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COMPARISON OF HIGH-PERFORMANCE LIQUID CHROMATOGRAPHIC AND ATOMIC SPECTROMETRIC METHODS FOR THE DETERMINATION OF Fe(III) AND Al(III) IN SOIL AND CLAY SAMPLES

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SUMMARY

A comparison has been made of high-performance liquid chromatographic and atomic absorption spectrometric methods for the determination of Fe(III) and Al(III) in soil and clay samples, following five different digestion/extraction schemes. Good correlations were obtained in the case of Fe(III) determinations in both matrices, but correlation was only achieved for Al(III) determinations following an hydrochloric acid digestion and a dithionite–citrate–bicarbonate extraction of the clay sample. Attempts have been made to explain the differences in results between the two methods in terms of the Al(III) species which are likely to be present following extraction. Confirmatory evidence to support some of the conclusions made with respect to the speciation of these metal ions in these matrices has been obtained using X-ray diffraction studies.

INTRODUCTION

The identification and quantitation of bioavailable metal species in soil and clay samples proves to be of continuing interest[1,2]. Consequently, the development of methodology for the "speciation" and quantitation of metal ions held in amorphous or semi-crystalline forms outside the formal, structural packets in soil and clay samples (*i.e.* "extra-framework" forms) is of considerable importance for bioavailability studies. To this end, a variety of different extraction procedures have been developed, principally to investigate the nature of iron oxides in soil and clay matrices. Mehra and Jackson[3] introduced the dithionite–citrate–bicarbonate (DCB) method for the extraction of iron oxides of different crystallinities, encompassing water-soluble, exchangeable and organic-bound iron species. McKeague and Day[4], however, pioneered the use of oxalate to extract amorphous, non-crystalline or poorly ordered iron oxides. In addition, various strong acid extractions have been reported which are

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supposed to approximate to "total" iron content[5,6], whereas the use of pyrophosphate is supposed to extract only organic-bound Fe(III) complexes[7].

Bloom *et al.*[8] developed a spectrophotometric method for the determination of "available" aluminium, which involved the use of 8-hydroxyquinoline (oxine) as extractant, at a wavelength of 395 nm. However, a 15-min extraction period was necessary to surmount the interference from Fe(III), and probably resulted in a change in the speciation of Al(III) during the extraction process. In an attempt to overcome this, James *et al.*[9] used a 15-s extraction period combined with an estimate of the Fe(III) interference from the absorbance at 600 nm. This type of background correction is, however, laborious and prone to large error.

The extraction method employed in the analysis of metal ions in soils and clays is therefore of obvious importance in the development of any "speciation" scheme. The detection of metal ions following these extraction procedures may be carried out using a variety of techniques; the most commonly employed methods being based on colorimetry or atomic absorption spectrometry (AAS). In recent years, however, much interest has been shown in the application of high-performance liquid chromatography (HPLC) for trace metal analysis. A variety of ligands have been investigated in this regard, including the dithiocarbamates[10,11], dithizone[12], 1,10-phenanthrolines[13] and oxine[14]. We have recently reported on the use of oxine as a ligand in an HPLC method for the determination of Cu(II) and Fe(III) in anaerobic adhesive formulations[15]. In this paper, we report on the use of this particular ligand for the determination of Fe(III) and Al(III) in soil and clay samples. A major potential advantage of using this ligand for this application is that it may also be used as the extractant of the metal ions from the original soil or clay sample.

EXPERIMENTAL

Materials

All chemicals used were of analytical grade. Soil samples were taken from a fixed locality on the NIHE campus, sieved to obtain a particle size of 2 mm or less, and dried in an oven at 110°C. The clay sample used was an untreated Wyoming montmorillonite described by Breen *et al.*[16]. All aqueous solutions were prepared in distilled water, further purified by passage through a Milli-Q water purification system. All organic solvents used were of HPLC-grade. Sample preparation cartridges (Sep-Pak) were obtained from Waters. The C_{18} column used in this study was obtained from Supelchem, and was a 25 cm × 4.6 mm steel column containing LC-18-DB (5 μm particle size) packing material. A Guard-PAK (Waters) guard column containing 10-μm μBondapak C_{18} packing material (end capped) was used to protect the analytical column.

Apparatus

The HPLC system used in this study consisted of an Applied Chromatography Systems (ACS) Model 352 ternary gradient pump connected to a Rheodyne 7125 injection valve and a Shimadzu Model SPD-6A variable-wavelength spectrophotometric detector. AAS was carried out using an Instrumentation Laboratory (IL) Model 357 AA/AE spectrophotometer.

