

# EVALUATION OF GEOCHEMICAL QUALITY CONTROL IN DETERMINATION OF Mn IN SOILS USING A SEQUENTIAL CHEMICAL EXTRACTION

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**ABSTRACT:** Sequential chemical extraction procedure has been widely used to partition particulate trace metals into various fractions and to describe the distribution and the statue of trace metals in geo-environment. One sequential chemical extraction procedure was employed here to partition various fractions of Mn in soils. The experiment was designed with quality controlling concept in order to show sampling and analytical error. Experimental results obtained on duplicate analysis of all soil samples demonstrated that the precision was less than 10% (at 95% confidence level). The accuracy was estimated by comparing the accepted total concentration of Mn in standard reference materials (SRMs) with the measured sum of the individual fractions. The recovery of Mn from SRM1 and SRM2 was 94.1% and 98.4%, respectively. The detection limit, accuracy and precision of the sequential chemical extraction procedure were discussed in detailed. All the results suggest that the trueness of the analytical method is satisfactory.

**KEY WORDS:** fraction; sequential chemical extraction; quality control

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## 1 INTRODUCTION

With the study on the toxicology of heavy metal elements, sequential chemical extraction procedure has attracted more and more attention in environmental science. The extraction method is based on the selective extraction of each leaching solution. It, although more time consuming, can furnish detailed information about the origin, mode of occurrence, biological and physicochemical availability, mobilization, and transport of trace metals (TESSLER *et al.*, 1979; PICKERING, 1986; JIANG *et al.*, 1993). Now sequential chemical extraction procedure has been widely used to partition particulate trace metals into various fractions and to describe the distribution and the statues of trace metals in environment (JIANG *et al.*, 1989; MAO *et al.*,

1981).

The purpose of this article was to evaluate the precision and the accuracy of a sequential chemical extraction procedure. Experiments were performed with three soil types, each with three different pH values. Typical element used in this study was trace metal Mn.

## 2 EXPERIMENT

### 2.1 Sampling

Three soil types were collected. Those were a sandy loam over Devonian shale, a sandy loam over granite, and a loamy sand over the lower greensand. Some properties of the soils used for the experiments are listed in Table 1.

Table 1 Some properties of the soils in the experiments

Soil No.	Parent material	Soil group	Clay(%)	LOI(%)	CEC(meq, 100/g)
1	Devonian shale	Brown earth	13.1	9.2	31.4
2	Granite	Brown earth	13.4	10.0	25.4
3	Lower greensand	Brown earth	4.1	3.0	9.1

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After collection, each of the three soil types was amended to give two other pH levels besides the natural one. As appropriate, the pH was lowered by adding finely divided elemental sulphur to dry soil, or it was raised using powdered calcium carbonate (DONG *et al.*, 1999). Equilibrium conditions in the amended soils were achieved by leaving the water-saturated soil in the greenhouse for 30 days (MERRY *et al.*, 1986).

In order to establish the statistical significance of the difference between results for each soil treatment, each treatment was replicated five times. Thus there were a total of 45 piles of soil. On the soils, soybean was grown in a greenhouse at 25°C over a period of two months. Then soil samples were collected after the plants were harvested. Representative soil samples for determination were air-dried, and then disaggregated to pass a 2mm mesh sieve prior to chemical analysis.

## 2.2 Leaching Procedure and Reagents (LI and COLES, 1995)

The extraction was carried out progressively on an initial weight of 1.000g of test material. The procedure and chemical fractions were described as follows:

(1) Exchangeable— sample was extracted with 8ml of 0.5M MgCl<sub>2</sub> at pH 7.0 for 20min, with continuous agitation, at room temperature.

(2) Bound to carbonate and specially adsorbed— residue from step (1) leached for 5h with 8ml of 1M NaOAc (adjusted to pH 5.0 with HOAc) at room temperature. Continuous agitation was maintained during the extraction.

(3) Bound to Fe-Mn-oxides— residue from step (2) was extracted with 20ml of 0.04 M NH<sub>2</sub>OH · HCl in 25% (v/v) HOAc for 6h. The extraction was performed at 96°C with occasional agitation. After extraction, the extract solutions were diluted to 20ml with DIW and subjected to continuous agitation for 10min.

(4) Bound to organic matter and sulphides— to the residue from step (3), 3ml of 0.02M HNO<sub>3</sub> and 5 ml of 30% H<sub>2</sub>O<sub>2</sub> (adjusted to pH 2.0) were added. The sample was then heated progressively to 85°C, and maintained at this temperature for 2 h with occasional agitation. A second 3ml of 30% H<sub>2</sub>O<sub>2</sub> (adjusted to pH 2.0) was then added, and the mixture was heated again at 85°C for 3h with intermittent agitation. After cooling, 5ml of 3.2M NH<sub>4</sub>OAc in 20% (v/v) HNO<sub>3</sub> were added, followed by dilution to a final volume of 20ml with DIW. The tubes were then continuously agitated for 30min.

