# ELECTRICAL TRANSPORT OF IONS THROUGH SAPWOOD OF *PINUS SYLVESTRIS* L.

BY

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Unless otherwise stated the research described in the Thesis is only that of the author.

# A B S T R A C T

A novel technique was developed for determining the electrical transport of ions and of water under an applied d.c. electric field in green sapwood of Pinus sylvestris L. (Scots pine).

Cylindrical samples of the wood were fitted horizontally into a special cell with silicon rubber O-rings. The ends of each sample were bathed in electrolyte solution contained in electrode compartments. Processes at the wood/solution interfaces were therefore separated from those at the solution/electrode interfaces. "Sweating" of the wood was reduced by coating the surface with Mobilcer R emulsion. Equal hydrostatic pressure was maintained across the cell by means of horizontal capillaries at each end, and by holding the cell in a horizontal frame.

Constant currents were passed through the cell, and the bathing electrolytes then analysed to determine the transference numbers of the ions in the wood. The endogenous current-carriers comprised inorganic ions, in the order: $K^+$, $Ca^{2+} > Mg^{2+} > Na^+ > NH_4^+$, $Cl^-$, $SO_4^{2-}$. These matched the levels of ion-exchangeable ions eluted by hydraulically flushing the wood. The endogenous current was virtually eliminated by prior electrolyte flushing, but only partially depleted by water flushing. Exogenous cations like $Cu^{2+}$ migrated fastest in the water-flushed wood. The tissue pathways for copper migration were identified.

These results are explained by a model of migration based on cation-exchange at successive carboxyl groups ($-COO^-$) attached to cell walls in the wood.

Electro-osmotic flow occurred from anode to cathode compartments, confirming that wood is negatively charged with respect to water. The rate of electro-osmosis was studied under various conditions.

A comprehensive survey of the literature is included, on the effects of applied d.c fields on wood and on its ion-exchangeable properties. The relevance of this project to wood preservation and to living wood is discussed.

# I N S C R I P T I O N

One and one are two,
  Two and two are four.
I only wish to goodness
  There wasn't any more!

Adding and subtracting,
  Really, what's the use?
When Winston Churchill was at school
  They say he was a goose.

Yet he became Prime Minister
  And help'd us win the war.
That's 'cause he didn't waste his time
  On two and two are four.

Spike Milligan (1963) 'The Little Pot Boiler', Tandem Books, London

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# CHAPTER 1

# BOTANY INTRODUCTION

## 1.1 Importance of timber

In an age of rapidly dwindling resources, timber is one of the few renewable materials widely available for construction, fuel and chemical uses. As populations and living standards rise, so the demand for timber increases. Total world consumption of wood and wood products in 1976 was 2524 x $10^6$ $m^3$ of roundwood, and is expected to increase by 80% by the end of the century (C.A.S., 1979). By the year 2025 world timber supplies will probably fall short of demand, as forestry investment is not keeping pace with the projected demand (Forestry Commission, 1977). As a result timber prices are expected to rise at an increasing rate.

An alternative approach to reducing the timber shortage is to preserve stocks of wood already in service against biodeterioration by insects, fungi, marine borers, and bacteria. Data on the cost of such deterioration in the U.K. are not available, but an estimated \$2000 x $10^3$ of damage to timber was caused in the U.S.A. in 1975 by fungal decay (Wilkinson, 1979). A wide range of methods for preserving timber has been developed during the long history of wood use. The contribution of this preservation towards conserving stocks of living trees has been estimated to have saved over 4000 x $10^3$ trees since 1909 (Wilkinson, 1979). Yet despite the sound economic sense in improving wood preservation and production, funds allocated to forestry research amount to less than 1% of the annual U.K. timber consumption (C.A.S., 1979). This is extremely low compared with the research allocation to other industries, particularly to agriculture. One aspect of wood research identified as needing more attention is "Timber drying and preservation; extending the life and determining the best use of home-grown and imported timber" (C.A.S., 1979). This project aimed to make a modest contribution towards such a research goal.

## 1.2 Introduction to *Pinus sylvestris* L. (Scots pine)

*Pinus sylvestris* L. (Scots pine, also known as Baltic or European redwood) is one of the few truly native conifers in the U.K., and at one time forests of it covered large areas of Scotland. During this century it has been planted extensively in East Anglia, and more recently the nutrient-poor uplands of Wales, Northern England, and Scotland. Over much of Northern Europe it is the principal source of softwood, and large quantities are shipped annually to the U.K. from the Baltic and from Russia.

Trees of Scots pine grow up to 30 m, and diameter up to 1 m. The physical properties of its wood largely depend on the conditions of growth, which affect the texture, density and the number and size of knots. Thus the wood from Northern Sweden and Russia has a fine texture due to its very slow growth rate, and is well suited for the manufacture of joinery. Wood grown in Southern Sweden and in the U.K. is coarser and is useful for fencing, boarding and other building purposes. Its working properties and uses depend to a large extent on the number and size of knots that it contains. In general it is very suitable for transmission and telegraph poles, as the broad band of sapwood is readily permeable, and so can be effectively impregnated with preservatives against biodeterioration, (Findlay, 1975).

## 1.3 Nature of Wood

Wood is most simply defined as the principal component of the stems and branches of trees. Although timber can be used to refer to wood in living trees, it will be used here to describe wood cut from felled trees.

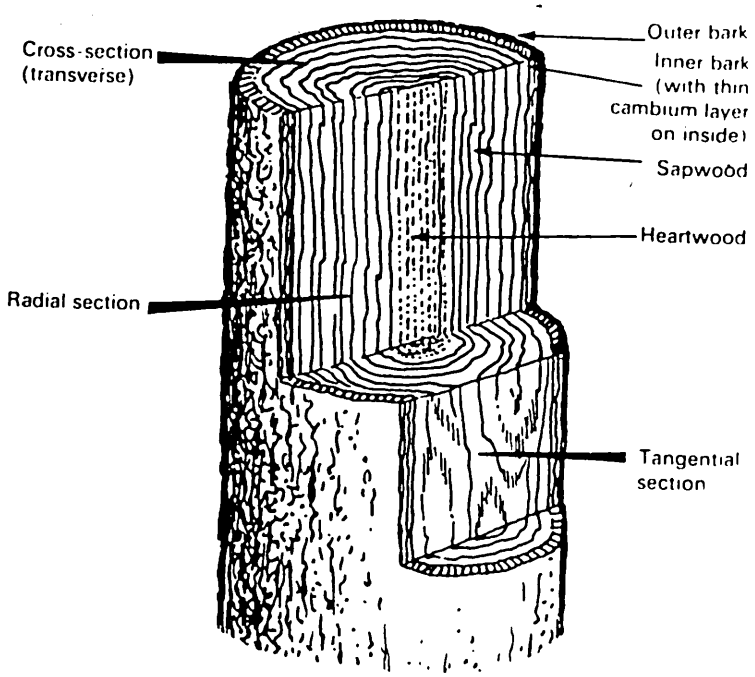
Woods are classed as 'softwood' or 'hardwood'. Softwoods are woods of the needle-bearing, coniferous trees, hardwoods those of broad-leaved, deciduous trees. A mature tree of either the softwood or hardwood type generally consists of a single woody trunk covered with a layer of bark. The woody tissue largely provides mechanical support; conducting channels for the upward or lateral passage of water, ions,

some organic compounds, and gases; and storage tissues where food reserves such as carbohydrates accumulate. The inner layers of bark conduct a variety of organic compounds, such as sugars and amino acids, and a few types of ions such as $Ca^{2+}$, and the outer layers of bark provide insulation and protection from physical and biological attack.

## 1.4 Gross features of wood

Wood is an anisotropic material - the majority of cells are elongated parallel to the stem axis with a relatively small component of cells elongated radially. In describing many features of wood it is convenient to refer to the three planes of dimension: transverse, radial longitudinal and tangential longitudinal planes (Fig. 1.1).

Figure 1.1 Gross anatomical features of a woody tree trunk in 3 dimensions



### 1.4.1 Sapwood and Heartwood

A mature tree trunk in transverse section comprises two zones of wood: an inner core of heartwood often dark coloured, and an outer, often lighter coloured ring of sapwood. Sap is conducted through the sapwood, and food materials stored in its living cells. As the tree matures the wood towards the centre of the trunk develops into heartwood, losing much of its moisture content, all the stored food substances, and usually becomes impregnated with various organic compounds such as oils, gums, resins, tannins, aromatic and colouring materials. Heartwood normally contains no living cells.

### 1.4.2 Growth rings

Another feature of wood often seen in transverse section is concentric rings of light and dark coloured wood. In temperate climates each ring represents one year's growth of wood, and is called an 'annual ring'. This pattern arises from the difference between wood produced in the early and later parts of one year's growing season - called 'earlywood' (or 'springwood') and 'latewood' (or 'summerwood'), respectively. The lighter coloured earlywood is usually less dense that the latewood, differing in cellular structure and sometimes in chemical composition. Within one growth ring, though, the contrast in colours can be less distinct, as the earlywood gradually merges with the latewood.

### 1.4.3 Grain

The grain of wood is, strictly speaking, the direction of the elongation of the majority of the wood cells in relation to the trunk (generally in a longitudinal direction parallel to the axis of the trunk).

### 1.4.4 Rays

Cells arranged radially and organised into bands of tissue are called wood rays. Primary rays extend from the pith at the centre of the trunk, to the cambium at the periphery of the xylem (Fig. 1.2);

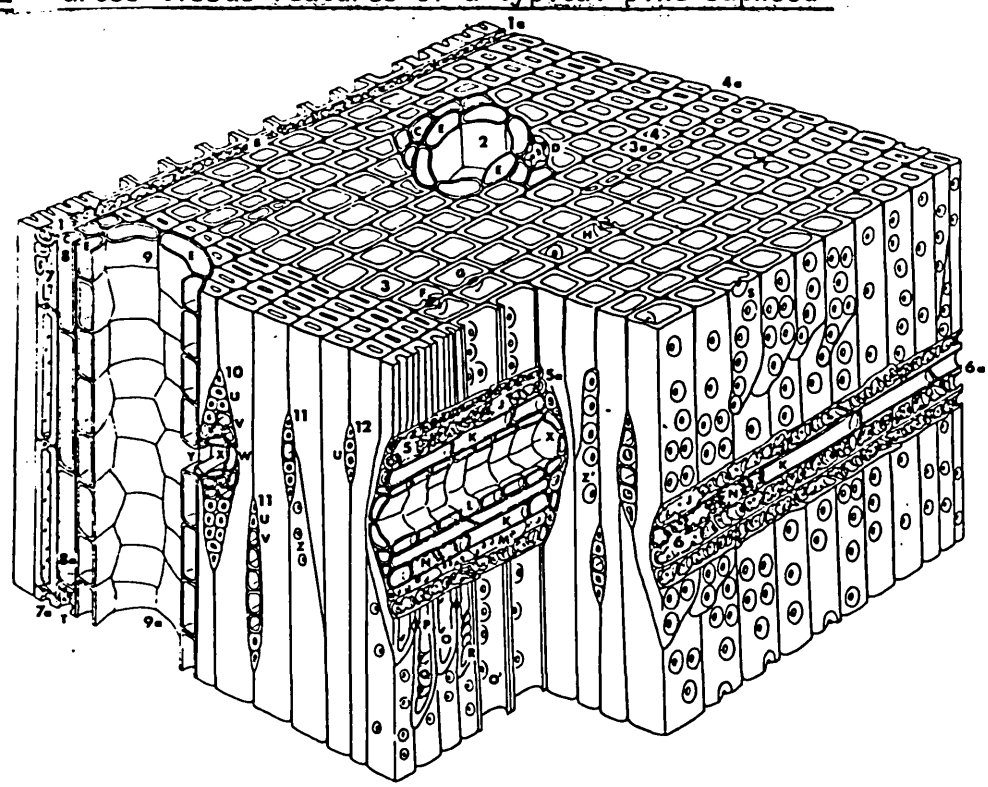
secondary rays are initiated later in the age of the tree, and do not extend as deep as primary rays. Rays appear as faint lines along radial sections of softwood.

## 1.5 Microscopic features

Wood is composed of millions of microscopic xylem cells. These cells differ in size and shape, depending upon their physiological role in the tree, most of them being many times longer than broad, and orientated in a longitudinal direction.

The xylem of softwood is much simpler than that of hardwoods, and consists of only two types of cell: parenchyma and tracheids, the former being restricted to rays and resin ducts in the majority of species (Fig. 1.2).

Figure 1.2 Gross tissue features of a typical pine sapwood



Transverse view. 1-1a, ray; B, dentate ray tracheid; 2, resin canal; C, thin-walled longitudinal parenchyma; D, thick-walled longitudinal parenchyma; E, epithelial cells; 3-3a, earlywood tracheids; F, radial bordered pit pair cut through torus and pit apertures; G, pit pair cut below pit apertures; H, tangential pit pair; 4-4a, latewood.

Radial view. 5-5a, sectioned fusiform ray; J, dentate ray tracheid; K, thin-walled parenchyma; L, epithelial cells; M, unsectioned ray tracheid; N, thick-walled parenchyma; O, latewood radial pit (inner aperture); O', earlywood radial pit (inner aperture); P, tangential bordered pit; Q, callitroid-like thickenings; R, spiral thickening; S, radial bordered pits (the compound middle lamella has been stripped away, removing crassulae and tori); 6-6a, sectioned uniseriate heterogeneous ray.

Tangential view: 7-7a, strand tracheids; 8-8a, longitudinal parenchyma (thin-walled); T, thick-walled parenchyma; 9-9a, longitudinal resin canal; 10, fusiform ray; U, ray tracheids; V, ray parenchyma; W, horizontal epithelial cells; X, horizontal resin canal; Y, opening between horizontal and vertical resin canals; 11, uniseriate heterogeneous rays; 12, uniseriate homogeneous ray; Z, small tangential pits in latewood; Z', large tangential pits in earlywood.

### 1.5.1 Parenchyma

Parenchyma cells are generally short, thin-walled, non-lignified brick-shaped cells (see Fig. 1.2), which remain alive in the mature sapwood. About 7 to 8% of the total volume of softwood xylem is composed of parenchyma cells, and is present in transversely orientated ray tissue, where they provide:

(a) horizontal transport of organic and inorganic material, and
(b) storage space for reserve materials, such as starch.

Parenchyma tissue also lines longitudinal channels known as resin ducts, into which they secrete resin.

Specialised parenchyma cells termed 'transfer cells' occur alongside tracheids, and are characterised by highly developed convoluted wall ingrowths; these cells can selectively extract or deposit ions from xylem sap.

### 1.5.2 Tracheids

Tracheids make up about 93% of the total volume of most coniferous woods. Tracheids are long, narrow cells (Table 1.1) with tapered ends along their radial surfaces (Figs. 1.2 and 1.3). The living cell contents of tracheids are lost the year they are formed, and the empty interior (lumen) of each cell provides an ideal channel for conducting fluids.

Earlywood tracheids are wider and have thinner walls than latewood tracheids. The earlywood tracheid lumina connect with other tracheid or parenchyma interiors by a large number of (50-300 μm) small, thin areas in their cell walls. These areas, known as 'pits', allow fluids to pass from lumen to lumen, and since most pits occur on the radial end faces of earlywood tracheids (where one tracheid dovetails with another), sap is conducted largely upwards through the earlywood tracheid lumina. Materials can also be transported through pits between rays and tracheids. The tracheids of latewood are thicker-walled, with narrower lumina, and smaller and fewer pits, and contribute more to the strength of wood. Tracheids occurring in the rays account for about 5% of total softwood volume.

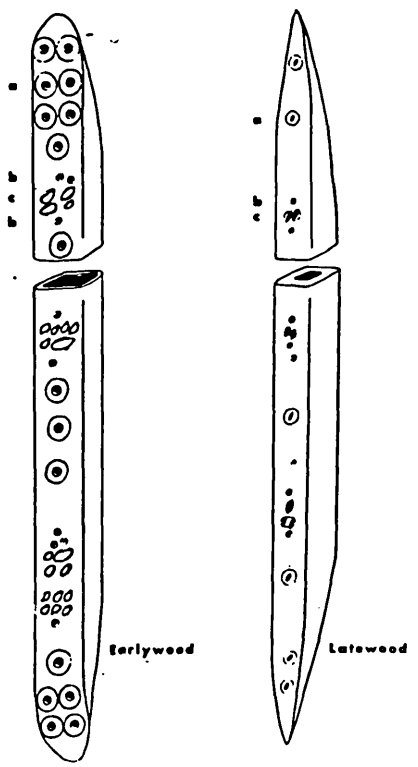
Table 1.1 Summary of dimensions of softwood structural elements

| Structural Element | Dimension, micrometers ($\mu$m) |
|---|---|
| Tracheid length | 3,500 |
| Tracheid diameter | 33 |
| Tracheid double cell-wall thickness, latewood | 10 |
| Tracheid lumen diameter | 20-30 |
| Thickness, true middle lamella, latewood | 1-4 |
| Thickness, primary wall | 0.1 |
| Thickness, $S_1$ layer, latewood | 1 |
| Thickness, $S_2$ layer, latewood | 4-10 |
| Thickness, $S_3$ layer, latewood | 1 |
| Overall diameter of pit chambers of bordered pits | 6-30 |
| Effective radii of pit openings | 0.01-4 |

## 1.5.3 Organisation of cell wall

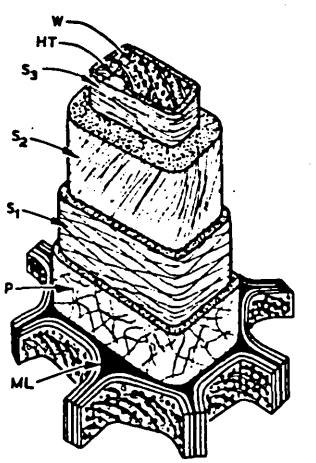
Wood cell walls are complex layered structures. Each cell has a primary wall, a thick secondary wall consisting of three concentric layers (known as $S_1$, $S_2$, and $S_3$) and, in tracheids of pine and some other species, a warty membrane lining the lumen. Individual cells are held together by a layer known as the middle lamella (Fig. 1.4).

Figure 1.3




Radial surfaces of earlywood (left) and latewood (right) tracheids: a, intertracheid bordered pits; b, bordered pits to ray tracheids; c, 13 pinoid pits to ray parenchyma.

Figure 1.4




A schematic diagram to illustrate the general structure of the cell wall of axially elongated wood elements and the dominant, helical orientation of the cellulose microfibrils within each wall layer. ML, middle lamella; P, primary wall, $S_1$, outer layer of the secondary wall, $S_2$, middle layer of the secondary wall; $S_3$, innermost layer of the secondary wall; HT, helical thickening; W, warty layer.

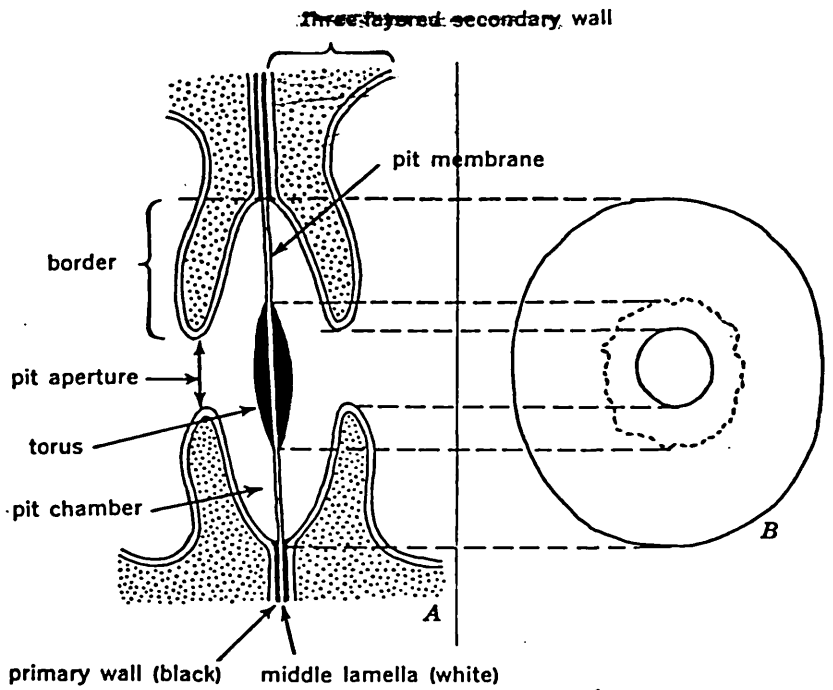
The cell walls are composed of a framework of elementary fibrils of cellulose organised into larger microfibrils which, in turn, form sheets (lamellae). The lamellae make up the various layers of the cell walls, and each wall layer is characterised by distinct microfibril arrangements. The dimensions of the various cell wall layers are given in Table 1.1. The cellulose lamellae are embedded in a matrix of hemicelluloses and other low molecular weight carbohydrates. Lignin is a major constituent of the middle lamella, and to a lesser extent the primary wall, contributing to the hardness of wood. A microcapillary system exists in the cell wall between the microfibrils, with capillary widths of the order of 0.1 nm, and between the elementary fibrils with capillary widths of the order of 0.01 nm, giving the cell wall porous properties.

### 1.5.4 Pit-pairs

A pit in the wall of one cell occurs opposite a complementary pit in the wall of an adjacent cell - a combination known as a 'pit-pair'.

The pit-pairs connecting wood cells are of two types: bordered pit-pairs, mainly between tracheids, and simple pits, mainly between parenchyma cells. The bordered pit-pair (Fig. 1.5) is in essence a valve-like channel. A pit membrane thickened into a 'torus' is suspended in the pit chamber by a network of fibrils (known as the 'margo'), which permit fluid to flow through spaces between them. When the pressure changes on one side of the bordered pit the torus is drawn across the aperture and seals it. This sealing is known as 'aspiration', and commonly occurs in wounded tissues and in heartwood formation.

