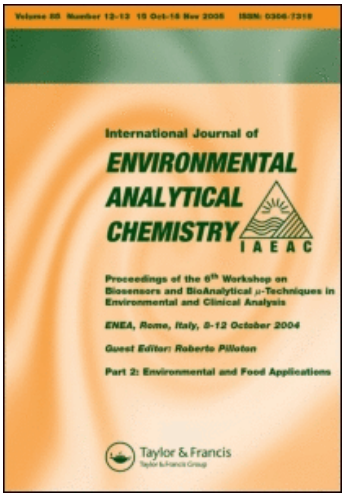

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SPECIATION OF HEAVY METALS IN SOILS, SEDIMENTS, AND SLUDGES USING D.C. PLASMA ATOMIC EMISSION SPECTROMETRY COUPLED WITH ION CHROMATOGRAPHY

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An analytical method has been developed that can provide more reliable analytical information than the classical fractionation method which has been used by soil scientists for years to determine heavy metal contents of soil, sediment, and sludge samples. The new approach utilizes d.c. plasma atomic emission spectrometry in combination with ion chromatography (DCPAES-IC), whereby the DCPAES provides element selective measurements of the chromatographic effluents. In this way, the combined analytical system provides information on all the species of a metal present in the different steps of the fractionation approach. The DCPAES-IC approach also addresses questions pertaining to completeness of extraction, interference, and reagent concentration effects.

KEY WORDS: Metals speciation, d.c. plasma atomic emission spectrometry, ion chromatography, element selective detector.

INTRODUCTION

The determination of heavy metals in soil, sediment, and sludge samples has relied to a great degree on a procedure developed by soil scientists more than thirty years ago[1-5], which is commonly referred to as the Tessier method. Typically, this method classifies heavy metals in soils, sediments and sludges into five categories or fractions, namely: exchangeable, adsorbed, organically bound, carbonate, and sulfide fractions. These fractions are determined by a successive extraction protocol requiring different reagents for each fraction. Accordingly, the exchangeable fraction is believed to contain metals retained in soils through cation exchange processes; the adsorbed fraction represents metal retained by sorption processes; the organically bound fraction represents metal species chelated or complexed by organic constituents of the soil; the carbonate fraction is that fraction existing as carbonates; and the sulfide fraction accounts for the metals precipitated as sulfides[6-12].

Even though the Tessier method has been modified somewhat over the years, several fundamental questions are yet to be sufficiently addressed in relation to the reliability and completeness of the analytical data provided by this general procedure. One concern

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is that it tends to generalize on the types and amounts of reagents to use notwithstanding the inherent differences among soils, sediments, and sludges in terms of their metal binding characteristics. Furthermore, and perhaps the more serious concern over the procedure is that it is a fractionation method; it classifies metals in soils, sediments, and sludges in broad terms without regard for the different forms in which they could exist, and how these species would be affected by the reagents employed[13]. Closely related to this point is the inability of the method to include in the analytical protocol a means of evaluating how a given step in the fractionation scheme could alter the original form of the metal(s), knowledge of which could be quite significant in environmental and biological considerations.

The purpose of the work reported in this paper was to reexamine the Tessier fractionation method, evaluating its overall reliability to provide accurate analytical information for use in assessing the pollution and toxic effects, and bioavailability of heavy metals. The research attempted to address the following questions: (1) What kind of speciation information can be discerned from the different steps of the Tessier fractionation protocol? (2) How do the reagents and procedures used in each step affect or influence metal speciation? (3) Are the procedures and reagents used equally effective for different types of sample, i.e., soils, sediments, and sludges?

EXPERIMENTAL SECTION

Instrumentation. Measurements of metal species in the various successive fractionation steps were accomplished by using ion chromatography, Dionex Model 2010i (Dionex Corporation, Sunnyvale, California), in combination with a d.c. plasma atomic emission spectrometry, Model Spectraspan IV (Fisons Corporation). Cationic and anionic metal species were separated on analytical columns obtained from Dinex Corporation, models HPIC-CS5 and HPIC-AS7 columns, respectively. The d.c. plasma served as an element selective detector for the chromatographic system. The effluents from the chromatographic column were directed to the d.c. plasma where all the moieties of a given metal were detected with equal efficiency at a fixed wavelength. To complement the speciation data obtained with the DCPAES-IC system, chromatographic effluents we also detected colorimetrically following postcolumn derivatization of the separated metal species. This mode of detection was accomplished by directing the chromatographic column effluents to a reaction coil containing 4-(2-pyridylazo)resorsinol (PAR) which converted metal ions into colored complexes. These were then detected by a variable wavelength uv-vis detector, Dionex (Corporation, used at a fixed wavelength of 520 nm.

The total metal contents of the successive extracts were determined by using the d.c. plasma operated in a direct sample injection mode, i e., while disconnected from the chromatographic column. Atomic absorption spectrophotometric measurements, employing a Perkin Elemer Model AAS 4000, (Perking Elmer Corporation, Norwalk, Connecticut) were also performed on the extracts to verify or complement the d.c. plasma data.