(5) Residual— residue from step (4) was digested with 10ml concentrated HNO<sub>3</sub> and 5ml HClO<sub>4</sub> to dryness. The remaining material was then taken up in 1M HNO<sub>3</sub>, and diluted to 10ml with 1M HNO<sub>3</sub>.

Following each extraction, the mixtures were centrifuged at 2000 r.p.m. for 20min at room temperature. An aliquot of the supernatant was decanted into clean glass test tubes using a pipette. The aliquot used for each extraction step was 4, 1, 15 and 15ml for steps (1), (2), (3) and (4), respectively. After that, to the aliquots of extractant solutions from steps (1) – (4), 1ml concentrated HNO<sub>3</sub> was added. And then, as for steps (1) and (2), the solutions were heated to dryness at 140°C. While as for steps (3) and (4), after the addition of HNO<sub>3</sub>, these extract solutions were left overnight on a heating block at 90°C and heated to dryness at 140°C to which the temperature was raised slowly. The residue in the tubes was then leached with 2ml of 5M HNO<sub>3</sub>, and made-up to final volume of 10ml with DIW.

Finally, the concentrations of Mn were determined by flame atomic absorption spectroscopy (FAAS) and reported on a dry weight basis.

## 3 ANALYTICAL QUALITY CONTROL

### 3.1 Analytical Precision

It is known that the precision of an analytical method is not constant but varies as a function of the analyte concentration. A linear relationship has been suggested (THOMPSON and HOWARTH, 1976) giving the standard deviation ( $S_c$ ) at a concentration ( $C$ ) by the equation (1):

$$S_c = S_0 + \theta \cdot C \quad (1)$$

where  $S_0$  is the standard deviation at zero analyte concentration and  $\theta$  is the precision constant to which the relative standard deviation tends at high analyte concentrations.

In this study, the analytical precision for each of the extraction steps was estimated by subjecting all of the soil samples in duplicate to the sequential procedure described above (THOMPSON and HOWARTH, 1976). These 90 samples were treated as separation test portions throughout the analytical process. Then the parameters of the analytical precision ( $S_0$  and  $\theta$ ) were estimated by comparing the mean value and the difference for each pair of duplicate results. Practically, the parameters were finally determined by regression analysis.

### 3.2 Analytical Accuracy

The analytical accuracy was controlled by analysis of standard reference materials (SRMs) and reagent blanks.

SRMs of appropriate matrix, SRM1 and SRM2, were selected and inserted into each batch of samples at random positions. For each SRM, the mean of the analysis results for individual fraction of Mn was obtained. The measured value was the sum of the means of the five fractions. The recovery of Mn from the SRMs was then given by a comparison of the measured values to the accepted values.

Reagent blanks were included as 10% of the samples at irregular intervals to detect possible contamination in the analytical system and laboratory environment. Moreover, they were also used to estimate detection limits of the analytical method.

## 4 RESULTS AND DISCUSSION

### 4.1 Detection Limit

The detection limits for the five fractions of Mn, based on twice the standard deviation on the blank sample, are listed in Table 2. As far as the values of the detection limits were concerned, they were low enough to determine each fraction of Mn in the samples.

As there were not any soil samples in reagent blanks, the completeness of extraction and the selectivity of leaching reagent would have little effect on the standard deviations of the blank samples and the detection limits. Attention would be paid to the effect of contamination from laboratory environment and reagents on the detection limits. This contamination is an im-

portant factor resulting in high blank values or irregular ones. In the air there is a lot of dust containing such metal elements as Na, K, Ca, Mg, Al, Fe, Zn, Cu, Mn, Pb etc. The concentrations of them are especially high in city's air. As a result, the longer the duration of extraction and sample preparation was, the more contamination would occur. Thus the detection limit might be deteriorated by long analytical period. Besides, contamination also comes from the reagents used in an experiment. In this study, many kinds of reagents were used during the extraction procedure. Although the purity level of these reagents was analytical grade, there still were some commonly found metals with low concentration which would influence blank values significantly. Moreover, detection limit would vary with the amount of reagents used. Generally, detection limit would tend to increase with the amount of reagents used. So the reagents used in the experiment would be considered as another factor affecting the detection limits.

From Table 2, it was shown that the first step whose leaching time was the shortest had the lowest detection limit, while the third step and the fourth step whose leaching time was the longest had the highest detection limits. When it came to the steps whose leaching time and digestion procedures before determination were roughly the same, the detection limits of them were much close. The third step and the fourth step were the case in point, whose detection limits were 1.99  $\mu\text{g/g}$  and 2.08  $\mu\text{g/g}$ , respectively. As for the second step and the fifth step, although they had same duration in the extraction procedure, the detection limits were obviously different. This reflects the effect of chemical reagents on it.

Table 2 The detection limits and preparation periods for the fractions of Mn

Fraction	Detection limit ( $\mu\text{g/g}$ )	Sample preparation period		
		Leaching time	Centrifuging time	Digestion time
1. Exchangeable	0.89	20min	20min	time of drying at 140°C
2. Bound to carbonate and specially adsorbed	1.55	5h	20min	time of drying at 140°C
3. Bound to Fe-Mn-oxides	1.99	6h and 10min	20min	one night and time of drying at 140°C
4. Bound to organic matter and sulphides	2.08	5h and 30min	20min	one night and time of drying at 140°C
5. Residual	1.35	--	--	about 5h

### 4.2 Analytical Precision

Analytical precision of each fraction of Mn is listed in Table 3. On the whole, the results in Table 3 showed that the analytical precisions were less than the target

of 10% (at 95% confidence level), which were considered acceptable in environmental analysis.