Figure 1.5 Cell Wall Bordered Pit-Pair




Bordered pit-pair of *Pinus* in sectional (*A*) and face (*B*) views. Details according to the concept of Kerr and Bailey (*Arnold Arboretum Jour.* 15, 1934). The pit membrane consists of two primary walls and the intercellular lamella but is thinner than the same triple structure in the unpitted part of the wall. The torus is formed by thickening of the primary wall. In *B*, outline of torus is uneven.

Simple pits essentially differ from bordered pits by lacking the overarching of the secondary wall - the pit border - and the open mesh of the margo. As a result, the aperture of the simple pit cannot be sealed. Half-bordered pit-pairs are usually located between tracheids and parenchyma, consisting of a bordered pit of a tracheid abutting a simple pit of a parenchyma cell. Although no openings are apparent, there is evidence of liquid flow through this type of pit-pair (Siau, 1971).

## 1.6 Chemical composition of wood

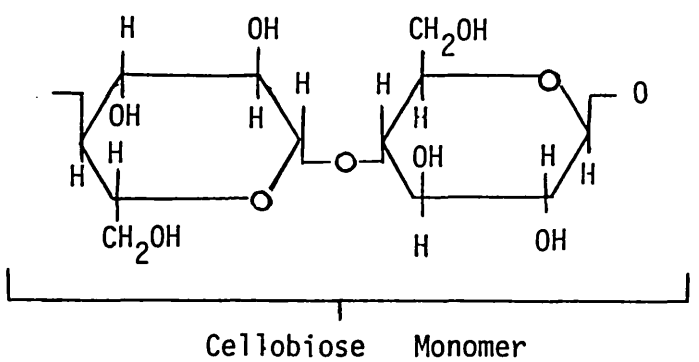
Many kinds of wood have been analysed into their major chemical constituents, and the average composition of a number of temperate timbers is given in Table 1.2.

Table 1.2 Average composition of 13 softwood and 10 hardwood trees, all from North America
(Findlay, 1975)

| | Softwood % | Hardwood % |
|---|---|---|
| Cellulose ..... | 66 | 76 |
| Holocellulose ..... | 46 | 49 |
| Hemicelluloses ..... | 8.5 | 19.5 |
| Lignin ..... | 27 | 21 |
| Inorganic ash ..... | 0.5 | 0.5 |

### 1.6.1 Cellulose

The cellulose molecule is a polymer based on the monomer cellobiose, which is composed of two glucose units:-

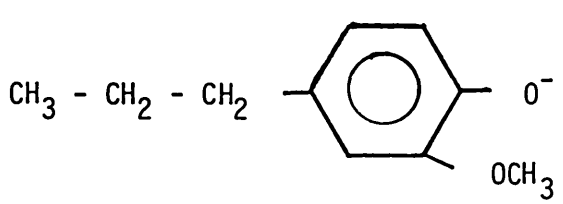


Water molecules can be adsorbed onto the hydroxyl groups of the cellulose polymer by hydrogen bonding, but hydroxyl groups can also be associated with other wall components, such as lignin.

Hemicelluloses, like cellulose, consist of large numbers of sugar units, but they differ in that they contain more than one kind of sugar. Some hemicelluloses are composed of pentosans (five carbon sugars), others contain hexosans (six carbon sugars). The molecular chains of hemicellulose are much shorter than in true cellulose, and often bear numerous short side chains. Because they do not build up long chains, hemicelluloses are of a more glutinous nature than cellulose. Pectic substances, such as calcium pectate, are similar to hemicellulose, but have different solubilities. They are amorphous colloidal, plastic and highly hydrophilic.

### 1.6.2 Lignin

The rigidity to the cell wall contributed by lignin arises through its complex three-dimensional structure. Although the chemistry of lignin within woods is still not completely understood, the general structure is known to be a three-dimensional polymer of phenylpropane units, and in softwood each unit carries one phenolic oxygen and one methoxy group:




The structure of lignin varies between species.

### 1.6.3 Inorganic constituents

The inorganic constituents of wood are extremely important in studies of its electrical properties. The earliest description of the mineral contents of a (unspecified) wood was published by Sacc in 1849. Although few experimental details were included, he listed the amounts of each element in the descending order: Ca, Na, Si, Mg, P, Mn, Fe,

K, and Cl. The inorganic chemistry of wood received wider attention in the late 19th Century in Germany, and high levels of Ca, K, Mg, and Mn were generally found (see review by Rennie, 1955). Because of the improvements made in ashing and especially analytical techniques in the past 30 years, all earlier data have been omitted from Table 1.3.

Sadly, much modern day literature only refers to the total ash content of a wood sample. For example, Côté (1968) describes the ash contents of "most woods" as "usually only between 0.2 to 0.3%" and lists the most common constituents in the order: calcium, potassium and magnesium, carbonates, phosphates, silicates, and sulphates. However, this description is highly deceptive: not only can ash content be as high as 4 to 5% in some tropical woods (Buchanan, 1963), but wide variations in inorganic contents have been shown to exist: between trees grown on different soils (e.g. Meyer and Siau, 1976); as trees age (Ovington, 1959); between wood from different parts of a tree (Orman and Will, 1960; Young and Guinn, 1966); in longitudinal gradients within a trunk (Orman and Will, 1960); in radial gradients within a tree - between early- and latewood (Galligan, Stern and Hohenschuh, 1965; McMillan, 1970), between different growth rings (Galligan, Stern and Hohenschuh, 1965), and especially between sap- and heartwood (Wardell and Hart, 1973); between hybrids (Bowersox, Blankenhorn and Murphey, 1979), and between species (e.g. Young and Guinn, 1966; Meyer and Langwig, 1973). Each element also appears to have a characteristic distribution pattern within a tree, and to vary in concentration during the year (Wardell and Hart, 1973). Even in woods taken from the same part of a tree, of identical species, age, and growing conditions, enormous differences in the levels of inorganic elements have been found (Ovington, 1959).

The decay of wood also causes marked changes in the concentrations of K, Ca, Mg, and Mn, of which the largest rise was found to be a roughly 3 to 10 fold increase in K (Safford, Shigo and Ashley, 1974). The increase in Mn, at least, has been closely associated with the growth of microorganisms such as hymenomycetes (Shortle and Shigo, 1973). Increases in moisture content and pH also occur in decaying wood, but these are thought more likely to be related to tree responses to wounding (Shigo and Sharon, 1970).

Ellis (1962) detected 28 elements in the wood of grand fir (*Abies grandis*), but more recent advances in ashing technique (Zicherman and Thomas, 1972) and in analysis by neutron activation (Meyer and Langwig, 1973; Osterhaus, Langwig and Meyer, 1975) indicate that other elements can be present, and that the total ash contents may be higher than previously supposed (Table 1.3). The dry ashing technique may lose the more volatile elements, or change the components of the wood, particularly by forming oxides and carbonates (Ellis, 1965). The most abundant inorganic elements in wood are in rough order of mass: Ca, Mg, K, Mn, Cl, Na, Mg, P and their concentrations roughly correspond to their nutritional importance in the living tree (Ellis, 1962; Osterhaus et al., 1975). Elements detected in appreciably lower quantities are B, Fe, Cu, Al, Br, S and in trace levels Mo, Zn, Ag, Co, Pb, Sr, Rb, In, V, Os, Si and Nd.

Table 1.3 Concentration of inorganic elements in chemically untreated wood (expressed as ppm of wood dry weight). Where not stated, data relates to sap- and heartwood combined.

Key: * Not measured
NAA Neutron activation analysis
AAS Atomic absorption spectroscopy/flame emission spectroscopy/flame photometry

| Element | *Abies grandis* (Ellis, 1962) | | *Pinus taeda* (McMillan, 1970) | | *Pinus taeda* (Zicherman & Thomas 1972) | *Betula alleghaniensis* (Langwig & Meyer, 1973) | *Eriotheca* sp. (Langwig & Meyer, 1973) | *Quercus alba* (Wardell & Hart, 1973) | | *Populus* [illegible] (Osterhaus, Langwig & Meyer, 1975) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | West of Cascades | East of Cascades | Earlywood | Latewood | Sapwood | | | Heartwood | Sapwood | | |
| | AAS | AAS | AAS | AAS | AAS | AAS | AAS | AAS | AAS | AAS | NAA |
| Ca | 495 | 1136 | 1141 | 885 | 739 | * | * | 708 | 1050 | 856 | 1171 |
| K | 615 | 442 | 116 | 98 | 27 | * | 449 | 900 | 1311 | 2270 | 2581 |
| Mg | 145 | 144 | 326 | 102 | 108.3 | * | * | 17 | 92 | 288 | * |
| Na | 42 | 31 | 223 | 180 | * | 12.6 | 253 | * | * | 940 | 112 |
| Cl | * | * | * | * | * | <0.1 | 1696 | * | * | * | 30 |
| Mn | 16.6 | 15.4 | 121 | 102 | 22.7 | 102.9 | 27.6 | 19 | 74 | 20 | 4.7 |
| P | * | * | 40 | 28 | * | * | * | 0 | 115 | * | * |
| Cu | 2.4 | 2.2 | * | * | 1.43 | * | * | * | * | * | * |
| Zn | 0.2 | 1.4 | * | * | 7.12 | * | * | * | * | 30 | * |
| Cr | * | * | * | * | * | * | * | * | * | * | * |
| Fe | 1.4 | 3.0 | * | * | * | * | * | * | * | 110 | * |
| B | 0.6 | 0.9 | * | * | * | * | * | * | * | * | * |
| Al | 3.6 | 7.7 | * | * | 3.03 | * | * | * | * | * | * |
| Ba | * | * | * | * | 3.03 | * | * | * | * | * | * |
| Pb | 0.03 | 0.06 | * | * | * | * | * | * | * | * | * |

However, these data on the presence and concentration of inorganic elements in wood only provide a rough guide to the types of ions present in the wood sap on or in the wood cells, because some of these elements can be covalently bonded in the wood cells.

There is also very little information on the location of the inorganic elements in the structure of the wood cells. The distribution

of the total ash content of individual earlywood cells of *Pinus taeda* (Loblolly pine) was studied by Zicherman and Thomas (1971), using an elegant oxygen plasma technique which vaporises organic materials at low ($< 200^{o}C$) temperatures without disturbing the conformation of the inorganic contents. Ashed cells were then carefully prepared for viewing by transmission electron microscopy, and ash particles were found intact and distributed throughout the cell wall. However, the ash was concentrated in the $S_1$, $S_3$, middle lamella layers and cell corners, and from delignification pretreatment the ash also appeared to be associated with the lignin content of the cells. Although these workers could not identify the ash components, electron probe X-ray analysis (as used for intact cells - see, for example, Greaves, 1974) may in future resolve the microdistributions of individual inorganic elements. Certainly the oxygen plasma method of ashing alleviates many of the problems encountered using the electron probe on wood, such as the difficulties in sectioning wood, and the considerable redistribution of inorganic elements during preparation for analysis.

Only brief mention of the microdistribution of endogenous minerals is made by other workers, often referred to as 'impurities' in literature dealing with the fixation of foreign, preservative, salts. For example, Klein and Bauch (1977) detected Na in the $S_2$ and middle lamella of cell walls of a number of soft- and hardwood species. Klein and Ginzburg (1960) showed that a variety of divalent cations ($Ca^{2+}$, $Mg^{2+}$, $Cu^{2+}$, $Fe^{2+}$, $Mn^{2+}$, and $Zn^{2+}$) have cementing properties in cell walls, as the chelating agent EDTA may remove these metals, thereby loosening the laminar structure of the cell wall.

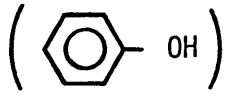
### 1.6.4 pH

Various reports of the pH of wood have been given in the literature, ranging from 2.5 for Western red cedar (Campbell and Bryant, 1935) to 7.5 for Kraft linerboard (Stamm, 1961). The pH of wood is generally determined by suspending wood blocks or sawdust in 5 to 10 times as much distilled water by weight, boiling and then cooling it, or simply stirring it without heating, followed by measuring the pH of water extract. Variations can arise from using this method, resulting from incomplete extraction of the wood, and from variations in the original pH of the water (Stamm, 1961). Campbell and Bryant (1935) measured

the pH of wood by equilibrating wood samples in dilute unbuffered solutions of acids and bases of different pH values, and finding the pH of the solution which is not changed by adding the wood. Unfortunately they gave no comparative values determined by the simpler water-extraction technique, but Stamm (1961) compared both these pH methods with measurements made using a pH glass electrode that can be pressed directly onto the wood surface. He found all three methods compared well, and obtained pH values ranging from 4.3 to 7.5 for different woods.

## 1.7 Ion-exchange

Most natural organic ion-exchange materials are cation-exchangers. They generally consist of a carbon-skeleton network to which are attached carboxylic groups (-COOH), and/or phenolic



and sulphydryl (-SH) groups.

The cation-exchange capacity of cellulose has received particular attention, since this property is an important feature in pulp-making, textile dyeing and manufacture of other cellulose-based materials (Sookne and Harris, 1954). Surprisingly though, ion-exchange in wood has been largely overlooked, and the literature about it is rather fragmented. Thus, ion-exchange in cellulose will be described first.

### 1.7.1 Cellulose

In naturally-occurring cellulosic fibres, cation-exchange capacity is largely accounted for by the non-cellulosic contents, such as lignin and uronic acids, $CHO-(CH-OH)_n-COOH$ (the latter contained in pectin and related compounds) (McLean and Wooten, 1939; Sookne and Harris, 1940). Exchange at the carboxyl groups of a uronic acid are considered much more plausible than at the far less (approx. $\times 10^5$ less) active hydroxyl (-OH) group of, say, a simple pentosan or of pure cellulose. In support of this idea, extracted pentosans and also hexosans have virtually no exchange capacity (McLean and Wooten, 1939). In fibres freed from all impurities the exchange capacity falls progressively, so that pure α-cellulose has virtually no exchange properties (McLean and Wooten, 1939; Kitchener, 1957). Davidson (1958) determined the affinity of several cations for the putative carboxyl groups of cellulose as:

$$N(CH_3)_4^+ < Li^+ < Na^+ < K^+ < Tl^+ < Ag^+ < Ca^{2+} < Ba^{2+}$$

This reflects the factors affecting ionic selectivity for an exchanger (such as the ionic radii of the ions), which are outlined further on in section 2.5.

### 1.7.2 Living plants

Despite the paucity of information of the microdistribution of ions in woody cells, increasing attention is being paid to the ion-exchange properties of lignified and non-lignified cell walls in living plants. Uronic acids and proteins are believed to play a major part in cation-exchanges in non-woody plant cells (ref. to Delmarty et al., 1978). These molecules carry carboxyl groups which can be ionised according to the pH and the ionic strength of the solution bathing the cell wall. The resultant formation of fixed $-COO^-$ groups attracts mobile cations (the physical chemistry of ion-exchange is described further in section 2.5).

The role of adsorption and exchange processes in the uptake and translocation of ions in living plants has long been recognised. The exchangeability of $Ca^{2+}$ with other divalent cations, increased mobility in the presence of chelating agents, and movement through the plant have been widely acknowledged (Ferguson and Bollard, 1976). It has been suggested that the xylem functions as an exchange column in which the carboxyl groups of the cell walls form the exchange sites (Knight, Crooke and Inkson, 1961). Such exchange sites are likely to participate in the cation-exchange transport reported in xylem translocation (Van de Geijn and Petit, 1979). Translocation in this respect occurs by cations passing along the xylem column at a rate dependent on solution concentration and transpiration (Van de Geijn and Petit, 1979). So for cation movement to occur all the exchange sites must be saturated (i.e. neutralised) irrespective of the cation concentration in the ambient solution, and any free cations accompanied by anions of equivalent charge, to maintain electroneutrality. Alternatively there must be as many floating cations as there are dissociated fixed negative charges, again to maintain electroneutrality.

The cation-exchange capacities found lead to charge densities that are too high (3.6 to 6 charges per 10 $nm^2$) to assume that the exchange

sites are only located on the xylem cell walls. Instead, Van de Geijn and Petit (1979) argue in favour of exchange sites present in many layers, as well as on the surface, of the xylem walls.

### 1.7.3 Wood

In contrast to those working on cellulose-based manufactured materials and on living plants, wood scientists have shown relatively little interest in the cation-exchange capacities of cell walls.

Perhaps the earliest recorded application of ion-exchange was the miracle by which Moses rendered the brackish water of the spring of Marah drinkable, by tossing a tree into the water (Exodus). It is possible that the "bitter" taste of the water was due to the presence of magnesium sulphate, which was removed by an ion-exchange reaction with hydrogen ions attached to the carboxyl groups in the wood:

$$Mg^{2+} + SO_4^{2-} + 2RCOOH \rightleftharpoons (RCOO)_2 Mg + H^+ + HSO_4^- \qquad (1.1)$$

followed by a neutralisation of the resulting $H_2SO_4$ by deposits of limestone:

$$H^+ + HSO_4^- + CaCO_3 \rightarrow CaSO_4 + CO_2 + H_2O \qquad (1.2)$$

The first scientific investigation of cation-exchange in wood was made by Sacc in 1849, who found that the ash content of wood was more extensively and rapidly removed by dilute acids than by using distilled water*. Because the electrolytic dissociation of ions was not known in those days, Sacc did not realise that the protons of the acids had exchanged with endogenous cations on the fixed charged sites of the wood, for example

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*Footnote

Whether Sacc's discovery was the first ever report of ion-exchange is debatable. Spence, an English analyst, found in 1845 that when a solution of ammonium sulphate percolated through a column packed with soil, the effluent from the column contained considerable amounts of calcium sulphate - instead of ammonium salts as expected. At the time the electrolytic dissociation of salts was unknown, and Spence's discovery was inexplicable. Perhaps the mystery of his finding was the reason behind the delay in his reporting the phenomenon - evidently his first report was not made until 1850, to the Royal Agricultural Society. Thus, Sacc's publication appears to pre-date Spence's.

$$\underset{\text{wood}}{-COO^- K^+} + \underset{\text{solution}}{H^+} \rightleftharpoons \underset{\text{wood}}{-COOH} + \underset{\text{solution}}{K^+} \qquad (1.3)$$

Little attention was paid to Sacc's work, and no further investigations of ion-exchange with wood were reported over the next 90 years. In 1939, McLean and Wooten briefly described (amongst the other cellulose-based materials they studied) the cation-exchange capacity of spruce (*Picea* spp.) sawdust. By measuring the change in pH when the sawdust was titrated against acids or alkalis, they found that the wood displayed a marked cation-exchange capacity, as shown by the ability of the wood partially to neutralise the acid or alkali titres.

Apparently unaware of the previous work, Kratzl and Stepnicka (1955) reported that the quantity of minerals removed from spruce sawdust using 0.1 M HCl was 5.6 times more than by using distilled water eluent. By using a sodium acetate titre they determined the total exchange capacity of the sawdust as 0.08 milliequiv. $g^{-1}$. When they treated the wood with sulphite or carboxylic acids, they added $-SO_3H$ or -COOH groups, respectively, thereby increasing the cation-exchange capacity of the wood to such an extent that it had about 1/5th the capacity of the best synthetic exchanger resins of the time.

Another interesting observation by these authors was that decayed wood (the type or extent of decay was not specified) possessed a cation-exchange capacity roughly ten times greater than that of fresh samples. Although they did not comment on this feature, it is a pertinent discovery in the light of the increased ionic content of decayed wood in trees reported by Ellis (1962) and Shigo and co-workers, as described previously in this chapter. The increase in the cation-exchange capacity of decaying wood (presumably as a result of microbial oxidation) may be the cause of the increase in ionic content. Klein (1978), for example, found that wood decayed with white or brown rot adsorbs more cations than uninfected wood, as measured by adsorption of $^{134}CsCl$.

Christensen and Williams (1951) found from electrolyte diffusion studies that wood behaves as a negatively-charged, semi-permeable, selective medium. They postulated that the diffusion of cations through the cell lumina appeared to be restricted by the presence of dissociated carboxyl groups on the cell walls, and Christensen (1951a) calculated the

cation-exchange capacity of *Eucalyptus regnans* as about 0.1 mg equiv. $g^{-1}$ (the details about how this figure was determined were not presented). Further evidence for the cation-exchangeability of wood was indicated by Bauch (1964) and Klein and Bauch (1977), in the preferential adsorption of cations over anions by fir and pine woods. Adsorption is meant here as uptake of ions into the bulk of the wood, as the wood structure is regarded as open and porous. From $^{134}Cs^{+}$ radioactive tracer studies it was found that the cation-adsorption of earlywood was greater than that of latewood (Klein and Bauch, 1977), and adsorption increased radially from sapwood to heartwood (Klein, 1978). The sapwood of two softwood and three hardwood species adsorbed roughly the same quantities of $^{134}Cs^{+}$, 2.5 to 5.0 mg cations $g^{-1}$ dry wood, whereas the heartwood adsorption was slightly more variable, from 2.8 to 7.8 mg cations $g^{-1}$ dry wood (Klein, 1978).

Although cation-exchange is probably only partly responsible for the adsorption of cations (Popper, 1978), several workers have reported that cation-adsorption increases with rising pH (Bauch, 1964; Klein and Bauch, 1977; Klein, 1978; Popper, 1978). Since the dissociation of the fixed acid groups in the wood will increase with rise in pH (e.g. Kitchener, 1957), the cation-exchange capacity of the wood will increase likewise. By adding varying amounts of different concentrations of $K_2SO_4$ to fir wood and measuring the change in pH of the solution, Popper (1978) found that the wood adsorbs cations in two steps, with dissociation constants (pK values) of around 5.8 and 10.4. As these pK values roughly correspond to those for carboxyl and phenolic hydroxyl groups in ion-exchange resins, respectively, Popper argued that these two acidic groups were probably the fixed cation-exchanger sites in the wood. Thus, with rising pH the dissociation of the two groups increased, releasing $H^{+}$ ions into solution. By potentiometric titration of these liberated $H^{+}$ ions, Popper determined the total cation-exchange capacity as $0.016 \pm 0.007$ m equiv. $g^{-1}$ dry weight wood.

