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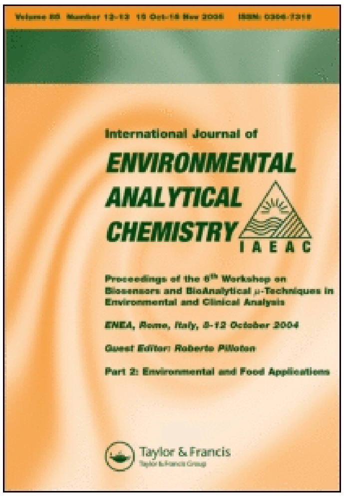

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Effect of Dissolved Humic Compounds on the Determination of Aqueous Aluminium by Three Spectrophotometric Methods

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Humic substances in solution constitute a generally overlooked source of interference in the spectrophotometric determination of aluminium. We investigated humic interference in the determination of total monomeric and acid-reactive aluminium using three methods: (1) 8-hydroxyquinoline/MIBK extraction, (2) flow injection pyrocatechol violet, and (3) flow injection eriochrome cyanine R/CTA. Interference was apparent in all three methods from both humic and fulvic acid concentrations above 10 mg $\mathrm{C\,L^{-1}}$ in the measurement of total monomeric aluminium. The 8-hydroxyquinoline/MIBK extraction method was not subject to interference in the determination of acid-reactive aluminium (<200 mg $\mathrm{C\,L^{-1}}$), while interference appeared in the other two methods at 20–50 mg $\mathrm{C\,L^{-1}}$. The observed interferences were pH-dependent and were minimized by performing the reaction at higher pH-values.

KEY WORDS: Aluminium, interference, humic compounds, 8-hydroxyquinoline, eriochrome cyanine R, pyrocatechol violet.

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INTRODUCTION

Aluminium is an important parameter in the study of soil acidification processes. Dissolved aluminium at elevated concentrations may also be toxic to aquatic and terrestrial biota. The development of methods for the determination of aluminium in leachate, soil pore and surface waters has therefore received considerable attention. It is generally recognized that determination of total dissolved aluminium is of little biological relevance since the various aluminium species differ greatly in toxicity. Therefore, the evaluation of potential environmental impacts of aqueous aluminium must include speciation, rather than simply total concentration. The fractionation scheme most commonly used is that by Driscoll,[1,2] which involves measurements of three aluminium fractions: acid-reactive aluminium (Al_r, after acidification to pH 1), total monomeric aluminium (Al_a, untreated samples) and non-labile monomeric aluminium (Al_o, cation exchange treated, mainly organic bound). Labile monomeric aluminium (Al_i, mainly inorganic), which is thought to contain the toxic species,[3,4] is obtained by difference, Al_a–Al_o. Speciation of the Al_i fraction is generally accomplished using thermodynamic equilibrium constants and a computer program such as MINEQL.[5]

A difficulty in extraction and spectrophotometric methods for aluminium determination is potential interference from dissolved humic compounds due to the formation of stable complexes between aluminium and humic ligands. In the presence of high concentrations of humic compounds, such as in some soil leachates, pore water and extracts, this interference would lead to underestimations of both total monomeric and nonlabile monomeric aluminium. Some of the monomeric aluminium bound to humic compounds would fall into the acid soluble aluminium (Al_s) fraction (Al_r–Al_a).

In developing a speciation procedure Driscoll was aware of this effect and included strong alumino-organic complexes in the acid soluble aluminium fraction. This is not very satisfactory, however, from an analytical chemical point of view. First, these strong alumino-organic complexes falling into the acid soluble fraction are monomeric. It is reasonable to assume that these compounds differ from polymeric aluminium hydroxides both in their reaction kinetics with chelating reagents and their thermodynamic stability in solution. Second, the fraction of organic aluminium compounds determined as acid soluble aluminium becomes very method-dependent. The stability of the various chelating agents used in extraction or spectrophotometric methods differ and the recovery of the organic aluminium compounds will therefore vary, making comparisons between methods difficult.

Recent laboratory and field research,[6,7] have suggested that dissolved humic compounds from upper soil horizons may be important in controlling the concentration of aluminium in both soil leachate and surface waters. Concentrations of dissolved organic carbon may be high in such situations (10–100 mg C L^{-1}). It is therefore important to ascertain the impact of elevated levels of humic compounds in solution on conventional speciation procedures for aluminium. The aim of the present work was to study the effect of humic compounds on the determination of aqueous acid-reactive and total monomeric aluminium. We used two well established methods (Barnes/Driscoll MIBK extraction method,[1,2] and pyrocatechol violet (PCV) method[8–11]) and a newly developed method using eriochrome cyanine R/CTA (ECR/CTA).[12] The PCV and ECR/CTA methods have been adapted to a flow injection analysis system[13,14] to increase speed of sample processing and reproducibility.