Methods

Digestion/extraction procedures

(1) Hydrofluoric acid digestion. Dried soil or clay (0.1 g) was shaken with 5.0 ml 40% hydrofluoric acid in a PTFE vessel for 24 h, and the extract diluted to 1 part in 300 parts water, prior to analysis.

(2) Hydrochloric acid digestion. Dried soil or clay (0.1 g) was shaken with 100.0 ml 36% hydrochloric acid for 24 h. Analysis was carried out on 1:100 and 1:25 dilutions in water for soil and clay samples, respectively.

(3) Dithionite–citrate–bicarbonate extraction. This was carried out according to the method of Mehra and Jackson[3].

(4) Oxalate extraction. This was carried out according to the method of McKeague and Day[4].

(5a) Oxine extraction for Fe(III). Dried soil or clay (0.5 g) was extracted for 4 h with 40.0 ml of (0.5%) oxine dissolved in 0.02 *M* acetate buffer, pH 4.0. A 2.0-ml aliquot of each extract was then passed through a silica Sep-Pak. The metal ion–oxine complex was then eluted with 4 ml methanol before analysis.

(5b) Oxine extraction for Al(III). This was carried out according to the method of James *et al.*[9], with the following modifications: (1) the oxine concentration was reduced to 0.5%, (ii) the reaction was stopped by centrifugation instead of extraction with butyl acetate, which interfered with subsequent HPLC analysis.

HPLC analysis

The conditions used for the HPLC analysis of Fe(III) and Al(III) were the same as those reported previously[15]. The mobile phase contained acetonitrile (containing $1 \cdot 10^{-2}$ *M* oxine)–0.02 M acetate buffer pH 6.0 (containing 0.2 *M* potassium nitrate) (50:50). Standard solutions of metal ions or extracts from soil or clay samples were injected directly onto the column through the injection port without any external formation of the complex.

Atomic absorption spectrometry

The conditions used for AAS measurements for Fe(III) are: light source, hollow cathode; lamp current, 8 mA; wavelength, 248.3 nm; slit width, 80 μm; burner head, single slot; band pass, 0.3 nm; flame description, air–acetylene, oxidising, fuel lean, blue. For Al(III) they are: light source, hollow cathode; lamp current, 8 mA; wavelength, 309.3 nm; slit width, 320 μm; burner head, nitrous oxide; band-pass, 1.0 nm; flame description, nitrous oxide–acetylene, reducing, fuel rich, red.

X-ray diffraction

Oriented samples for X-ray diffraction (XRD) analysis were prepared by evaporating an aqueous slurry of soil or clay onto a microscope slide (15 × 10 mm). The slide was then placed in the goniometer of a Phillips Model PW1050 diffractometer operating at 40 kV and 20 mA using CuK_α radiation (λ = 1.5418 Å). The XRD profiles were recorded at $2°(2\theta)\ \mathrm{min}^{-1}$ from $0–60°(2\theta)$. In the case of the hydrofluoric acid digestion, the extract contained almost no solid matter, and a small portion of the extract was poured onto the glass slide, where some crystals formed.

RESULTS AND DISCUSSION

X-ray diffraction studies

The XRD profile of the untreated soil sample is shown in Fig. 1, and illustrates that the major, indexable, crystalline component of this soil sample is α-quartz (Q). In contrast, the XRD profile of the untreated clay (C) sample (Fig. 1b) indicates the presence of several impurities including mica (M), kaolin (K), quartz (Q) and Feldspar (F), but exhibits no peaks commensurate with crystalline Fe- or Al-containing species such as goethite, lepidocrocite or gibbsite, respectively.

The effect of increasing severity of three of the extraction/digestion procedures reported in this paper on the XRD traces obtained for the clay sample is illustrated in Fig. 1c–e. The DCB extract was not washed prior to collecting the XRD data, and this accounts for the three characteristic sodium chloride (N) peaks shown in Fig. 1c. The XRD trace obtained for the hydrochloric acid digest is shown in Fig. 1d, and shows that treatment with this 36% hydrochloric acid causes no noticeable degradation of the structural clay lattice, and reflects the greater resistance of aluminous silicates to

