investigated in this study. As shown in Fig. 3b, when the digestion time exceeds 40 min, the recovery rate of the sample can reach over 98%. However, the relative standard deviation of six parallel samples at the time of 60 min (1.84%) is

Fig. 1 Recovery and precision of Pb in five reference materials by the conventional slurry sampling graphic furnace atomic absorption spectrometry (slurry sampling GFAAS).

Fig. 2 Recovery and precision of Pb in five reference materials by different acid combination digestion system.

lower than that of 40 min (3.6%), indicating that the Pb in the geological samples can be completely dissolved in 60 min with good reproducibility. Thus, the heat extracting time was optimized to 60 min to guarantee quantitative recovery for the different geological samples. Since Pb is typically a volatile element,³³ it is lost from the graphite atomizer at temperatures higher than 500 $^{\circ}\text{C}$ in the absence of a modifier. For soil with high organic material content, the pyrolysis stage at 500 $^{\circ}\text{C}$ temperature seems to be insufficient for carbonization of the organic substances and will affect the accuracy of the measurement results.^{34,35} A matrix modifier is usually used to assist in eliminating matrix interference in order to obtain accurate and reliable results.³⁶⁻³⁹ Matrix modifiers generally have two main functions: first, to convert the matrix into a volatile material at low temperature, such as $\text{NH}_4\text{H}_2\text{PO}_4$ and second, to protect the element being tested and to enhance its thermal stability, so that the pyrolysis temperature can be increased to remove the interfering material, such as $\text{Pd}(\text{NO}_3)_2$.³⁶⁻⁴⁰

In this paper, two types of matrix modifiers were used simultaneously to give full play of their effect and to ensure the accuracy of the results. The concentration of the $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{Pd}(\text{NO}_3)_2$ mixed matrix modifier was 0.5% (w/v) and 0.1% (w/v),

Fig. 3 Effects of the fast heat extracting slurry sampling ETAAS conditions on Pb recoveries from the geological SRM GSS-19. Effect of (a) heat extracting temperature, (b) heat extracting time.

Fig. 4 Effects of the fast heat extracting slurry sampling ETAAS conditions on Pb recoveries from the geological SRM GSS-19. Effect of pyrolysis and atomization temperatures.

respectively. The effect of the pyrolysis and atomization temperature on the integrated absorbance was studied by performing experiments on the GSS-19 SRM slurry with and without the mixed matrix modifier. As shown in Fig. 4, the mixed matrix modifier allowed the optimum pyrolysis temperature to

Table 1. Graphite Furnace Temperature Programs and Spectrometer Operating Conditions

Step	Temp. (°C)	Ramp times (s)	Hold time (s)	Inter. Flow (mL min ⁻¹)	Gas type
Drying 1	110	5	30	250	Ar
Drying 2	130	20	30	250	Ar
Pyrolysis	900	10	20	250	Ar
Atomization	1600	0	4	0	-
Cleaning	2500	1	3	250	Ar

increase from 500 °C (without the modifier) to 900 °C. The optimum atomization temperature was found to be 1900 °C, which is much higher than that without a modifier. The graphite furnace temperature programs are listed in Table 1.

Analytical performance

Calibrations were carried out using aqueous standard solutions with a linear range of 10 to 50 ng mL⁻¹ Pb. The fitted linear equation of the analytical curve of $Y=0.00225X+0.0007$ with the correlation coefficient of 0.999 and the relative standard deviation ranged from 0.12 % to 2.07%. The characteristic mass (m_0), defined as the mass of the analyte corresponding to 0.0044 absorbance units, was 14.8 pg. The limit of detection (LOD) was 0.035 mg kg⁻¹, which was calculated from 20 consecutive measurements of the blank solutions and a 500-fold sample dilution factor. By considering the time required for preparation of the sample slurries (1 hour for 52 samples per batch, depending on the number of holes in the heating block) and the determination by ETAAS, the analytical throughput of the method was estimated to be 52 samples per hour (while the traditional digestion method takes more than 4 hours). The digestion process only needs to use the conical polypropylene tube and the corresponding acid, does not require to transfer the sample, can be a directly fixed volume, and reduces the source of pollution. Conversely, traditional digestion methods require the use of digestion tanks, beakers, volumetric bottles and other containers, which greatly increases the risk of contamination.

