Chromic Anhydride-Chlorosilanes. An Application to Benzylic Oxidation

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Chlorotrimethylsilane reacts with chromic anhydride to form a very reactive neutral chromium (VI) oxidizing agent. The active oxidizing species is not trimethylsilyl chlorochromate as was previously reported but chromyl chloride generated in equilibrium concentration. This oxidizing agent was proved very suitable for benzylic oxidations of toluenes and alkylbenzenes to benzaldehydes and aralkyl ketones. Dichlorodimethylsilane and trichlormethylsilane also react with chromic anhydride to form chromyl chloride in an equilibrium concentration.

Introduction

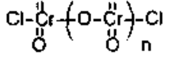
Neutral chromium (VI) oxidizing agents have not been popular in organic synthesis, because they generally produce mixtures of many products.[1,2] However, some of the neutral chromium reagents such as di-*t*-butyl chromate and chromyl chloride were very useful for certain type of oxidation reactions.[1] Using chromyl chloride, the oxidations of toluenes to benzaldehydes,[3] enol silylethers to α-hydroxyketones,[4] and disubstituted olefins to α-chloro ketones[5] can be easily achieved.

Recently, Palomo and Aizpurua[6] reported that both potassium dichromate and chromic anhydride easily react with chlorotrimethylsilane in dichloromethane forming a dark red chromium oxidizing agent. This neutral reagent was proved to be efficient for the oxidation of alcohols to ketones, thiols to disulfides, and oximes to the corresponding carbonyl compounds.[6] In the study of the application of chromic anhydride-chlorotrimethylsilane, we reported a few excellent reactions for the oxidation of toluenes,[7] alcohols[8] and olefins.[9] In this paper, we wish to describe our results on the identity of the actual chromium oxidant generated in the reaction of chromic anhydride and chlorosilanes and on the application of this reagent for benzylic oxidation of toluenes and other alkylbenzenes.

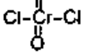
Results and Discussion

The Nature of the Oxidant. Chromic anhydride readily dissolves in dichloromethane, carbon terachloride and other polyhaloalkane solvents containing either chlorotrimethylsilane or dichlorodimethylsilane or trichloromethylsilane at room temperature.[6,7] The solution thus obtained is dark red and nearly homogeneous.

A simple insertion of chromium trioxide (CrO_3) into silicon-chlorine bond would produce trimethylsilyl chlorochromate (**3**) which Palomo *et al.* proposed as a possible active oxidant.[6] This type of insertion was reported in the formation of trimethylsilyl chlorosulfonate from the reaction of sulfur trioxide and chlorotrimethylsilane.[10] However, we believe that Palomo's hypothesis is less likely when the following facts and observations are taken into consideration.


$Cl-\overset{O}{\underset{O}{Cr}}\left(O-\overset{O}{\underset{O}{Cr}}\right)_n-Cl$

1


$Cl-\overset{O}{\underset{O}{Cr}}-Cl$

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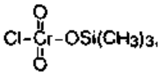
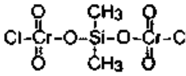
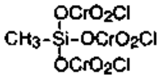

$Cl-\overset{O}{\underset{O}{Cr}}-OSi(CH_3)_3$,

3


$Cl-\overset{O}{\underset{O}{Cr}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{O}{\underset{O}{Cr}}-Cl$,