It is interesting to note that the pH-dependence of cation-adsorption was also found for isolated wood components, such as holocellulose, α-cellulose, and lignin (Klein and Bauch, 1977). However, the sum of the adsorption values of these three wood components at any particular pH value is far greater than the wood *in toto*, allowing for

their relative masses in the wood (Klein and Bauch, 1977). In addition, increasing the purity of each wood component decreases their respective adsorption capacity (as previously described in 1.7.1). The adsorption behaviour of wood therefore depends on a variety of factors, including pH and the chemical content of the wood.

Workers in the wood-preserving industry are now focusing their attention on the part that cation-exchange is likely to play in the preservation of wood by certain inorganic salts - although here again many workers appear to be unaware of the previous literature.

Dahlgren and Hartford (1972) claimed that the first step in the fixation of Cu into wood during treatments using conventional Cu-Cr-As preparations was a rapid ( $<3$ min) cation-exchange with the cell walls of the wood. By pressing a flat membrane glass electrode onto sapwood sawdust of Scots pine or spruce, they recorded increases in the pH of the preservation solutions 3 min after applying the solutions. The authors postulated that the protons in the acidic preservative solutions had exchanged with native cations in the wood (although no test for native cations was made). However, these pH increases could also have arisen as a result of complexing reactions of the chromate ions with the wood, or simply adsorption of protons into void spaces inside the cell walls. The possible role of ion-exchange in the leaching of inorganic salt preservatives from wood is discussed further on in 1.11.3.

## 1.8 Moisture content

Wood also contains varying amounts of water. In freshly felled green wood there may be free water present in the tracheid lumina, but as the wood slowly dries this 'free water' becomes depleted until all the remaining water is bound within the cell walls. It is here present in microcapillary channels, intermolecular spaces (such as those between microfibrils), and in chemical association with the wall framework, particularly the cellulose matrix. The point at which wood is saturated only with bound water is called the 'fibre saturation point', and corresponds in most woods to an overall moisture

content of 27 to 30% weight. The equation by which the moisture content, u, of wood is usually calculated is:

$$u = (w_u - w_o)/w_o \times 100 \qquad (1.4)$$

where $w_u$ is the original weight of wood and $w_o$ is the weight of the wood oven-dried for 24 h at 101°C.

Wood is said to be hygroscopic, and takes up moisture in equilibrium with its surroundings, given sufficient time. Changes in wood moisture content below fibre saturation point result in shrinkage or swelling of the wood. When this happens the dimensional changes are not the same in all directions, and nearly all distortion occurs across the grain - tangential being greater than radial distortion. In addition, the electrical conductivity of the wood is greatly affected, as described further in 3.1.

## 1.9 Diffusion

Three forms of diffusion through wood can occur: that of solutes, of gases and vapours, and of liquids bound to the cell walls. In all cases diffusion occurs as a result of a concentration gradient which causes a substance to move so as to equalise the difference in concentration. According to Fick's first law, the rate of this movement (diffusion) is proportional to the concentration gradient. The physical chemistry of diffusion is described further in section 2.4.

### 1.9.1 Fick's first law and diffusion coefficients

Several workers have studied the diffusion of electrolytes through a specimen of wood by clamping it between two water-tight compartments, one filled with an electrolyte solution, and the other with distilled water. The diffusion rate of the electrolyte is followed by drawing off small samples from the opposite compartment, and analysing them by measuring their electrical conductivity (e.g. Christensen and Williams, 1951).

For thin sections of wood we may apply Fick's first law:

$$dm/dt = - DA(dc/dx) \qquad (1.5)$$

where dm/dt is the amount of substance diffused in unit time, A is the cross-sectional area through which diffusion occurs, dc/dx is the gradient of concentration, and D is the diffusion coefficient (c.f. section 2.4.1 for magnitudes and units) (e.g. Christensen, 1951a; Fukuyama and Tsunoda, 1970). However, chemical or physical reaction between solute and wood - such as swelling, adsorption, or precipitation - appear to obscure the validity of the law. Thus Christensen and Williams (1951) found that increasing the thickness of specimens of *Eucalyptus obliqua* wood in such diffusion studies did not produce the theoretically expected effect. This they attributed to osmotic counter-diffusion of water moving out from the surface layers of the wood (which behaved as a semi-permeable membrane) into the bathing electrolyte solution.

Another complicating factor is the anisotropic nature of the wood tissues. As a result the diffusion coefficients of laminae cut in three directions are in the sequence longitudinal > radial > tangential (Kumar and Jain, 1973). As diffusing ions in a relatively large wood sample follow the path of least resistance, the direction of flow (and hence the apparent diffusion coefficient) may change inside the wood. Therefore the rate of flux of ions will not only depend on dc/dx (the gradient in direction x) but also on dc/dy and dc/dz - the gradients in the directions y and z (Kumar and Singh, 1978).

### 1.9.2 Temperature

Diffusion coefficients of electrolytes in wood increase with increasing temperature (Kumar and Purushotham, 1972). However, their temperature coefficient $Q_{10}$ (see 2.4) became smaller as the temperature rose, and decreased in the directions tangential > radial $\gg$ longitudinal for mango wood (Kumar and Jain, 1973), and radial, tangential > longitudinal for the heartwood of two eucalypt species (Christensen, 1951a).

In all cases $Q_{10}$ values for diffusion of salts through wood were greater than for their diffusion in aqueous solution. Thus greater activation energies were required for ions to diffuse through wood because of potential energy barriers in the wood structure. Christensen (1951a) believed that these barriers arose from fixed charges on capillary walls in the wood structure, and that the smaller the diameter of the capillaries, the greater the potential barrier. The

greater activation energies for diffusion in the transverse directions were suggested by Christensen to result from the passage of ions through cell wall capillaries, rather than through cell lumina as in longitudinal diffusion. Christensen (1951a) also found that the activation energies for diffusion of electrolytes in all three dimensions of a softwood, *Araucaria cunninghamii* (hoop pine), were considerably less than those for the hardwoods. Thus, softwood diffusion probably occurred through tracheid and ray lumina and apertures, all of which had lower potential barriers (probably because the capillaries were wider).

### 1.9.3 Effect of chemicals

In most cases the concentration of the salt had little effect on its diffusion coefficient (Christensen and Williams, 1951; Kumar and Purushotham, 1972). However, the diffusion of salts through eucalypt hoop pine, and bamboo woods was very dependent on the polarity and valency of the ions. (Christensen, 1951b; Bains and Kumar, 1979). In these experiments thin sections of wood (about 2 - 5 mm thick) were soaked in 1 mM HCl followed by 1 mM $Na_2CO_3$, so as to remove endogenous ions by ion-exchange. However, the reaction between these two electrolytes could have liberated $CO_2$ gas:

$$HCl + NaHCO_3 \rightarrow Na^+ + Cl^- + CO_2 + H_2O \qquad (1.6)$$

These bubbles of gas may have then interfered with the subsequent diffusion measurements. Nevertheless, the reported results indicate that diffusion of salts containing bivalent anions or cations was generally only a fraction of that for salts comprised of univalent ions. For univalent chlorides D increased in the order $LiCl > NaCl > KCl > NH_4Cl$ in two eucalypts and hoop pine (Christensen, 1951b). This is the inverse of the order of mobility of the hydrated cations in solution.

In contrast, the differences in diffusion rates in wood of salts with various univalent anions were relatively small. However, D values for salts containing bivalent anions were considerably smaller (a greater decrease than found in aqueous solution). This decrease was relatively more pronounced for hardwoods and high density species than for softwoods and less dense species. The structure of the wood clearly affected the diffusion of bivalent anions much more than that of univalent anions.

Christensen considered that cations and anions diffuse together through wood as ion-pairs to preserve electroneutrality, and that the size of these ion-pairs restricts their passage through narrow capillaries (particularly in cell walls). The differences between woods was attributed to the fixed negative charges on cell walls and lumen capillaries. The anion was considered the restricted ion of the pair needing sufficient activation energy to overcome the electrostatic repulsion at the fixed charge sites. Strangely, Christensen made no mention of probable restriction of cation diffusion arising from cation-exchange at the fixed charge sites.

Bains and Kumar (1979) directly related the diffusion coefficients of salts with common anions diffusing through bamboo culm to the limiting ionic conductance of their cations. Of the four electrolytes investigated, the unexpectedly low D value for copper sulphate was attributed to complexing within the wood structure. However, the leaching experiments of Dahlgren and Hartford (1976) and electrical conductivity determinations of Duran, Meyer and Siau (1978) suggest that such complexing of $CuSO_4$ with the wood does not occur. It is also strange that the zinc or aluminium sulphates tested by Kumar and Bains did not complex with the wood also.

## 1.10 Flow

One of the most important properties of wood is its porosity. Sapwood of a living tree conducts water and dissolved salts from the roots upward and sapwood of felled timber may be artificially impregnated with aqueous preservatives. In general, water can move through wood in three forms: vapour, free liquid, and that bound in the cell walls.

Water generally moves in wood with moisture content above fibre saturation. Fluid flowing through softwoods largely passes from one tracheid lumen to another via the interconnecting bordered pit-pairs. As the pit channels are considerably narrower than the tracheid lumina, they cause most of the resistance to flow. Flow is further impeded by air bubbles in the pit apertures, and considerable pressures are required to overcome the surface tension at the liquid-air menisci. Petty and Puritch (1970) have demonstrated that 13% of the resistance to flow in air-dried *Abies grandis* is caused by the tracheid lumina and the remaining 87% by the (aspirated) pit membrane pores. Bolton

and Petty (1975) later indicated that both pit channels and pit membrane apertures contribute towards resistance to fluid flow, in addition to the tracheid lumina. The greater permeability of latewood compared with earlywood has been attributed to the greater ability of latewood pit-pairs to resist aspiration, because of their thick pit channels and more rigid pit membranes. The degree of pit closure also affects the resistance to flow. Côté (1963) described three changes in pit-pairs of softwoods which account for decreased permeability, in order of increasing degrees:

(1) Pit aspiration, in which the torus is held tightly against the aperture (possibly by hydrogen bonding between adjoining cellulose chains);
(2) Pit occlusion with water-soluble extractives;
(3) Pit incrustation with water-insoluble lignins.

The heavily occluded and incrusted pit apertures in heartwood tracheids account for the poor permeability of heartwood.

Flow through cell wall microcapillaries has been shown by electron microscopy in eucalypt wood. Inorganic solutions can flow through pit membranes, cell wall capillaries, and across the middle lamellae - i.e. flow through and along cell walls (Rudman, 1966).

Although gross flow in wood is principally through the tracheid lumina, parallel flow of fluids and gases can also occur along resin ducts (presumably so long as resin does not completely block the ducts). In addition, resin ducts provide an initial path of entry for liquids penetrating wood specimens. Species containing longitudinal resin ducts, such as Japanese red pine (*Pinus densifolia*) and radiata pine (*Pinus radiata*) have been claimed by Hayashi, Nishimoto and Kishima (1966) to be much more permeable than softwood species without longitudinal resin ducts. Nevertheless, such a claim does not explain why felled spruce wood (which has resin ducts) is impermeable, whereas firs (which do have resin ducts) are permeable. Clearly other unknown factors are involved, at least in the impermeability of spruce.

Flow can also occur in the radial direction. Wardrop and Davies (1961) found ray parenchyma was more permeable to $CuSO_4$ solution than ray tracheids from the same tissue of pines and eucalypts. Erickson and Estep (1962) reported that radial flow in green Douglas fir heartwood

was about 25 to 50% of longitudinal flow, and a small tangential flow accounted for 5 to 10% of the radial flow. There is also evidence of flow from ray tissues to longitudinal tracheids (Hayashi and Kishima, 1965), and from radial resin ducts to longitudinal resin ducts (Behr et al., 1969).

The nature of the conducting fluid greatly affects the permeability of wood. Non-polar liquids, for example, flow much better than polar liquids, and surplus preservative previously passed through green wood (and therefore containing leached extractives) are far less able to penetrate wood than fresh preservative (Nicholas, 1972). De-gassed fluids also penetrate wood more easily and rapidly than solutions containing dissolved gases. Erickson, Schmitz and Gortner (1937) and Kelso, Gertsejansen and Hossfeld (1963) believed that this explained why the rate of flow of water through wood consistently decreases with time, and they proposed that air blockages are formed in the fluid streams during flow.

## 1.11 Preservation of wood against biodeterioration

The wood of many species of trees is resistant to biodeterioration by bacteria, wood staining fungi, mould fungi, brown-, white-, and soft-rot fungi, insects, or marine boring organisms. However, these durable timber species are becoming increasingly scarce and expensive. It is now generally more economical to treat non-durable timber, so as to make conditions unfavourable for the growth of the biodeteriorating organisms.

### 1.11.1 Chemical preservatives

A successful treatment must distribute preservative chemicals in sufficient concentration throughout the wood to prevent microbial attack. The amount of timber treated annually in the U.K. is about $2 \times 10^6$ $m^3$. Much of this is treated by water-borne salt mixtures, mainly copper-chrome-arsenic (CCA) preparations which are toxic to the wood-destroying organisms. Timber preserved in this way in the U.K. is mainly used in building (50%) and fencing (20%) and the balance for pit props in mines, cooling tower timbers, and miscellaneous uses (Cockcroft, 1979).

There are three general classes of chemical wood preservatives: oils, chemicals soluble in volatile oils or organic solvents, and water-soluble chemicals. There is no one wood preservative ideal for all purposes, as wood in different situations requires varying degrees of protection depending on the hazards to which it will be exposed. As a result a wide variety of preservatives is now available.

Impregnation of timber with CCA has proved highly successful owing to its strong fixation, penetration, and toxicity in many different types of wood. The general composition of commercially produced CCA's is approximately: Copper (as $CuSO_4.5H_2O$) 35%, Dichromate (as $K_2Cr_2O_7$) 45%, Arsenic (as $As_2O_5.2H_2O$) 20% (see BS 4072, 1974). The high retention of these preservatives is due to reactions between each component and the cell walls of the wood, such that copper and arsenic are precipitated as insoluble complexes which are resistant to leaching (Dahlgren and Hartford, 1972).

### 1.11.2 Impregnation treatments

#### 1.11.2(i) Full-cell pressure process

If wood is merely immersed in liquid preservatives their penetration is usually slow and irregular. In the Full-cell process, wood is sealed in large steel cylinders and a vacuum applied to extract air from the cells. After a suitable interval, pressure is applied to force the preservative into the wood. Surplus liquid is drawn off using a short period of vacuum. The amount of preservative absorbed by the timber is measured by weighing the wood before and after treatment, and the degree of treatment is usually expressed as weight of preservative absorbed per unit volume of wood, in kg $m^{-3}$ (or lb cu $ft^{-1}$).

#### 1.11.2(ii) Open-tank treatments

Pressure impregnation of wood is sometimes impractical because of the high costs of plant involved. The open-tank process offers a useful and much cheaper alternative which involves submerging seasoned timber in a tank of heated preservative solution for a few hours, and then allowing it to cool while the timber is still submerged. During the heating period the air in the wood cells expands and much of it

escapes as bubbles. When the timber cools the air remaining in the cells contracts, drawing in the preservative.

1.11.2(iii) Diffusion treatments

These are similar to open-tank treatments, but rely on the diffusion of water-soluble salts through wet wood using only warm solutions (ca. 50°C). After soaking in the preservative the wood is left to remain moist for a number of weeks.

It is possible to use two successive diffusion treatments with different salts that react together to form an insoluble precipitate in wood. This process is called double-diffusion.

1.11.2(iv) Injection treatments

A preservative paste containing soluble salts can be injected through a needle into wood parallel with the grain to a depth of 5 cm, in a technique known as the Cobra Process. This method is generally applied to timbers standing in the soil, where the wood is most susceptible to decay. Injections are usually made into a zone just above or below ground surface level.

1.11.2(v) Sap replacement

Freshly felled logs can be treated by forcing preservatives through the sapwood by hydrostatic pressure created by a reservoir of preservative held about 6 m above a horizontal log, a technique known as the Boucherie process. A cap is fitted over the butt-end of a log, and connected by hose to the reservoir. In this way pressure is applied to the wood, and treatment is complete when preservative passes out of the other end of the log.

1.11.3 Problems associated with wood preservation treatment

Considerable pressures have to be applied to overcome the blockage to flow of fluids through wood caused by air bubbles in the cell wall and pits. If, moreover, the wood has been dried significantly prior to

treatment, air entering the structure greatly retards or practically prevents treatment under low pressures. Drying also causes pit aspiration, which further retards preservative penetration. Green sapwood, though, is virtually saturated with water, and can be readily treated by a sap replacement method under a small head of liquid. In woods such as spruce, aspiration is so strong that pressure techniques are of no use without prior treatment to increase the wood permeability.

Pit aspiration, occlusion, and incrustation (see 1.10) are believed to cause the very poor permeability of heartwood. Although heartwoods are generally durable materials, treatment is often needed to prolong their durability but pressure treatments are usually ineffective.

Laboratory leaching studies, using distilled water and over short periods of time, have indicated that current CCA preservatives give lasting protection (Irvine and Dahlgren, 1976). However, leaching out of preservatives is particularly widespread in timbers in ground contact, in cooling towers, in marine sites, and other environments containing aqueous salt solutions. Irvine and Dahlgren (1976) have proposed a mechanism for the leaching of CCA preservatives from treated timbers in saline water, in which $Cl^-$ and $OH^-$ in the water complex with $Cu^{2+}$ and $Cr^{3+}$ in the wood and increase the leachability of these cations. Since chromium ions fix arsenic ions in the wood, leaching of arsenate also results. Thus Irvine and Dahlgren found that most of the copper in sawdust of *Pinus sylvestris*, which had been treated with copper sulphate, was eluted by stirring with sodium chloride solution. However, the significance of ion-exchange (e.g. sodium for copper) in preservative leaching was not commented on. Since specific elements such as copper can be retained in particular cell types or cell wall layers of many wood species in preference to other constituents of a preservative solution, complex formation with the wood structure may not occur. As a result ion-exchange leaching of preservatives may take place instead. For example, CCA pressure treatment of *Betula* sp. (birch) results in accumulations of Cr in the rays, high levels of Cu, Cr, and As in the vessels, and poor penetration of the fibres. In *Pinus sylvestris*, though, CCA is evenly distributed throughout the tissues and across the cell walls following pressure treatment (Dickinson, Sorkoh

and Levy, 1976). Thus ion-exchange leaching may only arise in timbers with uneven cellular or tissue element distribution patterns, as in many hardwoods (Levy and Greaves, 1978).

### 1.11.4 Natural preservation and fixation

The discovery of a copper-preserved cedar (*Cedrus* sp.) pit prop from a Roman copper mine in Cyprus (Biek, 1963) may be the oldest example of ion fixation in wood by natural causes. The copper had penetrated the wood specimen so thoroughly that bright specks of metallic copper were visible in the outer growth rings (confirmed by X-ray analysis). There was no question of any deliberate preservation treatment by the Romans, so that the metal must have been absorbed from the surrounding copper-rich soil. This idea is borne out by recent evidence from CCA-treated stakes of *Fagus sylvatica* (beech) and *Pinus sylvestris* exposed in the ground (Ofori, 1977). Calcium and/or magnesium was absorbed into the subterranean and/or ground level parts of the sticks, particularly in those samples in which the preservatives remained firmly fixed in the wood. Since these parts of the wooden stakes were saturated with water, it is likely that the elements moved into the wood as ions. The stakes with better CCA fixation attracted larger amounts of Ca, so that the preservation treatment may have increased the cation-exchange capacity of the wood.

# CHAPTER 2

# ELECTROCHEMISTRY INTRODUCTION

Ions in electrolyte solutions give rise to three major measurable flow properties: conductivity, transference numbers, and diffusion. Each of these properties will be dealt with, bearing in mind their relation to the behaviour of electrolytes in wood.

## 2.1 Electrolytic Conductance

### 2.1.1 Introduction

Electricity passes through electronic conductors (such as metals) by the flow of electrons, and through ionic conductors (such as aqueous salt solutions) by the flow of ions. In a few systems the electric charge is carried by both ions and electrons, e.g. $Cu_2O(s)$, $CuCl(s)$, Na in liquid $NH_3$ (Sheehan, 1970).

Like metallic conductors, homogeneous electrolytic conductors obey Ohm's law

$$I = V/R \qquad (2.1)$$

in which I is the current in amps, V is the potential across the conductor in volts, and R is the resistance in ohms. The conductance G (in $ohm^{-1}$) of an electrical conductor is the reciprocal of its resistance R:

$$G = 1/R \qquad (2.2)$$

When electricity passes through a resistance, heat (known as Joule heat) is liberated. The amount of heat H (in joules) can be calculated by the formula

$$H = I^2Rt \qquad (2.3)$$

in which t is the time in seconds.

The resistance R of a conductor of length l and cross-section A is inversely proportional to A and proportional to l. Thus the specific resistance $\rho$ or resistivity (in ohm cm, or ohm m) of a homogeneous conductor given by

$$\rho = RA/l \qquad (2.4)$$

expresses its resistance in a form which is independent of the dimensions. The specific conductance or conductivity $\kappa$ of a substance (expressed as $ohm^{-1}cm^{-1}$ or $ohm^{-1}m^{-1}$) is the inverse of $\rho$, that is

$$\kappa = 1/\rho = 1/AR = Gl/A \qquad (2.5)$$

The specific conductivity of a solution varies with its concentration. For electrolytes that are completely dissociated in water and called "strong" (e.g. KCl), $\kappa$ rises almost proportionately with increasing concentration. However, for so-called "weak" electrolytes such as $CuSO_4$ in water, $\kappa$ rises much more slowly with increasing concentration as the degree of dissociation becomes smaller.

