

Presentation of Predicted Results Based on Numerical Simulation and 'XRF' Analysis of Lead Contaminated Soil and Sequential Extraction

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Abstract

We carried out the 'XRF' analysis and sequential extraction of soils contaminated with lead using lead nitrate of known amount. Noting pertinently, that the nominal lead concentration obtained in the contaminated soil sample earlier in the experimental work is 2,415 mg/kg after appropriate procedures. Looking at our results, we found that the concentration of the solid contaminated samples: OL S 1-2, and OL S 3-2 (2,080.26, and 2,080.41 mg/kg) respectively in that order are very close to the concentration of lead also obtained using the 'XRF' analysis for the liquid solutions obtained from the sequential extraction procedures of soil samples: 'OL S 1-2, and 3-2 as (2,110 mg/kg, and 2,090 mg/kg) respectively in that order. It would not be necessary to carry out the long 'sequential extraction procedure in determining the lead concentration in contaminated soil as the 'XRF' analysis result can be relied on based on the closeness of the results obtained from the two different procedures. Most pertinently and interestingly, the results of the 'XRF and sequential extraction have been predicted numerically and randomly generated based on the 'Monte Carlo simulation technique. The predicted and numerically generated results are good estimates of the experimental results.

Keywords: Sequential extraction; Lead contaminated soil and transport; XRF analysis; Monte Carlo simulation technique

Introduction

Theoretical framework

To describe EDTA and its various protonated forms, chemists distinguish between EDTA^{4-} , the conjugate base that is the ligand, and H_4EDTA , the precursor to that ligand. At very low pH (*very acidic conditions) the fully protonated $\text{H}_6\text{EDTA}^{2+}$ form predominates, whereas at very high pH or very basic condition, the fully deprotonated EDTA^{4-} form is prevalent. In this case, the term EDTA is used to mean $\text{H}_{4-x}\text{EDTA}^x$, whereas in its complexes EDTA^{4-} stands for the tetra-deprotonated ligand (Figure 1).

In coordination chemistry, EDTA^{4-} is a member of the amino poly carboxylic acid family of ligands. EDTA^{4-} usually binds to metal cations through its two amines and four carboxylates. Many of the resulting coordination compounds adopt octahedral geometry. Although of little consequence for its applications, these octahedral complexes are chiral. The anion $[\text{Co}(\text{EDTA})]^-$ has been resolved into enantiomers. Many complexes of EDTA^{4-} adopt more complex structures due to either

the formation of an additional bond to water, i.e., seven-coordinate complexes, or the displacement of one carboxyl at arm by water. The Fe(III) complex of EDTA is seven-coordinate. Early work on the development of EDTA was undertaken by Gerold Schwarzenbach in the 1940s. EDTA forms especially strong complexes with Mn(II), Cu(II), Fe(III), Pb(II) and Co(III) [1].

Several features of EDTA's complexes are relevant to its applications. First, because of its high density, this ligand has a high affinity for metal cations:



Written in this way, the equilibrium quotient shows that metal ions compete with protons for binding to EDTA. Because metal ions are extensively enveloped by EDTA, their catalytic properties are often suppressed. Finally, since complexes of EDTA^{4-} are anionic; they tend to be highly soluble in water. For this reason, EDTA is unable to dissolve deposits of metal oxides and carbonates.

Experimentation

The previous activity was about the determination of lead concentration in contaminated soil. With a nominal concentration, a sequential extraction procedure was carried out to extract the lead in artificial contaminated soil (Table 1).

The initial concentration of lead in the non-contaminated soil was determined. We have an idea of the nominal lead concentration of the

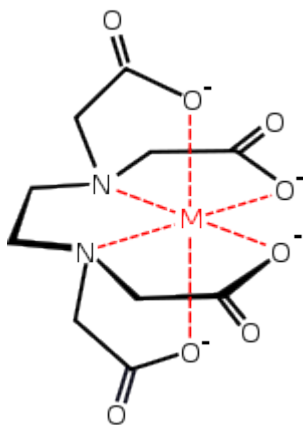


Figure 1: Metal-EDTA chelate.