MATERIALS AND SUPPLIES

Standard, samples, and other experimental materials

Calibration standards and synthetic samples of the metals used in the investigation were prepared from dilutions of appropriate volumes taken from 1000 mg/L stock solutions.

These stock solutions were prepared from high purity nitrates of the metals of interest. The metals studied included lead, copper, zinc, and manganese, which were supplied by Fisher Scientific, Fair Lawn, New Jersey; and ferric and ferrous nitrate which were supplied by Mallinckrodt Chemical Company, Paris, Ky. Solutions and dilutions were done with distilled-deionized water prepared in-house. Where acidification was required, it was done with ultrapure nitric and/or hydrochloric acids supplied by Fisher Scientific.

The environmental samples used in the study consisted of soils, sediments, and sludges. Soils were obtained locally from agricultural fields in the Hampton area. They were collected in plastic bags, dried at about 80°C, and then stored in a desiccator at room temperature. Experimental quantities were taken as needed and processed as discussed below.

Sediment samples were collected from the Hampton River by first scrapping off about two centimeters from the top layer during low tide. Samples were collected at depths ranging from 2–10 cm below the top layer. They were dried at 80°C, sieved to remove detritus, wood chips, shells, etc., and then stored at room temperature in a desiccator. Experimental quantities were weighed out as needed and processed as discussed below.

Composted sludge samples were supplied by Hampton Roads Sanitation District in Newport News, Virginia. After drying in an oven at 80°C, wood chips and other large materials were removed and then the sample was sieved into different particle size ranges.

General procedure

The objective in this research was to apply metal speciation methods which were previously developed in this laboratory[14–17] to determine the efficacy of the sequential fractionation method in providing reliable analytical data. The chromatographic and spectroscopic characteristics of the metals of interest were verified using synthetic samples prepared from standard solutions. The information obtained and other works previously reported from this laboratory were then used as reference and calibration for the soil, sediment, and sludge samples.

One to two grams of soil, sediment, and sludge samples were processed and treated according to the protocol developed by Tessier and others[18,19], which is summarized in Table 1. In each case, 25 mL aliquots of the respective reagent was employed in the extraction, except where reagent volume effects were investigated. The extraction mixture was separated by using an ultracentrifuge operated at 2000 rpm. The supernatant was then analyzed for the respective metal fractions. The extraction procedure was repeated as needed, evaluating other experimental parameters such as completeness of

Table 1 Summary of the Tessier Successive Extraction Protocol.

Reagent	*Stirring Time (hrs)*	*Metal Extraction*
(I) 0.5 M KNO_3	16	Exchangeable
(2) DDW	2 (done 3 times)	Adsorbed
(3) 0.5 M NaOH	16	Organically bonded
(4) 0.05 M EDTA	6	Carbonate
(5) 4 M HNO_3	16 (70–80)°C	Sulfide/residual

extraction, speciation, effects of reagent concentration, and solution parameters such as pH.

RESULTS AND DISCUSSION

Completeness of Extraction. The distribution of metal species among the extraction fractions obtained depended on the type of metal extracted, the type of sample used, and the degree to which the extraction process was carried out. Figure 1 shows data obtained for a single extraction of iron from a soil sample. It would appear from this single extraction that while some iron was found in each of the extraction steps, the majority of it was in carbonate form. However, upon repeating the extraction for a second time, the data obtained were quite different as depicted in Figure 2, which shows that the overwhelming amount of iron was extracted from the sulfide fraction during the second time around. This amount accounted for about 60% of the total iron extracted compared to the 12.5% obtained in the single extraction. Moreover, the total amount extracted in all