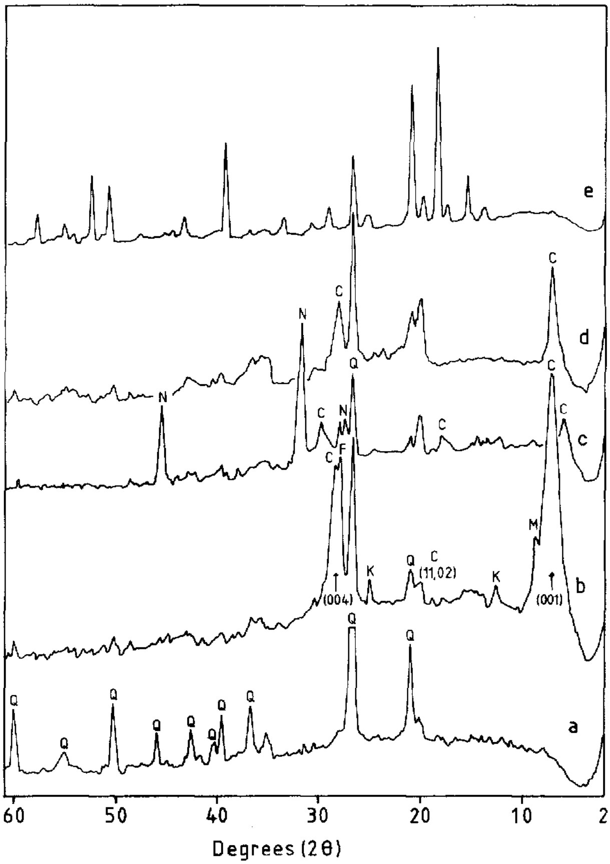

Fig. 1. XRD profiles for (a) untreated soil, (b) untreated clay, (c) DCB-extracted clay, (d) hydrochloric acid digested clay, and (e) hydrofluoric acid digested clay.

acid attack compared to the magnesium rich analogues. The reduced intensity of the Q and F peaks in the DCB extract most probably reflects the physical loss of sample rather than preferential extraction, whilst the Feldspar peak for the hydrochloric acid digested clay (Fig. 1d) lies below the 005 reflection marked C at around 28°(2θ). The XRD trace obtained for the hydrofluoric acid digest of the clay (Fig. 1e) illustrates emphatically that treatment with hydrofluoric acid has a devastating effect on the clay, leaving few identifiable reflections. In a similar manner, only the hydrofluoric acid digestion procedure had any marked effect on the diffraction profile of the soil sample.

Digestion/extraction methods

The results obtained using both HPLC and AAS for the percentages of Fe(III) and Al(III) in the soil and clay samples following the various digestion/extraction procedures detailed under Experimental are given in Table I. A typical trace obtained for the separation of Fe(III) and Al(III) using HPLC is shown in Fig. 2. A detection wavelength of 400 nm was employed, which lies between the λ_{max} values for the oxine complexes of Fe(III) and Al(III) at 450 and 375 nm, respectively. Limits of detection of the order of 1–2 ppm for Fe(III) and Al(III) were typically achieved using both methods.

Hydrofluoric acid digestion

The values obtained for the percentage Fe(III) in the soil and the clay represent the "total" metal content, because the hydrofluoric acid completely digests the samples, as shown from the XRD trace in Fig. 1e. The results obtained using both

TABLE I

CONCENTRATIONS OF Fe(III) AND Al(III) OBTAINED USING HPLC AND AAS FOLLOWING DIGESTION/EXTRACTION PROCEDURES

n.d. = not detected.

Extractant	*Sample*	*HPLC*		*AAS*	
		Fe(III) (%)	*Al(III) (%)*	*Fe(III) (%)*	*Al(III) (%)*
HF	Soil	2.38 ± 0.18	0.09 ± 0.002	2.36 ± 0.12	2.64 ± 0.09
	Clay	1.60 ± 0.05	0.25 ± 0.005	1.64 ± 0.12	7.51 ± 0.44
HCl	Soil	1.69 ± 0.04	0.20 ± 0.01	1.71 ± 0.02	0.42 ± 0.01
	Clay	0.75 ± 0.01	0.14 ± 0.01	0.75 ± 0.01	0.15 ± 0.01
DCB	Soil	1.39 ± 0.06	1.33 ± 0.04	1.46 ± 0.03	1.70 ± 0.04
	Clay	0.18 ± 0.01	$0.004 \pm 1 \cdot 10^{-4}$	0.16 ± 0.01	$0.003 \pm 1 \cdot 10^{-4}$
Oxalate	Soil	0.08 ± 0.01	0.04 ± 0.005	0.08 ± 0.005	0.07 ± 0.005
	Clay	0.04 ± 0.005	0.04 ± 0.001	0.04 ± 0.001	0.08 ± 0.001
Oxine	Soil	0.05 ± 0.005	n.d.	0.05 ± 0.005	n.d.
	Clay	0.02 ± 0.001	n.d.	0.02 ± 0.001	n.d.