Geological sample analysis

The proposed HESS-GFAAS method was used to analyze 12 geological SRM samples. For comparison, microwave digestion-ICP-MS was also used. The Pb contents obtained by the heat extraction slurry sampling method were in agreement with the certified values (Table 2), the results were also consistent with those of microwave digestion-ICP-MS, and the recoveries ranged from 96.05 to 102.4%. In addition, in order to further verify the feasibility of this method, we tested the long-term stability of the solution by selecting ten time points within one month to test the GSS-7 and GSS-19 solutions after heat extraction, as shown in Fig. 5. The results of the repeated analyses over a period of one month were found to be very stable, which further confirms that this method is reliable.

Table 2. Results of Pb Values in 20 Geological Standard Reference Materials (n=3)

Geological SRMs	Pb values (mean±SD), mg kg ⁻¹		
	Certified values	HESS-GFAAS (This work)	microwave digestion-ICPMS
GSS-4, Limestone soil	58±5	57.11±0.234	60.045±0.255
GSS-7, Basalt of Xuwen, Guangdong	14±3	13.64±0.129	12.48±0.134
GSS-14, Sichuan basin soil	31±1	31.53±0.126	31.58±0.19
GSS-18, Saline-alkali soil of Inner Mongolia	20±1	20.39±0.11	19.59±0.18
GSS-19, Qinghai haiyan county brown desert soil	18.7±0.9	18.52±0.08	18.13±0.13
GSS-20, Saline-alkali soil in Shanshan, Xinjiang	13.4±1.2	13.07±0.10	12.30±0.05
GSS-21, Limestone soil of Shihezi city, Xinjiang	17±1	16.49±0.21	17.38±0.12
GSS-22, Rizhao Yellow River tidal flat sediment	26±2	25.69±0.12	26.29±0.18
GSS-23, Shoal sediments from Xiangshan Shandong coastal area, Zhejiang province	28±1	28.42±0.17	28.62±0.12
GSS-24, Tidal flat deposits in south China sea, Yangjiang city, Guangdong province	40±2	41.37±0.	38.48±0.18
GSS-26, Anhui Wuhe huai River sediment	21±2	20.17±0.11	21.74±0.17
GSS-27, Changjiang River sediments in Zhangjiagang, Jiangsu province	41±2	42.01±0.28	41.94±0.21
GSD2a, Stream Sediments	32±8	36.15±0.12	34.12±0.16
GSD-6, Stream Sediments	27±5	29.41±0.13	28.64±0.19
GSD-9, Stream Sediments	23±4	23.11±0.21	23.77±0.14
GSD-10, Stream Sediments	27±3	28.00±0.20	26.94±0.21
GSD-13, Stream Sediments	13.5±2.4	13.51±0.19	13.16±0.14
GSD-16, Stream Sediments	31±2	31.27±0.22	30.99±0.18
GSD-20, Stream Sediments	24±2	24.49±0.17	24.81±0.17
GBW-37, Stream Sediments	42.6±2.5	42.88±0.24	43.09±0.21

Fig. 5 Results of repeated analyses of (a) Basalt laterite of Xuwen, Guangdong GSS-7, and (b) Qinghai Haiyan county brown desert soil SRM GSS-19. The average values of Pb in GSS-7 and GSS-19 are $13.12 \pm 0.13 \mu\text{g g}^{-1}$ and $19.07 \pm 0.149 \mu\text{g g}^{-1}$, respectively. Ten separate aliquots of the samples were analyzed during a period of one month.

CONCLUSIONS

An improved method using fast heat extraction slurry sampling GFAAS to accurately determine trace Pb in various soils, sediments, and rocks was evaluated and validated. This method requires only a conical polypropylene tube and 3 mL mixed acid, no need to transfer the sample, and a directly fixed volume. Thus, the problems related to conventional acid digestion, such as time consumption, risk of contamination, and possible analyte loss, are avoided. Using the proposed method, the Pb levels were determined in 20 geological SRMs, and the results were found to

be in good agreement with the certified values. The proposed method has great potential for the rapid trace level Pb determination in various geological samples.

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Notes

The authors declare no competing financial interest.