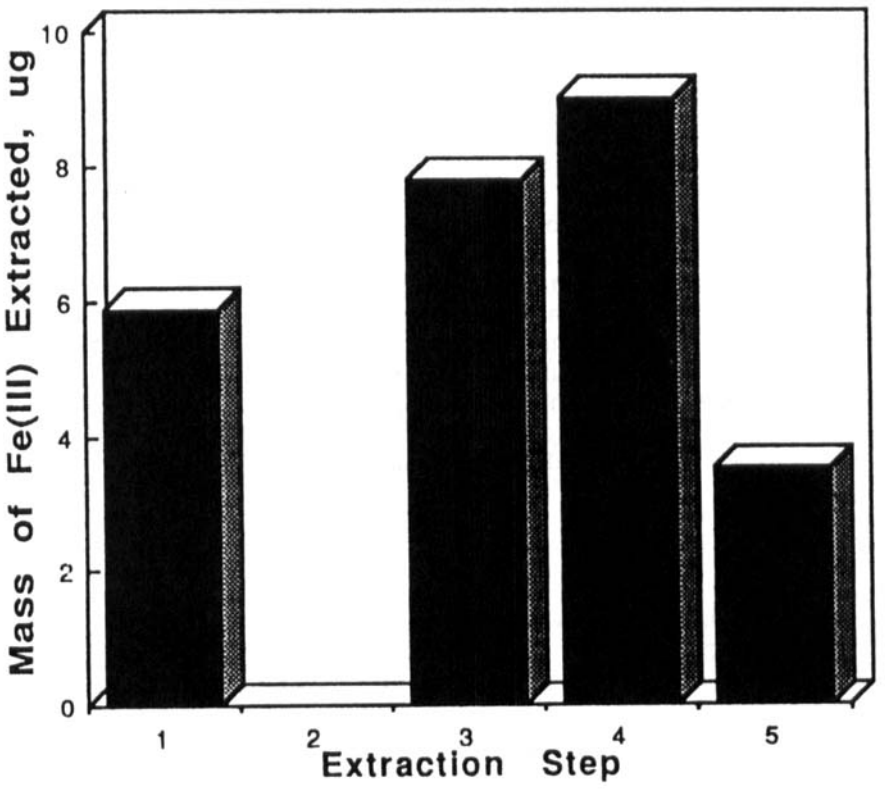

Figure 1 Mass of Fe(III) extracted from 1.0 gram of soil sample in each of the five extraction steps.

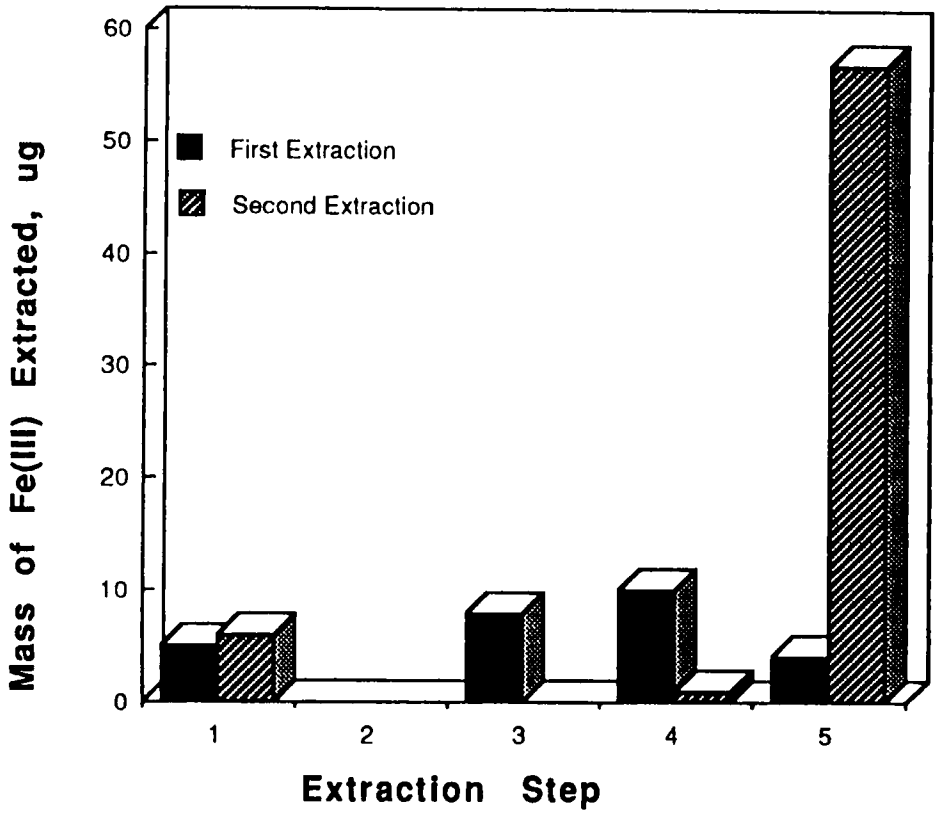

Figure 2 Mass of Fe(III) extracted from 1.0 gram of soil. Two extractions were performed at each step.

fractions with one extraction is 25% of that extracted with two extractions. In all cases, a third extraction did not produce significant amounts of iron from this particular sample.

These data point to the necessity of repeating the extractions to verify the accuracy of the analytical information obtained for a given fraction. While it would be more efficient, and preferred to use reagent volumes which would remove the desired fraction in one extraction, such volumes may not be known before hand. It is only by repeating the extraction that a determination can be made as to whether that particular fraction was exhausted. The results reported above and later below indicate that there can be variations in the extraction requirements depending on the nature of the sample, the metal being measured, and the extraction step itself.

Variations in fractional distribution among metals was studied by determining in the soil sample used above the amounts of copper and manganese extracted in each step in a single extraction. The results are shown in Figures 3 and 4, respectively. Copper appeared to be distributed among all the fractions, most of it occurring in the organic and sulfide portions. Manganese also appeared in all fractions, but in smaller relative amounts compared with the sulfide fraction, which accounted for over 80% of the total

