ON THE DETERMINATION OF WOOD PRESERVATIVES IN THE CELL WALL OF TREATED PINE POLES USING A LASER-MICROPROBE-MASS-ANALYZER (LAMMA)

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ABSTRACT

A Laser-Microprobe-Mass-Analyzer (LAMMA 500) was used for the determination of wood preservatives within the cell-wall layers of pine poles commercially impregnated either with CCF- or CCB-solution. The instrument allows a comprehensive analysis of the preservatives in the cell-wall layers within an area of less than 1 μm^2. All elements of the periodic system, including boron and fluorine, are apparently detectable.

Keywords: Scotch pine, wood preservatives, copper-chromium-fluorine (CCF), copper-chromium-boron (CCB), microanalysis.

INTRODUCTION

During the last few years, the application of new analytical methods has considerably facilitated the determination of important inorganic components contained in wood preservatives or impregnated wood. In particular, the application of microprobes in connection with the scanning microscope has led to significant results. It specifically allows analyzing a single cell as well as its structural components (e.g. Greaves 1974; Dickinson et al. 1976; Antoine and Giot-Wirgot 1977; Hulme and Butcher 1977; Liese and Peters 1977). This approach, however, fails to produce energy spectra from elements with mass numbers below that of sodium with the result that boron and fluorine, frequently used components in wood preservatives, cannot be verified. Although there are several effective methods known for the quantitative determination of these elements in impregnated wood (for fluorine: Gersonde and Kottlors 1961; Becker and Berghoff 1965; Williams 1969; Johanson 1974; for boron: Lämmke 1974; Schulz and Celik 1975; Hoffmann and Petrowitz 1976; Ermusch and Kalninsch 1979), they are not suitable for an exact localization within specific cell components.

A few years ago a laser-microprobe-mass-analyzer (LAMMA) was developed by the Leybold-Heraeus Company, Cologne, for solving biomedical problems (Wechsung et al. 1978a). It has proved to be a very effective tool for the detection of salt components within single cells of treated wood, and elements having a

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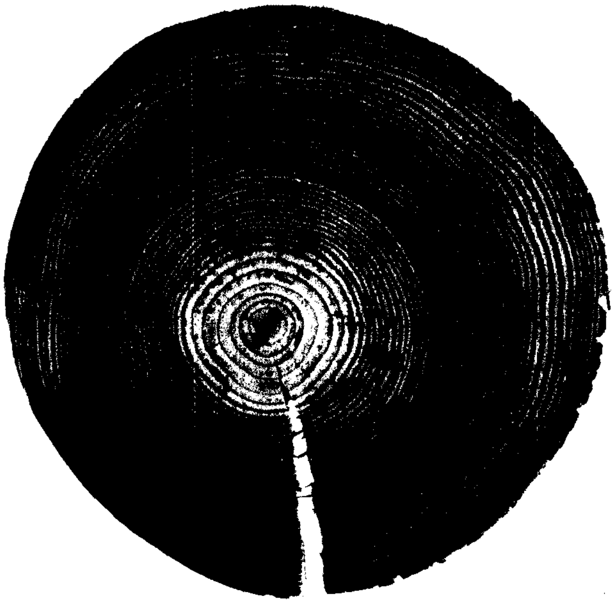

FIG. 1. Cross-section of a pole treated with 4% CCB-salt solution showing the measured annual rings.

relatively low mass number, i.e. boron and fluorine, can be detected quantitatively. After demonstrating possibilities of element localization in the cell wall of wood samples treated in the laboratory—by way of orienting analyses employing the LAMMA (Klein and Bauch 1979)—this study involves a similar experimental attempt to examine pine wood poles treated either with the CCF (chromium-copper-fluorine) or CCB (chromium-copper-boron) preservative on an industrial basis. Of special interest is the detection of B and F in the cell wall. By the same token, the proportions of the amounts of cations and anions taken up within the cell wall are studied, especially the ratio of Cr and Cu.

