

CHEMICAL INVESTIGATION OF 23-YEAR-OLD CDDC-TREATED SOUTHERN PINE

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Dedicated to the memory of our friend and colleague, Robert D. Arsenault

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ABSTRACT

The effect of 23 years' exterior exposure on copper dimethyl dithiocarbamate (CDDC)-treated southern yellow pine was evaluated by the application of solid state analytical instrumentation. Analytical methods including environmental scanning electron microscopy (ESEM), energy dispersive X-ray analysis (EDXA), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), inductively coupled plasma (ICP), and atomic absorption spectroscopy (AAS) were used to study CDDC-treated wood. Data from ICP and AAS analysis indicated that about 60% of copper and 81% of sodium dimethyl dithiocarbamate (SDDC) are lost from the 1/8-in. shell of the below-ground portion of the stakes after 23 years' field exposure. The molar ratio of SDDC to copper for freshly treated southern yellow pine is 2:1, while it is reduced to 1:1 after 23 years' field exposure. ESEM micrographs and EDXA data confirm the presence of solids rich in copper and sulfur similar to that of CDDC freshly treated samples. It is suggested that bidentate CDDC is modified to monodentate and bonded to wood to balance the available valence.

Keywords: Copper dimethyl dithiocarbamate (CDDC); sodium dimethyl dithiocarbamate (SDDC); environmental scanning electron microscopy (ESEM); X-ray diffraction (XRD); X-ray photoelectron microscopy (XPS); wood preservatives.

INTRODUCTION

Metal dimethyldithiocarbamates have been used since the 1940s in a variety of fungicidal and termiticidal applications such as plastics, textiles, and rubber. A 23-year field study of copper dimethyldithiocarbamate (CDDC)-treated wooden stakes installed in 1969 showed that CDDC is a highly effective wood preservative (Arsenault et al. 1991). The American Wood-Preservers Association has recently developed and published appropriate standards for CDDC as a wood preservative for below-ground and above-ground application (AWPA 1996).

The formation of CDDC in wood is an *in situ* two-step process. The first step consists of pressure-treating wood with a copper (Cu(II)) solution. Copper sulfate, copper hydroxide, copper amine, or copper carbonate may be used. The second step consists of impregnating the copper-treated wood with sodium dimethyl dithiocarbamate (SDDC), which reacts with copper to form the water-insoluble brown solid, copper dimethyl dithiocarbamate. The formation of CDDC in wood has been well investigated by comparing the X-ray diffraction (XRD) and the Fourier transform infrared (FTIR) spectra of

pure CDDC powder with the spectrum of CDDC-treated wood (Craciun et al. 1997; Gallacher et al. 1995).

The water-solubility of CDDC with a 2:1 molar ratio of SDDC to Cu was reported to be approximately 0.01 ppm (Arsenault et al. 1991; Cooper and Stokes 1993). Even at this low level of 0.01 ppm, CDDC was shown to be toxic to decay-causing fungi. It was also reported that the amount of copper leached from CDDC-treated wood was significantly lower than the amount leached from comparable samples treated with chromated copper arsenate (CCA-C) (Freeman et al. 1994). After 6 months' exposure in a soil bed test, copper leached at lower levels from CDDC than from either CCA- or ACA- (ammoniacal copper arsenate) treated stakes. CDDC samples lost less than 1% of the initial copper loading, whereas CCA- or ACA-treated samples lost 40 to 50%. The CDDC formed in wood is water-insoluble (i.e., fixed) within an hour or so, whereas the fixation of CCA in wood may take several days or weeks depending on the temperature and treating conditions.

Little is known about the effect of aging on the nature of CDDC present in wood. It was suggested that the N-alkyl dithiocarbamates of Cu(II) with two ligands are unstable and easily transformed into Cu(I) monodentates (Dwyer and Mellor 1964). Recently, it has been reported that metal dimethyldithiocarbamate complexes are candidates for the deposition of the corresponding metal sulfide semiconducting materials (Nomura et al. 1996). The decomposition of CDDC releases one SDDC ligand at a time, and the first fragmentation step is triggered by the breaking of metal-S bonds which may occur at 200°C. However, the effect of weathering conditions such as UV light, humidity, temperature, acid rain, etc., on CDDC solids in treated wood is unknown.