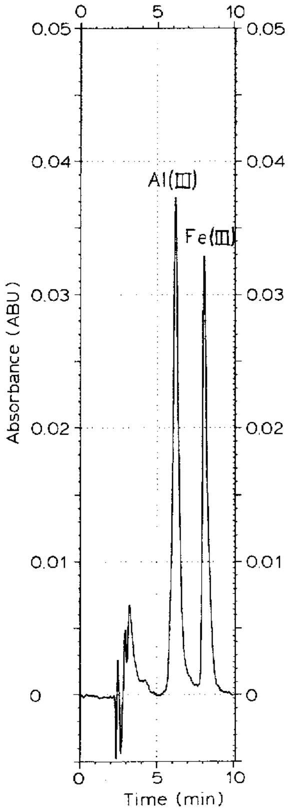

Fig. 2. HPLC separation of a 10 ppm mixture of Fe(III) and Al(III) with spectrophotometric detection. Conditions: flow-rate 1 ml/min; detection wavelength 400 nm.

HPLC and AAS are in good agreement, and show that the Fe(III) content of the soil sample exceeds that of the clay.

The values obtained for the percentage Al(III) in the soil and clay using HPLC were consistently lower than those obtained using AAS. This is probably due to the fact that Al(III) forms a much stronger complex with fluoride ions than with oxine, and hence prevents any *in situ* formation of the Al(III)–oxine complex on the column. With the high temperatures used in the rich nitrous oxide–acetylene flame, the Al(III)–fluoride complexes will be atomised, hence giving rise to a more accurate value of the Al(III) content in the soil or clay. Consequently, greater cognisance should be afforded the AAS results, particularly since the value of 7.51% Al(III) in the clay sample is close to that reported previously[16].

Hydrochloric acid digestion

The values obtained for the percentage Fe(III) in the soil and clay were shown to be in good agreement using both instrumental methods of analysis. In the case of Al(III), the results for the clay were in good agreement, but the percentage Al(III) in the soil was found to be nearly double using AAS when compared to HPLC. The reason for this discrepancy is not clear, but may be due to the nature of the "extra-framework" Al(III) in the respective matrices. From the results of the XRD studies, it is clear that the 36% hydrochloric acid digestion is not as effective as hydrofluoric acid at breaking down the structural units of the soil and clay matrices, and thus this digestion procedure can only yield results that approximate to "total" metal ion content.

Dithionite–citrate–bicarbonate extraction

This extraction technique, which is based on the strong reducing properties of dithionite, was developed to extract oxides of different crystallinity, including water-soluble, exchangeable and organic-bound metal[3]. The optimum pH for this extraction is 7–8, and this is maintained by the buffering capacity of the bicarbonate anion. Citrate is employed to complex the reduced metal ion.

The values obtained for the percentages of Fe(III) and Al(III) (Table I) show that whilst the HPLC and AAS results for percentage Fe(III) are in good agreement, the HPLC results for percentage Al(III) in the soil sample are somewhat lower than those obtained by AAS. This probably reflects competition between citrate and oxine for Al(III), which is a problem in the HPLC assay, but not in AAS where the citrate complex would be broken down. Consequently, since the HPLC method relies on complexation of free metal ion with oxine, the difference between the two results may relate to the amount of Al(III)–citrate complex present following extraction. One further interpretation, which cannot be ruled out, is that the DCB method extracts organic-bound Al(III) which would be determined by AAS but not by HPLC. The higher values for the percentage Al(III) in the soil compared to those obtained following hydrochloric acid digestion may be explained by the possible presence of semi-crystalline iron oxides containing a substantial amount of Al(III). It is difficult to obtain evidence for the presence of these phases, because as Schulze and Schwertmann[17] have found in both naturally occurring and synthetic goethites, the substitution of Fe(III) by Al(III) substantially reduces the intensity of peaks in the diffraction profile.