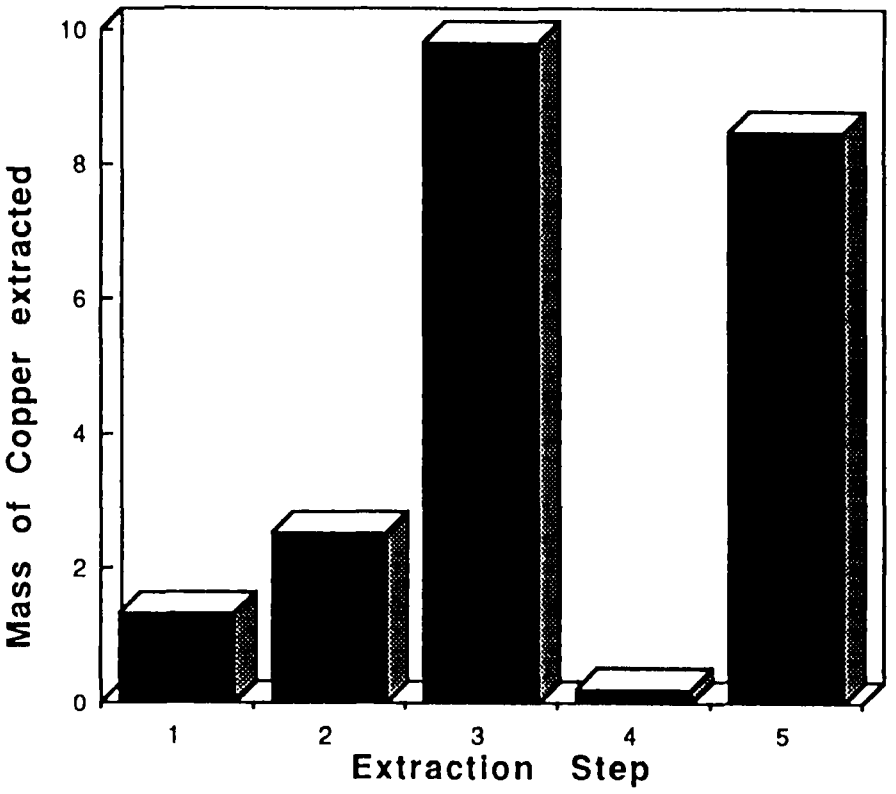

Figure 3 Mass of copper extracted from 2.0 grams of soil sample in each extraction step.

manganese in the sample. An important observation made in connection with this sample was the large amount of manganese found, which was more than one hundred times the amount of copper. What this means is that the experimental procedures used, including reagent volumes, to determine the metal contents of soils, sediments, and sludges may not be equally suitable for different materials and metal species. In some cases there may be need to develop protocols tailored specifically for metals of interest.

While in some cases the extraction is progressively exhausted with repeated extractions, in others, completeness of extraction can occur abruptly. In those cases where more than one extraction is necessary, there are two consequences; first, the subsequent fraction will contain an amount of the metal carried over from the previous steps, which leads to erroneous interpretation of the results of both steps.

Secondly, the amount carried over to the next step contaminates the fraction to be determined in that step.

Variations associated with sample type are depicted in Figure 5, which shows the relative amounts of copper extracted in the organic fractions of soil and sediment samples, respectively. While the amount of organically bound copper in soil increased with the number of extractions, the reverse was true for the sediment sample, pointing to

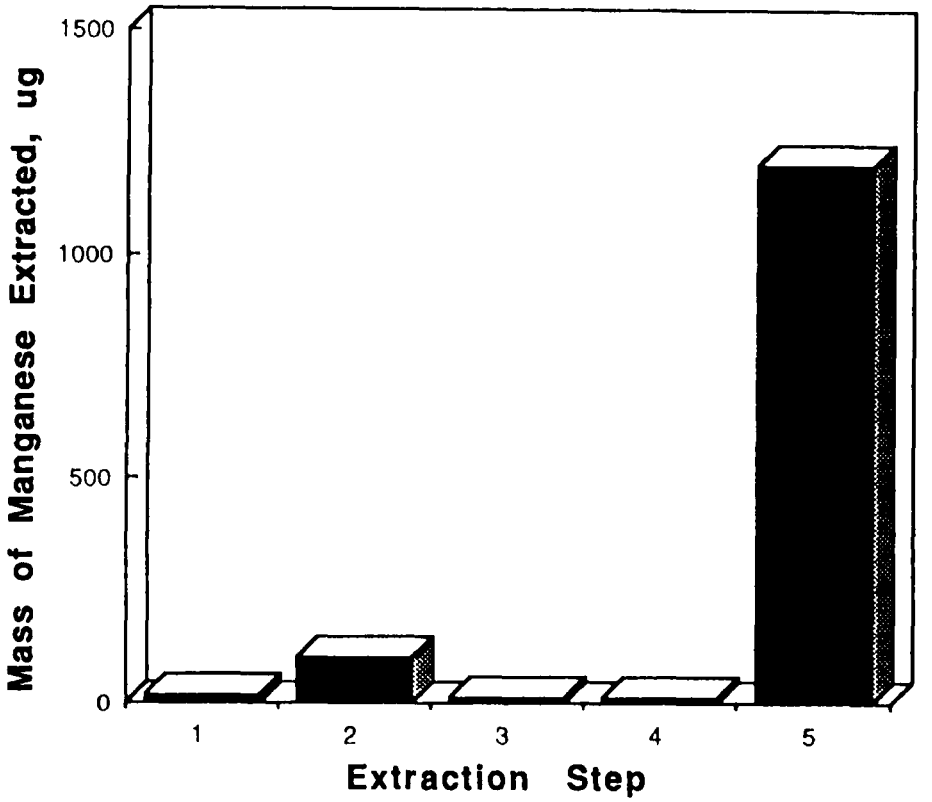

Figure 4 Mass of manganese extracted from 2.0 grams of soil sample in each of the extraction steps.

inherent differences in the mechanisms involved in metal binding. This is a reflection of the functional group differences of the complexing ligands in the samples. Therefore, applying the same procedure to soils and to sediments can lead to erroneous results. However, this conclusion can only be made for the samples used in this study.