The objective of this work is to chemically characterize CDDC or the remaining copper-based preservatives in CDDC-treated stakes after 23 years' field exposure.

MATERIAL AND METHODS

Treatment

Southern yellow pine sapwood stakes measuring 19 by 19 by 91 mm ($0.75 \times 0.75 \times 36$ in.) were pressure-treated with copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), then air-dried, and retreated with a SDDC solution. The average retentions were 3.60 kg/m^3 (0.225 pcf) for copper and 16.0 kg/m^3 (1.00 pcf) for SDDC (Arsenault et al. 1991).

Field sites

The 23-year-old stakes were installed in Orange Park, Florida, from 1969 to 1976, then removed and relocated at Bainbridge, Georgia, in January 1977 until 1991 (Arsenault et al. 1991). The Orange Park test site has a warm climate and an average annual precipitation of 1.37 m (54 in.). The soil is a sandy organic type (Lakeland sand). The termite attack is rated greater in the Orange Park site than in the Bainbridge one. The Bainbridge soil is sandy with more organic matter (Tifton fine sandy loam) than in Orange Park. Untreated control stakes failed earlier at Bainbridge than at Orange Park. After 7 years' exposure in Orange Park, the average logscore of CDDC-treated stakes was 95.5. The stakes were then installed in Bainbridge from 1977 to 1991 and were rated at 92.3 for decay and 81 for termites at the end of this period. This logscore was comparable to the 92 of CCA-C treated to 6.4 kg/m^3 (0.4 pcf) retention. The CDDC stakes were analyzed for their copper and SDDC residual content in 1991 after their removal from Bainbridge.

Chemical analysis

Copper, nitrogen, and sulfur were analyzed by using inductively coupled plasma (ICP) and/or atomic absorption spectroscopy (AAS). Environmental scanning electron microscopy (ESEM-EDXA) was used to examine the surface of uncoated and wet samples. This instrument allows access to the scanning electron images of uncoated samples or deposits in

TABLE 1. Initial and final copper and SDDC retentions in CDDC-treated stakes after 23 years' field exposure.

	Initial		Final (23 years)	
	SDDC	Cu	SDDC	Cu
Retention, kg/m ³	16.02* (0.80)	3.52* (0.16)	3.52* (0.66)	1.41* (0.27)
pcf	1.00* (0.05)	0.22* (0.01)	0.22* (0.041)	0.088* (0.017)
Moles	0.0070	0.0035	0.0015	0.0014
Mole ratio (SDDC : Cu)	2:1		1.07:1	

* Mean of 10 replicates. Standard deviations are shown in ().

wood structure as well as the X-ray microanalysis of the same sample. ESEM-EDXA was used on thin cuttings to visualize and to microanalyze the solids present on the wood cell walls.

XRD was employed to acquire diffraction patterns of solids present in treated wood and XPS to determine the oxidative state of copper. XRD patterns of 23-year-old stakes were collected and compared to that of pure CDDC powder and to freshly treated stakes. X-ray photoelectron spectroscopy (XPS) yielded information on the valence of copper, carbon, oxygen, and sulfur present on the first 50 to 100 angstroms of the sample surface.

Conventional mass spectrometry (MS) yielded molecular information on the pure CDDC or the CDDC formed in treated wood as well as the 23-year-old CDDC treated samples. A 50:50 mixture of methanol and chloroform was used to extract freshly treated and 23-year-old CDDC-treated southern yellow pine, and to dissolve pure CDDC powder for mass spectrometry analysis. The mass fragmentation was initiated by electron impact with 70 eV at 10^{-7} Torr with the heating and ionization source at 200°C.

