

International Journal of Soil, Sediment and Water

Volume 3, Issue 2

2010

Article 10

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Abstract

Field tests for the detection of lead in soil are not frequently accepted, since the tests are rather cumbersome or not reliable for screening determinations. Recently, we developed the LEADQuick field test kit for the detection of lead in water with 3 $\mu\text{g/L}$ sensitivity. This test is further modified to detect lead in soil with a sensitivity 0.03 μg . We developed an extraction protocol using nitric acid and potassium nitrate for the extraction of lead from soil. Most of the organic and inorganic compounds of lead are readily extracted as Pb²⁺ using the developed extraction procedure and are detected using the LEADQuick field test kit. The solubility of the lead salts in the soil is adequate for a quick extraction procedure without any heating. The experimental details, results of the soil testing and interferences are presented. This will demonstrate the potential application of our extraction procedure along with LEADQuick field test kit for soil lead monitoring.

KEYWORDS: Soil Reference Materials, Extraction, LEADQuick field test kit, Interference study, Standard addition method

*The authors would like to thank Mr. Howard Ray for critically reviewing the manuscript.

NEW FIELD TEST FOR LEAD (Pb²⁺) IN SOIL

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ABSTRACT

Field tests for the detection of lead in soil are not frequently accepted, since the tests are rather cumbersome or not reliable for screening determinations. Recently, we developed the LEADQuick field test kit for the detection of lead in water with 3 µg/L sensitivity. This test is further modified to detect lead in soil with a sensitivity 0.03 µg. We developed an extraction protocol using nitric acid and potassium nitrate for the extraction of lead from soil. Most of the organic and inorganic compounds of lead are readily extracted as Pb²⁺ using the developed extraction procedure and are detected using the LEADQuick field test kit. The solubility of the lead salts in the soil is adequate for a quick extraction procedure without any heating. The experimental details, results of the soil testing and interferences are presented. This will demonstrate the potential application of our extraction procedure along with LEADQuick field test kit for soil lead monitoring.

Keywords: Certified Reference Materials, Soil field samples, Extraction, LEADQuick field test kit, Interference study, Standard addition method.

1. INTRODUCTION

Lead is a most troublesome toxic metal. Government agencies have taken many preventive steps to control lead in the environment, but still large-scale incidents of metal poisoning have occurred (Lau, 1994). The principal target organ systems of lead poisoning are the blood, brain, nervous system, kidney and reproductive system. Acute exposure to lead leads to shock, severe anemia, acute nervousness and irreversible brain damage. Lead poisoning also causes a range of health effects such as behavioral problems, learning disabilities, seizures and death. Lead is transferred to animals and human beings through the food chain system of soil-plant-animal-human (Melaku et al., 2005; Prasad et al., 2006).

Many consumers felt that lead was the first toxic metal when metal poisoning was mentioned. The government and industry organizations reluctantly accepted the dangers of lead in the 1900's and new laws and regulations were enacted to safeguard the consumer. In view of this, the extraction and detection of Pb²⁺ at very low concentrations in the soil was very critical for environmental monitoring.

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The extraction of lead from the soil was a most laborious and time consuming procedure. In general, the wet digestion methods were the most common methods used for soil analysis (Hoenig and Thomas, 2002). However, the selection of an acid or acid combination was very critical to obtaining the maximum extraction of metal (Hoenig and De Kersabiec, 1996). Among the acids, HCl never used for soil analysis, but HNO₃ digests many common metals either alone or in combination of some other acids (Thompson and Nathanail, 2003). However, some of these acids were interfered in the analysis. Gryschko et al., (2005) studied the extraction efficiency of NH₄NO₃ and KNO₃ on heavy metals. He observed that the high ionic strength also decreases the activity of metal-OH⁺ species and the electrostatic potential of the particle surfaces. This lead to increased desorption of heavy metal cations from negatively charged soil surfaces.

Based on this result, a mixture of HNO₃ and KNO₃ were used for the extraction of lead from the soil. Similarly, we were also performed extraction experiments using HNO₃ alone. We observed that the extraction efficiency for lead was almost identical for both the reagents, except in few samples. However, due to the less corrosive nature of HNO₃ and KNO₃ mixture, we optimized the HNO₃ and KNO₃ mixture concentration for further studies.