Oxalate extraction

The oxalate extraction was introduced by McKeague and Day[4] to extract the "active" fraction of metal ions from soils. This includes amorphous, non-crystalline or poorly ordered metal oxides and also includes organic-bound metal. The technique is based on complexation of metal ions by oxalate at pH 2–3. In this study, extractions were carried out at pH 2 and 3, but little difference was noticed in the percentage metal ion concentrations obtained. The results obtained for the percentage Fe(III) and Al(III) in soil and clay samples following this extraction procedure at pH 3 are given in Table I. Once again there is good agreement between the HPLC and AAS values for the percentage Fe(III), but not for the percentage Al(III). However, it is unlikely that the source of this discrepancy is due to the competitive chelation observed in the DCB method because there is a digestion step using nitirc acid–sulphuric acid prior to analysis, which should break down any Al(III)–oxalate complex and/or organic-bound Al(III). Unfortunately, this acid digestion step lowers the pH of the extract prior to the analysis stage, and studies with comparable standard solutions indicate that these low pH values suppress absorbance readings in AAS and affects the complexation of Al(III) with oxine, resulting in lower values than anticipated for the HPLC method. The reason that the values obtained for the percentage Al(III) using HPLC are higher in the soil and lower in the clay following the oxalate extraction compared with the dithionite–citrate–bicarbonate extraction may be due to the fact that oxalate is a better extractant of amorphous Al(III) species[4] which are suggested to be more prevalent in the soil than the clay from the XRD studies.

Oxine extraction

Methods employing oxine as an extractant for "available" Al(III) in soils have been reported in the literature[8,9], but this extractant has not been widely used for determinations of Fe(III) in soil and clay samples. We have therefore investigated the use of oxine for Fe(III) determinations in these matrices based on the method of James *et al.*[9] reported for Al(III).

The extraction method involving oxine was optimised with respect to time of extraction, pH and isolation of the complex using Sep-Pak cartridges. The extraction time was varied between 2 and 72 h, but periods in excess of 4 h gave comparable results. Previous studies[14,15] have shown that the formation of the oxine–Fe(III) complex is optimal in the pH range 4–6, although analysis of the soil extracts indicated that slightly higher values were obtained at pH 4 than at pH 6. Furthermore, the use of a silica Sep-Pak was found to be an effective means for isolation of the complex formed, in addition to acting as a means of sample "clean-up", as observed previously[15]. It was found that 4 ml of methanol was required to quantitatively remove 20-μg of oxine–Fe(III) complex from the Sep-Pak.

The results in Table I show that there is good agreement between the HPLC and AAS results for the percentage Fe(III) in soil and clay samples using this extraction method. No detectable concentrations of Al(III) were found in any of the oxine extracts by either HPLC or AAS, although spiking a soil sample with 5 ppm Al(III) resulted in HPLC and AAS values of 5.03 and 5.30 ppm Al(III), respectively. This suggests that oxine will only extract extremely labile Al(III) from these matrices.

CONCLUSIONS

A comparison of the results in Table I show a good agreement in the percentage Fe(III) values obtained from both soil and clay using both HPLC and AAS. The percentage Fe(III) extracted using the various methods decreased in the order HF > HCl > DCB > oxalate > oxine. This is to be expected considering the different mechanisms by which these extractions/digestions operate. It is interpreted from the results that the hydrofluoric acid extraction yields a value relating to the "total" Fe(III) content. Because of the specific nature of the DCB and oxalate extraction procedures for crystalline and non-crytalline oxides, respectively, the different values for the percentage Fe(III) arising from these procedures can be explained. The difference between the hydrofluoric acid results and those obtained using the DCB extraction can be attributed to the amount of Fe(III) which forms an integral part of the lattice structure of the clay, and perhaps also that of the soil. The difference between the DCB and oxalate extractions for Fe(III) can be attributed to the amount of crystalline iron oxides present in these matrices, even though they were too small in particle size to be observed using XRD analysis. The difference between the oxalate results and those obtained using the oxine extraction is most probably due to "exchangeable" Fe(III) species.

The results obtained with the 36% hydrochloric acid digestion suggest a small ingress of acid into the octahedral layer, thus leaching out a small amount of Fe(III) associated with the lattice structure. In the case of Al(III), the percentage values obtained in both soil and clay were found to be in good agreement for the hydrochloric acid digestion and the DCB extraction for the clay using both HPLC and AAS. The results obtained using the other extraction procedures, however, were found to be much lower using HPLC compared to AAS, especially for the soil. This is mainly due to the competition between oxine and the various extractants employed for Al(III).

Although this paper has necessarily limited itself to the analysis of a single soil and a single clay sample, it has, however, highlighted the possibility of employing HPLC (i) as a multi-element approach to the determination of metal ions in soils and clays, and (ii) to provide information on the speciation of metal ions, provided that experiments have been carried out taking into consideration the matrix involved as well as the sample preparation. If lower limits of detection were required than are possible using the approaches described in this paper, then these could be achieved for the HPLC method by employing the technique of "external formation" of the oxine–Fe(III) or oxine–Al(III) complex prior to injection onto the column, and for the AAS method by employing a flameless approach to atomisation.

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