RESULTS AND DISCUSSION

ICP

The average copper, SDDC, and CDDC retentions of ten stakes originally treated in 1969 and after 23 years' field exposure are listed in Table 1. The SDDC retention is determined by using the sulfur content. The molar ratio of SDDC to copper is 2:1 for freshly treated samples. Arsenault et al. (1991) reported the cop-

per retention for a matched stake to this set after 7 years' exposure in Charleston, to be 86% of the original; no SDDC data were given. The molar ratio of SDDC to copper for the 23-year-old sample determined in this study is 1:1. The molar ratio corresponds to a monodentate CDDC; this means a core copper atom with one dimethyldithiocarbamate links.

A further elemental analysis of copper, sulfur, and nitrogen yielded 0.0014 mole of copper, 0.009 mole of sulfur, and 0.0016 mole of nitrogen in the 23-year-old CDDC-treated sample. The molar ratio of the three elements confirmed that CDDC is still present as a monodentate species with one copper for 1.6 to 2 sulfur and 0.8 to 1 nitrogen atom based on the molar ratio. On a weight basis, wood freshly treated wood with CDDC contains 0.28% copper, 0.93% nitrogen, and 1.86% sulfur. After 23 years' exposure, CDDC-treated wood contains 0.23% nitrogen and 0.28% sulfur, while only 0.03 to 0.1% nitrogen and 0.02% sulfur are typical in untreated southern pine (Panshin and de Zeeuw 1980). The levels of sulfur and nitrogen found in old stakes represent an $85 \pm 5\%$ sulfur loss and $75 \pm 5\%$ nitrogen loss during the 23-year exposure.

In 23-year-old stakes, the overall copper retention is reduced from 3.60 kg/m³ (0.225 pcf) to 1.41 kg/m³ (0.088 pcf), while SDDC decreased from 16.0 kg/m³ (1.00 pcf) to 3.0 kg/m³ (0.188 pcf). About 60% of the copper and 81% of the SDDC are removed after 23 years, and the loss of SDDC is higher than that of copper. The loss of SDDC corresponds to the removal of one ligand per mole of the proposed CDDC bidentate structure.

TABLE 2. *Repartition of copper and SDDC in one stake after 23-years' field exposure (3 replications).*

	Above ground				Below ground			
	0.32 cm (1/8") shell		Core		0.32 cm (1/8") shell		Core	
	SDDC	Cu	SDDC	Cu	SDDC	Cu	SDDC	Cu
AVG, kg/m ³	3.28	1.78	3.49	1.67	3.17	0.99	4.27	1.23
pcf	0.205	0.111	0.218	0.104	0.198	0.062	0.267	0.077
SD** (pcf)	(0.114)	(0.028)*	(0.118)	(0.021)	(0.051)	(0.019)	(0.162)	(0.031)
Moles	0.0014	0.0017	0.0015	0.0016	0.0014	0.0010	0.0019	0.0012
Mole ratio (SDDC : Cu)	0.82:1		0.94:1		1.4:1		1.58:1	

* Shell is outer 1/8 in. (3.1 mm) of 3/4 in. (19 mm) stake while core is the remainder. Standard deviations are shown in ().

More copper is lost from the outer 1/8-in. shell of the below-ground portion of the stake than in the above-ground portion or from the core for both above- and below-ground portions (Table 2). This could be explained by possible copper absorption by the surrounding soil. Almost 45% of copper is lost in the 1/8-in. shell and 36% in the core below ground compared to respective above-ground sections. Table 2 also shows that more SDDC is removed from 1/8-in. shell than in the core samples.