Analytical instruments such as atomic absorption or atomic emission spectroscopy, voltametry etc., were used for the detection of Pb²⁺ (Jones and Szutka, 1966; Li et al., 2004; Tarley and Arruda, 2005; Ostrega and Piekarska, 2005). Even then, there was a significantly greater need to provide inexpensive and remote monitoring methods and instruments for the on-site detection of this highly deleterious element in the soil. In view of this, emphasis was focused on the development of field test kits for the detection of toxic ions (Wang et al., 2002; Metivier et al., 2004). This type of test kit offered higher sensitivity, short response time and selectivity for remote identification. Among these, colorimetric test kits allowing onsite, real-time qualitative or semi-quantitative detection without the use of any complicated spectroscopic instrumentation were particularly very attractive (Palomares et al., 2004; Liu and Lu, 2004). We recently developed a field test kit for the detection of lead in water (Jaunakais and Anand, 2008) and applied for the detection of lead in certified reference materials and field soil samples.

2. MATERIALS AND METHODS

2.1 Materials

US-EPA Certified soil reference materials (RM) (CRM-020, CRM-021, CRM-025, CRM-030, CRM-033 and CRM-036) were collected from Resource Technology Corporation, WY, USA and used for the detection of lead. The certified compositions of the various elements are given in Table 1. The 1000 and 10 ppm of lead standard solutions were procured from Ricca Chemical Company and Hach, USA, respectively. Nitric acid, potassium nitrate and sodium hydroxide chemicals were obtained from Sigma-Aldrich, USA. Stock solutions of various anions and cations were prepared by taking appropriate amounts of sodium salt of anions and chloride salt of cations. Unless indicated, analytical reagent grade chemicals and lead free water were used throughout the experiment.

Table 1. Certified values of the soil certified reference materials used in the analysis

Ion	Reference value (mg/kg)					
	CRM 020	CRM 021	CRM 025	CRM 030	CRM 033	CRM 035
Al	1750	2725	7637	4811	10600	5320
As	397.4	24.8	339	13.1	129	148
Ba	22.3	586	1839	56.1	220	61.4
Be	NR	0.18	0.33	5.97	2.55	5.38
B	NR	13.8	17.2	5.29	48.4	67.8
Ca	25584	5426	28320	14184	13500	14300
Cd	20.8	1.19	369	58.4	89.2	254
Co	7	2.7	4.07	NR	95.2	67.1
Cr	13.2	10.7	441	43.8	105	41
Cu	753.3	4792	7.76	5.68	95.5	66.4
CN ⁻	NR	NR	NR	10.4	NR	NR
Fe	191645	6481	9439	8315	11800	8210
F ⁻	NR	NR	NR	29.4	NR	NR
Pb	5194.8	144742	1447	7.13	60.6	132
Hg	1.2	4.68	99.8	6.55	6.45	27.9
Mg	2832.3	2367	4376	2466	4180	2590
Mn	969.4	174	173	127	248	138
Mo	NR	NR	<0.8	8.78	58.3	87.4
Ni	15.9	12.6	12.2	6.63	56	119
K	856.5	1006	1992	1476	3140	3558
Se	NR	NR	518	18.5	88.9	16.2
Si	NR	NR	171	169	NR	NR
Ag	34.2	6.52	132	0.04	0.78	0.335
Na	75.9	380	313	997	109.9	1952
Sr	24.7	NR	408	54.4	NR	NR
Sn	NR	304	NR	NR	386	183
Sb	NR	4955	< 3.2	2.32	79	1.59
Th	NR	0.6	< 4.8	NR	33.1	0.347
V	NR	8.66	19.3	29	112	23.3
Zn	3021.7	546	51.8	74.8	227	18.2

NR = Not Reported

The extracting mixture (HNO₃ and KNO₃) used to extract the lead from the soil was designated as Pb-1P. Pb-2 was a buffer reagent that contains tris-hydroxy methyl amino methane and 2-amino 2-methyl 1, 3 propanediol. The Pb-3 test strip has α , β , γ , δ -Tetra (3-N-methylpyridyl) porphin (TMPyP) reagent and the Pb-4 test strip contains ethylene diaminetetraacetic acid tetra sodium (EDTA) and hydrochloric acid. Recently, we developed a portable compact exact LEADQuick photometer (Jaunakais and Anand, 2008) and used it for the analysis of lead concentration in the soil extracted samples. The pH of the samples was measured using Jenco model 6171 microcomputer based bench pH meter. Small size spatula (weighs-0.15 g) from Measurex, USA was used to collect the soil material for the extraction.