MATERIALS AND METHODS

Wood samples

The localization of wood preservatives based on LAMMA involved samples from two selected poles of Scotch pine (*Pinus sylvestris* L.) that had been commercially treated with 4% CCF or 4% CCB solutions. For the analysis small wood blocks were taken from the annual rings No. 7, 16, 30 of the CCF-treated poles and from No. 5, 16, 30 and 40 of the CCB-treated ones (Fig. 1). The samples were air-dried and embedded in butyl-methyl-methacrylate (3:2); and cross-sections of 1-μm thickness cut with an ultramicrotome. Such sections were placed on copper grids to be inserted into the LAMMA-instrument for direct measurements.

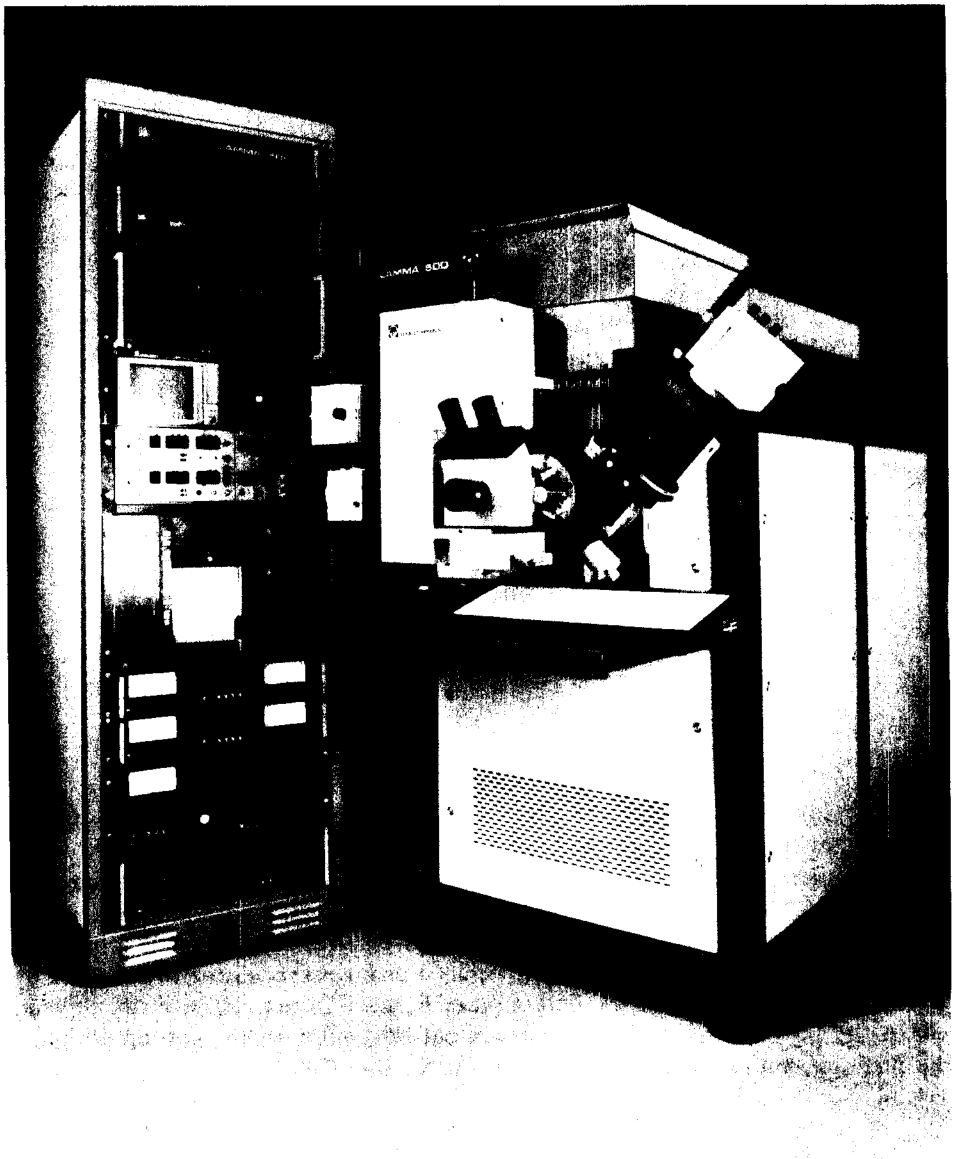

FIG. 2. General view of the Laser-Microprobe Mass-Analyzer (LAMMA).