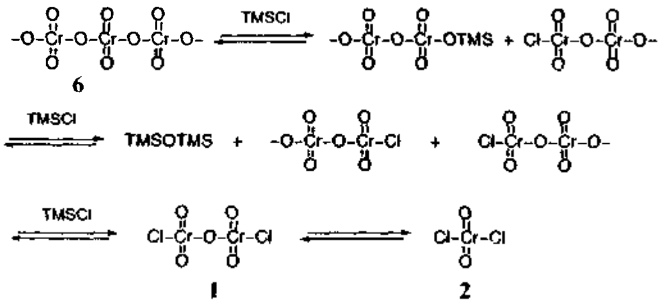
4


$CH_3-\overset{OCrO_2Cl}{\underset{OCrO_2Cl}{Si}}-OCrO_2Cl$

5

The reagent can prepared from chromic anhydride and chlorotrimethylsilane in carbon tetrachloride. The NMR spectrum of this nearly homogeneous solution showed only types of singlet methyl peaks characteristic of the methyl protons of chlorotrimethylsilane and hexamethyldisiloxane. No NMR peak other than these two types of protons was observed. This means that trimethylsilyl esters of chromate, polychromate and chlorochromate can exist only as transient species. The ratio of methyl protons of chlorotrimethylsilane and hexamethyldisiloxane did not vary on standing for 2-3 days or on heating the mixture for several hours. The NMR spectrum of the regent prepared from equimolar mixture of chromic anhydride and chlorotrimethylsilane in carbon tetrachloride showed that 30-35% of chlorotrimethylsilane was converted to hexamethyldisiloxane. In a mixture of two equivalents of chlorotrimethylsilane and one equivalent of chromic anhydride, about 55% of chlorotrimethylsilane turned into hexamethyldisiloxane. Addition of increasingly more chlorotrimethylsilane resulted in increasingly more hexamethyldisiloxane. Addition of hexamethyldisiloxane to the reagent prepared from chlorotrimethylsilane and chromic anhydride, on the other hand, increased the relative proportion of chlorotrimethylsilane. Also found was that considerably less than an equivalent of chlorotrimethylsilane almost completely dissolve chromic anhydride.

This phenomena can be better understood, when one considers the structure of chromic anhydride. The structure of chromic anhydride has been determined by X-ray analysis[11] to be a linear polymer of chromium and oxygen atoms with two additional oxygen atoms linked to each chromium atom as was depicted in **6**. Like other metal oxides of linear structure,[10] it can be easily depolymerized in reactions with water, *t*-butyl alcohol, and acetic acid and other unoxidizable protic acid.[1] The reaction of chromic anhydride with chlorotrimeth-



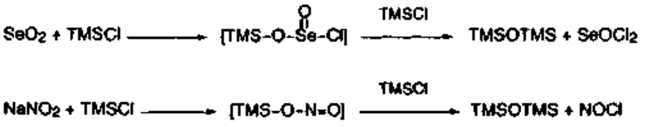
Scheme 1

ylsilane is believed to be a similar depolymerization process as can be illustrated in Scheme 1.

In Scheme 1, the polymeric chain of chromic anhydride (**6**) is cleaved by chlorotrimethylsilane forming O-Si and Cr-Cl bond. The Cr-OTMS bond is replaced in reaction with another molecule of chlorotrimethylsilane forming hexamethyldisiloxane and another Cr-Cl bond at the terminal chromium atom. This process repeats elsewhere along the chain and results in the fragmentation of the chromic anhydride chain to polyoxochromium dichloride (**1**) and finally to chromyl chloride (**2**). Hexamethyldisiloxane will be the only by-product.

All these steps are believed to be reversible and are in equilibrium as was illustrated in Scheme 1. Thus, the addition of extra chlorotrimethylsilane to the reagents generated more hexamethyldisiloxane. Whatever excess chlorotrimethylsilane were added, quantitative formation of hexamethyldisiloxane was not observed. Moreover, the addition of extra hexamethyldisiloxane to the system caused an increase in the relative proportion of chlorotrimethylsilane. Attempts to isolate the reagent by distillation resulted in occasional violent explosions. Removal of lowest boiling chlorotrimethylsilane cause the lengthening the chain of chromium oxidant by the reverse reactions, raising the boiling point of the oxidant.

Chromic anhydride is known to be dissolved readily in hexamethyldisiloxane forming bis (trimethylsilyl) chromate (BTSC).[12] This reagent is a red, distillable liquid. The methyl protons of BTSC show up at 0.3 ppm in the NMR spectrum. These methyl signals of BTSC almost completely disappeared upon the addition of excess chlorotrimethylsilane, and hexamethyldisiloxane reappeared as evidenced by NMR. Addition of hexamethyldisiloxane to chromyl chloride solution in carbon tetrachloride also resulted in the appearance of chlorotrimethylsilane. These findings are in good agreement with the reaction scheme proposed above.

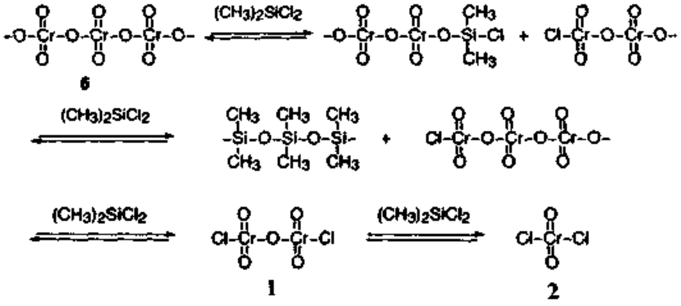


$$SeO_2 + TMSCl \longrightarrow [TMS\text{-}O\text{-}\overset{O}{\overset{\|}{Se}}\text{-}Cl] \xrightarrow{TMSCl} TMSOTMS + SeOCl_2$$

$$NaNO_2 + TMSCl \longrightarrow [TMS\text{-}O\text{-}N\text{=}O] \xrightarrow{TMSCl} TMSOTMS + NOCl$$