ESEM-EDXA

ESEM images in Fig. 1a and 1b show solids in both freshly treated and 23-year-old CDDC-treated SYP; no solids are seen in untreated wood (Fig. 1c). No significant difference was noticed between the above-ground and below-ground portions of the stakes. The EDXA in Fig. 2 confirm that the solids in both freshly treated (Fig. 2b) and 23-year-old samples (2a) contain carbon, copper, and sulfur. Although EDXA is only a semi-quantitative technique, it was evident from the sulfur peak that the 23-year-old CDDC sample contained less sulfur than freshly treated wood. The solid deposits in the 23-year-old CDDC sample appeared smaller in size than those in freshly treated wood, suggesting that the size of CDDC solids in wood is reduced by aging.

XRD and XPS

XRD of the 23-year-old sample indicates the presence of very small amounts of CDDC

crystals compared to freshly treated wood. This is illustrated by the low intensity of the spectrum in Fig. 3. The most visible peaks were at $2\theta=10.9, 11.8, 24.6,$ and 27.4 similar to those of freshly treated CDDC (Craciun et al. 1997; Gallacher et al. 1995). The low intensity of XRD spectrum indicates the more amorphous nature of the solids after 23-year field exposure.

The formation of CDDC with only one ligand in CDDC-treated wood was hypothesized and for comparison, the XRD of copper (I) dimethyldithiocarbamate was obtained. No similarity with the XRD of the 23-year-old exposed sample was found. The XPS Cu spectrum did not reveal any modification of the copper valence after 23 years' exposure. The binding energy was similar to that of Cu(II).

The presence of solids in ESEM images combined with the low XRD intensity for 23-year-old CDDC-treated sample suggests that with time the CDDC crystals might be reduced to amorphous solids undetectable by XRD. An analysis of electron spin resonance was conducted on CDDC in southern pine sapwood by Ruddick (1993). The study revealed that copper in the wood sample recovered after 23 years' exposure was still bound to oxygen.

It can be suggested that with the time, CDDC-treated wood released one of its dithiocarbamate ligands. The monodentate CDDC is easily leachable, less stable, and more bioavailable than bidentate (Cooper and Stokes 1993). Since copper is still present as