LAMMA

Because detailed instrumental data have been given by Wechsung et al. (1978a) and Heinen et al. (1979), the following description will be related to the experiments only. The LAMMA consists of a microscope in conjunction with a time-of-flight mass spectrometer (Fig. 2). The section, mounted on the grid, is subjected to vacuum, rendering it observable by transmitted light of the microscope, and permitting the laser beam to be focused exactly at the analyzing area. The

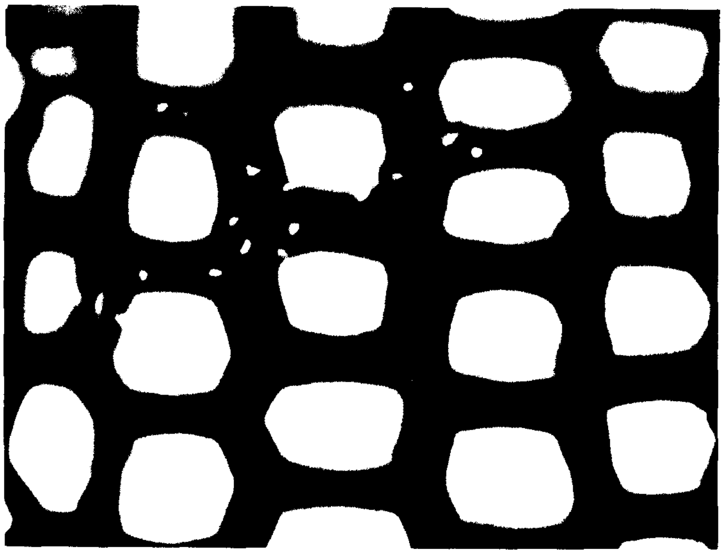

FIG. 3. Micrograph of a cross section of pine wood based on several laser shots, indicating the site of the individual analysis.

ions generated by the laser are extracted by the ion optics and analyzed with the mass spectrometer.

Each laser shot through the selected thin wood section (Fig. 3) generates a spectrum of either positive or negative ions. All elements of the periodic system, including their isotopes, can be detected by LAMMA. The focus of the laser beam allows selective measurements of an area less than 1 μm^2 of the individual layers of the cell wall. In the following study, more than a thousand positive and negative mass spectra have been recorded from different cell-wall layers of earlywood and latewood in order to obtain representative mean values.

RESULTS

Localization of the CCF-preservative components in the cell wall

From each cross-section of the CCF-treated pine poles, positive and negative mass spectra were recorded. Evaluating the negative mass spectra (Fig. 4) of all annual ring samples showed that F can be confirmed not only in the preservative (Fig. 4a) but also in the cell wall (Fig. 4b). It is surprising, however, that only a very slight amount of F may be detected in the cell wall, requiring a sensitivity factor of 40 for its clear identification (Fig. 4c). The distribution of anions in the cell-wall layers appeared to be irregular; this was also observed for cations. By comparison of the anion spectrum with the cation spectrum, it becomes clear that the F concentrations occurring in the cell walls were considerably less than those of Cr and Cu.