The replacement of silyloxy group by chlorine upon reaction with chlorotrimethylsilane apparently seems to be very easy. Hence, no methyl protons other than those of chlorotrimethylsilane and hexamethyldisiloxane appeared in the NMR spectrum of the reagent solution. Similar type of cleavage of in-situ generated trimethylsilyl chloroselenite by chlorotrimethylsilane to form selenium oxychloride and hexamethyldisiloxane was reported for the reaction of selenium dioxide with chlorotrimethylsilane.[13] Selenium dioxide, like chromic anhydride, has a linear polymeric structure.[11] A similar cleavage was also observed when trimethylsilyl nitrite was reacted with chlorotrimethylsilane.[14]

Therefore the actual chromium oxidant is believed to be chromyl chloride (**2**) or the chromium trioxide insertion product of chromyl chloride (**1**), where n is an interger which varies depending upon the relative proportion of chlorotrimethylsilane and hexamethyldisioxane. When chromic anhydride was stirred with one equivalent of chlorotrimethylsilane, 30-35% of the Cr-O single bonds in polymeric chromic anhydride were replaced by Cr-Cl bonds. With two and three equivalents of chlorotrimethylsilane, the NMR spectrum showed that about 50 and 65% Cr-Cl bonds were formed, respectively.



Scheme 2

Chromic anhydride (**6**) was also found to be completely dissolved in methylene chloride or carbon tetrachloride containing a half or one third of dichlorodimethylsilane or trichloromethylsilane. Palomo postulated the insertion of two equivalents of chromium trioxide into two Si-Cl bonds of dichlorodimethylsilane and the formation of a new chromium oxidant **4**. However, we rather believe that there exists an equilibrium similar to in chromic anhydride-chlorotrimethylsilane system. Scheme 2 shows that chromium oxidant **1**, and to the chromyl chloride (**2**) postulated in Scheme 1 can be generated from chromic anhydride and dichlorodimethylsilane through a sequence of equilibrium steps. Polydimethylsiloxane was the only silane produced as a by-product.

The reaction of trichloromethylsilane with chromic anhydride is also believed to proceed in a similar manner. Instead of a complicated new methylsilyl tris (chlorochromate) **5**, chromium species **1**, or chromyl chloride (**2**) could be postulated to be formed following the Schemes similar to 1 to 2. The only difference is that the Si-Cl bond in trichloromethylsilane is more reactive than that of chlorotrimethylsilane. This would shift the equilibrium in favor of the siloxane and chromyl chloride.

The chromium oxidant generated from chromic anhydride and chlorotrimethylsilane was reported to be very useful for the reactions previously done with commercial chromyl chloride. The reactivity of chromyl chloride could be reduced by adsorbing it on silica-alumina. The chemiadsorbed chromyl chloride was shown to be an efficient reagent for the oxidation of various alcohols to aldehydes or ketones under nonaqueous conditions. Similarly, the present reagent was used successfully used for the same purpose in the presence of basic alumina.[8] Equimolar chromic anhydride and chloro-

Table 1. Benzylic Oxidation of Arylmethanes and Analogous Compounds by Chromic Anhydride-Chlorotrimethylsilane, Dichlorodimethylsilane, and Trichloromethylsilane in Refluxing CCl_4

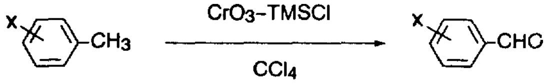
Substrate	Product	% Yield[a]		
		CrO_3-Me_3SiCl[b]	CrO_3-Me_2SiCl_2[c]	CrO_3-$MeSiCl_3$[d]
Toluene	Benzaldehyde	76	80	70
o-Bromotoluene	*o*-Bromobenzaldehyde	34	54	60
o-Nitrotoluene	*o*-Nitrobenzaldehyde	<5[e]	<5[e]	<5[e]
p-Xylene	*p*-Tolualdehyde	62	64	81
p-Nitrotoluene	*p*-Nitrobenzaldehyde	<5		
p-Methoxytoluene	*p*-Anisaldehyde	59	52	44
Mesitylene	3, 5-Dimethylbenzaldehyde	32	36	34
Ethylbenzene	Acetophenone	56	85	87
Propylbenzene	Propiophenone	82	80	85
Benzyl chloride	Benzaldehyde	78		
Styrene	Benzaldehyde	45		
Diphenylmethane	Benzophenone	94	93	96