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Received August 11, 2017; Accepted September 06, 2017; Published September 10, 2017

Citation: Mayowa A, Luigi P (2017) Presentation of Predicted Results Based on Numerical Simulation and 'XRF' Analysis of Lead Contaminated Soil and Sequential Extraction. J Chem Eng Process Technol 8: 351. doi: [10.4172/2157-7048.1000351](https://doi.org/10.4172/2157-7048.1000351)

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contaminated soil.

Subsequently the samples from sequential extraction were analyzed with the 'AAS' and the concentration of the solid sample were determined by 'XRF' analysis method, both before contamination, and after contamination with lead.

The deductions, findings, and observations are reported in subsequent sections.

Sample preparation and method

After sample preparation, and characterization of the soil sample, the previous laboratory activities comprise:

Sequential extraction: Results of the sequential extraction and column experiments are presented briefly. The sequential extraction is a four stage process with the acid strength for the attack of the soil sample increasing with the steps involved in the experimental process. It was based on a 'BCR' sequence of 4 steps procedure, with the acid strength for attack increasing with each step in the sequential order (Table 2).

The BCR procedure of the sequential process was adopted, which is available in manual for explicit description of the procedures involved [2].

The four (4) steps of the sequential extraction process are listed below:

1. Acetic acid to extract all exchangeable, acid and water soluble metals.
2. Hydroxy ammonium chloride to extract all reducible metals.
3. Hydrogen peroxide to extract all oxidizable metals.
4. Aqua regia to extract all remaining, non-silica bound metals.

The 3 new values in Table 3a are obtained based on 'XRF', and 'AAS' analysis of the (new) contaminated soil samples for the column experiment after seasoning, and their residues after sequential extraction from 'aqua regia' attack, and the mean value with standard deviation is shown in Table 3b.

Discussion

The above Table 3b is obtained based on the 'XRF' analysis. Our

Samples	Analysis Name: OL S	'XRF' Solid (mg/kg)	'MC' Solid (mg/kg)	'XRF' Liquid (mg/kg)	'MC' Liquid (mg/kg)	'AAS' Liquid (mg/kg)	'Predicted: based on MC' Estimated (mg/kg)
1	1-1	2035.82	2046	1943	1979	2727	2740
2	1-2 *	2080.26	2092	2110	2114	3065	3005
3	1-3	2116.75	2109	1920	1921	2866.5	2893
4	2-1	2006.78	2027	-	-	-	-
5	2-2	2014.29	2027	-	-	-	-
6	2-3	1833.72	1828	1825	-	-	-
7	3-1	2077.79	-	-	-	-	-
8	3-2 *	2080.41	2091	2090	2060	2906.5	2915
9	3-3	2034.9	2028	1816	1886	2640	2671
1	1.1 (NC)	138.199	-	306	-	155.2	-
2	1.2 (NC)	-	-	312	-	146.6	-

Table 1: Table of Values obtained (new): "based on XRF analysis" 17, 13, and 14 -06- 2016, and 'AAS' 13-07-16 and Predicted based on numerically random generated Monte Carlo.

Sol (mg/kg) 'XRF'	Liq (mg/kg) 'XRF'	Liq (mg/kg) 'AAS'
$M_1=2078$	$M_1=1991$	$M_1=2886$
$M_2=1952$	$M_2=1825$	$M_2=2659$
$M_3=2064$	$M_3=1953$	$M_3=2773$
$\sigma_1=40.53$	$\sigma_1=84.67$	$\sigma_1=169.86$
$\sigma_2=102.25$	-	-
$\sigma_3=25.55$	$\sigma_3=137$	$\sigma_3=188.44$
$\sigma_{ave}=56.08$	-	-
$M_{ave}=2031$	$M_{ave}=1951$	$M_{ave}=2810$
$\sigma_{ave,2}=69.25$	$\sigma_{ave,2}=126.28$	$\sigma_{ave,2}=165.00$

Table 2: Table of Values (means and stdv).

Analysis (new) Samples	'XRF' Solid (mg/kg)	'Predicted' (mg/kg)	'XRF' Liquid (mg/kg)	'Predicted' (mg/kg)	'AAS' Liquid (mg/kg)	'Predicted' (mg/kg)	'XRF' (residues) Liquid (mg/kg)
1	1855.0	1875	1890.2	1893	2285	2266	37.4
2	1724.4	1718	1836.6	1838	2409	2496	42.3
3	1804.6	1804	1729.9	1727	2543	2519	35.5

Table 3a: Table of Values of the (new) contaminated samples, and residues from 'XRF', and 'AAS'.