Conductances (i.e. resistances) can be measured by direct or alternating current methods (see Robinson and Stokes, 1955). In the d.c. technique a current is passed through the solution under investigation and through a standard resistance in series. The potential developed between two fixed points in the solution is compared with that across the standard resistance. However, polarization effects at the electrodes can arise with direct current, and as a result alternating current at about 1000 Hz is generally used instead.

### 2.1.2 Molar conductance

Since the specific conductivity of strong electrolyte solutions is almost proportional to the molarity c, it is convenient to introduce the molar conductance $\Lambda_m$ defined by

$$\Lambda_m = 1000\,\kappa/c \qquad (2.6)$$

where $\kappa$ is in $ohm^{-1}\ cm^{-1}$, c in mol $dm^{-3}$, and $\Lambda_m$ in $cm^2\ ohm^{-1}\ mol^{-1}$. The molar conductance can be regarded as the conductance, G, of the amount of solution that contains 1 mole of solute when measured between parallel (unpolarised) electrodes 1 cm apart and large enough in area to include the necessary volume of solution.

The literature often refers to equivalent conductance, $\Lambda$, defined by

$$\Lambda = 1000\,\kappa/C \qquad (2.7)$$

in which C is the concentration in equivalents per litre (normality). For an electrolyte of formula $m_{\nu_+}^{z+} x_{\nu_-}^{z-}$ ,

$$C = \nu_+ z_+ c = \nu_- |z_-| c \qquad (2.8)$$

where z is the algebraic charge number of the subscripted ion. If the electrolyte is composed of univalent ions, $\Lambda_m = \Lambda$.

The specific conductance of an electrolyte solution is also proportional to the sum of the products of molar conductances and concentrations of all the ions in the solution:

$$10^3 \kappa = \Lambda_m c = \sum_i \lambda_i c_i \qquad (2.9)$$

where $\lambda_i$ is the molar conductance of ion i in $cm^2\ ohm^{-1}\ mol^{-1}$.

### 2.1.3 Variation of conductance with concentration and temperature

$\Lambda_m$ decreases with increasing concentration of an electrolyte, but decreases much more for a 'weak' than a 'strong' electrolyte. This arises because the degree of dissociation ($\alpha$) of the electrolyte becomes smaller as the concentration increases.

$\Lambda_m$ increases with increasing temperature, ca. 2% for most ions per $1^oC$ rise in water. This rise is associated with a corresponding fall in the viscosity of the water.

### 2.1.4 Molecular interpretation of conductance

Conductance depends on three properties of the electrolyte:

(1) the number of ions of different kinds (1, 2, ....i..);
(2) their electrical charges ($z_i$); and
(3) their velocities ($v_i$) in the electric field (x).

Since the velocity (in $cm\ s^{-1}$) is proportional to the field or potential gradient x (in $V\ cm^{-1}$), one can write

$$v_i = u_i x \qquad (2.10)$$

where $u_i$ is the mobility of ion i in $cm^2\ s^{-1}\ V^{-1}$. It can be shown by dimensional analysis that the mobility is related to the molar

conductance of the ion $\lambda_i$ and to its equivalent conductance $(\lambda_i)_{eq}$ by

$$\lambda_i = (\lambda_i)_{eq}|z_i| = u_i|z_i|F \qquad (2.11)$$

where F is the Faraday constant (96487 C $mol^{-1}$). Thus in a solution of the strong electrolyte referred to above, from equations (2.9) and (2.11):

$$\Lambda_m = (\lambda_+ c_+ + \lambda_- c_-)/c = F(u_+ z_+ \nu_+ + u_- |z_-| \nu_-) \qquad (2.12)$$

If the electrolyte is only partly dissociated with a degree of dissociation, $\alpha$, then

$$\Lambda_m = F\alpha(\nu_+ z_+ u_+ + \nu_- |z_-| u_-) \qquad (2.13)$$

By equation (2.8):

$$\Lambda_m = F\alpha\nu_+ z_+ (u_+ + u_-) \qquad (2.14)$$

At infinitesimal concentration (infinite dilution), where the properties are designated by a superscript o, the degree of dissociation becomes unity. Thus

$$\Lambda_m^o = F\nu_+ z_+ (u_+^o + u_-^o) \qquad (2.15)$$

where $\Lambda_m^o$ is the limiting molar conductance. If the mobilities do not change very much with concentration we obtain the Arrhenius equation

$$\alpha = \Lambda_m/\Lambda_m^o \qquad (2.16)$$

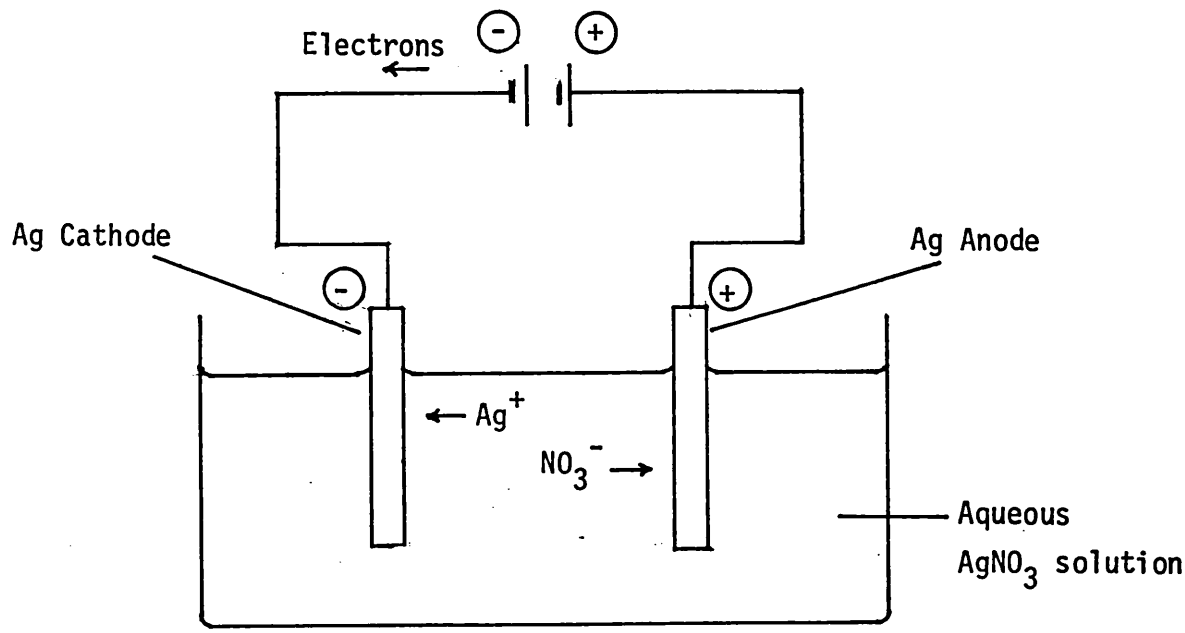
In strong electrolyte solutions $\alpha = 1$ at all concentrations, and here the small decrease in $\Lambda_m$ with increasing concentration is due entirely to inter-ionic attraction effects which decrease the ionic mobilities.

## 2.2 Electrolysis

Electrolytic conduction can be demonstrated using an electrolytic cell (Fig. 2.1). Electric current is led into and out of the aqueous $AgNO_3$ electrolyte solution by metallic Ag electrodes immersed in it. The electrode connected to the positive pole of the electricity supply is called the anode, and the electrode connected to the negative one the

cathode. During electrolysis electrons carry current through the external part of the circuit, passing into the cathode, where they cause reduction at the electrode/solution interface, and out of the anode where they cause oxidation.

Figure 2.1 Schematic diagram of an electrolytic cell




The amount of reduction or oxidation does not depend on the potential, but on the quantity of electricity passed through the circuit. This quantity is measured in coulombs, and equals the product of the current in amperes (amps) and the time in seconds

$$q = \Sigma It = \int I dt \qquad (2.17)$$

According to Faraday's laws, the passage of 96487 coulombs (= 1 faraday of charge) will reduce or oxidise one mole ($6.023 \times 10^{23}$ molecules or ions) of singly charged ions, e.g.

$$Ag^+ + e^- \rightleftharpoons Ag(s) \qquad (2.18)$$

For an ion/metal couple where the ion is doubly charged, two faradays are needed to reduce one mole of metal, as in the reaction:

$$Cu^{2+} + 2e^- \rightarrow Cu(s) \qquad (2.19)$$

Referring again to Fig. 2.1, during electrolysis the cathode becomes negatively charged, and the anode positively charged. This potential difference creates an electric field across the solution, and causes $Ag^+$ cations to migrate towards the cathode, and $NO_3^-$ ions to migrate towards the anode. This is how the solution conducts electricity. Electricity passes across the electrode/solution interfaces by reactions (2.18): at the cathode electrons are donated to $Ag^+$ ions

$$Ag^+ + e^- \rightarrow Ag(s) \qquad (2.20)$$

and the silver metal is deposited on the cathode surface. At the anode solid Ag is oxidised to $Ag^+$ by the loss of an electron

$$Ag(s) \rightarrow Ag^+ + e^-$$

It should be noted that the ions that conduct electricity in the solution are not necessarily the ones that are oxidised or reduced at the electrodes. Take for example a platinum cathode in a KCl solution. The $K^+$ and $Cl^-$ ions migrate and conduct electricity in the solution, but at the cathode the electrode reaction is

$$H_2O + e^- \rightarrow 1/2\ H_2(g) + OH^- \qquad (2.21)$$

because this is the most energetically favourable reaction. In other words, water molecules are selectively discharged at the cathode in preference to $K^+$ ions.

## 2.3 Transference or Transport Numbers

### 2.3.1 Introduction and definition

The electrical conductance of an electrolyte solution indicates the extent to which all the ions present in the solution migrate in an electric field, thereby carrying the electric current. In order to describe the proportion of current carried by a particular type of ion, i, we must introduce the ionic or electric transport number $t_i$.

Consider a solution containing a completely dissociated electrolyte of molarity c (mol $l^{-1}$ or mol $dm^{-3}$). The transference number of either ion is defined as the number of faradays of electricity carried by the ion concerned across a reference plane, fixed with respect

to the solvent, when one faraday of electricity passes across the plane. Since the number of faradays transported by any ionic species i depends directly upon the magnitude of its algebraic charge number z, its molarity c, and its mobility u, it follows that

$$\frac{t_+}{t_-} = \frac{z_+c_+u_+}{|z_-|c_-u_+} = \frac{c_+\lambda_+}{c_-\lambda_-} \tag{2.23}$$

Moreover,

$$t_+ + t_- = 1 \tag{2.24}$$

since the total number of faradays carried in both directions is equal to 1 when 1 faraday passes. Thus

$$t_+ = \frac{z_+c_+u_+}{z_+c_+u_+ + |z_-|c_-u_-} \tag{2.25}$$

More generally, for a solution containing several types of ions (the situation dealt with in the present research)

$$t_i = \frac{|z_i|c_iu_i}{\Sigma|z_i|c_iu_i} = \frac{|z_i|Fc_iu_i}{\Sigma|z_i|Fc_iu_i}$$

$$= \frac{c_i\lambda_i}{\Sigma c_i\lambda_i} = \frac{c_i\lambda_i}{1000\kappa} \tag{2.26}$$

Ions in solution are often complexed. The transference property then measured is not that of an individual type of ion but of a particular ion-constituent, R. For example, the ion-constituent $H^+$ exists in oxalic acid as part of the species $H^+$, $HOx^-$, and $H_2Ox$. The transference number of an ion-constituent is given as $t_R$. It is defined as follows: "The transference number, $t_R$, of a cation- or anion-constituent R is the net number of faradays carried by that constituent in the direction of the cathode or anode, respectively, across a reference plane fixed with respect to the solvent, when one faraday of electricity passes across the plane" (Spiro, 1971). $t_R$ is dimensionless and

$$\sum_R t_R = 1 \tag{2.27}$$

Numerically, $t_R$ is equal to the net number of moles of R transferred for every $|z_R|$ faradays passed. The relations between $T_R$ and $t_i$, and between $T_R$ and $\lambda_i$, are

$$T_R = \sum_i (z_R/z_i) N_{R/i} t_i \qquad (2.28)$$

$$= \sum_i (z_R/z_i) N_{R/i} c_i \lambda_i / \sum_i c_i \lambda_i \qquad (2.29)$$

where $N_{R/i}$ is the number of moles of ion-constituent R in each mole of ion i (Spiro, 1971).

## 2.3.2 Conductance and mobility of ion-constituent

Combination of the conductance and transference equations leads to the following expression for the molar conductance and the mobility of an ion-constituent R:

$$\lambda_R = F|z_R|u_R = \frac{t_R \Lambda_m}{\nu_R} = \Sigma N_{R/i} \left(\frac{\lambda_i}{z_i}\right)\left(\frac{z_R}{\nu_R}\right)\left(\frac{c_i}{c}\right) \qquad (2.30)$$

For a single binary electrolyte that consists of 2 ions only per molecule, e.g. $CH_3COOH$ or $CuSO_4$, where $N_{R/i} = 1$, $z_R = z_+$ or $z_-$, $\nu_R = 1$, and $c_i = \alpha c$ we have

$$\lambda_R = \alpha \lambda_i \qquad \text{or} \qquad u_R = \alpha u_i \qquad (2.31)$$

If the electrolyte is strong, $u_R$ is simply equal to $u_i$, and $\lambda_R$ to $\lambda_i$. The mobility or ionic conductance of an ion is the only property of an individual ion that can be unambiguously determined, by the combination of conductance and transference data.

The mobility of an ion in water largely depends on the radius of the hydrated ion. Thus the order of the mobilities of the alkali-metal cations is the order of increasing hydration (and the inverse order of their crystallographic size):

$$K^+ > Na^+ > Li^+$$

So although $Li^+$ possesses the smallest crystal radius of the alkali metals, it is the most strongly hydrated and therefore large and slow-moving.

### 2.3.3 Variation of $t_R$ with concentration

Transference numbers at infinitesimal ionic strength are called limiting transference numbers. For a single binary electrolyte they are simply related to the limiting equivalent conductances of the constituent ions and of the electrolyte as a whole by:

$$T^o_{\pm} = \frac{(\lambda^o_{\pm})_{eq}}{(\lambda^o_{\pm})_{eq} + (\lambda^o_{\pm})_{eq}} = \frac{(\lambda^o_{\pm})_{eq}}{\Lambda^o} \qquad (2.32)$$

whatever the valence type of the ions. Transference numbers are therefore essentially ratios of conductances, and so usually vary less with concentration than do conductances themselves. At finite concentrations ionic atmosphere effects come into play; the transference number therefore changes somewhat with increasing concentration. Theory shows (MacInnes, 1961) that for a single binary electrolyte, $T_R$ increases with increasing concentration if $T_R > 0.5$, and decreases with increasing concentration if $T_R < 0.5$. For electrolytes in which complex ions form the transference numbers will vary in different and specific ways with changes in concentration.

### 2.3.4 Variation of $t_R$ with temperature

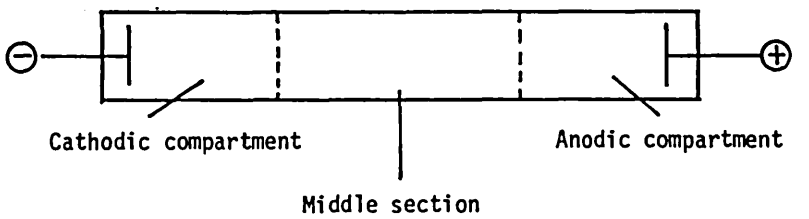
Transference numbers, being functions of ionic conductances, are relatively insensitive to changes in temperature and pressure, when compared with the ionic conductances themselves. For example, in water at 25°C most ionic conductances increase by ca. 2% per 1°C, while transference numbers change by amounts of the order of 0.1% per 1°C (Spiro, 1971).

### 2.3.5 Measurement of transference numbers

Several methods are available for determining transference numbers. The most suitable method for a given purpose depends on the concentration range of interest, the accuracy desired, and the properties of the solution in question. So far no attempt has ever been made to investigate transference numbers in wood, and the most practical method for this purpose is a modification of the Hittorf method. This will now be briefly described.

The Hittorf method is the simplest technique of determining transference numbers. The method involves passing known quantities of electricity through a cell filled with the solution whose transference numbers are to be determined (Fig. 2.2). The solutions in various sections of the cell are then directly or indirectly separated, weighed, and quantitatively analysed.

FIGURE 2.2 Simplified Hittorf Cell for Measuring Transference Numbers




Dotted lines are arbitrary section boudaries, considered fixed with respect to the solvent throughout the experiment.

The middle section or sections are designed to ensure that all chemical changes occur entirely within the two electrode compartments, and that no intermixing occurs.

For every faraday of electricity passed through the cell, $T_R$ moles of cation-constituent R migrate across the dotted lines in the direction of the cathode. Clearly the composition of the middle section remains the same, and analysis for R in the electrode sections at the ends of the cell yields the transference number $T_R$ of this cation-constituent. A similar method is used for determining the transference number of the anion-constituent migrating in the opposite direction. In practice the electrode reactions must also be taken into account if these involve the constituent under investigation.

## 2.4 Diffusion

Diffusion is the name given to the movement of a substance along a concentration gradient from higher to lower concentration, so as to equalise the concentration of that substance. Reverse movement of the substance is only possible by expending external energy, such as via an electric field.

### 2.4.1 Fick's first law and the measurement of D

The rate of transfer of matter by diffusion in unit time, dm/dt (mol $s^{-1}$) is given by Fick's first law under steady state conditions

$$dm/dt = - DA(dc/dx) \qquad (2.33)$$

where A is the cross-sectional area ($cm^2$) through which diffusion occurs, dc/dx is the gradient of concentration (mol $cm^{-3}$) per unit distance ($cm^{-1}$), and D is the diffusion coefficient ($cm^2$ $s^{-1}$). The equation contains a negative sign because the mass transfer occurs in the direction of decreasing concentration.

### 2.4.2 Effect of temperature

The variation of the diffusion coefficient with temperature (T) has been expressed in three different ways.

(i) The ratio of the D values when the temperature has risen by $10^{o}C$

$$Q_{10} = (D_{T+10})/D_T \qquad (2.34)$$

where Q is sometimes called a temperature coefficient.

(ii) The rate of change in D with change in temperature

$$\alpha = dD/dT \qquad (2.35)$$

where $\alpha$ is the temperature coefficient.

(iii) The activation energy E as given by the Arrhenius equation

$$D_T = D_0 \exp(-E/RT) \qquad (2.36)$$

where $D_T$ is the diffusion coefficient at the absolute temperature T, $D_0$ is a constant, and R is the gas constant. This equation is based on the concept that ions must possess a minimum activation energy to overcome the energy barrier present before each diffusion step. The value of E is obtained from the slope of a plot of ln D versus 1/T.

In addition to increasing the probability that an ion will have sufficient energy to overcome the energy barrier, a rise in temperature will also increase the actual ion velocity according to the relationship

$$N m \bar{u}^2/3 = RT \qquad (2.37)$$

where N is the Avogadro number, m the mass of the ion, and $\bar{u}^2$ the root mean square velocity (Christensen, 1951a). This leads to a modified Arrhenius equation

$$D_T = D_0' T \exp(-E'/RT) \qquad (2.38)$$

It can be shown by differentiation that $E = E' + RT$.

### 2.4.3 Effect of concentration

The diffusion coefficient D varies with the concentration of the diffusing material

$$D = D_0 + f(c) \qquad (2.39)$$

where $D_0$ is the limiting diffusion coefficient at infinitesimal concentration. This variation with concentration is usually not large (Robinson and Stokes, 1955).

The value of $D_0$ of a single electrolyte can be related to the limiting molar conductances ($\lambda$) and algebraic charge numbers (z) of the ions by the equation

$$D_0 = \frac{RT}{F^2}\left(\frac{z_+ + |z_-|}{z_+ |z_-|}\right)\left(\frac{\lambda_+^0 \lambda_-^0}{z_+\lambda_-^0 + |z_-|\lambda_+^0}\right) \qquad (2.40)$$

The self- or trace diffusion of a particular ion species, i, can be measured by radioactively labelling the ion. The limiting value of the trace diffusion coefficient is related to the limiting molar conductance of the ion by the Nernst equation

$$(D_0)_i = (RT/F^2)(\lambda_i^0/|z_i|^2) \qquad (2.41)$$

## 2.5 Ion-Exchange

An ion-exchange material may be broadly defined as "an insoluble matrix containing labile ions capable of exchanging with ions in the surrounding medium without any major physical change taking place in its structure" (B.D.H., 1977). Exchange only occurs between ions

of the same electrical polarity, so that exchange materials are either cation- or anion-exchangers. Ion-exchange is a stoichiometric and reversible process; for every ion equivalent entering the exchanger, one ion equivalent of like charge leaves it and enters the solution. However, ions of different valency may exchange with each other.