[a] Absolute yields. An appreciable amount of starting meterial was recovered. [b] CrO_3: Me_3SiCl = 1: 2, 48 hr. [c] CrO_3: Me_2SiCl_2 = 2: 1, 20 hr. [d] CrO_3: $MeSiCl_3$ = 2: 1, 20 hr. *e*. Not isolated. by NMR and GC after filtration through wet silica gel. f. 20 hr reflux.

trimethylsilane in carbon tetrachloride was found suitable for the oxidation of disubstituted olefins to α-chloro ketones at room temperature.[9] With commercial chromyl chloride, the reaction had to be done in acetone at −78℃.

On the ground of all these findings, we believed that chromyl chloride or the oxidant **2** is the responsible oxidizing species. Chromium insertion products such as **3**, **4** and **5** are less likely, considering the fact that the reagent generated from chlorotrimethylsilane and chromic anhydride dose not show any sign of the presence of trimethylsilyl ester of chlorochromate and polychromate. It can be successfully used for most reactions developed using chromyl chloride. The mildness of the chromic anhydride-chlorotrimethylsilane pair compared to chromyl chloride due to the formation of the oxidant in low equilibrium concentration. This in-situ generated oxidant provides many advantages over chromyl chloride itself. It is less expensive, more convenient to handle. Its reactivity can be easily controlled by the mode of mixing and the ratio of chromic anhydride and chlorotrimethylsilane.

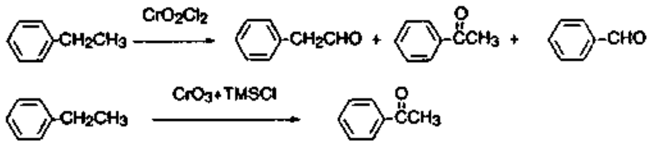
Benzylic Oxidation. The chromium (VI) oxidant prepared from chromic anhydride and chlorotrimethylsilane in carbon tetrachloride was proved effective in oxidizing toluene derivatives to the corresponding aromatic aldehydes.[7] The procedure is very simple and straightforward. The product was isolated either by silica gel chromatography or by aqueous work up. The yields of the reactions were generally good, but varied widely depending on the substituents on the aromatic ring. The reaction conditions and yields of these oxidations are summarized in Table 1.



In the reaction with chromyl chloride[3] or chromium anhydride-acetic anhydride,[15] toluene derivatives are known to form an Etard complex or an acylals. A similar complex is believed to be formed in the oxidation with chromium anhydride-chlorotrimethylsilane. Investigation by NMR revealed that no free aldehyde proton was present in the reaction mixtures. Nevertheless the reaction could be monitored by silica gel TLC. They all showed the spots of free aldehydes. Free aldehyde protons appeared on the NMR spectra only after an aqueous work up or wet silica gel column chromatography. The complex seemed to be very unstable and easily hydrolyzed by the moisture adhered on silical gel. The structure of the complex and the route of its formation are believed to closely resemble those of Etard reaction.

The reaction of *o*-nitrotoluene with chromic anhydride-chlorotrimethylsilane is of particular interest. A complex similar to Etard complex was apparently formed. But it gave only a trace of *o*-nitrobenzaldehyde on treatment with water. Most of *o*-nitrotoluene was recovered unoxidized. Similar result was obtained with *p*-nitrotolene. In contrast, oxidation with chromyl chloride is known to produce *p*-nitrobenzaldehyde in good yield (70%). The difference in reactivity between chromyl chloride and chromium anhydride-chlorotrimethylsilane also found in the oxidation of *p*-methoxytoluene, mesitylene. They were oxidized to the corresponding aldehydes in fairly good yields. For example *p*-methoxytoluene produced *p*-anisaldehyde in better than 60% yield, Etard oxidation of *p*-methoxytoluene was failed to produce the aldehyde.