2.2 Extraction Method

One level scoop (0.1 ml volume scoop, which holds ~ 0.15 grams) of soil sample was added to a clean 50 ml graduated plastic conical tube. Twenty drops of reagent Pb-1P was added to the conical tube. The material was swirled for a few seconds until all soil was suspended, thoroughly mixed. After five minutes wait the sample volume was adjusted to 50 ml using deionized, distilled, or lead free tap water. The conical tube was capped, mixed, and identified as the Soil Extracted Solution (SES). The sample was left for five minutes to allow the suspended soil particles to settle. The analysis of the SES was carried by the below test method.

2.3 Test Method:

1. To a clean 50 ml graduated conical tube, 1 ml (1000 μ l) of SES sample was added. The volume was adjusted to 50 ml using lead free tap water. The sample was mixed thoroughly before testing.
2. The meter was turned on by pressing the ZERO/ON button. The display showed all annunciators and then the current MENU selection with last reading.
3. The MENU button was pressed and re-pressed until the display showed the parameter PB2.
4. The cell was rinsed 3 times with the above test sample. Finally, the cell was filled to capacity (4ml) with the test sample. The meter was tilted forward to allow excess sample to flow out in order to make room for Pb-2 Reagent addition below.
5. Five (5) drops of eXact® Reagent Pb-2 were added to the cell.
6. The eXact® Strip Pb-3 was dipped into the CELL and the READ button was pressed. This started the 20 SECOND countdown timer. During this time the strip was moved in a gentle back and forth motion. The strip was removed and discarded after "1" on the display disappeared. The display flashed (- - -) and begin immediately counting from 1 to 60. After the 60 seconds, the meter automatically zeroed. The cursor moved across the display followed by 0 μ g (μ g/L).
7. The eXact® Strip Pb-4 was dipped into the CELL and the READ button was pressed. This started the 20 SECOND countdown timer. During this time the strip was moved in a gentle back and forth motion. The strip was removed and discarded after "1" on the display disappeared. The display flashed (- - -) and begin immediately counting from 1 to 60. After the 60 seconds, the cursor moved across the display, indicating that it was about to measure the sample as μ g (μ g/L). The displayed result was recorded (the meter automatically stored this result in the PB2 menu). The sample was discarded and the cell was rinsed immediately after the test was completed.
8. To convert the value in step 7 from μ g/L to mg/kg use 17.86 as the multiplication factor: (For example: $65 \mu\text{g/L} \times 17.86 = 1161 \text{ mg/kg}$)

NOTE: If lead was not found when the 1.0 ml SES sample was used in step 1, then use either 2, 5 or 10 ml of the SES for lower detection. . If the result read “HI”, then the SES sample was retested using a 0.01 ml sample in Step 1. Convert the value using the multiplication factor in the table 2

Table 2: Parameters used for the detection of lead in various dilutions

SES volume used (ml)	Pb-1P drops	Pb-2 drops	Multiplication factor	Range (mg/Kg)	Accuracy
0.01	0	5	1786	Up to 300,000	± 25%
1	0	5	17.86	18 to 1500	+ 15%
2	0	5	8.93	9 to 1500	+ 15%
5	0	7	3.57	3 to 750	+ 10%
10	0	7	1.79	1 to 250	+ 10%

2.4 Spiked recovery test method

This was also referred to as the Standard Addition method and was used to verify the accuracy of the results. The percentage of recovery was calculated using the following formula:

$$\% \text{ Recovery} = 100(C_s - C_u)/K$$

Where: C_s = Concentration of the spiked sample found

C_u = Concentration of the Un-spiked sample found

K = Concentration of the spike added to the sample

The results for the reference materials along with spiked data were given in table 3.

2.5 Interference study

The interferences study was carried out to determine the effect of other coexisting ions on the extraction and detection of lead. The experiment was performed by the addition of one interfering ion at a time. To summarize this interference study:

1. The interference study was carried for CRM-025 sample using 1000 μ l of SES. The spiked recovery of CRM-025 sample was performed for 1000 μ l of SES using 100 mg/kg of lead concentration. It gave a recovery of 102.1 % (Table 3). The percentage of recoveries indicates that only a small positive interference was observed.
2. Deionized water was spiked with a lead level 100 μ g/L and was used for a second confirmation of the level of interfering ions.

The ion interference level was identified as positive or negative interference, if the recovery is > 120 or < 80%, respectively.