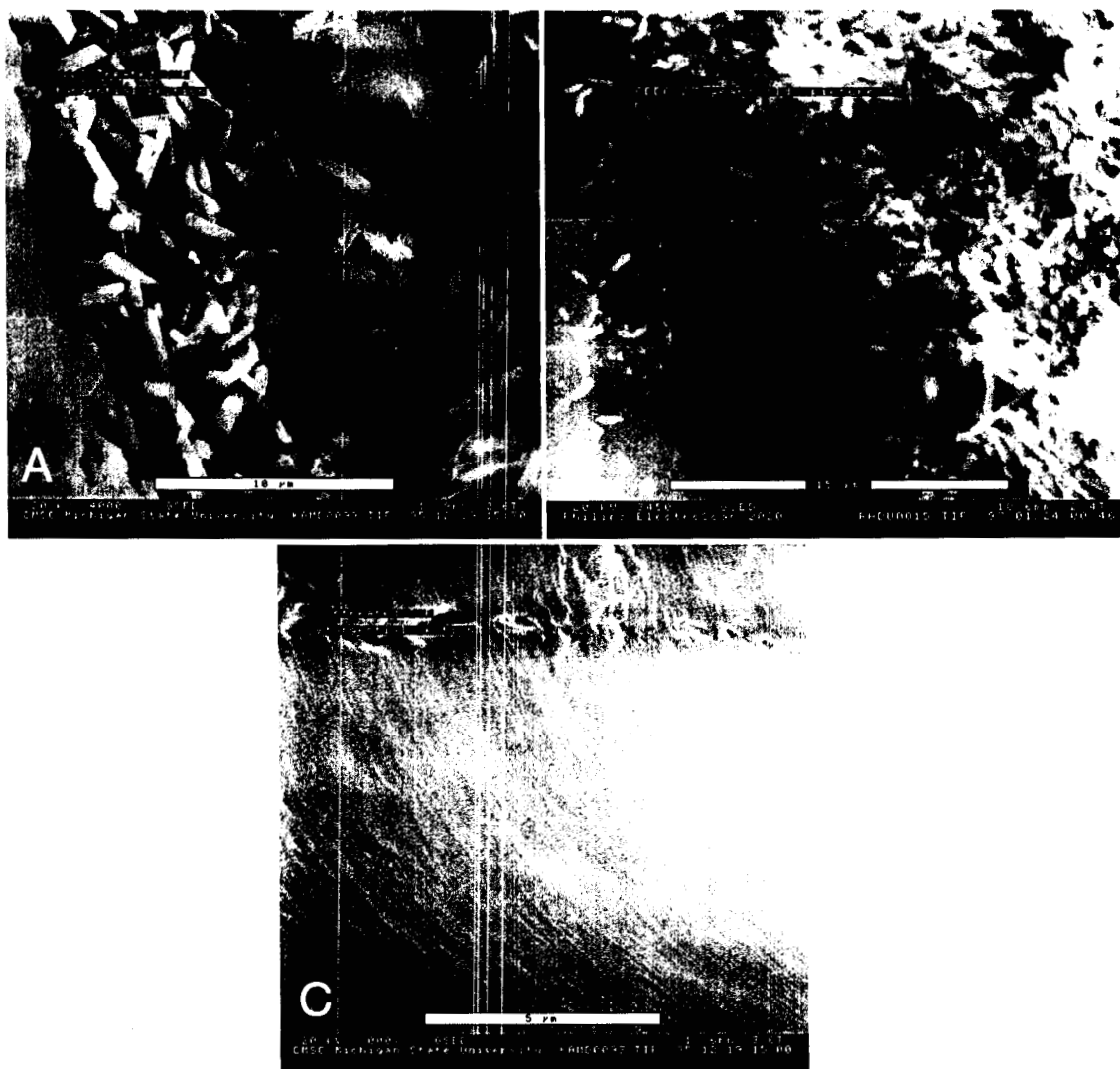
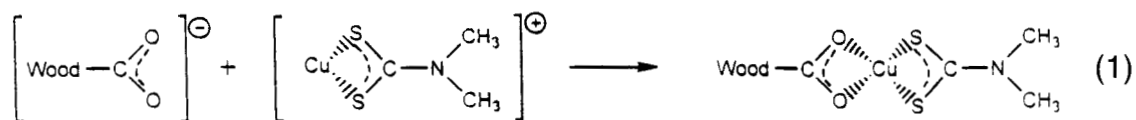


FIG. 1. ESEM images of: A. Freshly treated wood; B. 23-year-old sample; C. Untreated wood.

copper (II) plus(+) and the ligand dimethyldithiocarbamate is (I) minus(-), monodentate CDDC will use whatever wood component is available to act as the counter-ion and stabilize, as illustrated in Eq. (1). The copper of

CDDC monodentate could react with the carboxylic acid or phenolic hydroxyl groups of wood as suggested in the equation below. Further study is needed to validate this proposed mechanism.



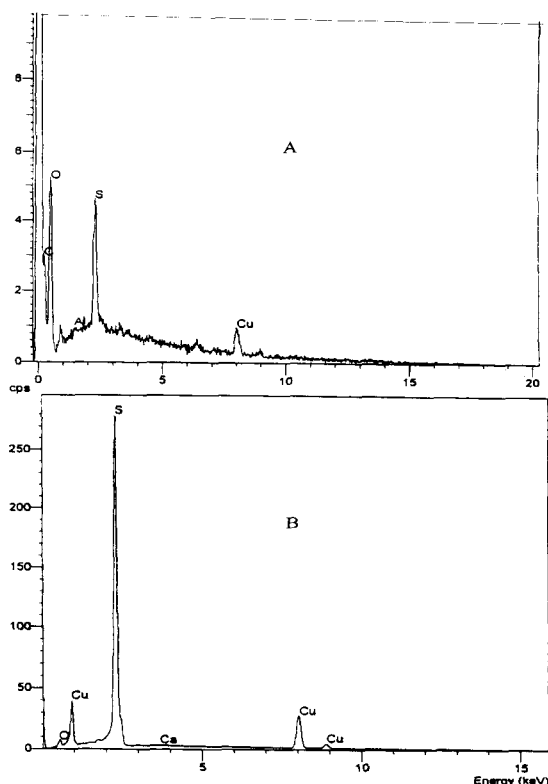


FIG. 2. EDXA of: A. 23-year-old sample; B. CDDC freshly treated wood.