Ion-exchangers show preferences for particular types of ions, and this preference is quantitatively described by the 'selectivity coefficient', K. The more strongly an ion of given type is attracted to exchange sites, the greater its K value. Consider a simple exchange system involving two univalent ions A and B:

$$A_{aq} + B_s \rightleftarrows A_s + B_{aq} \tag{2.42}$$

where the subscripts aq and s represent the solution and exchange material phases, respectively. The selectivity coefficient is then defined by:

$$K_B^A = \frac{[A]_s\ [B]_{aq}}{[B]_s\ [A]_{aq}} \tag{2.43}$$

For ions of different charges, K is given by:

$$K_B^A = \frac{[A]_s^b\ [B]_{aq}^a}{[B]_s^a\ [A]_{aq}^b} \tag{2.44}$$

where the exponents a and b are the charge numbers of ions A and B respectively. If $K_B^A > 1$ the exchanger shows a preference for A compared with B; if $K_B^A < 1$ a preference for B over A, and if $K_B^A = 1$ it shows no selectivity. The following factors affect selectivity:

(i) the greater the charge number of an ion, the greater its attraction for the exchanger,

(ii) for different ions of the same charge number, the larger the surface electrostatic charge on the ion (which is in turn related to the ionic radius and degree of hydration), the more strongly are the ions attracted to the exchanger,

(iii) ions having stronger hydrophobic and Van der Waals' interactions with an exchanger are selected over ones with weaker interactions.

Clearly the concentration of the electrolyte solution affects the position of the exchange equilibrium, and an excess of aqueous ions of type A (say) will displace almost all the ions of type B from the exchanger. The total extent of the exchange is also determined by the exchange capacity of the material. This is defined as the number of exchange sites per unit volume or mass, and is usually expressed as milliequivalents per g or per ml. The exchange capacity is greater the more the exchange groups ionise (taking into account the pH range of ionisation). Strong acid and base groups attached to the matrix ionise more highly and over a greater pH range, than weak ones. This is very relevant in the case of wood (section 1.7.3).

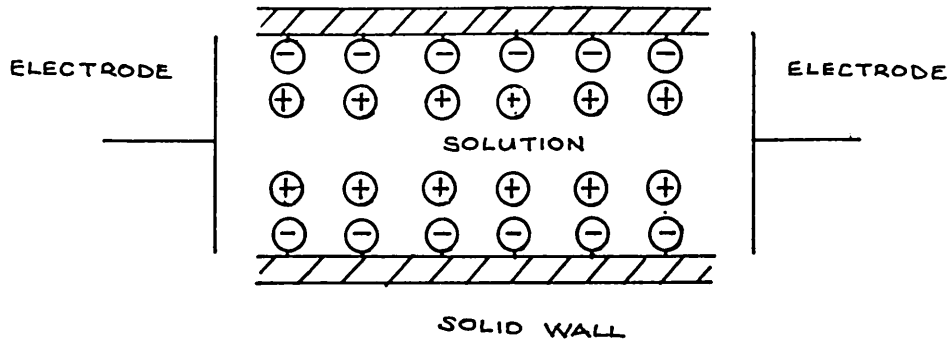
## 2.6 Electrokinetics

The movements of solids or fluids arising from potential differences at phase interfaces are grouped together as electrokinetic phenomena. The three main types of electrokinetic phenemona are: electro-osmosis, electrophoresis, and streaming potentials. Electro-osmosis is the movement of a liquid with respect to the surface of a solid under an applied potential difference; electrophoresis is the movement of suspended solid or liquid particles in an electric field; streaming potential is the potential difference created by a fluid being forced through a capillary under pressure. For electrical studies of wood, electro-osmosis is the most relevant electrokinetic phenomenon, and will therefore be dealt with in most detail.

A net electrostatic charge resides on the face of a solid in contact with a liquid. An equivalent number of counter-ions of opposite charge form a diffuse "ionic double layer" in the liquid (aqueous) phase adjacent to solid (Fig. 2.3). Thus, an electrical potential is created, of the order of millivolts, between the solid/liquid interface and a point in the liquid beyond the double layer. The double layer potential is called the zeta potential $\zeta$.

If an electric field is applied in a direction perpendicular to such an interface (Fig. 2.3), the liquid layer adjacent to the interface will move to the pole of opposite charge. This movement of liquid is

Figure 2.3 Schematic illustration of ionic double layer on the face of a solid in contact with a solution




known as electro-osmosis. The velocity, v, with which the liquid moves through such a capillary is proportional to the applied potential gradient dE/dx and to the zeta potential, and is given by the c.g.s. equation

$$v = (\zeta D/4\pi\eta)(dE/dx) \qquad (2.45)$$

where D is the dielectric constant of the liquid and $\eta$ its viscosity (MacInnes, 1961). In some experiments the current rather than the potential gradient is measured. We can therefore apply Ohm's law (2.1) and (2.5) in the form

$$E/I = R = \rho x/A = x/\kappa A \qquad (2.46)$$

and assume a uniform potential gradient so that

$$dE/dx = E/x = I/\kappa A \qquad (2.47)$$

Since the rate of volume flow dV/dt may be written as Av if we assume that the whole end of the material of cross-section A consists of capillaries, then (2.45) becomes

$$dV/dt = (\zeta D/4\pi\eta)(I/\kappa) \qquad (2.48)$$

The zeta potential can be determined by applying this equation or (2.45).

Electrophoresis is the movement in an electric field of particles of solid (or liquid) suspended in a liquid medium. It is therefore the converse of electro-osmosis. The electrophoretic mobility of a particle depends on its size and charge, as well as on its zeta potential. If the particle is only an atom or a few atoms in size, i.e. if it is an ion, the phenomenon becomes simply ionic migration in an electric field.

# CHAPTER 3

# ELECTRICAL PROPERTIES OF WOOD

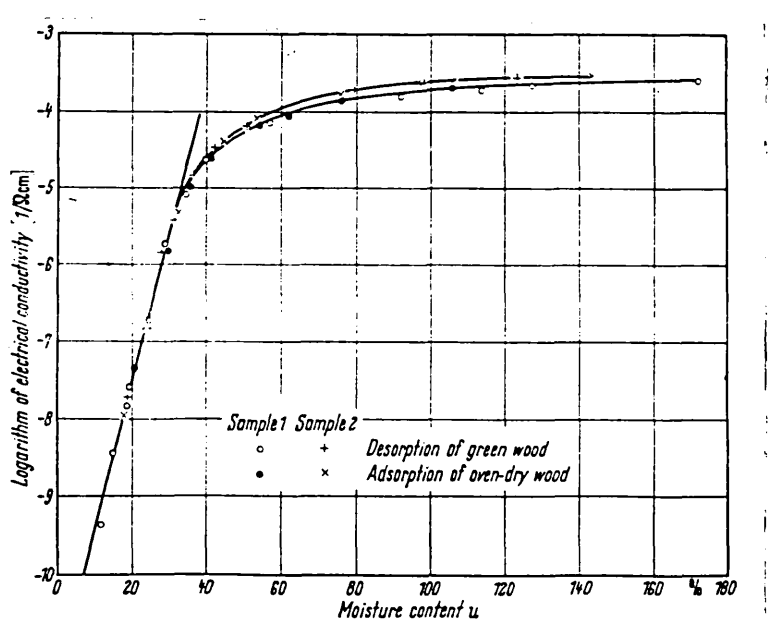
We usually think of wood as an excellent electrical insulator. This is true for oven-dried wood with moisture contents well below fibre saturation (i.e. ca. 30% water), but with rising moisture content the wood increasingly conducts electric currents. Although certain electrical properties of wood, such as d.c. and a.c. conductance, have been studied for 70 years, several other aspects of the electrochemistry of wood remain badly neglected. Unless otherwise stated, the literature refers to d.c. conductance.

## 3.1 Factors affecting electrical conduction

### 3.1.1 Moisture content

The a.c. resistivity of oven-dried wood at room temperature is around $10^{17}$ to $10^{18}$ Ωcm, i.e. a conductivity of $10^{-17}$ to $10^{-18}$ $\Omega^{-1}cm^{-1}$. Fig. 3.1 shows how steeply the electrical conductivity rises as the moisture content increases, particularly below the fibre saturation point.

Figure 3.1 Relationship of logarithm of conductivity to moisture content of wood (Stamm, 1927)



Stamm (1927) confirmed Butterfield's (1911) and Hasselblatt's (1926) findings of an almost linear relationship between moisture content and logarithm of conductivity from 7 to 30%, and that within this range the conductivity increases a millionfold. Above the fibre saturation point this relationship abruptly changes, and from 30 to 200% moisture content the conductivity only increases 50 times (Stamm, 1959). This change is believed to correspond with a change from conduction along continuous water channels inside the cell walls, to lower resistance channels in the cell lumina of the wood (Siau, 1971).

### 3.1.2 Temperature

Although moisture content has a predominant effect on conduction, temperature also has a considerable influence. Butterfield (1911) first found that increasing temperature increases electrical conductivity, G, in wood, and Clark and Williams (1933) reported the following relationship at moisture contents below 10%:

$$\log_{10} G = (a/T) + b \qquad (3.1)$$

where a and b are constants, and the temperature T is in $^{o}K$. Such an equation would be expected from an Arrhenius-type relationship (c f. 2.17).

Although other investigators have confirmed the positive temperature coefficient, dG/dT, of wood conductivity (e.g. Davidson, 1958; Brown, Davidson and Skaar, 1963), Lin (1965) has shown that log G is not linear with 1/T at moisture contents greater than about 10%. The deviation from linearity occurs with increasing temperature, and is possibly caused by changes in the moisture content during measurements, decrease in the fibre saturation point, and the high thermal expansion coefficient of wood at high moisture contents. The activation energy then decreases with increase in temperature.

### 3.1.3 Chemical content

Butterfield (1911) found that treating various species of wood at several different moisture contents with zinc chloride greatly reduced the electrical resistance of all woods. He calculated that for a rail 1 mile long laid on wet, salt-treated, wooden railway sleepers

resting on wet ballast and with wet rail bearings, 30% of the power of an electrical current passed along the rail could be lost through the sleepers into the ground.

Butterfield also found that the resistances of the woods were roughly inversely proportional to the concentration of the impregnating salt solution. This was later confirmed by Stamm (1927), using wood soaked in various concentrations of NaCl, but surprisingly little carefully-controlled work has since been made on the effects of single salt electrolytes on electrical conduction in wood.

Attention has turned instead to the effects of sea water or combinations of water-soluble preservative salts on lowering the electrical resistance of timber poles used for carrying power cables, since this presents an electrical hazard to men working on the cables. Soaking timber poles in sea water decreases their electrical resistance (Katz and Miller, 1963a; Breeze and Vitins, 1965). The increase in conductivity was roughly proportional to the square of the sodium chloride content of the soaked poles. The effect of other salts like those of magnesium was ignored. In contrast, long-term soaking of logs in fresh water increased resistance in proportion to the duration of the soaking period (Katz and Miller, 1963a). Freshwater re-soaking of timber poles saturated with sea water only partially restores either the original resistance of the green wood, or the resistance of wood soaked only in fresh water (Breeze and Vitins, 1965). This could have been due either to insufficient soaking or to ion fixation.

Different salts have a marked effect on the resistance of wood. Kininmonth (1962) found that an oxide preservative $CuO$-$ZnO$-$CrO_5$-$As_2O_5$ had no appreciable effect on the resistance of radiata pine (*Pinus radiata*) and three New Zealand hardwood species, but that $CuSO_4$-$K_2Cr_2O_7$-$As_2O_5$ and several boron compounds, including sodium borate, all lowered the electrical resistance over the three levels of moisture content tested. Increasing the concentrations of these salts decreased the resistance even further. Katz and Miller (1963b) also found that wood impregnated with $CuSO_4$-$K_2Cr_2O_7$-$As_2O_5$ had a consistently lower resistance than untreated wood at several different moisture

contents, but that impregnation with $CuO-CrO_3-ZnO-As_2O_5$ had negligible effect on resistance. Katz and Miller concluded that the oxide preservatives react almost completely with the wood, and that there are relatively few surplus ions remaining to conduct current, whereas the excess of ions in the copper sulphate preservative increased the conductivity.

The effects of the chemical constituents of wood itself have been little studied. Variations in the ash content are not generally considered important because the concentration of water soluble salts are thought to be too small to matter (e.g. Lin, 1967; Kollman, 1951).

A close correlation between conductivity and % lignin content was claimed by Venkateswaran (1972) for a variety of different soft- and hardwood species at fixed moisture contents and temperature. However, the variation in lignin content within each species, or possible effects of other chemical constituents of the wood, were not taken into account nor was the variation in types of lignins between different species.

### 3.1.4 Grain direction

The direction of the grain of wood has a large effect on its electrical conductivity. Butterfield (1910, 1911) first found that electrical resistance is less along than across, the grain. The resistivity is 2 to 3 times greater across the grain than along the grain in softwoods, and 2 to 8 times greater in hardwoods, the exact ratio varying among different species (Hiruma, 1915; Stamm, 1960). Resistivity in the tangential direction is the same or 10% greater than in the radial direction. All these ratios are independent of moisture content below fibre saturation point (Stamm, 1960), but there are no data available for moisture contents above fibre saturation point.

These differences in conductivity with direction are believed to be due to the high electrical resistance across cell walls, so that current tends to pass along rather than across the cells (Hart, 1964; Siau, 1971) - analogous to the pathways of diffusion (1.9) and flow (1.10) of electrolytes. Radial flow can be accounted for by the presence

of rays and radial resin ducts (Hart, 1964), although no correlation has been sought between volume of radial tissues and radial conductivity. Growth ring density gradients have also been claimed to reduce radial conductivity, and slightly increase tangential conductivity (Hart, 1964), although other workers have found gross wood density has a negligible effect on electrical conductivity (Wood Handbook, 1955; Venkateswaran,1972).

### 3.1.5 Mechanism of electrical conduction

Electronic conduction in wood is unlikely since it does not contain the molecular structure necessary for passage of electrons, i.e. overlapping electron levels as in metals, or single-double bond conjugation as in graphite or certain organic semiconductors. Instead it is generally agreed (e.g. Lin, 1967) that electrical conduction in wood arises from the movement of ions (ionic conduction), and this belief is borne out by the following observations:

(i) conductivity increases with increasing temperature (whereas conductivity in metallic conductors decreases with increasing temperature),

(ii) conductivity increases with rising moisture content,

(iii) conductivity increases roughly in proportion to the square of the concentration of a simple binary electrolyte contained in the wood,

(iv) ions migrate during passage of current.

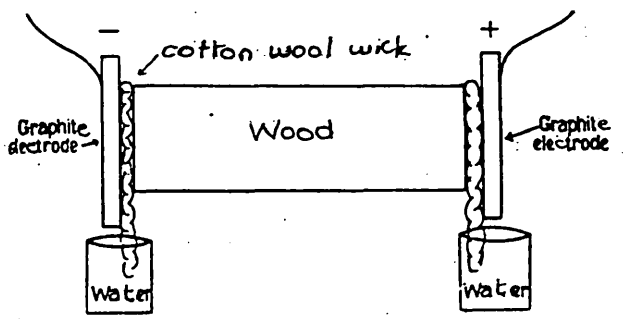
## 3.2 Migration of ions

Migration of endogenous (i.e. native) wood ions, of electrode reaction products, and of exogenous electrolytes through wood have been reported from time to time when a constant potential was applied. These phenomena have generally been studied for their wood-preserving prospects (see 3.5.1), but little is known about the electrical transport of ions through wood. Nevertheless, the literature will be described in detail, given its relevance to this project.

### 3.2.1 Endogenous ions

The literature on electrical transport of endogenous ions through wood is extremely sparce. Bechhold and Heymann (1927) first determined the changes in ash content of wood after passing d.c. electricity, using the apparatus shown in Fig. 3.2.

Figure 3.2 Apparatus of Bechhold and Heymann (1927) for passing electrical current through wood



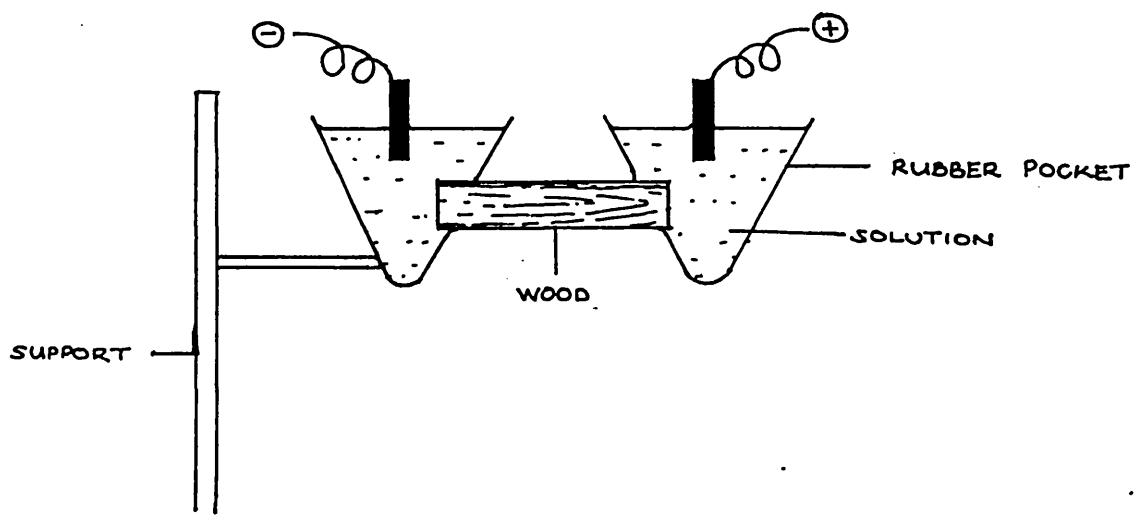

Endogenous ions migrating out of the wood samples were drawn down into the collecting bowls through cotton wool wicks, which during some experiments were regularly rinsed with water to remove the migrated material. However, the nature and levels of the migrating ions, or the constituents of the remaining ash were not determined. Instead, the total ash content of the wood samples was measured after each electrical run, and compared to a (presumably almost identical) untreated piece of wood of the same size.

In all cases, for oak, spruce, and pine sap- and heartwood, the passage of current caused marked falls in the ash content. Nearly all the ash was removed from wood in electrical runs using the rinsing technique - e.g. the ash content of a pine sample 180 mm long x 70 mm diameter (containing sap- and heartwood) fell from 0.31 % to 0.02% after applying 120 V for 15 days (approx. 45 000 C). The original ash contents of sap- and heartwood were not given, but the percentage of ash in both types of wood were almost identical after electrical treatment. It was also not possible to compare the extent of ash removal between the species, as different sizes of wood with varying lengths of treatment were used for each species. Nevertheless, the wood-preserving

qualities of the treated wood were attributed to the de-ashing process, as shown by the inhibited growth of 4 species of fungi (presumably as a result of the fall in nutrient ions required for fungal growth).

Similar results were found by Schwarz (1928a, b,c) using a set-up in which the ends of a wood sample were bathed in various electrolyte solutions contained in water-tight rubber electrode compartments (Fig. 3.3).

Figure 3.3 Apparatus of Schwarz (1928a, b,c) for passing electrical current through wood




Unfortunately Schwarz also failed to analyse the ions migrating from the wood into the electrolytes in most of his experiments. Instead he measured the levels of ash remaining after passing current in the two halves of the wood facing the cathode and anode, and compared these to a (presumably almost identical) untreated piece of wood of the same size. With all the salt electrolyte solutions tested the ash content increased (as described further in the next sub-section), but with "distilled" water, HCl, or $H_2SO_4$ the levels of ash throughout the wood samples fell.

Schwarz (1928b) did analyse the contents of both electrode compartments when these had initially contained "distilled" water. However, because the wood was left to soak in the water-filled apparatus

for several hours before current was passed, ions probably leached out of the wood. After passing approx. 3000 C (using unspecified electrodes) through a 82 mm long x 31 mm diameter sample of maritime pine (*Pinus maritima*) sapwood, the catholyte contained 20 mg inorganic material with none detected in the anolyte. In addition, there was five times less ash remaining in the cathode-facing half of the wood, than the anode-facing half. Although Schwarz had no explanation for these results, they indicate that the endogenous inorganic ion current comprised only cations, which had migrated towards the cathode. However, 29 mg and 27 mg organic material was also detected in the cathode and anode compartments, respectively. Electro-osmotic flow of water was thought to flush this organic material out of the wood (Schwarz, 1928c), but as electro-osmosis in this experiment almost certainly flowed from anode to cathode it cannot account for the organic substances present in the anolyte. More likely, the electrolytes (being exposed to the atmosphere) had become contaminated during the 3 day experiment with foreign organic bodies, such as bacteria or rubber particles from the electrode compartments. The levels of organic matter in the electrolytes were not recorded in other runs.

Muraoka (1929), too, showed that passage of current resulted in marked decreases in the ash content of the softwood species Japanese cedar (*Cryptomeria japonica*), although it is not clear what apparatus was used for these experiments. Analysis of the organic contents of fresh and electrically-treated (using roughly 1000 C) wood samples revealed apparent decreases in various components - such as lignins or "volatile oils" - and (inexplicably) increases in other constituents, such as α cellulose. These results are suspect as the organic content of the wood sample Muraoka used as a control may not have provided a reliable comparison - replication of treated and untreated wood samples would have given a more realistic comparison.

Herzner (1932) pointed out the disadvantages of placing electrodes onto the surface of wood samples, as unidentified negatively charged colloidal substances migrating out of the wood coated the anode. Furthermore, gassing at the electrodes resulted in formation of acid at the anode ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$), and alkali at the cathode ($2e^- + 2H_2O \rightarrow H_2 + 2OH^-$), which could both pass into the wood. To

counteract the colloidal, $H^+$, and $OH^-$ migrations, Herzner developed an "electrodialysis" process in which a variety of mesh electrodes was separated from the wood by absorbent membranes such as asbestos fibre and parchment. These were frequently washed with water to remove electrode reaction products and migrated ions.

D.c. potentials of 110 to 220 V were applied across 100 mm long x 25 mm wide x 50 mm thick pieces of beech wood. Further experimental details were scarce and no illustration of the apparatus was given.