The positive ion mass spectra (Fig. 5) were also received for the CCF-solution (Fig. 5a) as well as from the cell walls of impregnated wood (Fig. 5b). As Fig. 5a indicates, all preservative elements—namely sodium (mass number: 23), potassium (39, 41), calcium (40), chromium (50, 52, 53, 54), and copper (63, 65) in

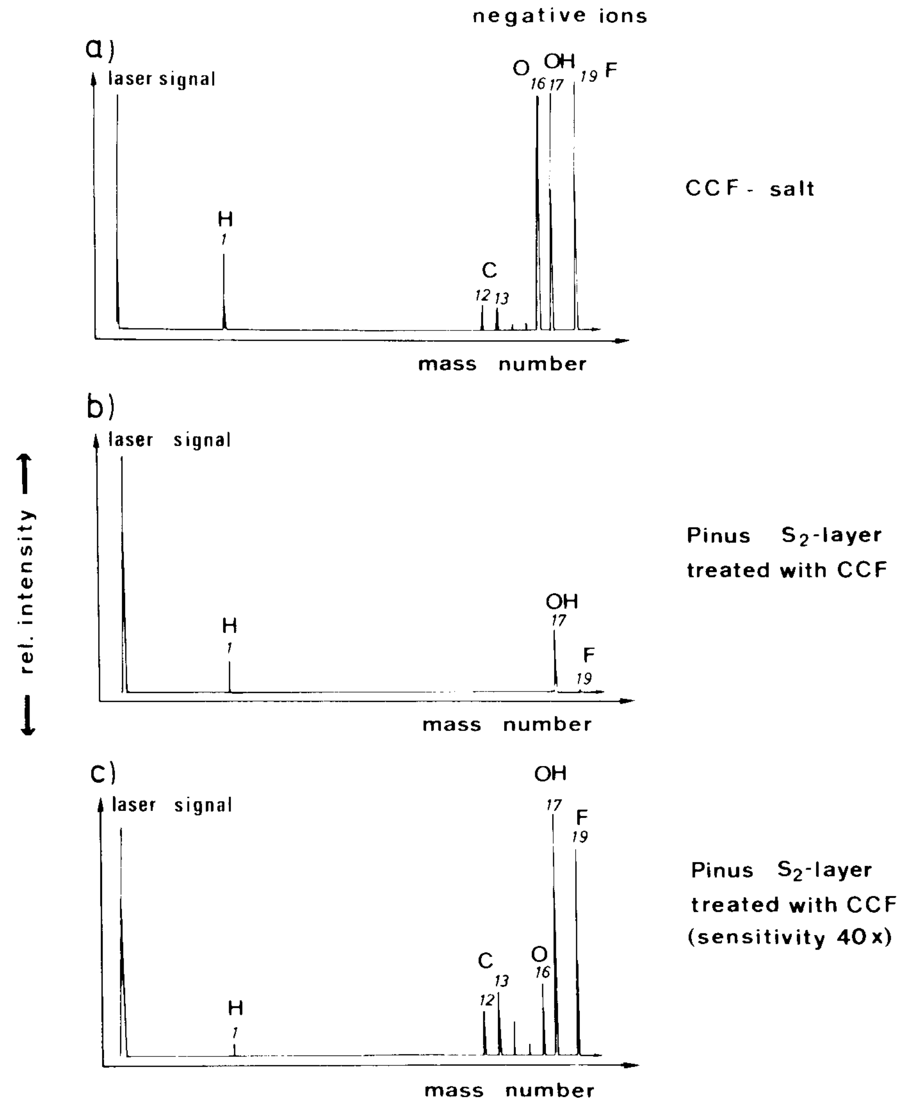

FIG. 4. Negative mass spectra: a) 4% CCF-salt solution, b) treated secondary cell wall of pine wood, c) spectra shown in b) intensified by a factor of 40.

particular— are detectable. The LAMMA system, however, has a greater sensitivity for Cr than for Cu, as demonstrated by the analysis of the original CCF solution. The original CCF solution had a ratio of 3.8 of Cr to 1 of Cu, but the LAMMA analysis gave a ratio of 8 of Cr to 1 of Cu. This means that the LAMMA system is twice as sensitive to Cr as to Cu.

The average ratio of chromium to copper measured in the cell wall (Fig. 5b) amounts to 60 to 1, suggesting that about 30 times more chromium is adsorbed in the cell wall than copper, on the basis of all sapwood measurements.