Mass spectrometry

The mass spectra (MS) of CDDC powder, freshly treated, and 23-year-old field exposed samples are represented in Fig. 4. The MS of pure CDDC and freshly treated southern pine have an m/z of 303 and 305, which correspond to CDDC. The two peaks at 303 and 305 are attributed to the copper isotopes with mass 63 and 65. The fragmentation peak at 240 corresponds to CDDC without copper; the 208 is from CDDC without CuS, and the 183 corresponds to a monodentate CDDC. The peak at 121 is attributed to one ligand with a hydrogen attached to nitrogen. The peak at 88 is from the loss of one sulfur atom from the 121 ion, and the peaks at 73 from the loss of one methyl group, while the 76 may be from carbon disulfide.

The MS of the 23-year-old sample did not show any peak at 303 or 305, nor any pattern comparable to pure CDDC or freshly treated

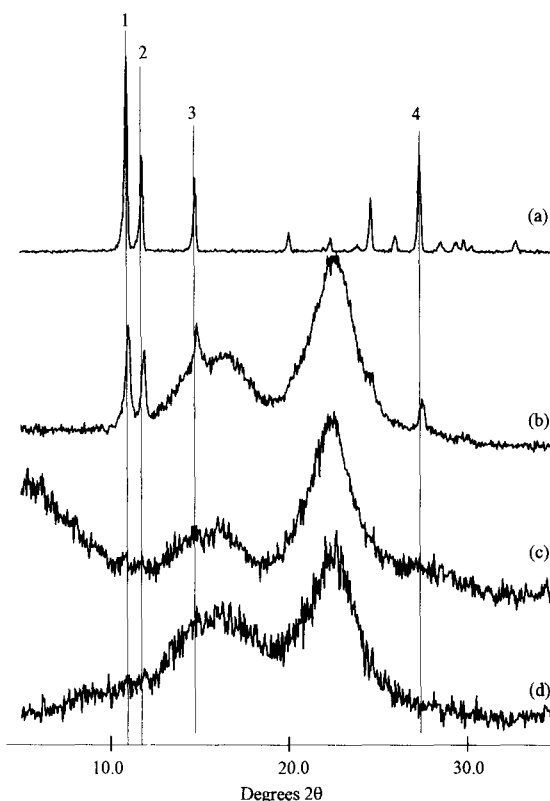


FIG. 3. XRD of: (A) CDDC pure powder; (B) CDDC freshly treated wood; (C) 23-year-old CDDC-treated wood; (D) untreated wood.

CDDC. However, the MS did show a peak at 183, a fragment at 76, and another at 44, which can be attributed to monodentate CDDC and to carbon disulfide. Based on the MS, it is concluded that after 23 years' field exposure, copper and sulfur in CDDC-treated wood are most likely present as the monodentate copper dimethyl dithiocarbamate.

CONCLUSIONS

1. ICP and AAS data indicated that after 23 years' of field exposure, bidentate CDDC originally formed *in situ* was modified. A change in copper valence state was not detectable.
2. ESEM-EDXA confirmed the presence of smaller sized solids in the 23-year-old sample compared to the size of crystals of the freshly treated sample.