Metal speciation in successive extraction fractions

The constituents of the successive extraction solutions were separated on an ion chromatographic column under conditions previously developed in this laboratory and published in the literature[14–17]. Ion chromatograms of standard metal solutions were obtained for use in interpreting the data obtained with the soil and sediment samples. Some of the samples appeared to have only one metal species in the extracts; however, their chromatographic retention times were significantly shorter than the retention times of respective standards prepared from inorganic salts. This would suggest that the metal species found in the extracts may have been in a different form than the standards; most likely in some form of organic compound.

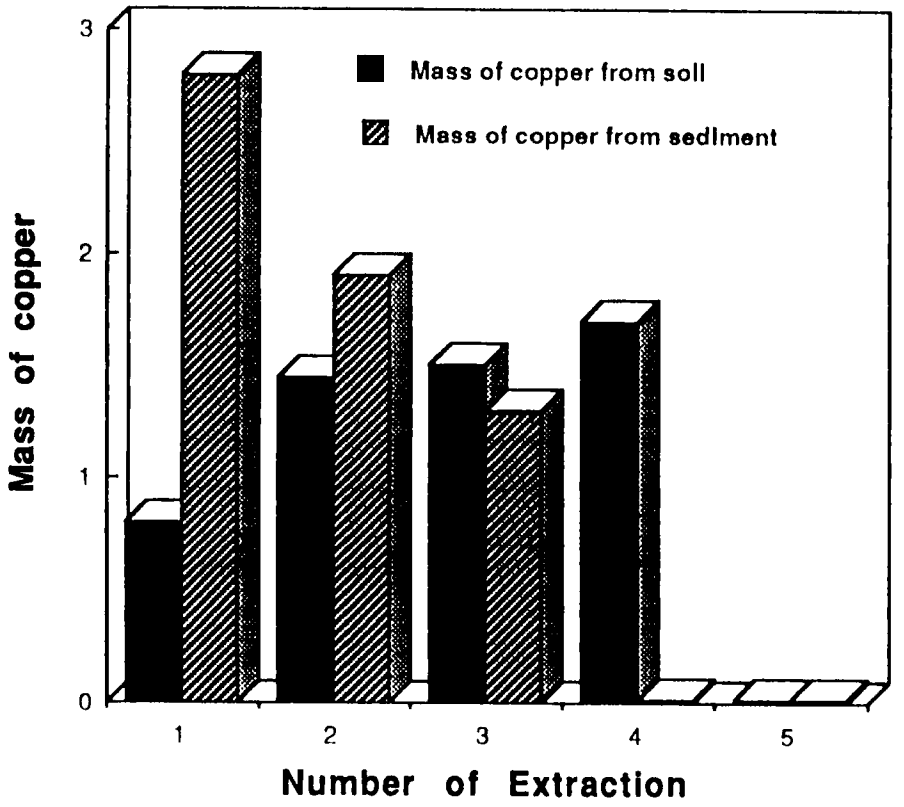

Figure 5 Extracts of copper from soil and sediment samples.

Some of the river sediment sample extracts had two forms of iron, Fe(III) and Fe(II). As shown in Figure 6, the two forms of iron were clearly separated in each of the several extracts obtained from step five of the protocol, using HCl instead of HNO_3, and skipping the first three steps. The first three steps, which call for reagents such as KNO_3, and NaOH, produced extracts which contained only one form of iron, Fe(III). This points to the inability of the successive extraction approach to provide information on the different species of metal that may be in the sample, knowledge of which is vital in assessing the bioavailability and environmental impact of the metal.

Completeness of extraction

In step four of the successive extraction protocol, metals are extracted as EDTA complexes. The question is whether the amount of the reagent used would be enough to complex all the metal species present, notwithstanding the fact that this ligand has affinity for a large number of metals. The successive extraction method does not put into consideration the possible existence of the metals in the natural environment as complex ions in association with ligands with similar characteristics as EDTA.