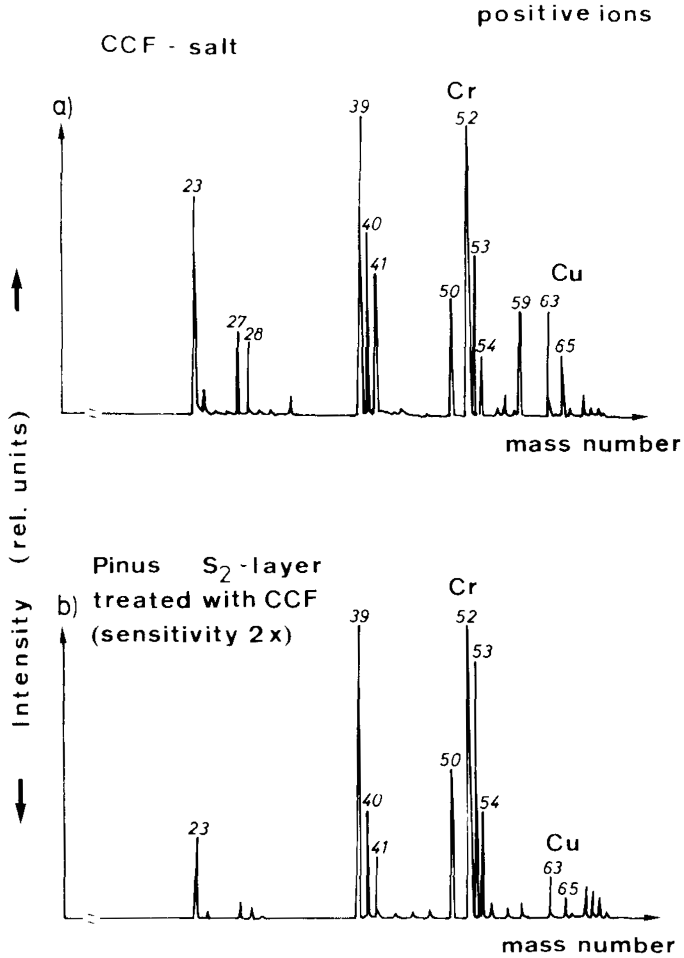

FIG. 5. Positive mass spectra: a) 4% CCF-salt solution, b) treated scondary cell wall of pine wood.

Localization of the CCB preservative components in the cell wall

The mass spectra of the solution of CCB preservative (Fig. 6a) reveal that boron (mass number 10 and 11) is part of the positive spectrum, displaying, however, a lower sensitivity than for copper or chromium. For the 4% CCB, it can be calculated that the analytical sensitivity of boron amounted to about 10% of that of copper. The mass spectroscopical measurements of CCB in the cross section of the treated pole, as shown in Fig. 6b, suggest that the cell walls of all annual rings adsorb boron at greatly varying concentrations. For a single measurement this may even result in a cell-wall concentration of boron corresponding to that of copper.