Table 3. Determination of lead in soil certified reference materials along with lead % recovery

Reference material	SES Volume (S), μ l	spiked Pb con. (mg/L), (Sp)	Con. of Pb in soil sample (S) (mg/kg)	Standard deviation (SD)	Con. of Pb in soil sample (Sp) (mg/kg)	Reference value (mg/kg)	% recovery
CRM-020	1000	100	10.23	5.4	124.24	5194.8	98
	2000		17.86				
	2000		26.78				
	5000		17.86				
	5000		21.43				
	2000						
CRM-021	100		142856			144742	
	100		142856				
CRM-025	1000	100	1232	67.41	1360	1447	102.1
	1000		1214				
	2000		1151				
	2000		1036				
	2000		1090				
	1000						
CRM-030	10000		10.71	1.78		7.13	
	10000		7.14				
CRM-033	10000	200	42.86	2.78	223.2	60.6	91
	10000		48.42				
	10000						
CRM-036	10000	300	123.24	0.88	369.25	132	85
	10000		125.0				
	10000						
*FS-1	200	---	0		72		100
	200	200+70					
*FS-2	200	---	0		74		100
	200	200 + 70					

SES = Soil Extracted Solution; *FS-1 = Loomy soil collected from Edisto Island beach
 FS-2 = Rock Hill soil sample

3. RESULTS AND DISCUSSION

The soil analyses result indicates that using HNO_3 - KNO_3 better extraction efficiency is observed compared to HNO_3 alone (Table 4). The data in table 4 also indicates that the extraction efficiency of nitric acid in most of the studied samples is almost on par with potassium nitrate and nitric acid. But due to highly corrosive nature of nitric acid, we decided to use HNO_3 - KNO_3 for further experiments. Our extraction procedure has many advantages in terms of selectivity, simplicity, speed and cost effectiveness compared to microwave, EDTA extraction, and dry, and wet ash digestion methods (Prasad et al., 2006; Gryscho et al., 2005; Chrastny et al., 2008; Tuzen, 2003) and will be highly useful for field detection. In addition to this, our method also uses less sample and reagent

compared to conventional digestion methods, thereby reducing waste and enhancing operator safety.

Table 4. Comparison of extraction efficiency of KNO₃- HNO₃ with HNO₃

Soil sample	Con. of Pb in soil sample (mg/kg)		Reference value (mg/kg)	Remarks
	KNO ₃ - HNO ₃	HNO ₃		
CRM-020	26.78	30.24	5194.8	HNO ₃ extraction is very corrosive.
CRM-021	142856	185234	144742	
CRM-025	1232	1158	1447	
CRM-030	10.71	5.25	7.13	
CRM-033	48.42	40.42	60.6	
CRM-036	125	115	132	

The analyses of soil samples were performed using the test procedure described in the Materials and Methods section using 100 to 10000 µl of SES. The volume of SES depends on the concentration of lead in the sample. The data in table 3 indicates that the reference material with high lead concentration (CRM-021) uses 100 µl of SES. The data also showed that the reference materials with low concentrations of lead (CRM-030, CRM-033 and CRM-036) use 5000 to 1000 µl of SES for further experiments. Very importantly, the data in table 3 and figure 1 indicate that using our extraction procedure and field test strip kit, we can detect very low concentration of lead (7 mg/kg, 10⁻⁹ M) in a wide range of soil samples. The sensitivity of our method is very high (0.03 µg), with a detection limit much below the USEPA permissible level of 400 mg/kg. The precision of our results was verified by analyzing replicate samples and found to be excellent. Basing on the data in table 3, we have optimized to use 1000 µl of SES for further studies. The spiked recovery experiments showed that percentage of recovery in majority of the samples was > 85% (Table 3). This indicates that the high concentration of coexisting ions did not interfere in the detection and also specifies that our extraction protocol was not strong enough to break all of the lead complexes from the soil.

The spiked recovery experiment results (Table 3) showed that the percentage of recovery varied from 85 to 102.1%. The data also specified that with the increase in the volume of SES, the percentage of recovery generally decreases. This was due to increasing the concentration of coexisting ions in the test solution, which affected the lead detection.