	Solid (mg/kg) 'XRF'	Liq (mg/kg) 'XRF'	Liq (mg/kg) 'AAS'	Res. (mg/kg) 'XRF'
M_{ave}	1794	1819.9	2412	38.4
σ_{ave}	65.86	81.60	129.03	3.51

Table 3b: Table of Values (mean, and stdv.) of the (new) contaminated sample from 'XRF' and 'AAS'.

samples were oil samples both contaminated, and non-contaminated with 'nitrate di piombo: $Pb(NO_3)_2$.

Samples serial number, 1-9 are soulo samples contaminated with lead nitrate, while the remaining two samples 1 and 2 last bottom of the Table 1 in that sequence were non-contaminated with lead [3,4].

The solid samples of all the contaminated soils with, lead nitrate were analyzed with 'XRF' analysis, and also the non- contaminated soil samples and the results are displayed in the above Table 1.

Out of the 9 soil samples contaminated with lead, we initially selected soil samples: 'OL S 1-2, and 3-2 indicated by the asterisks, with 2 soil samples: OL S' non-contaminated for sequential procedures, arriving at a total of 4 samples: 'OL S' altogether comprising contaminated (C), and non-contaminated (NC).

After the long process of sequential extraction, the liquid samples obtained in 100 ml flask were analyzed by 'XRF' procedure to obtain the lead concentration, and the results were presented in the tables for 1 samples consisting (OL S 1-2, and OL S 3-2 contaminated, C, and OL S 1.1, and OL S 1.2 non-contaminated with lead nitrate).

The sequential extraction was subsequently carried out also on more soil samples: OL S 1-1, OL S 1-3, OL S 2-3, and OL S3-3, and the 'XRF' analysis done to obtain the lead concentration which is presented in Table 1 above [5].

Further discussion and deductions

Looking at our results, we found that the concentration of the solid contaminated samples: OL S 1-2, and OL S 3-2 (2,080.26 and 2,080.41 mg/kg) respectively in that order are very close to the concentration of lead also obtained using the 'XRF' analysis for the liquid solutions obtained from the sequential extraction procedures of soil samples: 'OL S 1-2, and 3-2 as (2,110 mg/kg, and 2,090 mg/kg) respectively in that order.

Noting that the nominal lead concentration obtained in the contaminated soil sample earlier is 2,415 mg/kg after appropriate procedures [6,7].

Finally, since the values of the lead concentrations obtained for the soil samples: OL S 1-2, and 3-2 from the 'XRF' analysis of the solid contaminated soil samples, and the solutions of the sequential extractions of the contaminated solid soil samples: OL S 1-2, and 3-2 respectively, and other results presented are quite close, we can confidently conclude that the 'XRF analysis' procedure is very good enough, and appropriate in obtaining the lead concentration of the contaminated solid soil sample, without necessarily carrying out the

sequential extraction procedures.

Conclusion

Finally, since the values of the lead concentrations obtained for the soil samples: OL S 1-2, and 3-2 from the 'XRF' analysis of the solid contaminated soil samples, and the solutions of the sequential extractions of the contaminated solid soil samples: OL S 1-2, and 3-2 respectively, and other results presented are quite close, we can confidently conclude that the 'XRF analysis' procedure is very good enough, and appropriate in obtaining the lead concentration of the contaminated solid soil sample, without necessarily carrying out the sequential extraction procedures.

Most pertinently and interestingly, the results of the 'XRF has been predicted numerically and randomly generated based on the Gaussian random number generator and 'Monte Carlo simulation technique.

The predicted and numerically generated results are good estimates of the experimental results. Since the 'XRF results are in quite close agreement with the results from the 'AAS analyzed results of the sequential extraction procedure and aqua regia attack, there won't be need to go through the long process of sequential extraction.

In addition, achieving very good numerical estimates of the 'XRF, AAS and others perimentally obtained results would offer very good platform to be able to theoretically predict the lead concentrations of contaminated sites and other heavy metals based on extrapolation of previous and extant literature data and available past experimental results without having to go through rigor of long experiments by finding a very robust predicting tool or model at work.

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