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REFERENCES

1. Y. E. Peng, W. Guo, P. Zhang, and L. L. Jin, *J. Food Comp. Anal.*, 2015, **42**, 78-83. <https://doi.org/10.1016/j.jfca.2015.03.007>
2. J.-Y. Yang, Z.-L. He, X.-E. Yang, and T.-Q. Li, *Pedosphere*, 2014, **24**, 817-826. [https://doi.org/10.1016/s1002-0160\(14\)60069-2](https://doi.org/10.1016/s1002-0160(14)60069-2)
3. Y.-X. Liu, X.-Y. Sun, S. Li, S.-Y. Li, W.-J. Zhou, Q.-X. Ma, and J.-L. Zhang, *Environ. Sci. Pollut. R.*, 2020, **27**, 7693-7701. <https://doi.org/10.1007/s11356-019-07505-9>
4. J. Ren, Z. Zhang, M. Wang, G.-L. Guo, P. Du, and F. S. Li, *Front. Environ. Sci. Eng.*, 2019, **2**, 97-105. <https://doi.org/10.1007/s11783-018-1006-2>
5. O. A. Lourdes, G. J. Alberto, F. P. Luis, C. Jose, and S. Francisco, *Environ. Sci. Pollut. R.*, 2019, **26**, 30386-30398. <https://doi.org/10.1007/s11356-019-06197-5>
6. M. T. Kolo, M. U. Khandaker, Y. M. Amin, W. H. B. Abdullah, D. A. Bradley, and K. S. Alzimami, *Results Phys.*, 2018, **11**, 755-762. <https://doi.org/10.1016/j.rinp.2018.10.003>
7. I. Maja, F. Željka, M. Gordana, F. T. Martina, M. Gordana, S. Jasminka, and K. Goran, *Chemosphere*, 2018, **215**, 668-677. <https://doi.org/10.1016/j.chemosphere.2018.10.108>
8. A. Gałuszka, Z. M. Migaszkowski, S. Dołęgowska, and A. Michalik, *Scie. Total Environ.*, 2018, **639**, 397-405. <https://doi.org/10.1016/j.scitotenv.2018.05.174>
9. Y. T. Li, W. Guo, Z. C. Hu, L. L. Jin, S. H. Hu, and Q. H. Guo, *J. Agric. Food Chem.*, 2019, **67**, 935-942. <https://doi.org/10.1021/acs.jafc.8b05479>
10. M. Žemberyová, R. Jankovič, I. Hagarová, and H.-M. Kuss, *Spectrochim. Acta Part B*, 2007, **62**, 509-513. <https://doi.org/10.1016/j.sab.2007.05.004>
11. We. Guo, R. Wang, W. X. Wang, and Y. E. Peng, *J. Food Comp. Anal.*, 2020, **91**, 103517. <https://doi.org/10.1016/j.jfca.2020.103517>
12. D. K. Benbi, *Commun. Soil Sci. Plant Anal.*, 2018, **49**, 2103-2112. <https://doi.org/10.1080/00103624.2018.1495732>
13. D. V. Babos, A. I. Barros, E. C. Ferreira, and J. A. G. Neto, *Spectrochim. Acta Part B*, 2017, **130**, 39-44. <https://doi.org/10.1016/j.sab.2017.02.005>
14. W. Guo, L. L. Jin, S. H. Hu, and Q. H. Guo, *J. Agric. Food Chem.*, 2017, **65**, 3407-3413. <https://doi.org/10.1021/acs.jafc.7b00535>
15. R. Jing, W.-D. Jian, W. Can, B.-L. Ji, Z.-J. Cheng, and Y.-L. Peng, *Spectrosc. Spect. Anal.*, 2014, **34**, 3113-3118. [https://doi.org/10.3964/j.issn.1000-0593\(2014\)11-3113-06](https://doi.org/10.3964/j.issn.1000-0593(2014)11-3113-06)
16. H. Lenka, U. Iva, Š. Michaela, and Š. Tereza, *Talanta*, 2017, **175**, 93-100. <https://doi.org/10.1016/j.talanta.2017.07.031>
17. D. Ryszard, A. Agnieszka, and O. Magdalena, *Talanta*, 2013, **113**, 19-25. <https://doi.org/10.1016/j.talanta.2013.03.085>
18. N. Salehi, A. Azhdarpoor, and M. Shirdarreh, *Chemosphere*, 2020, **246**, 125845. <https://doi.org/10.1016/j.chemosphere.2020.125845>
19. Y.-Z. Yi, S.-J. Jiang, and A. C. Sahayam, *J. Anal. At. Spectrom.*, 2012, **27**, 426-431. <https://doi.org/10.1039/C2JA10314A>