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MATERIAL AND METHODS

The MIBK extraction method was used as described by Barnes[2] and Driscoll[1] with extraction at the recommended pH (8.3). In the interference study the extraction was also performed at pH 7.0 and 6.1 using piperazine (pH 6.1) and imidazol (pH 7.0) buffers. The flow injection analysis methods with ECR/CTA and PCV were used as described previously[12–14] at their recommended pH values (7.5 and 6.1 respectively). In addition the ECR/CTA method was run at pH 6.1 using hexamethylenetetramine buffer.[13]

For the interference studies samples containing 1.0 mg Al L^{-1} and increasing amounts of humic compounds (10–200 mg C L^{-1}) were prepared. To avoid the formation of polymeric aluminium hydroxide species during the preparation of these samples, the pH of the solution containing the humic compounds was first adjusted to 3.5–

4.0. Aluminium standard solutions (from a 10.0 mg Al L^{-1} stock solution in 1 mM HCl) were then added and the final pH was adjusted to 4.0 ($\pm$0.1) and diluted to volume by 0.1 mM HCl. At pH 4.0 and a total aluminium concentration of 1.0 mg L^{-1} no polymeric aluminium hydroxide species are expected to form.[15] Any observed decreases in aluminium recovery would therefore be due to interference, rather than polymerization.

The humic and fulvic acids used in this study were prepared by alkaline extraction of raw humus from the O_h-layer of a podsolic forest soil in southeastern Norway.[16] We also analysed soil extracts prepared from four soils from the O_h-layer of a beach and pine forest in the Solling research area, Federal Republic of Germany, described by Dietze.[17] The extracts were prepared by mixing 10 g of soil with 90 ml of demineralized water, which was shaken over night, centrifuged and filtered through 0.45 μm cellulose acetate membrane filters. Results obtained in aluminium analyses of the four soil extracts using the three aluminium methods were also compared to Al determinations after digestion (UV/H_2O_2) to remove organic compounds.

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RESULTS AND DISCUSSION

Interference from a humic and a fulvic acid

Figure 1 shows the effect of humic and fulvic acids (concentration expressed as dissolved organic carbon, DOC) on the determination of acid-reactive aluminium. The ECR/CTA method is not affected by this interference at DOC <50 mg C L^{-1}. The PCV method seems to be slightly more affected by this interference especially at lower concentrations of fulvic and humic acids (<50 mg C L^{-1}). The MIBK method is very little influenced by this interference; the presence of up to 200 mg C L^{-1} has little effect on recovery (when the extraction is performed at pH 8.3). The small increase in recovery which appeared for the fulvic acid at concentrations above 100 mg C L^{-1} is probably due to the extraction of organic compounds into the MIBK phase (which absorb at the wavelength of photometric Al determinations, 395 nm).

In the determination of total monomeric aluminium (Figure 2) interference from humic and fulvic acid in the MIBK method

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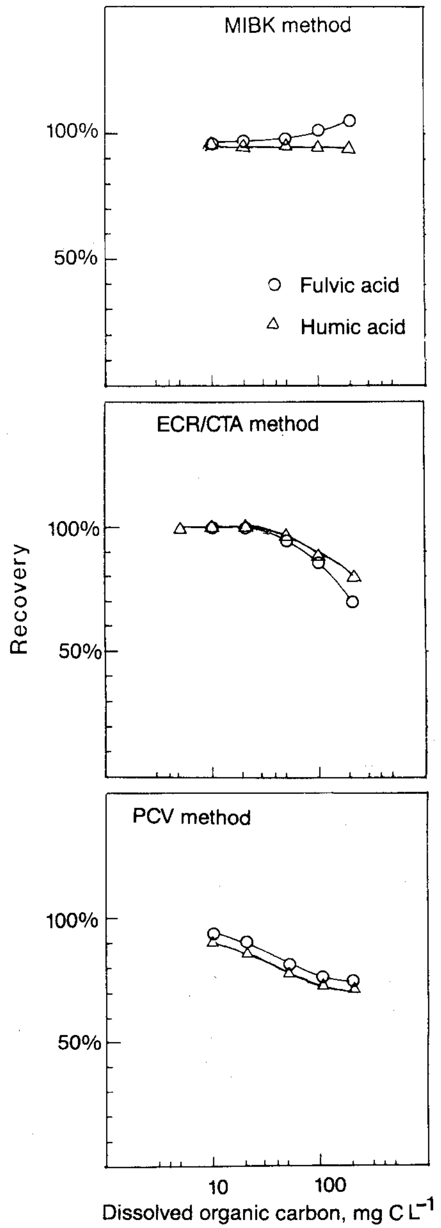

FIGURE 1 Recovery of acid-reactive aluminium from samples containing fulvic and humic acid by the MIBK, ECR/CTA and PCV methods. Reactions were performed at the recommended pH values for each of the methods, 8.3, 7.5 and 6.1, respectively.