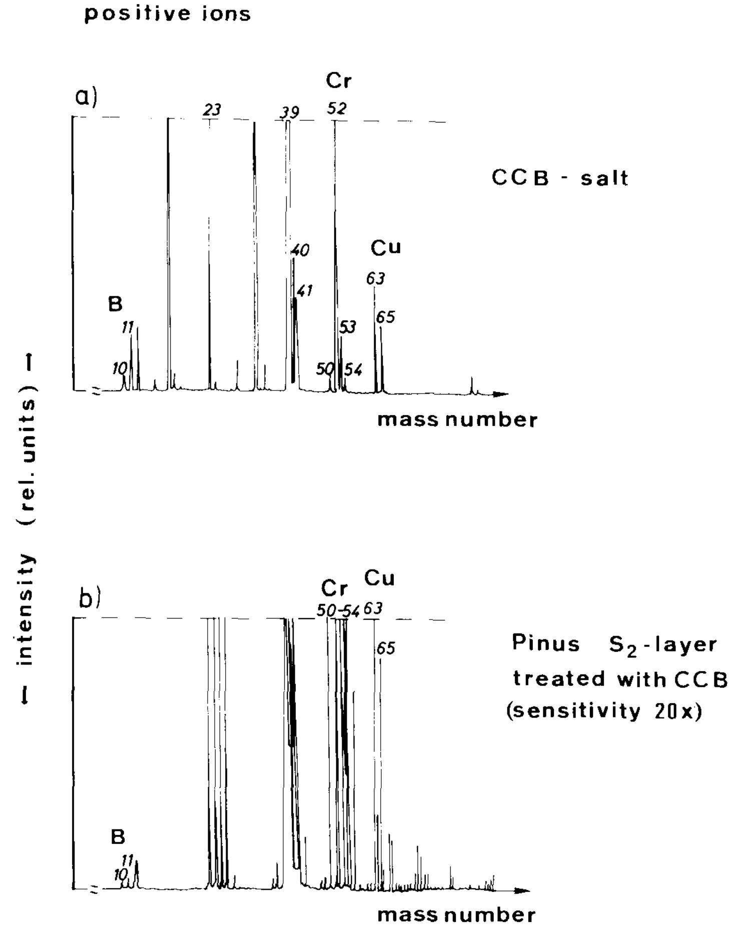

FIG. 6. Positive mass spectra: a) 4% CCB-salt solution, b) treated secondary cell wall of pine wood.

Relative concentration of chromium and copper in the cell walls of CCF- and CCB-treated pine poles

Besides locating the two preservatives CCF and CCB in the cell wall, an attempt was made to determine the relative concentration gradient of Cr and Cu extending from the cambium to the pith (Table 1).

For the 4% CCF-solution the ion ratio of chromium to copper amounts to 3.8 to 1. However, the proportions found in the treated wood are different. In the 7th annual ring, the Cr concentration exceeded that of Cu by a factor of 40. The relative ratio decreased at the 30th annual ring to a ratio of 22 to 1; at the same time the absolute amount of adsorbed chromium and copper was reduced.

A similar trend was observed in samples treated with the CCB preservative. For the 4% CCB-solution, the ratio of Cr to Cu amounted 1.9 to 1, whereas the

TABLE 1. *Relative concentrations of chromium and copper in the cell walls of CCF or CCB treated pine poles. (Annual ring number related to the outermost ring.)*

Relation of ions Cr:Cu	Concentration (rel. units) Cr:Cu			
4% CCF-solution	Annual ring number			
	7	16	30	
3.8:1	40:1	30:1	22:1	
4% CCB-solution	Annual ring number			
	5	16	30	40
1.9:1	13:1	11:1	8:1	7:1

relative concentration ratio measured for the 5th annual ring of the treated wood increased to 13 to 1. The trend towards the inner sapwood at the 40th annual ring corresponded to a ratio of 7 to 1, which is comparable to the results obtained from samples involving the CCF-treatment.

DISCUSSION

The results obtained from this investigation emphasize that LAMMA instrumentation is very effective in the determination of chemical components of wood preservatives in the cell wall. The previous investigation with laboratory-treated samples (Klein and Bauch 1979) served as an experimental basis for this study of commerically treated pine poles.

Nevertheless, the LAMMA-analysis of preservatives, using methacrylate-embedded sections, is not suitable for evaluating deposits in the lumina because of leaching from the embedding process itself. As shown by Klein and Bauch (1979), cured polymethacrylate itself does not have an apparent effect on the measurements. As opposed to X-ray energy analysis EDAX (e.g. Becker et al. 1974) or other analytical approaches applied to single cells (Lämmke 1974), all elements of the periodic table, including B and F, appear to be determinable in the cell wall by using LAMMA.

According to our analytical data, the concentration of F found to be present in the cell wall is low, which corresponds with earlier findings, generally showing that anions are less adsorbed than cations (Bauch 1964; Patt 1970; Klein 1976).