20. U. B. Ibrahim, S. Yahaya, I. Yusuf, and A. H. Kawo, *Micro. Res. J. Inter.*, 2020, **30**, 36-47. <https://doi.org/10.9734/mrji/2020/v30i330203>
21. R. Proshad, D. Zhang, M. Uddin, and Y. Wu, *Environ. Sci. Pollut. R.*, 2020, **27**, 18355-18370. <https://doi.org/10.1007/s11356-020-08160-1>
22. A. S. El-Hassanin, M. R. Samak, G. N. Abdel-Rahman, Y. H. Abu-Stee, and E. S. Saleh, *Toxic. Rep.*, 2020, **7**, 10-15. <https://doi.org/10.1016/j.toxrep.2019.11.018>
23. C. Ma, F.-Y. Liu, B. Hu, M.-B. Wei, J.-H. Zhao, K. Zhang, and H.-Z. Zhang, *Ecotox. Environ. Safe.*, 2019, **185**, 109688. <https://doi.org/10.1016/j.ecoenv.2019.109688>
24. T. Feng, C.-J. Wang, Y. Liu, M. Chen, M.-M. Fan, and Z. Li, *Int. J. Env. Res. Pub. He.*, 2019, **16**, 5059. <https://doi.org/10.3390/ijerph16245059>
25. A. L. Oropesa, J. A. Gala, F. P. Luis, J. Cabezas, and F. Soler, *Environ. Sci. Pollut. Res.*, 2019, **26**, 30386-30398. <https://doi.org/10.1007/s11356-019-06197-5>
26. R. Dobrowolski, A. Adamczyk, and M. Otto, *Talanta*, 2013, **113**, 19-25. <https://doi.org/10.1016/j.talanta.2013.03.085>
27. R. Dobrowolski, A. Adamczyk, M. Otto, and J. Dobrzyńska, *Spectrochim. Acta Part B*, 2011, **66**, 493-499. <https://doi.org/10.1016/j.sab.2011.02.006>
28. D. Ryszard, A. Agnieszka, and O. Magdalena, *Talanta*, 2010, **82**, 1325-1331. <https://doi.org/10.1016/j.talanta.2010.06.049>
29. T. Nilgun, *J. Hazard. Mater.*, 2007, **143**, 87-94. <https://doi.org/10.1016/j.jhazmat.2006.08.068>
30. D. Barańkiewicz, H. Gramowska, K. Ren, and M. Mleczek, *Open Chem.*, 2006, **4**, 363-374. <https://doi.org/10.2478/s11532-006-0002-8>
31. O. Acar, *Anal. Chim. Acta*, 2005, **545**, 244-251. <https://doi.org/10.1016/j.aca.2005.04.081>
32. I. López-García, R. E. Rivas, and M. Hernández-Córdoba, *Anal. Bioanal. Chem.*, 2008, **391**, 1469-1474. <https://doi.org/10.1007/s00216-007-1805-y>
33. M. Savio, S. Cerutti, L. D. Martinez, P. Smichowski, and R. A. Gil, *Talanta*, 2010, **82**, 523-527. <https://doi.org/10.1016/j.talanta.2010.05.017>
34. P. Török and M. Žemberyová, *Spectrochim. Acta Part B*, 2010, **65**, 291-296. <https://doi.org/10.1016/j.sab.2010.03.007>
35. Z.-X. Yang, S.-Q. Liu, D.-W. Zheng, and S.-D. Feng, *J. Environ. Sci.*, 2006, **6**, 1135-1141. [https://doi.org/10.1016/s1001-0742\(06\)60051-x](https://doi.org/10.1016/s1001-0742(06)60051-x)
36. R. Adhikari, H. Mingtarja, G. Freischmidt, K. L. Bristow, P. S. Casey, P. Johnston, and P. Sangwan, *Agr. Water Manage.*, 2019, **222**, 346-353. <https://doi.org/10.1016/j.agwat.2019.05.020>
37. X. Zhao, X.-D. He, and J.-L. Zhang, *J. Agri. Res. Environ.*, 2017, **34**, 384-389. <https://doi.org/10.13254/j.jare.2016.0306>
38. Y.-Q. Liang, C. Zhou, Z.-H. Guo, Z.-T. Huang, C. Peng, P. Zeng, X.-Y. Xiao, and Z.-F. Xian, *Environ. Sci. Pollut. Res.*, 2019, **26**, 28319-28327. <https://doi.org/10.1007/s11356-019-06041-w>
39. A. B. Volikov, V. A. Kholodov, N. A. Kulikova, O. I. Philippova, S. A. Ponomarenko, E. V. Lasareva, A. M. Parfyonova, K. Hatfield, and I. V. Perminova, *Catena*, 2016, **137**, 229-236. <https://doi.org/10.1016/j.catena.2015.09.022>