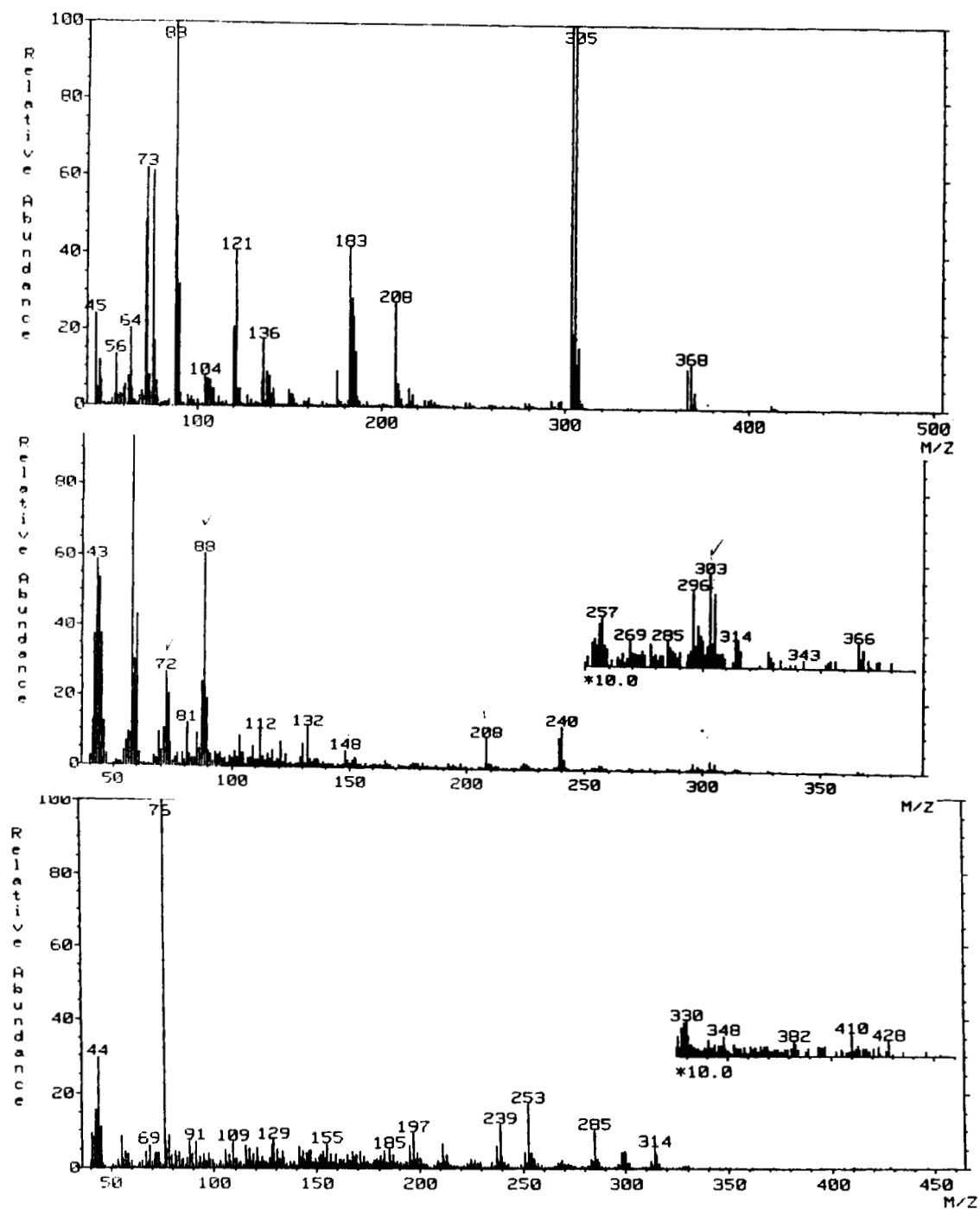


FIG. 4. MS of: A. CDDC powder; B. Freshly treated wood; C. 23-year-old CDDC-treated sample.

3. No significant XRD pattern was obtained from the 23-year-old sample, suggesting the transformation of crystalline CDDC to amorphous solids. The amorphous solids were tentatively identified as monodentate CDDC bonded to wood through oxygen interaction.

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