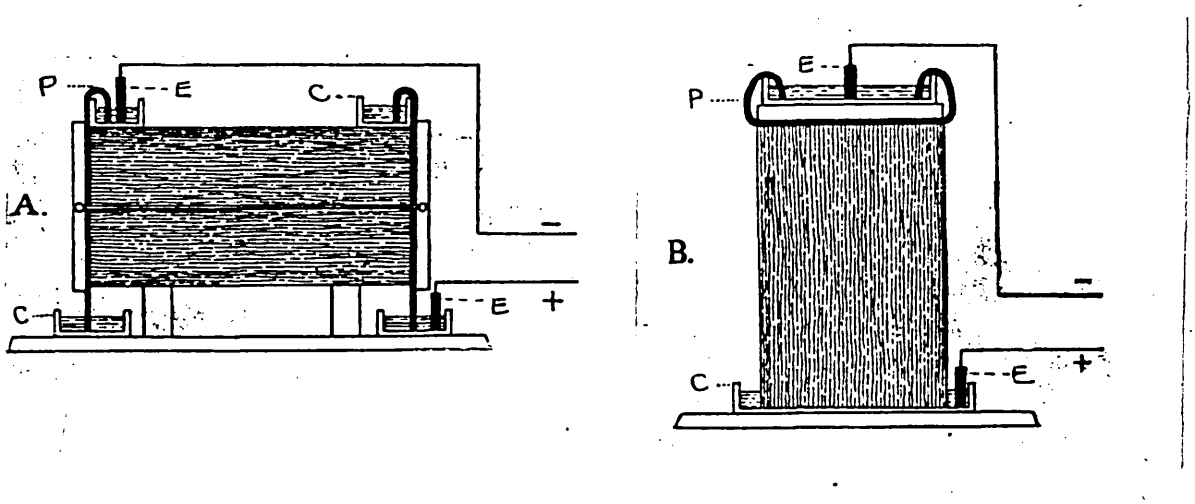
Wood treated by electrodialysis for 1 to 2 weeks took up 18 - 20% less water from the atmosphere than untreated controls. This fall in hygroscopicity increased with the durations of treatment. The samples of wood shrank, presumably as a result of electro-osmosis, although this was not stated. There was also no mention of the exact nature of the migrating endogenous material, although in a later patent in 1934 (see section 3.6.1) xylan appeared to migrate to the anode, and rust-brown discolouration occurred at the cathode. In addition, electrodialysis was thought to sterilise bacteria and other single-celled micro-organisms present in the wood, by "electro-plasmolysis". However, no evidence for this was presented.

More recently the electrical transport of endogenous ions through wood has been verified by Langwig and Meyer (1973), using samples of wood from 3 species of Venezuelan jungle trees (the original location of the samples from within each tree was not given). Current was passed by clamping copper electrodes onto the surface of the wood and applying constant voltages for known lengths of time. By cutting the wood into sections perpendicular to the electric field after each experiment, they were able to analyse for ion concentrations in different parts of the samples. Native cations (particularly $K^+$ and $Na^+$) migrated towards the cathode, and native anions (particularly $Cl^-$ and $Br^-$) towards the anode. Although they only reported the <u>elements</u> present in each section, and not the types of <u>ions</u>, Langwig and Meyer's results did distinguish between mobile and fixed ions. Manganese, for instance, remained immobile in the electric field in all the woods tested, including one specimen in which current was passed across, rather than along, the grain. They suggested that manganese may be chelated in the wood, and was therefore not available for carrying charge through the electric field.

### 3.2.2 Exogenous ions

Petri (1921) pioneered the study of the electrical transport of exogenous ions through wood, using approx. 10 $cm^3$ samples laid either horizontally (Fig. 3.4a) or vertically (Fig. 3.4b). Absorbent pads, P, were clamped tightly onto the wood specimens, drawing electrolyte solutions from electrode compartments C. Constant potentials of 110-200 V were applied across a variety of soft- and hardwoods, using carbon rod electrodes, E, mounted in the electrode compartments.

Figure 3.4 Electrical Apparatus of Petri (1921)
Explanation of figure in text.




At low voltages (60 - 70 V) with 5 wt% $CuSO_4$, beechwood was discoloured blue-grey - presumably by the migration of $Cu^{2+}$ ions - whereas at higher voltages (120 - 150 V) the wood was stained brick red, probably by the formation of copper oxide. Red deposits and copper precipitates were formed on the surface of the cathode and on the wood surface. Interestingly, reddening did not occur in softwoods nor in wood used in the electro-osmotic apparatus (Fig. 3.8) with a $CuSO_4$ solution. These observations are difficult to explain.

By following the course of discolouration, Petri found that copper migrated first through the core, and then to the periphery of a wood sample. Discolouration also began at the cathode-facing side,

implying (although this was not stated) that copper anions had migrated from cathode to anode. However, the vertical apparatus (Fig. 3.4B) may have forced $CuSO_4$ into the wood from the top, cathode, compartment against the electric current. Slightly less hydrostatic pressure differences would also have occurred in the horizontal apparatus, and these results should therefore be treated with caution. Greater discolouration occurred with current alternated every 10 min.

Microscopic examination showed the cell walls of all the treated wood tissues to be homogeneously discoloured throughout the secondary wall layers. With the higher voltage treatments Cu deposits were observed in cell lumina, and starch granules in the parenchyma had disappeared, apparently by hydrolysis to glucose, although no supporting evidence for this phenomenon was presented. Copper was also deposited as granules in the rays and some vessels.

Petri's report appeared to be highly subjective. His claim that electrical impregnation with $CuSO_4$ (and also $ZnCl_2$ and $HgCl_2$) was greater in speed and extent of penetration, than by immersion or pressure/vacuum treatments was not quantified. Nevertheless, electrically treated wood thoroughly washed in distilled water (to leach out unfixed preservative) was more resistant to innoculations of *Coniophora cerebellum* than comparable pressure/vacuum preservation. The fixation of metals in the wood was confirmed by the (unspecified) levels of Cu remaining in the ash of leached wood.

Physical tests of electrically impregnated wood cast doubts on the commercial feasibility of this treatment. Petri found that the electrical treatment resulted in poor mechanical strength of the wood, which was partly attributed to physical damage to the cell walls of the wood tissue (as seen by cracked and deformed walls). Such damage may have been caused by Joule heating which split the wood at larger currents. Furthermore, the electrical conductivity was unequal in single pieces of wood, so that Joule heating (and probably also impregnation) would have been expected to be unevenly distributed. Partially dried wood was also unsuitable for electrical impregnation, even if re-wetted

(presumably because of pit aperture aspiration - see section 1.10). Thus, electrical treatment was only recommended for fresh wood, using < 100 V to avoid mechanical damage.

Petri's pioneering research remained unnoticed by all later workers. Bechhold and Heymann (1927) briefly studied the migration of metallic cations through pine wood, using the apparatus described in Fig. 3.2. Metallic salt solutions were contained in the anodic bowl. With 5 wt % $CuSO_4$ anolyte, $Cu^{2+}$ migrated into the cathodic bowl after passing approx. 5000 C (48 h of treatment), using 230 mm long x 100 mm diameter wood previously treated electrically to remove the endogenous ions (see previous sub-section). In partly de-ashed wood (ca. 0.1% ash) the $Cu^{2+}$ appeared to migrate more slowly, passing into the cathode bowl only after 80 h treatment (the current was not recorded for this experiment, so the number of coulombs passed is not known). The endogenous ions, particularly cations, may therefore have retarded the passage of $Cu^{2+}$.

The distribution of impregnating metals in the wood was determined by analysing ashed samples. Higher levels of Hg (0.7% $HgCl_2$ anolyte) and of Cu (3% $CuSO_4$) were generally found in the sap- than the heartwood. Proportionately more metal was contained in the middle portions of the heartwood, and lower levels in the end parts. In contrast, the gradient of metals in the sapwood was greatest in the anode-facing part of the sample, and least in the cathode-facing part, resulting from metallic cation migration from anode to cathode.

The passage of $Cu^{2+}$ resulted in a blue-green discolouration of the wood, but in many (unspecified) species the heartwood was stained red or red-brown, like that described by Petri for his high voltage-treated wood. Compared to Boucherie-treated (i.e. hydraulically flushed) wood samples of similar size, electrical impregnation with $CuSO_4$ was slow but penetration (particularly into the heartwood) was greater.

Bechhold and Heymann considered that exogenous metal cation migration occurred primarily by electro-osmosis, and that electrolysis

only played a minor part. They showed that the acid fuchsin (anion) dye migrated through the wood from anode to cathode, i.e. against the electrical current. They reasoned that the dye must have been carried with the electro-osmotic flow, although the dye did not penetrate the whole sample evenly.

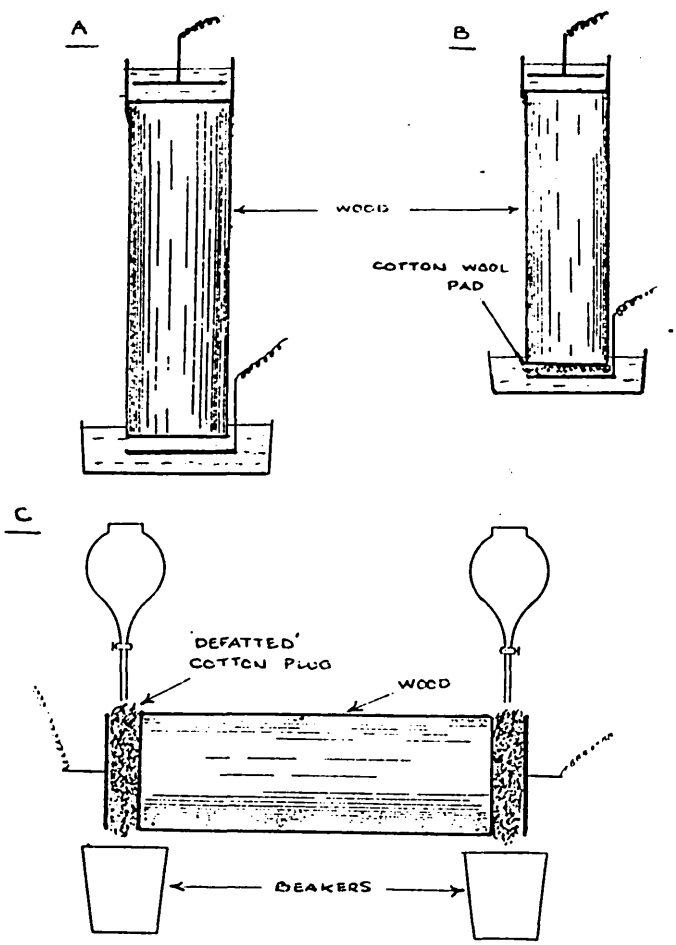
Schwarz (1928) electrically impregnated samples of maritime pine, *Pinus maritima* using the apparatus in Fig. 3.3. Solutions of KI, $ZnCl_2$, $CaCl_2$, $MgSO_4$, and $CuSO_4$ were placed in both electrode compartments, and after passing d.c. the ash content was raised, particularly in the anode-facing side of the wood. Although the nature of these changes in ash was not analysed, they probably resulted from migration of metallic cations from anode to cathode compartments. However, the ash content of the cathode-facing side of the wood was slightly greater in $CaCl_2$ treated wood, and this is difficult to explain.

Metallic precipitates were formed in the wood in runs using $MgSO_4$ and $CuSO_4$, but the wood became charred by excessive Joule heating in the $CuSO_4$ runs. These precipitates were considered to be the cause of the poor conductivity of the wood, particularly as Cu deposits were more concentrated at the anode face where they could block the entry of fresh $CuSO_4$ solution. A precipitate of $PbCrO_4$ was also obtained with a $K_2Cr_2O_7$ catholyte and $Pb(NO_3)_2$ anolyte. Since more of this precipitate was deposited in the wood on the anode side, it was reasoned that the $CrO_4^{2-}$ anions had migrated faster than $Pb^{2+}$ cations. $PbCrO_4$ was also deposited in all the wood tissues, including heartwood, indicating that anion and cation currents had passed through all the tissues.

Muraoka (1929) studied the migration of $CuSO_4$ by applying 100 V potentials (mainly d.c.) across Japanese cedar wood (*Cryptomeria japonica*), previously dried and then re-wetted in distilled water or NaCl solutions for 20 d. In contrast to Schwarz, this re-wetting procedure apparently restored the conductivity of the wood, although no fresh wood control was used. However, microbial contamination during the re-wetting period may have affected ion migration through the wood (c.f. sections 1.6.3, 1.7.3, 1.9).

In a vertical arrangement, Muraoka (1929) held 'saturated' $CuSO_4$ solutions at the top and bottom of the wood (Fig. 3.5A), or inserted a moistened cotton wool pad between the wood and lower electrode (Fig. 3.5B) (unspecified electrodes). However, hydrostatic pressure from the top electrolyte bath could have forced solution into the wood (c f. Petri, 1921) - $CuSO_4$ impregnation was greatest in the uppermost parts of the wood whether the top electrode was anode or cathode. Nevertheless, more homogenous electrolyte penetration was achieved using a.c. (of unspecified frequency) rather than d.c.

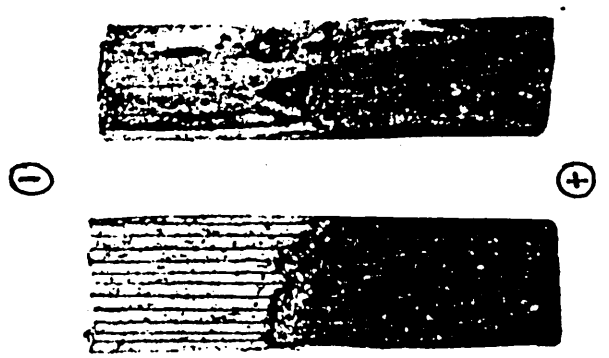
Figure 3.5 Electrical apparatuses of Muraoka (1929)



Muraoka also adapted Bechhold and Heymann's apparatus, by pouring (rather than dipping) solutions onto 'de-fatted' cotton plugs at both ends of a horizontal wood sample (Fig. 3.5C). Impregnation with copper was increased by using higher currents or more concentrated $CuSO_4$ solutions. Electro-osmosis was claimed to cause the bulk of copper migration.

Wood samples previously re-wetted and then electrically impregnated with NaCl carried larger amounts of copper in subsequent $CuSO_4$ runs, than did wood only soaked in NaCl. (Unfortunately Muraoka presented insufficient data to compare water- with NaCl-soaking pretreatments on the later migration of copper). Photographs published of wood electrically pre-treated with NaCl and then $CuSO_4$ show an apparent sharp boundary of copper migrating from anode to cathode through all the wood tissues (Fig. 3.6).

Figure 3.6 Wood treated electrically by Muraoka's method
Wood soaked in water, electrically impregnated with NaCl (0.5 wt. %), and then with 'saturated' $CuSO_4$ solution, using the horizontal electrical apparatus.




Migration of exogenous ions has often been reported to interfere with moisture measurements using d.c. resistance meters (see section 3.5.3). Skaar (1964) observed the passage of $Ag^+$ derived from a silver-coated anode across thin (approx. 1.5 mm) segments of aspen wood at 21% moisture content. The ion migrations led to artificially high "moisture contents" and eventually short-circuited the wood between the two silver-coated electrodes.

Perhaps the clearest demonstration of exogenous ion migration was by Lin (1965), using radioactively labelled ions whose transport can be followed during the passage of electrical current. Unfortunately his work remains unpublished as a Ph.D. thesis.

More recently Duran, Meyer and Siau (1978) studied ion migration in specimens of hard red maple (*Acer saccharum*) pressure/vacuum-impregnated with various permutations of $Cu(NO_3)_2$, $CrO_3$, and $As_2O_5$, using the methodology and neutron activation analysis described by Langwig and Meyer (1973). Copper and arsenic readily migrated when present individually - copper moving towards the cathode, and arsenic towards the anode. The quantity of migrating copper was considerably less than that of arsenic, possibly because their respective ion-constituent mobilities differed. If copper migrated as $Cu^{2+}$ it would probably have associated with the negative carboxyl groups in the wood, whereas arsenic may have passed as $H_2AsO_4^-$. Chromium, though, showed little migration, possibly due to the formation of chromium complexes with the wood cellulose.

The profile distribution of the individual ions along the wood specimens reflected their respective mobilities. Thus, appreciable copper or chromium migration was only distinguishable close to the electrodes, whereas the concentration of arsenic increased from cathode to anode. In addition, a slight increase in sodium concentration was noted, particularly near the anode, possibly due to contamination. Similarly, penetration of copper from the Cu anode resulted in marked increases in its concentrations in segments near the anode. Langwig and Meyer (1973) had also detected copper as well as potassium penetration into the wood from a Cu anode. The copper penetration increased with time, and became visible as a turquoise-green coating on the surface of wood directly exposed to the anode.

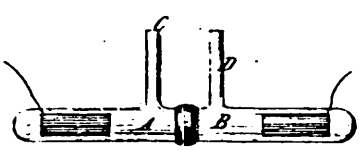
The presence of copper or chromium impaired the transport of arsenic, and was attributed to the formation of copper or chrome arsenates in the wood. When all three elements, Cu, Cr, and As, were present together there was no significant migration of any of them. It was concluded that no ionisable species of these elements were present to move in the applied field, probably as the result of formation of

complexes with the wood. Other ions, such as endogenous $Na^+$, and ions produced "in the electrolysis of the available moisture in the samples" (presumably $H^+$ and $OH^-$) were considered to conduct all the current in this case. However, the possible role of the counter ions from the preservatives (such as $NO_3^-$) was ignored.

## 3.3 Electrokinetic Phenomena

An electrokinetic phenomenon in wood was first studied by Quinke (1859), who measured streaming potentials through diaphragms of sawdust wrapped in silk, and sealed with wax into a glass cell (Fig. 3.7). Aqueous solutions forced through one of the vertical tubes, C, D, resulted in a change in electrical potential (i.e. streaming potential) across the wood. This indicated that the wood was negatively charged with respect to water (i.e. had a negative zeta potential). Addition of acids or salts to the water diminished the current (i.e. decreased in zeta potential).

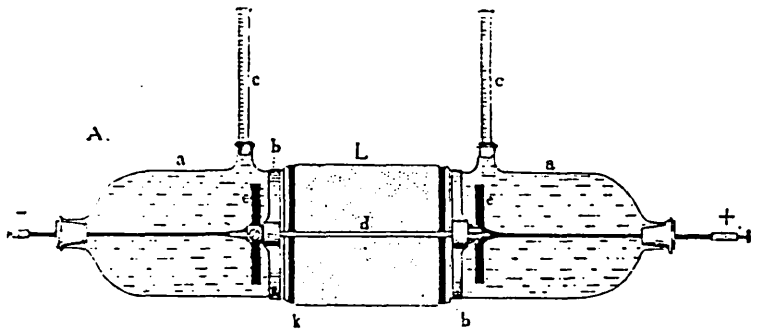
Figure 3.7 Streaming potential apparatus of Quinke (1859)
(explanation of figure in text)




Later measurements of streaming potentials (Bethe and Toropoff, 1915; Anderson, Gortner and Schmitz, 1941) and electro-osmosis (Petri, 1921; Stamm, 1926; Bechhold and Heymann, 1927; Schwarz, 1928) confirmed that wood has a negative zeta potential with respect to water. The techniques for measuring electro-osmosis through wood were varied. Petri (1921) held a cylinder of wood, L, 50 to 55 mm long x 60 mm diameter between two 30 $cm^3$ glass compartments, a, using metal rings, b, and screw rods, d, and sealed with rubber gaskets, k (Fig. 3.8). Carbon, Cu, or Pt electrodes, e, were held near the wood by insulated Cu rods. Electrolyte volume changes were measured using two graduated vertical tubes, c. However, differences in electrolyte levels between

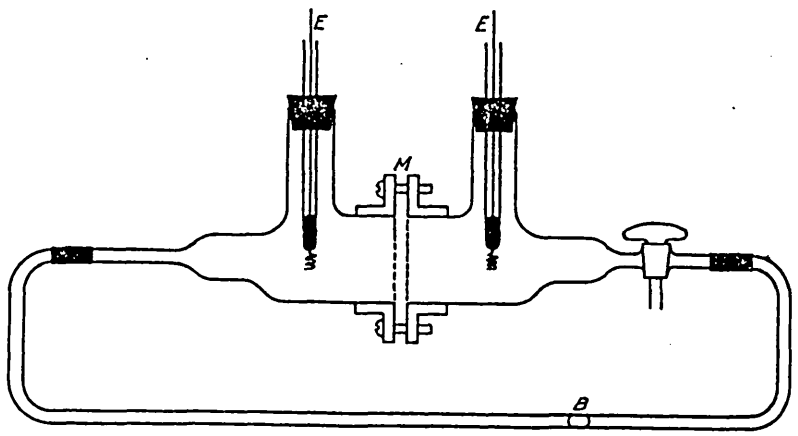
these tubes would have created unequal hydrostatic pressure across the cell, and this, together with possible gassing at the electrodes, would have interfered with the electro-osmotic measurements.

Figure 3.8 Electro-osmosis apparatus of Petri (1921)
(Explanation of figure in text)




Stamm (1926) overcame the hydrostatic pressure problem by using a horizontal tube in a closed cell filled with salt, acid, or alkali solutions (Fig. 3.9). A membrane of wood, M, 0.04 - 1.45 mm thick was clamped into the cell, which was immersed in a thermostat at $25 \pm 0.05^{o}C$. A potential was applied between two Pt coil electrodes, E, and the rate of electro-osmosis followed with a bubble, B, trapped in the horizontal tube. Stamm's apparatus may also have suffered gassing problems, although this was not mentioned.