The effect of diverse ions on lead detection was examined following the optimized protocol in drinking water and CRM-025. The results in Table 5 showed that no interference was found for sulfate and chloride for both the samples. We observed positive interference for Cd(II), Cu(II) and Hg(II) and negative interference for the remaining ions for both the samples. The other studied ions interfered at high concentration only. The interference data for CRM-025 showed that a majority of the studied ions interfere at low concentrations compared to the same ions studied in a drinking water sample. This could be due to the presence of coexisting ions in the soil reference materials. The presence of any particulate materials may affect the results and to make sure about this, we filtered the sample and carried the interference study. The results show that no affect was observed.

Table 5. Effect of co-existing ions on the detection of Lead

Ion	Soil S2 testing		Drinking water testing	
	Interference level (mg/kg)	Type of Interference	Interference level (mg/L)	Type of Interference
Al(III)	2	Negative	6	Negative
Cd(II)	0.006	Positive	0.02	Positive
Co(II)	5	Negative	13	Negative
Cr(VI)	0.2	Negative	0.6	Negative
Cu(II)	5	Positive	10	Positive
Cl ⁻	>500	None	>500	None
Fe(II)	0.1	Negative	0.5	Negative
Fe(III)	0.2	Negative	0.2	Negative
Hg(II)	0.05	Positive	0.02	Positive
Mg(II)	150	Negative	200	Negative
Mn(II)	0.35	Negative	0.45	Negative
Mo(VI)	20	Negative	80	Negative
Ni(II)	1	Negative	35	Negative
PO ₄ ³⁻	0.5	Negative	16	Negative
Sn(II)	0.5	Negative	0.8	Negative
SO ₄ ²⁻	> 750	None	>750	None
V(V)	2	Negative	6	Negative
Zn(II)	3	Negative	8.5	Negative

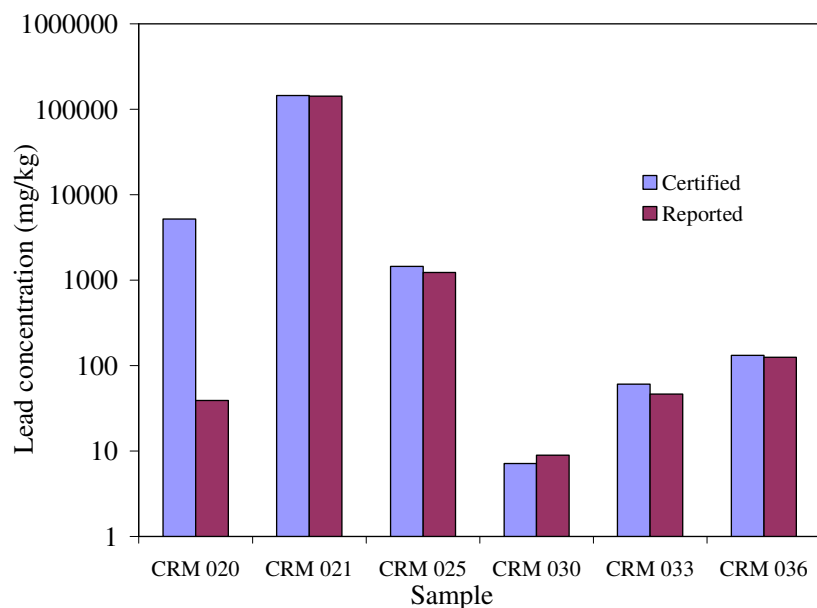


Figure 1: Comparison of the lead concentration with certified data using soil extracted solution of the certified reference materials.

4. CONCLUSION

In conclusion, the experimental data indicates that the developed extraction technique and detection kit was very good to detect lead over a wide range of concentrations. The results showed that using 10000 µl of SES, we can detect very low concentration of lead (7 mg/kg) and also using 100 µl of SES, we can detect very high concentration of lead (142856 mg/kg). This study has confirmed that the LEADQUICK field test kit can be successfully used for the on-site screening of lead in soil samples. The comparison of KNO₃- HNO₃ and HNO₃ for lead extraction showed the advantages of KNO₃- HNO₃ over HNO₃. The kit also demonstrates the high reliability, minimal interference, and low detection limit, which is well below the maximum levels permissible by the USEPA and WHO. The results also suggests that this type of extraction protocol and field test kit has potential application for the analysis of lead arsenate which, until 1988, was used as a pesticide in apple orchards to prevent ravages of insect damage (Environews, 2006).

5. ACKNOWLEDGEMENT

The authors would like to thank Mr. Howard Ray for critically reviewing the manuscript.

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