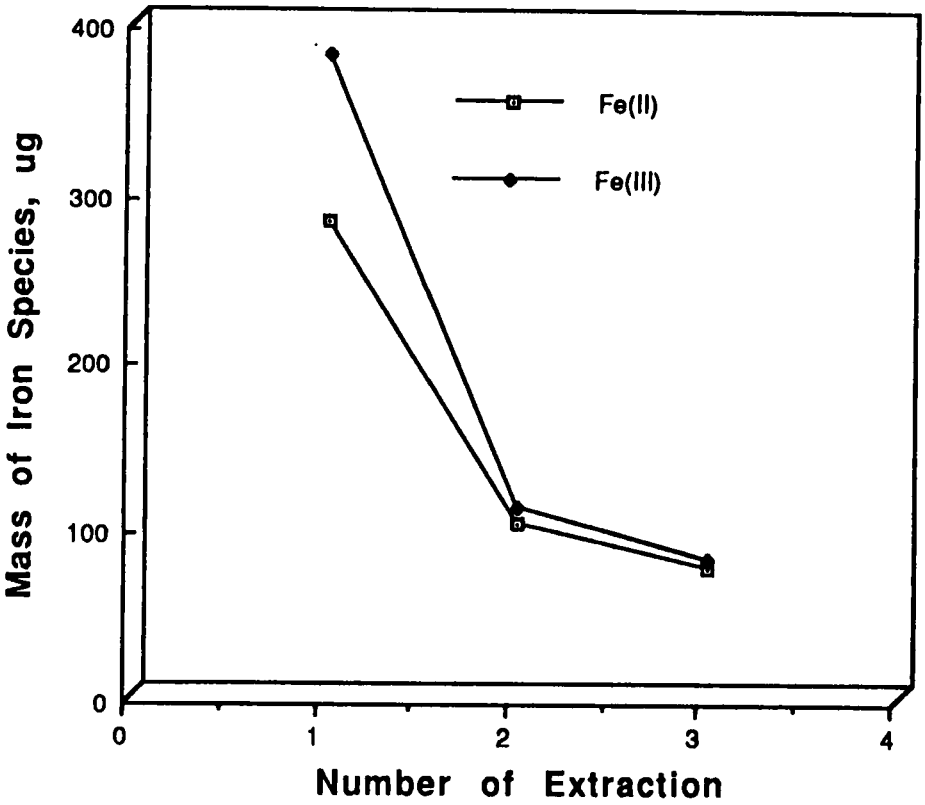

Figure 6 Mass of Fe(II) and Fe(III) extracted from 2.0 grams of river sediment.

Experiments were conducted to demonstrate that if the procedure does not use an excess amount of the ligand to ensure complexation of all the metals present, and depending on the measurement method used to measure the metal complexes, erroneous results will be produced. This was done by measuring EDTA extracts of a soil sample using IC coupled with both DCPAES and UV-Vis spectrophotometry as detection methods.

The UV-Vis method is based on colorimetric determinations done at a fixed wavelength, 520 nm. Therefore, in order for the chemical entity to be detected, it must absorb at this wavelength. For metal ions, post-column derivatization is followed by spectrophotometric measurement. If the effluent has both free and derivatized forms of a given metal, only the derivatized form will be measured. Indeed this was the case for the free metal-PAR complexes measured using the UV-Vis detector. Only single peaks of the metals present were obtained.

When the same solutions were detected with d.c. plasma however, two peaks were obtained, one due to the free uncomplexed metal, and the other due to the metal-ligand complex. This was observed when EDTA and PAR were employed. As depicted in Figure 7, with the d.c. plasma detector, as long as there are two species of a given metal,

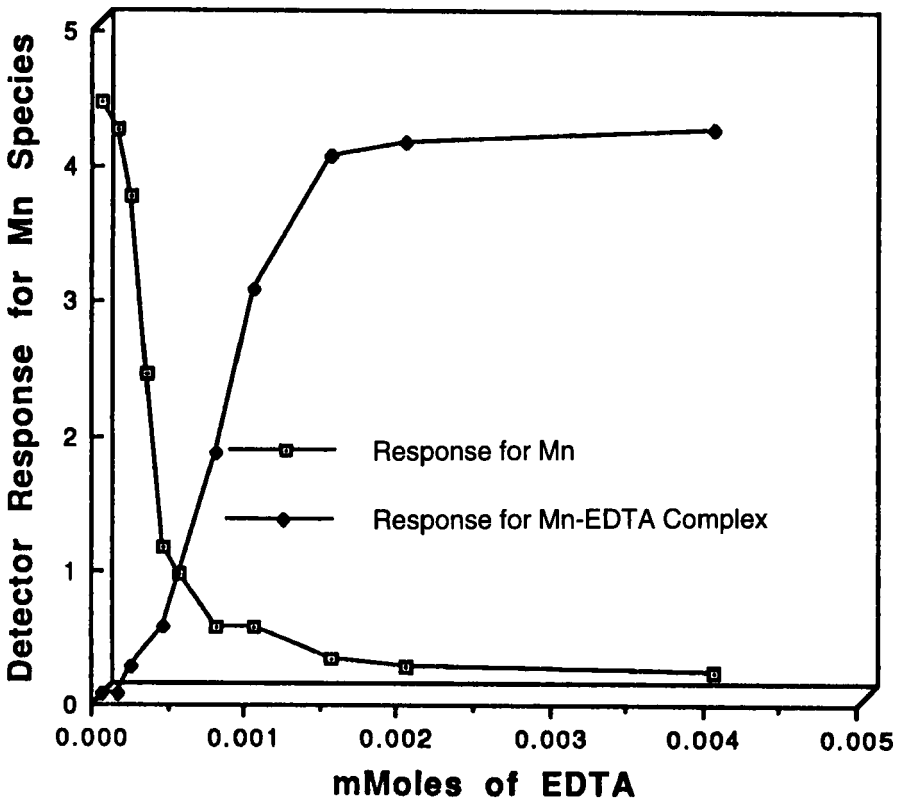

Figure 7 Speciation of manganese using d.c. plasma as element selective detector for Ion Chromatography.