Figure 3.9 Electro-osmotic apparatus of Stamm (1926)
(Explanation of figure in text)

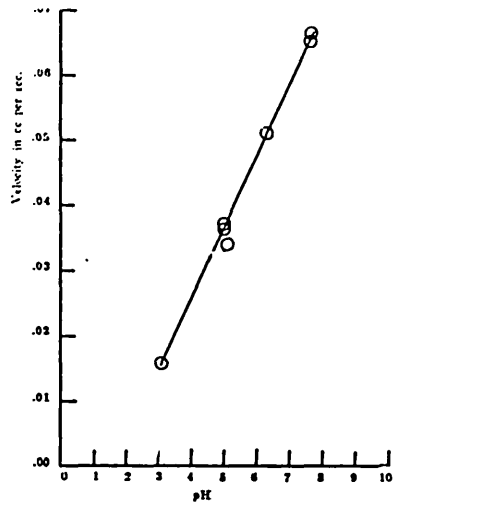


Bechhold and Heymann's apparatus avoided pressure and gassing problems, but variations in the porosity of the cotton wool plugs held between the electrodes and wood may have given misleading results (Fig. 3.2; section 3.2.1). In Schwarz's system the electrolyte baths fitted over the ends of the wood sample were not calibrated; furthermore, unequal hydrostatic pressure would have developed across the cell during electro-osmosis (Fig. 3.3; section 3.2.1).

Despite the shortcomings in the techniques outlined, all workers found that electro-osmosis through wood generally flowed from anode to cathode - i.e. wood usually has a negative zeta potential. Stamm (1926) calculated an average zeta potential of -13.6 mV from electro-osmotic data for a variety of softwoods and one hardwood. The negative zeta potential probably originates from the fixed, negatively-charged, carboxyl groups on the cell walls of the wood tissue (see section 1.7.3), although only Bechhold and Heymann appreciated the likelihood of such fixed charged sites. Since the dissociation of these fixed acidic groups is pH-dependent, the velocity of electro-osmosis falls, and its direction sometimes reversed, when the pH of the bathing electrolyte decreases - i.e. fewer fixed acid groups dissociate. Conversely, the velocity rises with increasing pH as more acid groups dissociate (Petri, 1921; Bechhold and Heymann, 1927; Stamm, 1928) (Fig. 3.10).

The zeta potential and electro-osmotic velocity are also affected by ions present in the bathing solution, and particularly by their charges. For example, Stamm (1928) found that monovalent chlorides increase the electro-osmotic velocity with increasing concentration, but bi-, tri-, and tetravalent chlorides have varying effects. During electrical impregnation of wood with $CuSO_4$, Bechhold and Heymann (1927) recorded a steady fall in electro-osmotic velocity. This fall was attributed to: (a) $Cu^{2+}$ ions binding (tightly) to the fixed negative sites (as supported later by Anderson et al. 1941, who found the zeta potential decreases during penetration of wood by electrolytes), and (b) an increase in conductivity of the wood - i.e. a decrease in the potential gradient across the wood.

Figure 3.10 Effect of pH on electro-osmosis through cedar wood (Stamm, 1927)
(1.12 mm thick wood sections)




## 3.4 Other Electrical Phenomena

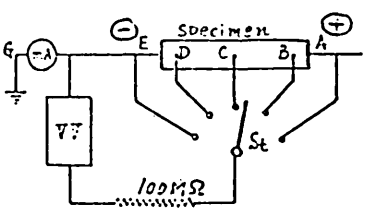
When direct current is applied to a wood specimen its apparent resistance may either increase or decrease with time, although studies have not been made for periods longer than several minutes, and a final steady state has not been determined. Three main factors are involved: changes of composition within the wood (section 3.2.1); polarisation at interfaces (electrode/wood, electrode/solution, wood/solution); and Joule heating in the wood. These latter two time-dependent factors will be discussed here, together with the so-called Evershed effect.

### 3.4.1 Polarisation at interfaces

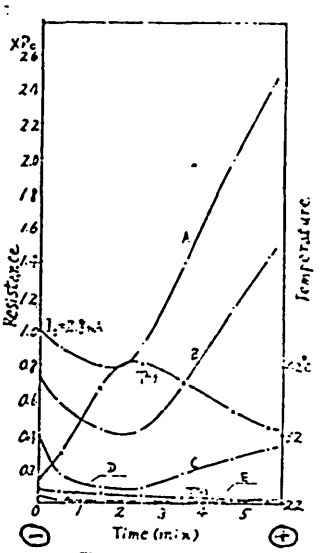
When current is passed it produces an e.m.f. at the electrodes, tending to oppose the polarity of the applied e.m.f. This opposing or "back" e.m.f. is observed as a "residual e.m.f.", and decays exponentially after the external field is removed (Skaar, 1964). Polarisation at electrode/solution interfaces is a well-documented field (Bockris and Reddy, 1973), but little is known of wood/solution polarisation. In most of the literature the electrodes were mounted directly onto the wood, so that several types of polarisation will have

been present and interacted in unknown ways. Ito (1960a, b, c) measured the potential gradient along specimens of *Cryptomeria* during passage of current, but had his electrodes mounted directly onto the wood. Using copper electrodes, Ito (1960a, b) found that the resistance rapidly increased around the anode, and wood facing towards the anode, but remained low and virtually constant at the cathode, and the wood facing the cathode (Fig. 3.11). This contrast in resistances may have been partly caused by electro-osmotic migration of water towards the cathode, resulting in increased solvent for electrolysis to occur. In addition, the Cu anode would have formed $Cu^{2+}$ ions which would have migrated into the wood to displace endogenous cations such as $K^+$. Since $Cu^{2+}$ ions are more tightly bound to the wood matrix, the conductance would have fallen.

Figure 3.11 Change in electrical resistance and temperature during passage of current through specimens of *Cryptomeria* wood (Ito, 1960a)




Measurement of potential distribution.




Change of electric resistance of each part.
22°C, 86%; Cu electrodes; Rain-water; Supply volt. 500 V

## 3.4.2 Joule heating

When electric current passes through a conductor, a proportion of the current is converted into heat (see section 2.1). This so-called Joule heating equals $I^2R$ (I = current, R = resistance). It has been

recorded during passage of d.c. electricity through wood (Muraoka, 1929; Ito, 1960a,b; Skaar, 1964). Joule heating is particularly marked near the anode end of the wood, but generally declines during the course of an electrical run (Ito, 1960a, b).

Joule heating has been exploited in industrial drying of wood, and is discussed further in section 3.6.2.

### 3.4.3 Evershed Effect

There are conflicting reports as to whether wood obeys Ohm's law ($V = IR$, equation (2.1)), where V is the applied d.c. potential. For virtually all materials, the resistance of a given sample is independent of the applied voltage. For wood, however, the d.c. resistivity is affected by the voltage used, decreasing markedly with increasing voltage over the range 1 to 100 V $cm^{-1}$. This phenomenon has been termed the 'Evershed Effect'. Above 150 V $cm^{-1}$ the resistance no longer decreases significantly with increasing voltage until a critical voltage is attained, when the resistance drops abruptly at the point of dielectric breakdown. When conductivity is measured with a.c. at 60 Hz or higher frequencies, the Evershed Effect is not observed (Brown 1962, cited by Lin, 1967).

This phenomenon appears to be a characteristic of ionic conduction in polar dielectrics (Murphy, 1929), and has been attributed to the dependence of the degree of polarisation of polar substances on field strength (Lin, 1967). No attempts have been made to see if the Evershed Effect can be explained by the polarisation phenomena at the electrodes mentioned in section 3.4.1.

## 3.5 Industrial Applications

### 3.5.1 Electrical Impregnation

Bretonneau and Nodon (1897) impregnated wood across or along the grain using direct current density < 30 mA $cm^{-2}$ by immersing wood blocks between two (preservative) electrolyte-filled electrode compartments (Fig. 3.12). Nodon and Bretonneau (1900) later modified

Figure 3.12 Electrical Impregnation Apparatus of Bretonneau and Nodon (1897)

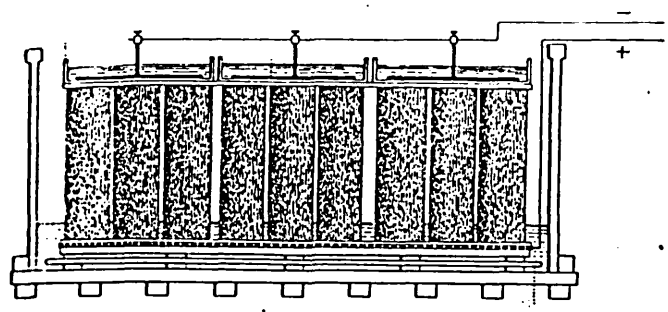



Figure 3.13 Electrical Impregnation Apparatus of Nodon and Bretonneau (1900)

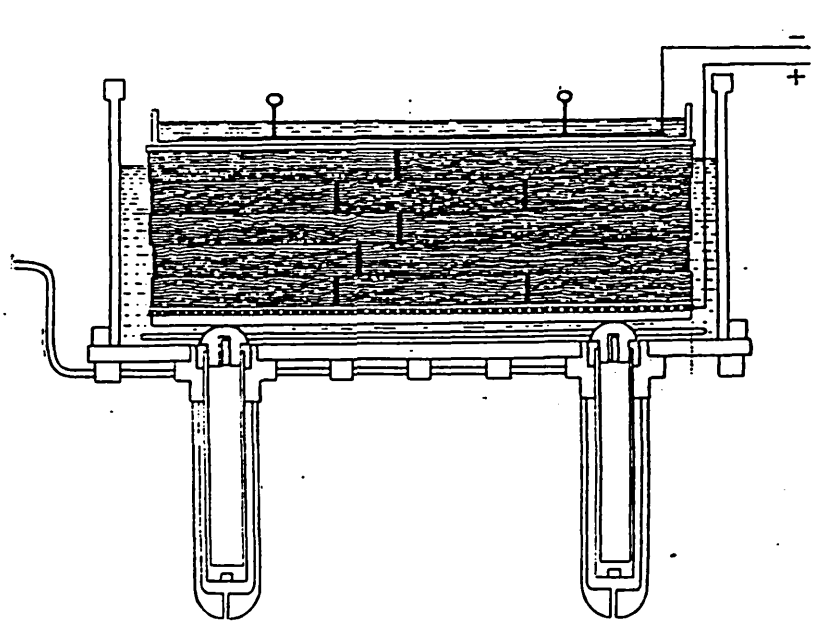
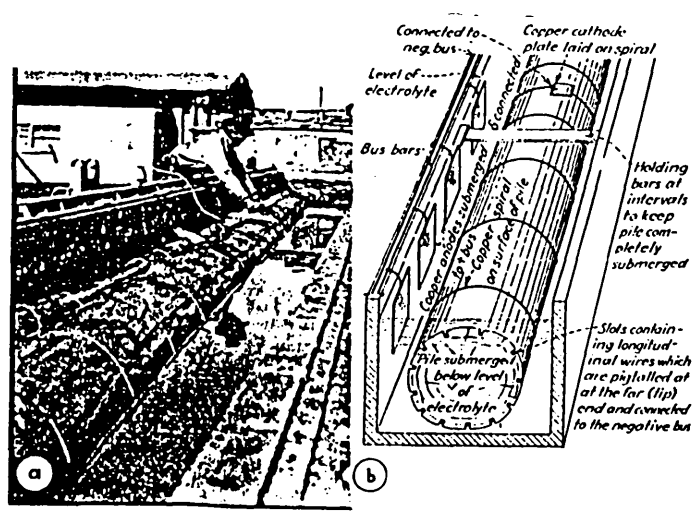



Figure 3.14 Electrical Impregnation Apparatus of Andrews (1925)




(a) Close-up of one of the tanks just before the pile is completely submerged; placing a cathode plate on one of the wire spirals. Anodes for the cell are hung below the surface of the electrolyte along the left side, where the buses are located; (b) schematic drawing of tank and pile

their technique by totally immersing planks of wood, and gradually raising the timber out of solution using a hydraulic jack (Fig. 3.13). In both cases, though, the treatment may have been partly caused by diffusion of solution bathing the wood.

The electrical impregnation technique of Andrews (1925) of the Olympia Wood Preserving Co., U.S.A. was put into commercial operation (1943)*. Several lengths of copper wire were fixed into grooves 18 mm deep, about 200 mm apart along the surface of timber poles 18-36 m long (Fig. 3.14). A coat of conductive metallic graphite paint was applied over these longitudinal wires, and a spiral of copper wire fixed over the painted surface. Each pole was then submerged horizontally into an electrolytic tank containing $CuSO_4$, $H_2SO_4$, and "other elements" in solution. Copper plate anodes were suspended along one side of the tank, all the Cu wires connected to a cathode source, and d.c. electricity (6-16 mA $cm^{-2}$ timber surface) passed for unspecified durations. Loadings of $>3 \times 10^{-3}$ g $cm^{-3}$ copper in the outer 18 mm core of wood were claimed, giving a "copper-colored sheen" over the surface of the log. Copper did not penetrate deeper than 18 mm, but impregnation was uniform. However, uneven loadings were more likely, since: (1) $Cu^{2+}$ ions migrating from the longitudinal wires on the side of the log facing the anode would be unlikely to penetrate the wood; (2) the migrating $Cu^{2+}$ would probably have passed along the more conductive coat of metallic paint; (3) the cathodic wires covered a relatively small area of the log surface; and (4) $Cu^{2+}$ migrating from the spiral wires were unlikely to have penetrated the metallic paint into the wood (in fact their function was not explained).

Andrews' treatment was said to preserve and harden the wood - a treated wood pile used in a marine environment for 17 years was found to be completely preserved. However, this success may be partly due to decomposition of the longitudinal Cu wires, kept in place after

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*Footnote. Despite extensive investigations it has not been possible to trace Andrews' patent. The description here is taken from the article in Electrical World (1943) which unfortunately omitted the number of the patent.

electrical treatment. Possibly because of the high electrical, material, and labour costs involved, this technique did not seem to become widely used.

Herzner (1934) patented an 'electrodialysis' preservation technique, described previously in his 1932 scientific paper (section 3.2.1). The patent gives few practical details, and was not illustrated. Potentials of 220 V d.c. electricity were applied to beech wood for a few days, until the current had fallen to a constant level (which was assumed to indicate the completion of treatment). After 2d treatment the wood surface facing the anode became increasingly covered in a jelly-like substance - mainly pure xylan - and the surface facing the cathode turned a rust-brown colour (presumably with ash components). The treated wood was said to be preserved by the removal of minerals from the wood, sterilised against micro-organisms, and to possess reduced swellability by removal of the xylan. As a side-product of the treatment, the waste products (ash and xylan) were recommended for uses such as fertilisers.

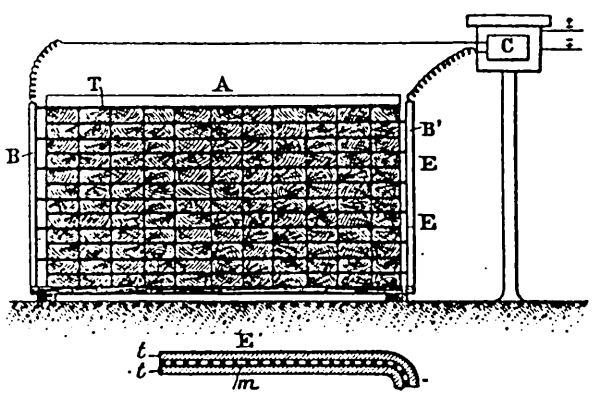
A variety of other early patents used a.c. electricity to impregnate wood with preservatives (Bazin and Hemery, 1865; Oncken, 1891; Belfort, 1897; Guide, 1902; Nodon, 1905, 1913; West, 1903, Alcock & Co. Ltd., 1910). In these, and the d.c. techniques described, large metallic electrodes were generally applied directly onto the wood, or current passed through a bathing electrolyte. The electrode/wood interfaces were usually kept moist to improve electrical conduction and prevent excessive heating. A.c. was often preferred to d.c. fields, to avoid electrolytic damage to the electrodes; or a reversible d.c. field was used instead. In many cases, though, the current probably passed outside the wood, and only heated the preservative and wood, so speeding up the diffusion of ions through the wood. Useful preservative effects may have also resulted from electrode reactions - e.g. release of $Cu^{2+}$ from Cu anodes - although none of the authors commented on this.

### 3.5.2 Electrical Drying

Alcock & Co. Ltd. (1910) dried wood by clamping metal plate electrodes (such as lead) at regular intervals between planks of wood,

and circulated air between the planks to promote moisture loss. Electrical fields of up to 400 V were applied with "low" amperage (probably direct) current for about 3 h, resulting in moisture oozing out from the ends and sides of the timber. Current was passed until the resistance of the wood became too high. Tiemann (1938) reported that this technique was used by Alcock & Co. Ltd. until 1920, but was finally discarded. Nodon (ref. to Dary, 1914) sandwiched layers of moistened jute between copper or zinc-alloy electrode nets and planks of wood (Fig. 3.15). D.c. electricity (5-6 mA $m^{-3}$ wood) was passed, but reversed at regular intervals to minimise electrolytic damage to the electrodes.

Figure 3.15 Electrical Apparatus of Nodon
(Ref. to Dary, 1914)




**Pile of lumber ready for treatment. Below, section of mat-electrode.**

*C*, switch-box; *B*, *B'*, poles connected with alternate mat-electrodes, E; *T*, lumber; *m*, flexible metal web; *t*, *t*, jute cloths.

Voight, Krischer and Schauss (1940) found that passing d.c. electricity through wood could only reduce its total water content to about 60%. The drying process also suffered from a gradient of moisture content and temperature along the wood - the greatest moisture and lowest temperature occurring at the cathode end of the wood. These gradients probably resulted from electro-osmotic water flow towards the cathode, although the authors did not mention this.

### 3.5.3 Electrical Resistance Meters

#### (a) Moisture measurements

The linear relationship between electrical resistance and moisture content of wood from 7 to 30% (section 3.1.1) has been exploited in a variety of resistance meters. These meters are basically d.c. or a.c. resistance bridge circuits with metal probes, which can record the high resistances (MΩ to GΩ) encountered in woods of <30% moisture content.

The resistance measurements are affected by ambient temperature, angle of grain, ion and electrolyte content, decay, tree species, surface moisture on the specimen, weather conditions, and operator handling (James, 1975). Skaar (1964) also reported effects on resistance measurements by polarisation phenomena caused by electrolytic conduction, the voltage used (Evershed effect), electrode geometry, contact resistance, Joule heating, and variations in these factors between different pieces or species of wood. Nevertheless, resistance meters provide a cheap, convenient, and sensitive method of measuring wood moisture content (Skaar, 1964; James, 1975).

#### (b) Decay measurements

Shigo and Shigo (1974) modified a d.c. resistance meter to determine discoloured and decaying wood. A pulsed current was passed through Cu wire probes inserted into holes drilled close together in the tree. By this means it is claimed to detect decay in living trees (Shigo and Shigo, 1974), and in utility poles (McGinnes and Shigo, 1975) before decay is visible on the exposed wood surface.

## 3.6 Effects of Applied Electricity on Living Trees

Potentials applied to excised maple stems can produce a small, transient electro-osmotic flow, and with potentials >45 V a sustained and large flow was induced in young, growing stems. (Fensom, 1962). Since potentials recorded from living trees are only of the order

of mV, electro-osmosis probably plays no signficant role in gross water transport in wood of living trees (Fensom, 1963).

Molitorisz (1966) passed approx. 1.6 mA for 28 d (about 4000 C) through the branches of young citrus trees, and claimed to induce greater "leaf density", some abnormalities in leaf shape, and the abscission of ripe fruits. However, few other experimental details were given.

Applied potentials enhance the uptake of K, Ca, and P in tomato plants, passing 3-30 μA through Ag/Ag Cl electrodes (Black et al., 1971). This stimulation was not proportional to current density, and was interpreted as an effect on metabolically driven ion uptake mechanisms in the cell membranes.

## 3.7 Electrical Currents and Wood Decay

Localised softening of wood often occurs around metal fastenings, particularly in wooden craft used in sea water (Cartwright and Findlay, 1958). This damage probably arises from using dissimilar metals in contact with wood soaked with salt solutions, e.g. NaCl, such that the wood conducts an electric current by migration of $Na^+$ and $Cl^-$. Caustic soda and metal formed by electrolysis accumulate in the wood around the metal that acts as a cathode, and chloride ions collect at the anode.

Passing current through metal fixtures in contact with wet, CCA-treated wood causes heavy corrosion of the anode and cathode where they are in contact with the wood (Gunnarsson, 1969). However, far less cathodic corrosion occurs when using wet, untreated wood, and this difference may arise from preservative $Cu^{2+}$ ions migrating to, and reacting with, the cathode.

An electric current may kill fungi already present in wood. Hattori and Tamura (1939) exposed cultures of *Poria vaporaria*, *Polystictus sanguineus* and *Schizophyllum commune* growing on agar and on wood to d.c. and a.c. electricity. D.c. was more effective than a.c. in checking growth of the fungi, and in the case of *P. sanguineus* led to leakage of cell contents.

# CHAPTER 4

# OBJECTIVES

## 4.1 Protocol

The germ of the project was originated by I.S. Stalker over 10 years ago (Stalker, personal communication). Stalker thought that blocks of green wood could be electro-osmotically dried using applied d.c. potentials, and that this might be of commercial value. Unknown to him, similar experiments performed long ago had little lasting commercial success (section 3.5.2).

Stalker placed flat electrodes onto the wood surface, passed current, and found that water was removed from the wood. However, after an (undetermined) amount of moisture had been removed, the water began passing back into the wood. This was attributed to an osmotic effect resulting from the rising concentrations of ions in the wood as its moisture content decreased.