The oxidation of ethylbenzene with Etard reagent produces mainly phenylacetaldehyde along with varying amount of acetopheneone, and benzaldehyde.[1] With chromic anhydride-chlorotrimethylsilane, however, ethylbenzene was oxidized to give exclusively acetophenone along with a trace amount of phenylacetaldehyde. Propylbenzene also produced propiophenone in good yields. The oxidation of ethylbenzene by chromyl chloride[16] is known to proceed through α-phenylethyl chromate, which produces either acetophenone by the abstraction of an α-proton or styrene by β-elimination. Phenylacetaldehyde is believed to be formed by the oxidation of styrene. The β-elimination leading to styrene is believed to be the predominant pathway in chromyl chloride oxidation of ethylbenzene. The elimination is almost completely suppressed for chromium anhydride-chlorotrimethylsilane.



Chromic anhydride and either dichlorodimethylsilane or trichloromethylsilane pairs were found equally or more effective than chromium anhydride-chlorotrimethylsilane pair in inducing Etard oxidation. For example, *o*-bromotoluene was easily oxidized to *o*-bromobenzaldehyde in good yield after 24 hour reflux with either chromic anhydride-dichlorodimethylsilane or chromic anhydride-trichloromethylsilane. These pair of reagents are expected to be more reactive than chromic anhydride-chlorotrimethylsilane due to the more reactive Si-Cl bonds. Therefore, dichlorodimethylsilane and trichloromethylsilane are expected to be more effective than chlorotrimethylsilane in depolymerization of chromic anhydride. The results are also summarized in Table 1. The failure of nitrotoluenes to produce nitrobenzaldehyde seems to result from the interaction of trimethylsilyl group with nitro substituent, which greatly diminishes the electron density of the aromatic ring. Although in less extent, the tendency was found in the oxidation of *p*-methoxytoluene. The use of stronger coordinating dichlorodimethylsilane and trichloromethylsilane in place of chlorotrimethylsilane resulted in poorer yield of anisaldehyde.

For all benzylic oxidation reactions, the molar ratio of chromic anhydride: chlorotrimethylsilane of 1: 1 and chromic anhydride: dichlorodimethylsilane of 2:1 was maintained in spite that a larger amount of chlorosilanes facilitates the depolymerization of chromic anhydride. Use of more chlorosilane resulted in the formation of dichloromethylbenzenes, which are reluctant to hydrolysis upon simple treatment with wet silica gel.

Conclusion

Chlorotrimethylsilane, dichlorodimethylsilane, and trichloromethylsilane react with chromic anhydride to produce chromyl chloride in equilibrium concentration. The reactivity of this in-situ generated chromyl chloride was milder than chromyl chloride itself but can be adjusted by controlling the degree of depolymerization of chromic anhydride. Benzylic oxidation of toluene and analogs to the corresponding benzaldehydes can be successfully carried out using chromic anhydride and any of chlorosilanes.

Experimental

Oxidation of *p*-Methoxytoluene. The oxidizing agents were prepared by stirring chromic anhydride (2 g, 0.02 mol) and chlorotrimethylsilane (2.2 g, 0.02 mol) in 10 m*l* carbon terachloride. *p*-Methoxytoluene (1.2 g, 0.02 mol) was added to the cold solution of oxidizing agents. The reaction mixture was heated to reflux for 48 hours. After cooling, the reaction mixture was slowly poured into a stirred mixture of water and ice and 5 g of sodium sulfate. Dilute (10%) hydrochloric acid was added to the mixture to dissolve chromium salts. The organic layer was separated, and the aqueous layer was extracted with carbon tetrachloride. The combined organic extract was washed with water, dried and evaporated in vacuo to afford 0.79 g (59%) of *p*-anisaldehyde.

Oxidation of Toluene. A mixture of chromic anhydride (2 g, 0.02 mol) and chlorotrimethylsilane (2.2 g, 0.02 mol) in 20 m*l* of carbon tetrachloride. A solution of toluene (0.02 g, 0.01 mol) in 5 m*l* of carbon tetrachloride was then added slowly. The reaction mixture was heated to reflux for 40 hours. The cooled mixture was filtered through a column of silica gel and washed with dichloromethane. The colorless filtrate and washings were combined and concentrated under reduced pressure to afford benzaldehyde (78 g, 76%).

Oxidation of Ethylbenzene. Ethylbenzene was slowly added to the prestirred mixture of chromic anhydride (2 g, 0.02 mol) and dichlorodimethylsilane (1.06 g, 0.01 mol) in 7 m*l* of carbon tetrachloride. After 21 hour reflux, the reaction mixture was filtered through a pad of silica gel. Evaporation of the volatile sovlent afforded 1.05 g of acetophenone (85%).