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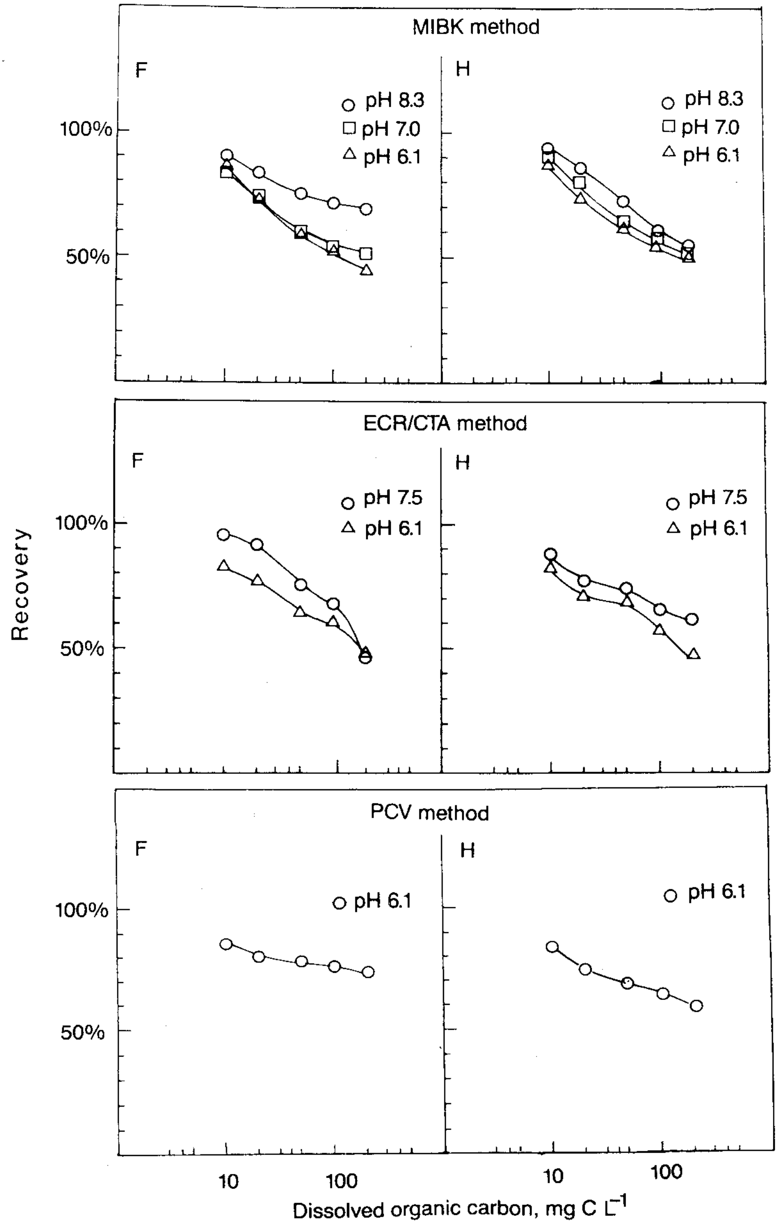

FIGURE 2 Recovery of total monomeric aluminium in presence of fulvic and humic acids by the MIBK, ECR/CTA and PCV methods. Reactions were performed at pH values of 8.3, 7.0 and 6.1 in the MIBK, 7.5 and 6.1 in the ECR/CTA and 6.1 in the PCV method. H: humic acid. F: fulvic acid.

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decreased at pH 8.3 compared to 7.0 and 6.1. The same pattern was obtained from the ECR/CTA method (Figure 2), with somewhat more interference at pH 6.1 than at 7.5. The three methods were similar at DOC $<50\,\mathrm{mg\ C\ L^{-1}}$, but the ECR/CTA method was more affected at higher concentrations of humic compounds.