Comparison of the analytical precisions of the five fractions, it would be implied that the precision might increase with the extraction step. This was possible

Table 3 Analytical precision of the sequential chemical extraction

Fraction	Regression equation	Correlation coefficient	Coefficient of variation	Precision* (%)
1. Exchangeable	$S_c = 0.27 + 0.015 C$	0.8134	0.036	7.20
2. Bound to carbonate and specially adsorbed	$S_c = 0.68 + 0.005 C$	0.9115	0.021	4.13
3. Bound to Fe-Mn-oxides	$S_c = 2.38 + 0.023 C$	0.7531	0.039	7.89
4. Bound to organic matter and sulphides	$S_c = 0.26 + 0.013 C$	0.5950	0.028	5.67
5. Residual	$S_c = 1.07 + 0.039 C$	0.9572	0.046	9.24

\* Precision was taken to be twice the coefficient of variation (95% confidence level).

because the errors would accumulate during the extraction procedure. However, the analytical precision of fraction 1 and fraction 3 were higher than expected. That might result from the completeness of extraction and the selectivity of leaching reagent, which should be important criteria of evaluating an extraction method (XU and ZENG, 1982; ZHOU, 1993). Moreover, the re-adsorption of trace elements and superimposition of leaching reagents might also be the reasons causing the poor precision according to recent studies (BELZILE *et al.*, 1989; KIM and FERGUSSON, 1991).

The clay minerals are chemically significant components of soils. These secondary minerals consisting basically of hydrated aluminium and iron silicates serve to adsorb trace metal cations. When the soil samples were extracted with 1M MgCl<sub>2</sub>, the exchangeable Mn would exchange with similar ion Mg<sup>2+</sup> in the solution. The leachate then had the exchangeable Mn from the soil samples. As the reaction that occurs in ion exchange is a reversible reaction, enough time should be required to achieve the equilibrium condition when the concentration of exchangeable Mn in leachate would be constant (WU *et al.*, 1986; GIBSON and FARMER, 1986). Thus, leaching time might be one of the important factors which would affect the analytical precision of this extraction step (1). In this study, 20 min was chosen, which might not be sufficient compared with that suggested in some studies (TESSLER *et al.*, 1979; GIBSON and FARMER, 1986). This would be the reason why the precision associated with the leaching step was high though the extraction procedure began with it.

The most successful methods for leaching iron and

manganese oxides involve the combined action of reagents reducing these metals to their ferrous and manganous forms respectively, and of agents capable of keeping in solution the relatively large amounts of metals liberated (TESSLER *et al.*, 1979). In this study, hydroxylamine hydrochloride—acetic acid was used to extract metals bound to Fe-Mn-oxides. Under the selected leaching condition, the extraction might be complete. Furthermore, organic matter was not significantly leached after treatment with NH<sub>2</sub>OH · HCl—HOAC. And only slight attack of the major silicate components occurred during this extraction step. However, the possible liberation of some metals from labile organic complexes could not be excluded at the same time (TESSLER *et al.*, 1979). This might result in the high coefficient of variation.

The analytical precision of the fraction 5 was the highest. This would be caused by the accumulation of errors for this step was the last one of the sequential chemical extraction procedure.

#### 4.3 Accuracy

The analysis of SRM1 and SRM2 was used to estimate the accuracy of the analytical method. The overall recovery of Mn for the reference materials in this study is listed in Table 4. The recovery obtained, based on a comparison of the sums of the amounts of the fractions extracted in the five steps with the accepted values, averaged 94.1% and 98.4% for SRM1 and SRM2, respectively. The high recovery of Mn from SRMs suggests that the trueness of analytical method is satisfactory.

Table 4 Overall accuracy estimate of Mn from SRMs

SRM	Concentration of each fraction of Mn (μg/g)					Total (μg/g)	Accepted value (μg/g)	Recovery efficiency (%)
	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5			
SRM1	6.68	15.50	52.30	2.26	30.10	106.84	113.59	94.1
SRM2	68.20	207.00	747.00	58.10	298.00	1378.30	1400.92	98.4

## 5 CONCLUSION

In this study, the detection limits were low enough to determine the concentrations of the five fractions of Mn in soils.

They were influenced by the duration of the extraction procedure and reagents used in the study. The analytical precision was less than 10% at 95% confidence level. It increased with the extraction step. This was possible owed to the accumulation of error during the sequential extraction procedure. The factor causing the high precision of the analysis of fraction 1 and fraction 3 might be the leaching condition and the extraction reagent used.

The recovery of Mn in soils (94.1% and 98.4% for SRM1 and SRM2, respectively) suggests that the trueness of analytical method is satisfactory.

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