Oxidation of Diphenylmethane. The oxidant solution was prepared by stirring chromic anhydride (1.5 g, 0.15 mol) and trichloromethylsilane (0.75 g, 0.05 mol) in carbon tetrachloride (6 m*l*). Diphenylmethane (0.84 g, 0.05 mol) was completely oxidized after 3 hours of reflux to afford benzophenone in 96% yield.

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Characterization of Humic Acids from Kuye San Soil

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Three humic acids, two from uranium bearing coal shale and one from the neighbouring limey shale region, are extracted from soils by dissolution in 0.1 M NaOH followed by acid precipitation. After purification cycles, they are characterized for their elemental composition, contents of inorganic impurities, molecular size distribution and proton exchange capacities. The results are compared with the data of reference and aquatic humic acids characterized under the project MIRAGE II at TUM and also with other literature data. The proton exchange capacity determined by direct titration, is found to be 3.60 and 2.01 meq/g for coal shale and limey shale humic acids, respectively.

Introduction

A wide variety of natural and man-made organic species are present in the environment which can play an important role in the migration of heavy metal ions ($Z \geq 2+$) by complexation in natural aquifer systems.[1,2] Among natural organics, the most preponderant species are humic and fulvic acids which are polyelectrolytes with high complexation affinity for metal ions in particular with Fe^{3+}, Fe^{2+}, Ca^{2+} and rare earth metal ions present in water. The aquatic humic acid loaded with metal ions forms colloidal particles which are called humic colloids.[3,4] Such colloids, by their ion exchange property in solution, can also form pseudocolloid of actinide or other toxic metal ions.[4] An enhancement of migration or retention of heavy metal ions in a given aquifer system, with particular filtration and sorption properties, can thus be affected by humic substances. Since humic substances are structurally similar but have different size distribution and functional group content which depend on their origin,[5-7] a basic knowledge on the nature of humic and fulvic acids and their complexation behaviour are indispensible in establishing better understanding of such processes.

The present work deals mainly with the characterization of soil humic acids from the coal shale containing uranium deposite and limey shale region around Kuye-San, Korea where prospecting for uranium occurred in the past. The characterization of soil humic acids, KS-T1-HA, KS-T2-HA and KS-T3-HA, is necessary for the determination of complexation constant and other key paramenters in the accessment of the migrational behaviour of actindes and other heavy metal ions. Analytical data of the humic acids will also provide an insight into the complexation behaviour with naturally occuring U^{4+} and UO_2^{2+} ions of the region.

Experimental

The humic acids (HA) from the Kuye-San soil are extracted by a procedure similar to that described for the north Illinois soil near Joliet.[8] They are isolated by alkaline digestion of soil and precipitation with addition of an acid to pH 1. The precipitates are redissolved in 0.1 M NaOH and after addition of 0.2 g NaF/g HA left overnight to remove silicate impurities. By repeated cycles of dissolution (0.1 M NaOH) and precipitation (pH 1 by HCl), the humic acid precipitates are washed with 0.1 M HCl until no Na^+ is detected in the supernatant. The protonated final products are freeze dried and stored in a dessicator under vacuum due to hygroscopic property.

C, H and N contents are analyzed by burning some 25 mg of humic acid in O_2 atmosphere and resulting CO_2, H_2O and N_2 (reduced from NO_x) gases are analyzed by a heat conductivity measurement with CHN Rapid instrument (Heraeus Co.). The oxygen content in the samples is analyzed by a cracking process which oxidize carbon to CO then further to CO_2 over I_2O_5, and resulting CO_2 quantified by titration. Sulphur is analyzed by oxidizing the sample in H_2O_2 under O_2 atmosphere and titrating H_2SO_4 acid produced with $Ba(ClO_4)_2$.

Inorganic impurities in humic acids are determined by neutron activation analysis (NAA), sealing 10 mg sample in 5 mm suprasil quartz tube (Heraeus Co.), and irradiating in the FRM (Forchungsreaktor Munchen) at the position with neutron flux of $2 \times 10^{13}\ sec^{-1}\ cm^{-2}$ and subsequently by gamma spectrometry against Au/Co monostandard.

Experiments for the determination of proton exchage capacity is conducted in an argon inert gas box ($O_2 \leq 4$ ppb) with solutions and chemicals free of O_2 and CO_2 (known to cause interferences). About 10 mg HA weighed to 1.0 μg accuracy is dissolved in 1.00 ml of 0.1 M NaOH (carbonate free, Baker Co.) and diluted to 50 ml with 0.1 M $NaClO_4$.