one free and the other complexed, two sets of chromatographic peak data will be obtained. For a fixed amount of metal, an increase in the amount of EDTA leads to a diminished free metal peak, until a point is reached where all the free metal is complexed. From this point on, only one peak, that of the complex, will be present. This is an effective and accurate way of monitoring the completeness of extraction of the metal in this particular step of the fractionation method.

Reagent concentration effects

The Tessier extraction protocol specifies the volumes and concentrations of the reagents to be used in each step. While this information can serve a guide in planning experimental conditions, it can seriously compromise the outcome of the analysis since as was indicated above, the distribution of metals in different samples can vary widely. Therefore, specifying the amount and concentration of the reagent can be misleading.

This was demonstrated in this work by performing the acid extraction step with several portions of a sludge sample using HCl. Each of the 2.0 grams of sludge used was

extracted with different concentrations of HCl, starting with 0.1 M. The extractions were analyzed for Cu, Fe, and Zn. The results for Cu and Fe are shown in Figure 8. While in both cases the amount of metal extracted increased as the acid concentration increased, the relative amounts of the metals extracted differed significantly. As the amount of HCl increased, three iron species were identified, apparently as the Fe^{2+} specie was converted into a chlorocomplex. The conversion of Fe(II) into a chlorocomplex in the presence of high concentrations of Cl^- has been previously studied using d.c. plasma in combination with ion chromatography[17].

These data point to the potential problems that can be encountered by not using enough reagent or using more than is necessary. In either case the risk of obtaining erroneous speciation data is quite significant.

However, a close observation of the data in Figure 8 will show that the inverse relationship between the amounts of Fe and Zn extracted can be used to selectively extract one metal in the presence of the other. As shown in Figure 9, an acid concentration can be determined to allow this selectivity.

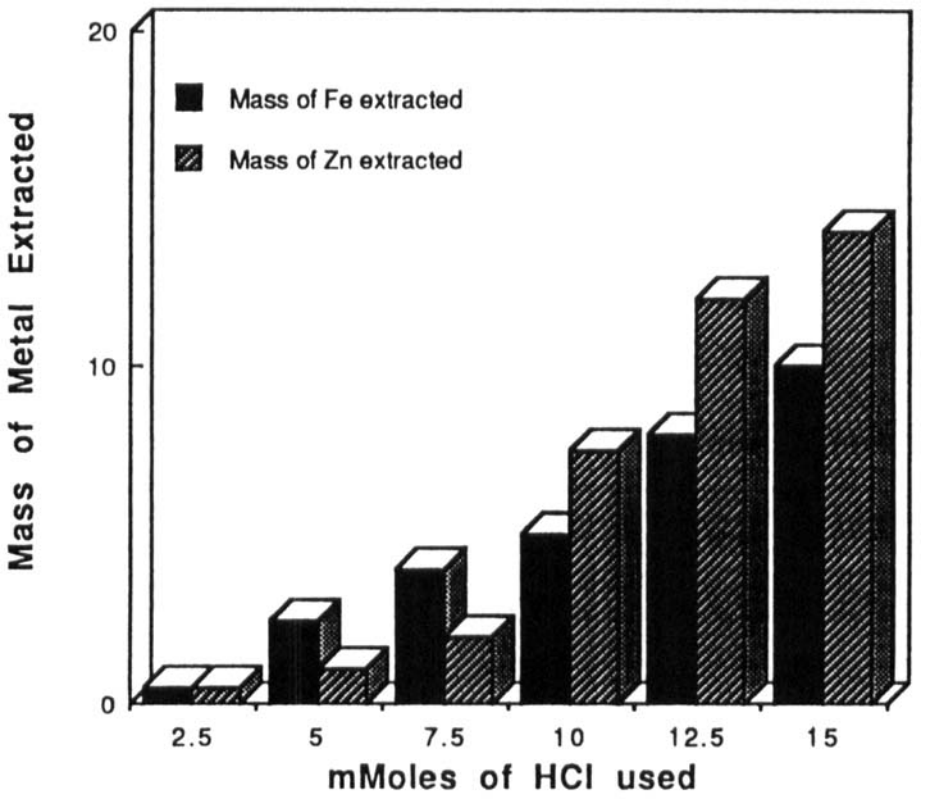

Figure 8 Influence of acid concentration on the extraction of metal species from sludge samples.