However, considering that quantitative analyses carried out by Becker and Berghoff (1965), Becker (1973), and Johanson (1974) have shown a sufficiently protective amount of F being present in the wood, it also means that the largest quantity of this element must have been deposited at the lumina surface and subsequently have become leached by the embedding process.

The fraction of boron observed to be present in the wood similarly is considered to be adequate as to protective requirements (e.g. Findlay 1959; Johanson and Howick 1975; Hoffmann and Petrowitz 1976). It has been pointed out repeatedly that B easily leaches from the cell-wall layers—a phenomenon also observed during this study. Boron is irregularly distributed in the cell wall and compared to copper is present in a lower concentration. However, some measurements revealed that boron was occasionally accumulated in the cell wall. In comparison to chromium, both elements are retained by the cell wall to a lesser extent.

The fixation of Cr in commercially treated poles is surprisingly strong considering the obtained Cr:Cu ratio in the sapwood for the CCF-solution of 30:1 and for the CCB-solution of 9:1. Based on EDAX-analyses, Hulme and Butcher (1977) found respective values of about 2:1 in the S2-layer of radiata pine samples treated with CCA-salt.

In order to explain the considerable differences for cation and anion adsorption obtained with LAMMA, the same samples were subsequently subjected to X-ray energy analysis EDAX (Klein, unpubl.). The measurements of single cell walls produce data of Cr and Cu concentration ratios similar to the preceding LAMMA-analysis. Subjecting cell tissues to overall measurements, however, amplified the occurrence of Cu as compared to single cell-wall analysis. The Cr-fraction appeared to be constant. With regard to the EDAX Cu detection in single cells, there are indications that, as an additional complexity, the working limit of sensitivity may be nearly reached. On the other hand, LAMMA proved to possess a significantly higher detection probability, with limits ranging from 10^{-18} to 10^{-20} g (Wechsung et al. 1978b), allowing a more effective differentiation of the kind of ion present in the individual cell-wall layer.

It also needs to be emphasized that these studies involved commercially and not laboratory-treated samples. The laboratory samples showed considerably less variation of adsorption between Cr and Cu (Dickinson 1974; Greaves 1974; Hulme and Butcher 1977; Duran et al. 1978). Moreover, depending on the specific species involved (Levy and Greaves 1978) and the treatment method applied, there are large differences of retention and distribution of preservatives between softwoods and hardwoods (Dickinson et al. 1976; Greaves and Levy 1978; Peters 1978).

Observed differences in Cr adsorption are, at first, explainable in terms of a higher Cr fraction present in the CCF-solution. Second, because boron is a cation in the CCB solution, it may have occupied more binding sites within the cell wall than the anion fluorine.

The data based on LAMMA additionally showed a decrease of adsorption associated with the internal region of the sapwood for all ions studied. This trend could be verified by applying EDAX-analysis.

In conclusion, it may be generalized that because of the very high detection sensitivity of LAMMA, an exact localization of wood preservative components in cell walls is possible. Although almost all LAMMA-analyses so far involved merely coniferous species, there is some promising evidence that this method is similarly applicable to the determination of preservatives in cell walls of broad-leaved trees.

SUMMARY

Based on the Laser-Microprobe-Analyzer (LAMMA), more than a thousand single analyses on preservatives retained in cell walls of pine poles, commercially treated either with CCF- or CCB-solutions, were carried out.

LAMMA is generally suitable for the determination of ions present in a treated single cell. Localization as well as evaluation of the relative concentration of all elements is possible.

Even elements such as boron and fluorine, with a mass number below that of sodium, are identifiable in the cell wall.

Fluorine—as anion—becomes adsorbed at a very low amount.

Boron and copper are likewise scarcely retained by the cell wall; boron shows an irregular distribution pattern across the cell wall, its fraction lying above or below that of Cu.

Chromium becomes more strongly fixed than copper.

There exists an overall gradient of ion concentration from the outer to the inner region of the sapwood of poles either treated with the CCF- or CCB-preservative.

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