The observed reduced interference at elevated pH is probably due to a shift in aluminium speciation. At pH above 7.5 a significant fraction of the monomeric aluminium is present as the anionic species $Al(OH)_4^-$ which probably does not show the same affinity for the anionic humic compounds as the cationic aluminium hydrolysis products formed at lower pH (the pK value for the hydrolysis reaction $Al(OH)_3^{\circ} + H_2O = Al(OH)_4^- + H^+$ is 8.3).[18]

Comparison of Figures 1 and 2 shows that interference from humic compounds is more pronounced (at least at low concentrations) in the determination of total monomeric aluminium than in acid-reactive aluminium, particularly for the MIBK and ECR/CTA methods. This is probably due to a reaction kinetic effect. In all three methods the reaction time between mixing of reagents and extraction/measurment is short (20 seconds). In the acidification of samples (for acid-reactive aluminium determination) most of the aluminium previously bound to humic compounds is released due to protonation of binding sites. When the pH is adjusted during mixing of reagents, the complexing agents are added in a high excess compared to the humic compounds. Although one might expect that the humic compounds would recombine with aluminium when pH is increased (to 6.1, 7.5 or 8.3), the high excess of reagent and short reaction time minimize this recombination.

Interference from organic compounds in soil extracts

Four different soil extracts were analysed for acid-reactive aluminium and total monomeric aluminium by the three different methods. The results obtained were also compared to the determination of total aluminium after digestion (UV/H_2O_2) to remove humic compounds. For the determination of acid-reactive aluminium the results obtained by the MIBK method agree most closely with total aluminium after digestion (Table I). The results for acid-reactive aluminium obtained by the ECR/CTA method (pH 7.5) and the PCV method are similar, but significantly lower than for the

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TABLE I

Determination of acid-reactive aluminium and total monomeric aluminium in four soil extracts by three different methods[a]

	Sample composition				Aluminium determinations					
					ECR/CTA		PCV	MIBK		
Aluminium fraction	Sample type[b]	pH	DOC[c] $mg\,C\,L^{-1}$	Total aluminium (UV/H_2O_2-digested)	pH 7.5	pH 6.1	pH 6.1	pH 8.3	pH 7.0	pH 6.1
Acid reactive aluminium[d]	FI	1.0	72	0.48	0.35	0.32	0.45	0.62	—	—
	FD	1.0	25	0.40	0.32	0.33	0.36	—	—	—
	BI	1.0	47	0.51	0.41	0.34	0.39	0.58	—	—
	BD	1.0	61	0.80	0.71	0.55	0.65	0.90	—	—
Total monomeric aluminium	FI	3.8	as above	as above	0.30	0.28	0.29	0.51	0.31	0.29
	FD	6.1			0.18	0.08	0.17	0.35	0.17	0.17
	BI	3.7			0.29	0.26	0.25	0.47	0.32	0.25
	BD	6.3			0.45	0.26	0.26	0.61	0.26	0.26

[a] All determinations of aluminium given in $mg\,L^{-1}$. Reproducibility was $< \pm 0.02\,mg\,L^{-1}$ in all three methods.

[b] B and F are soil extracts from O_h-layer in a beech stand and a spruce stand, respectively. I and D are untreated and limed soil, respectively.

[c] Dissolved organic carbon.

[d] Samples acidified to pH 1.0 by HCl.

MIBK method. Sullivan *et al.*[10] also found higher estimates of Al_r using the MIBK, as compared to the PCV method.

A similar pattern was obtained for the determination of total monomeric aluminium (untreated samples). The highest results were obtained by the MIBK method (pH 8.3). The recovery of aluminium in the MIBK and ECR/CTA methods was pH-dependent with greater interference at lower pH values (pH 6.1 and 7.0 compared to 8.3 and pH 6.1 compared to 7.5, respectively). Both the ECR/CTA and PCV methods gave lower values than the MIBK method (pH 8.3), indicating that the interference from humic compounds was stronger in the former methods.

CONCLUSIONS

Our results demonstrate that high concentrations of dissolved humic substances interfere in the determination of aluminium in all methods investigated. There are, however, some interesting differences. The interference from humic compounds is lower in acidified samples (as for acid-reactive aluminium) compared to untreated samples (as for total monomeric aluminium), particularly in the MIBK method. Underestimation of acid-reactive aluminium is therefore not expected to occur in the MIBK method, while this may occur in the PCV and ECR/CTA methods at DOC$>$20–50 mg C L^{-1}.

Interference from fluoride and phosphate decreases when the analytical reaction is performed at elevated pH using both the MIBK and ECR/CTA methods.[2,12] The results obtained in this study show that interference from humic compounds also decreases at elevated pH in these two methods.

Our results further demonstrate that interference from humic compounds is not significant in any of these spectrophotometric methods at DOC below 10 mg C L^{-1}. Most surface waters in acidified areas of Scandinavia and North America would be expected to fall in this range. This type of interference increases, however, at higher DOC, and results in the inclusion of organic monomeric aluminium in the acid-soluble aluminium fraction. Although the Driscoll fractionation scheme is operationally defined, interpretation of aluminium speciation becomes difficult at increased DOC concentrations. This is particularly relevant for studies investigating the role of organic

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soil horizons in controlling aluminium in streamwater[6,7] and in pore water.

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