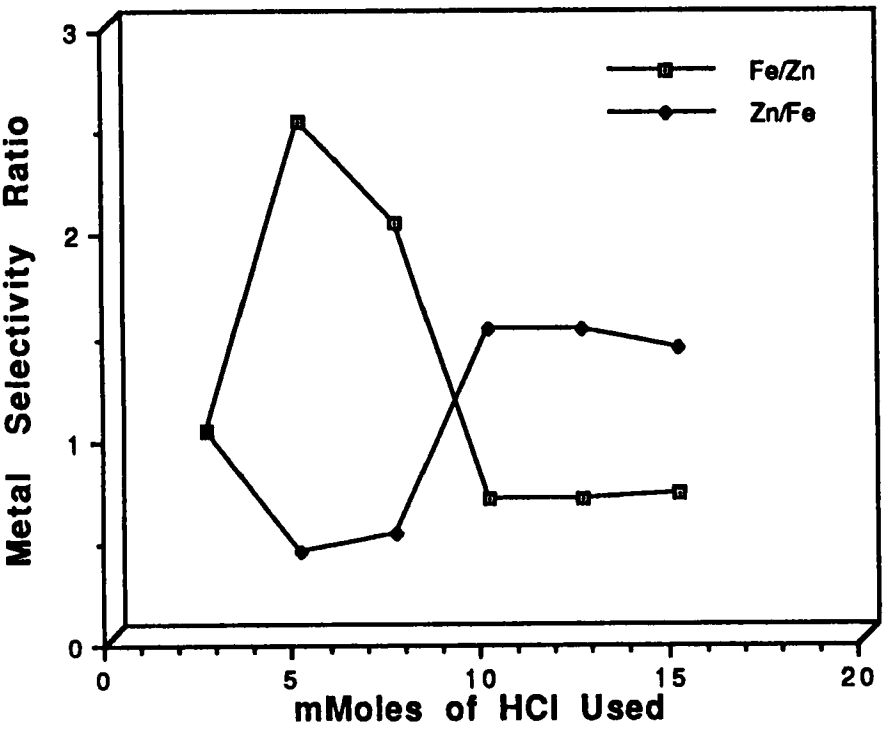

Figure 9 Metal extraction selectivity as a function of the amount of acid used.

CONCLUSION

The work presented in this paper identifies some of the inadequacies of an analytical procedure which has been used widely by soil scientists and other environmental scientists to determine the heavy metal content of soils, sediments, and sludges. Several factors have been identified which must be evaluated critically and carefully so that the importance of the analytical information obtained can be accurately interpreted. The paper shows that the classical fractionation procedure does not provide accurate information on speciation; that depending on the nature of the sample and the metal being determined, the data obtained may not be complete; and that the reagents used can have different effects on different samples and analytes. The accuracy of speciation measurements done by following the Tessier and similar protocols can be improved by incorporating in this protocol procedures that are tailored for specific metals and/or samples. In other words, experimental specifications should focus on the type of sample and analyte and not the quantities of the reagents.

Acknowledgments

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Literature cited

1. S. H. Jenkins and J. S. Cooper, *Int. Air & Water Poll.*, (G.B.), **8**, 695–703 (1964).
2. R. G. McLaren and D. V. Crawford, *J. Soil. Sci.*, **24**, 172–181 (1973).
3. A. C. Chang, A. L. Page, J. E. Warneke and E. Grgurevic, *J. Environ. Qual.*, **13**, 33–38 (1994).
4. D. L. Lake, P. W. Kirk and J. N. Lester, *Water Poll. Control*, **84**, 549–558 (1985).
5. R. C. Stover, L. C. Sommer and D. J. Silviera, *J. Water Poll. Control Fed.*, **48**, 2165–2175 (1976).
6. W. E. Emmerich, J. J. Lund, A. L. Page and A. C. Chang, *J. Environ. Qual.*, **11**, 178–181 (1982).
7. M. G. Hickey and J. A. Kittrick, *J. Environ. Qual.*, **13**, 372–376 (1984).
8. G. Sposito, J. Lund and A. Chang, *Soil Sci. Soc. Am.*, **46**, 260–264 (1982).
9. A. Tessler, P. Campbell and M. Bissom, *Anal. Chem.*, **51**, 844–851 (1979).
10. G. Petruzzeli, L. Lubrano and G. Gurdi, *Environ. Technol. Lett.*, **2**, 449–456 (1981).
11. G. Petruzzeli, L. Lubrano and G. Gurdi, In: *"Int. Conf. on Chemicals in the Environment"* edition in proof, (1986), pp. 772–778.
12. A. Anderson, *Swed. J. Agric. Res.*, **6**, 19–25 (1976).
13. A. Anderson, *Swed. J. Agric. Res.*, **7**, 1–5, (1977).
14. I. T. Urasa and S. H. Nam, *J. Chromatogr. Sci.*, **27**, 30–37 (1989).
15. I. T. Urasa, W. J. Mavura, V. D. Lewis and S. H. Nam, *J. Chromatogr.*, **547**, 211–223 (1991).
16. I. T. Urasa, V. D. Lewis and S. H. Nam, *J. Chromatogr. Sci.*, **27**, 468–473 (1989).
17. I. T. Urasa and W. J. Mavura, *Intern. J. Environ. Anal. Chem.*, **48**, 229–240 (1992).
18. S. Xiao-Quan and C. Bin, *Anal. Chem.*, **65**, 802–807 (1993).