Stalker next studied ion migration in wood using a sheet-metal Cu anode and an unspecified cathode in direct contact with fresh or pre-frozen sapwood of *Pinus sylvestris*. $Cu^{2+}$ ions released from the anode passed into and through the wood blocks (measuring approx. 20 x 20 x 20 mm). The migration of $Cu^{2+}$ through the wood was clearly visible on the surface of the blocks as a distinct boundary moving towards the cathode (Stalker, personal communication). Unfortunately no specimens or photographs of these experiments exist. Stalker proposed further experiments, but pressure of other work prevented him carrying these out.

## 4.2 Aims

Previous work on the effect of applied d.c. fields on wood has all been unsatisfactory in various respects. The object of the present project was to undertake a better designed and more systematic investigation. One of the principal aims was to identify all the endogenous ions in wood that migrate in an electric field, and to measure their contributions quantitatively. It was also important to measure the

allied phenomenon of water flow - electro-osmosis - in the same wood samples. Both ion migration and electro-osmosis were related to Joule heating and electrical resistance of the wood. Following on from these experiments it was planned to study the migration through such samples of exogenous (foreign) ions like $Cu^{2+}$. Thus, it was hoped to better understand the mechanism of ionic conduction through wood. The electrical impregnation of wood with ion species such as $Cu^{2+}$ also offers potential commercial applications in timber preservation. Because of time limitations, it was decided to restrict the research to green sapwood of *Pinus sylvestris*, and to place most emphasis on studying ion migration in the longitudinal direction.

### 4.2.1 Literature

The only review on d.c. electrical conduction in wood published in the past 60 years has been Lin's 1967 paper, which although extensive was by no means comprehensive. Thus, a more thorough and critical survey of relevant literature was urgently needed to update and extend Lin's review article, not only on conductance but also on diffusion and other electrochemical research carried out with wood.

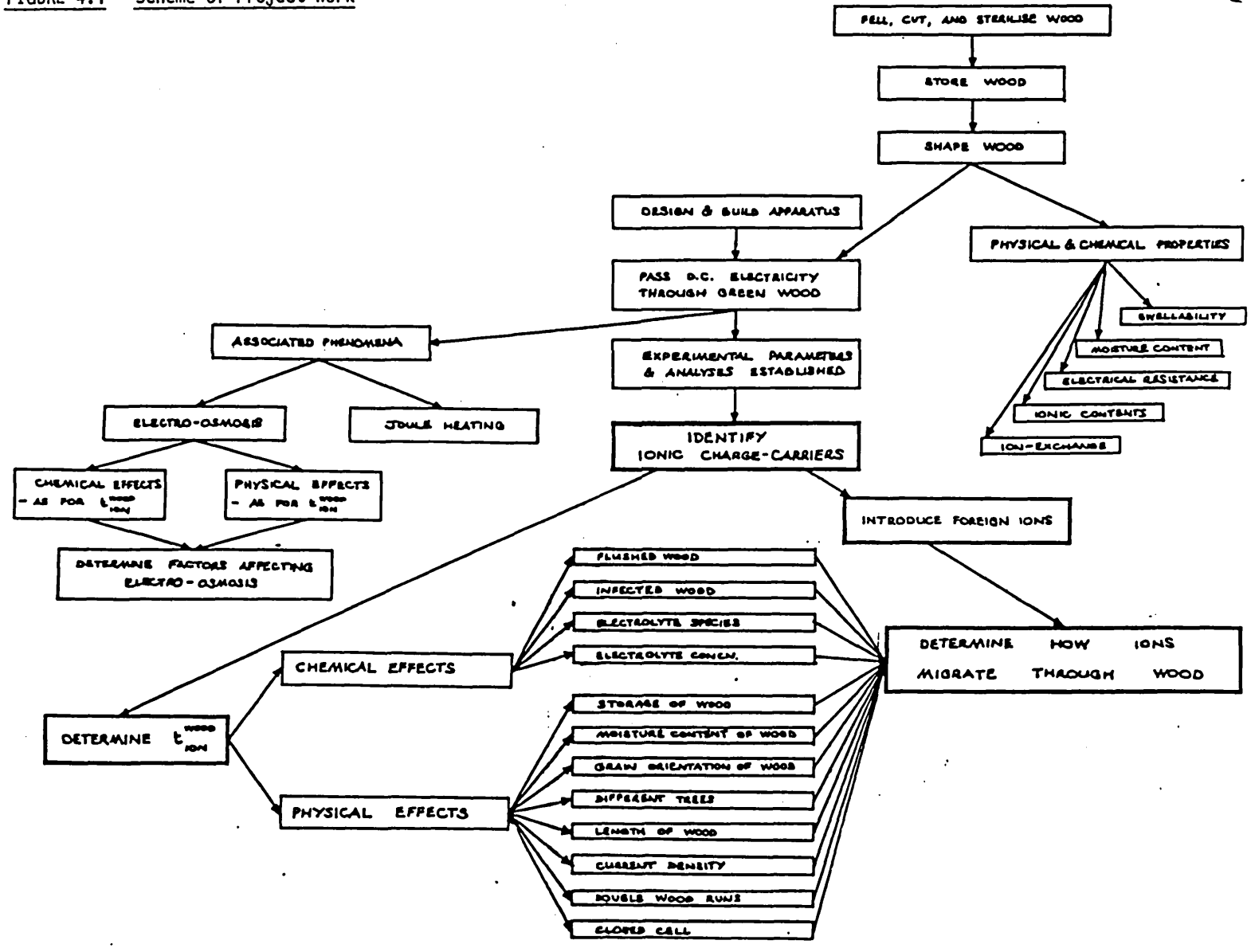
### 4.2.2 Experimental aspects

A new cell was designed in which a block of wood was tightly held between 2 electrode compartments. These compartments contained electrolyte solutions of the experimenter's choice, as well as the cathode and anode, respectively. The electrode/solution and solution/wood interfaces were therefore physically well separated to avoid interaction between them. Cations migrating out of the wood into the cathode compartment could be analysed in the catholyte solution, and likewise anions migrating into the anode compartment could be analysed in the anolyte. To obtain quantitative measures of transport, constant currents (rather than constant voltages as in previous work) were applied for known periods of time. Furthermore, each electrode compartment was fitted with a horizontal capillary at the same level above the work bench. This prevented differences of liquid levels developing between the 2 sides of the cell, and subsequent hydrostatic flow of

solution through the wood. It also allowed easy measurement of the electro-osmotic water flow through the sample. Foreign ion impregnation could be studied simply by filling one of the electrode compartments with the appropriate solution (e.g. $CuSO_4$ in the anolyte). In a few later experiments a modified cell was tried containing two wood samples in series, separated by a solution-filled bridge which could also be analysed (a 'double' cell).

The samples of wood were carefully handled and stored to minimise contamination and replication of experiments was carried out where possible. The general scheme of study is illustrated diagrammatically in Fig. 4.1.

FIGURE 4.1 Scheme of Project Work



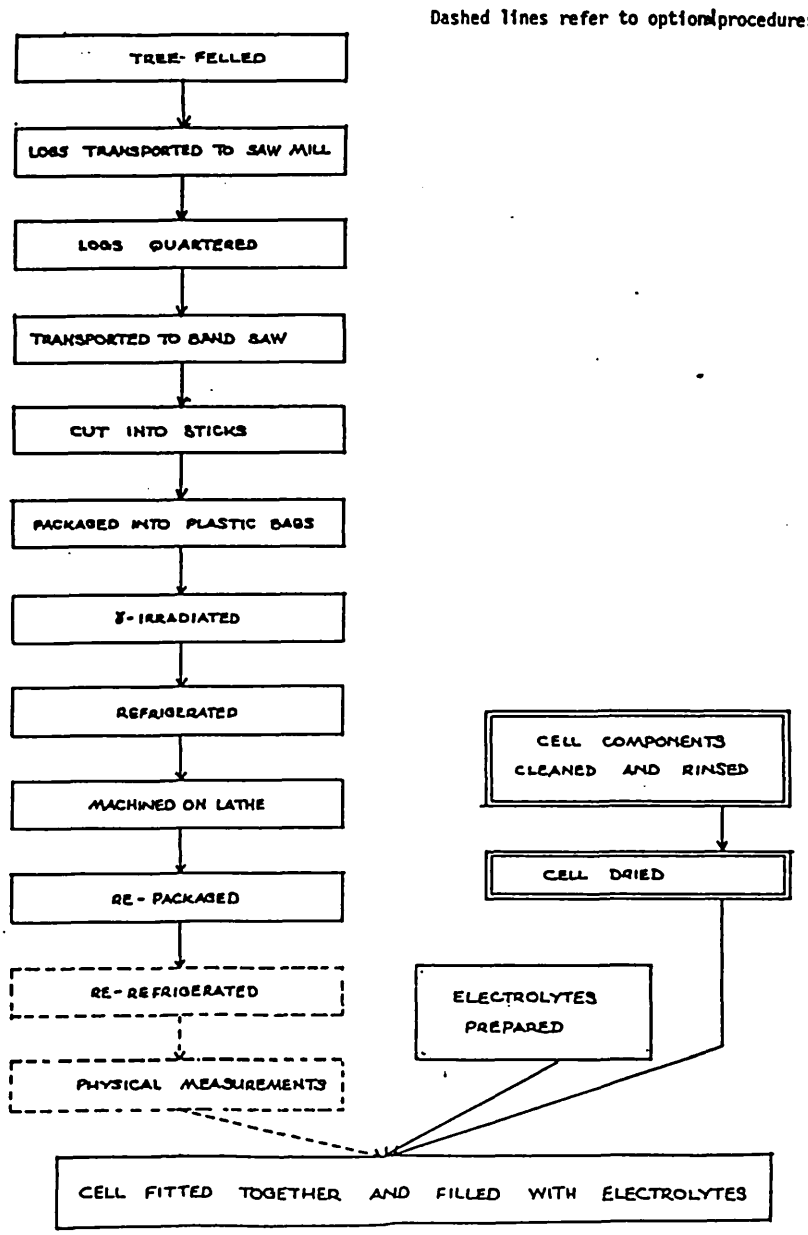
# CHAPTER 5

# MATERIALS & METHODS

## 5.1 Wood

The research required a continuous supply of healthy, straight-grained, green (i.e. unseasoned), uncontaminated wood. In addition, the timber had to be felled, shaped and stored without drying or contaminating the sample. Each wood sample then had to be machined to critical dimensions before being fitted into the electrical apparatus. The overall preparation of the wood is summarised in Figure 5.1.

FIGURE 5.1 Overall Preparation of Wood Prior to Electrical Runs



### 5.1.1 Selection of trees

Healthy Scots pine ( *Pinus sylvestris* L.) trees were selected from a site at Paddock Hurst, Whitely Hill, East Sussex. Trees were about 60-70 years old, growing in a well-managed plantation which had been thinned out and brashed (i.e. lower twigs and branches removed) so as to obtain high quality timber. The soil at Paddock Hurst is described as Hastings Bed, on a bedrock of soft sandstone with pockets of clay, and the plantation floor was covered in a thick layer of pine needles; the pH of the soil was 6 (N.P.Skinner, personal communication).

Four trees in all were used from the Paddock Hurst estate, and an additional supply of Scots pine timber was later used from a timber yard at Rowsant Sawmills, Copthorne, West Sussex. The locations and dates of felling of all the timber are given in Table 5.1 .

TABLE 5.1 Location and Felling Dates of Wood Used

| Tree Number | Location | Date of Felling | γ-irradiation | Storage |
|---|---|---|---|---|
| I | Paddock Hurst | 31/ 3/78 | x | Frozen or refrigerated |
| II | Paddock Hurst | 8/12/78 | ✓ | Refrigerated |
| III | Paddock Hurst | 11/ 7/79 | ✓ | Refrigerated |
| IV | Paddock Hurst | 22/ 1/80 | ✓ | Refrigerated |
| V | Copthorne | 7/11/80 | x | Refrigerated |

Key

x No γ-irradiation

✓ γ-irradiation performed

The following criteria were used in choosing suitable trees:

(1) Healthy, as indicated by:
   (a) reddish coloured bark,
   (b) there was minimal growth of epiphytes (such as mosses, liverworts and lichens),
   (c) there was no fungal growth on the bark,
   (d) bark was shedding half-way up the trunk.

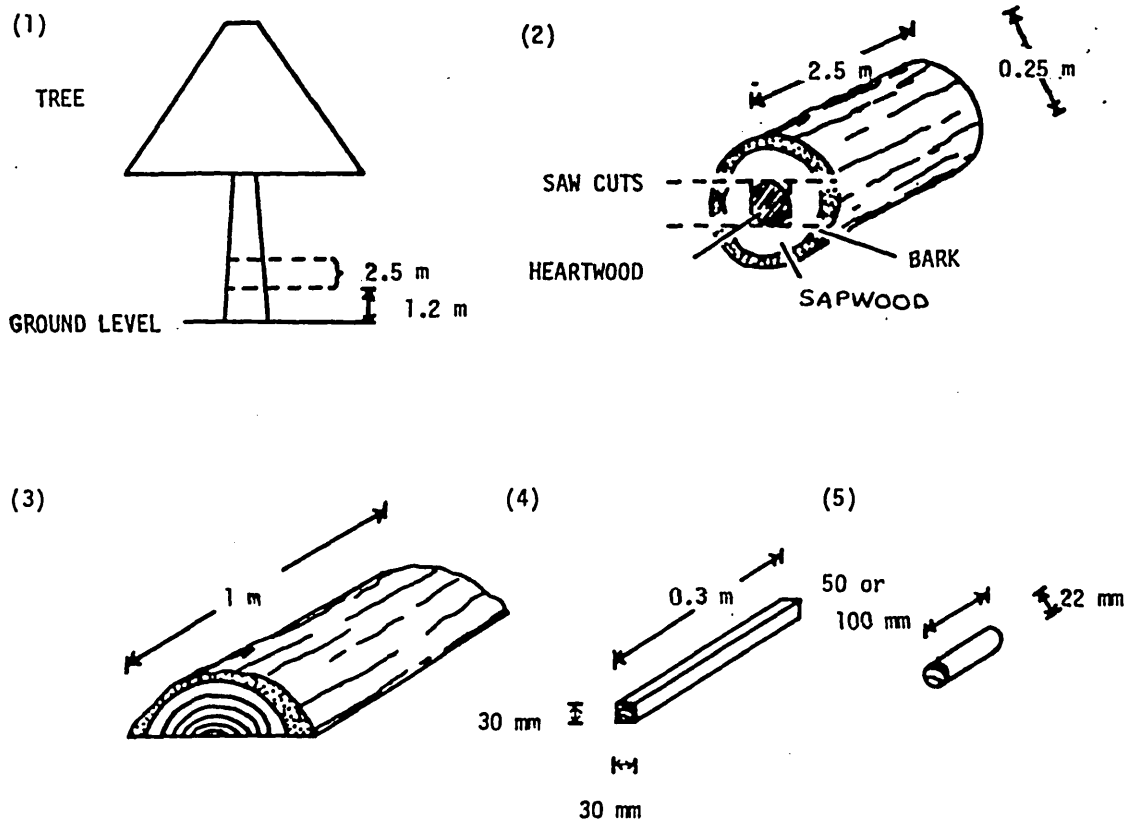
(2) Straight grain, as selected by:
   (a) trees with few sidebranches on the lower 50 m of trunk, so as to minimise the number of knots in the wood,
   (b) avoiding trees without perpendicular and tapered trunks, to eliminate distorted grain.

(3) Adequate amounts of softwood were needed, and trees with a girth of over 260 cm were chosen. A test sample of wood was extracted from the tree using a timber test borer (manufactured by 'Matteson' of Sweden). The amount of sapwood was determined by staining for heartwood using $\sigma$-anisidine solution (stains heartwood deep red, sapwood remains pale yellow).

### 5.1.2 Felling & cutting procedures

Trees were felled using a chain saw 1.2 m up from the ground level, and sawn into approximately 2.5 m long logs (Fig. 5.2).

FIGURE 5.2 Scheme of Felling and Cutting of Wood



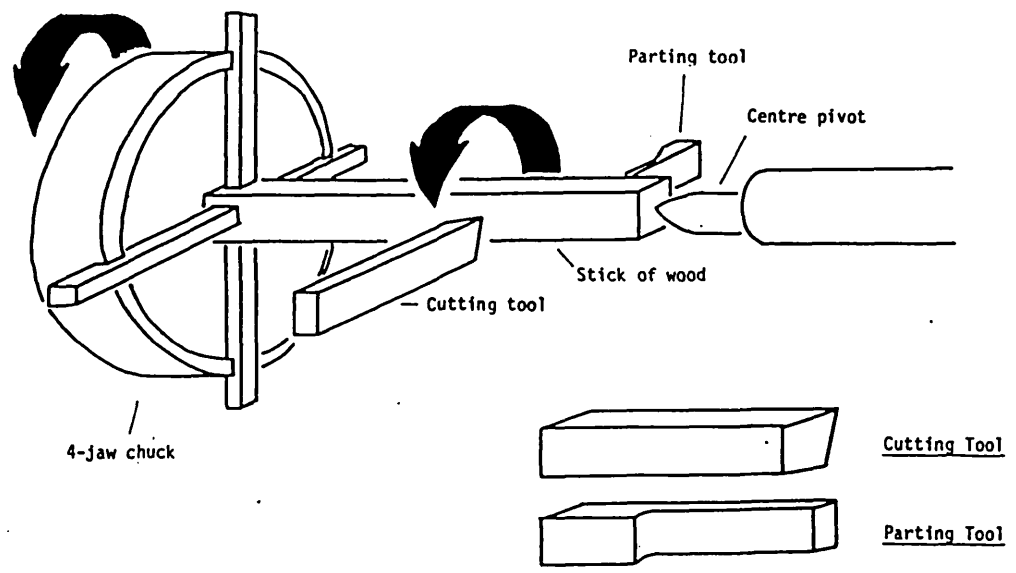
Felled logs were transported to a saw mill and cut down with a circular or band saw into quarters approx. 1 m long. Each quarter contained the minimum of heartwood, maximum of sapwood and also bark; the central core of heartwood was discarded.

Quartered logs were transported to a smaller saw and cut down further into 30 x 30 x 300 mm sticks. Bark, heartwood, knots, and any other visible defects were discarded. The remaining straight-grained sapwood sticks were packed in a random order (to avoid using contiguous samples of wood from any one part of a log) into thick polythene bags, stretching the polythene over the sticks as tightly as possible to prevent water evaporating out of the wood. The bags were then sealed using electrical tape or heat-sealing treatment (a Bunsen burner flame and asbestos board were used to sandwich the open flaps of the bags shut).

The sticks of wood were turned, when required, into cylinders $22 \pm 0.2$ mm diameter x 50 or 100 mm length using a metal-working lathe. A four-jaw chuck was used to secure the stick into place, and the wood cut at a fast (1480 revs $min^{-1}$) speed with a clean metal cutting tool (Fig. 5.3). A clean micrometer was used to check the diameter of the wood cylinder.

FIGURE 5.3 Machining of Wood Sticks on Lathe

(Arrows indicate direction of motion)



The 22 mm diameter sticks of wood were coated with a rubber emulsion, Mobilcer R (kindly supplied free of charge by Mobil Chemical Incorp. Ltd., London SW3). The emulsion was applied as a thin, even coat along the entire length of the wood using a paint brush which had previously been soaked and stored in distilled water, before being dried on clean tissue paper. As the emulsion takes a few hours to set firm, it tended to run to the underside of the cylindrical stick of wood. This problem was overcome by turning the wood in the lathe at a slow speed (280 revs $min^{-1}$), which not only helped give an even coat and remove excess emulsion, but also accelerated the drying process. To prevent moisture loss from the wood itself, this 'spin-dry' procedure was only used for approx. 15 min, and the emulsion then allowed to dry with the sample held stationary in the lathe for 2-3 h. Once the Mobilcer R had set firm (the emulsion turning from a milky-white liquid to an almost colourless solid), the stick of wood was then cut into required lengths with a parting tool (Fig. 5.3) at a slow speed (120 revs $min^{-1}$). Cut and coated cylinders of wood were re-packed into polythene bags and sealed with electrical tape.

### 5.1.3 Prevention of contamination of wood

Felling, sawing and packaging of the wood was carried out in less than 72 h in order to reduce the chances of colonisation or attack by micro-organisms and insects, and leaching of extractives from the wood by rainwater. With one exception, wood was felled during cold ($<8^{o}C$) weather to help reduce infection. Tree III, however, was felled during hot weather (up to $25^{o}C$), which resulted in more rapid contamination in later storage (cf. section 6.1).

The method of storing fresh wood without contamination was chosen by eliminating methods with the most undesirable side-effects, as shown in Table 5.2 .

TABLE 5.2 Methods of Preserving Stored Wood, Before Electrical Treatment

| Method | Description | Undesirable effects on: | | | | |
|---|---|---|---|---|---|---|
| | | Specific fungi | Moisture content | Ion content | Permeability | Organic components |
| Refrigeration | Sealed bags of wood stored at 7°C. | ✓ | x | x | x | x |
| Deep freeze | Sealed bags of wood stored at 0°C. | x | x | x | ? | x |
| Dry & re-wet | Wood dried to 12% moisture content, and re-wetted prior to experiment. | x | ✓ | ✓ | ✓ | x |
| $\gamma$-irradiation | Sealed bags irradiated before further preservative treatment. | x | x | ? | ? | ? |
| Volatile preservative | Naked wood stored in sealed tank over volatile organic preservative + water, e.g. propylene oxide. | x | ? | ? | ? | ✓ |
| Methanol | Wood sprayed and sealed into bags with small amount of methanol. | x | ✓ | ✓ | x | ✓ |
| Inorganic preservative | Wood sprayed and sealed into bags with small amount of inorganic preservative, e.g. Cu, Cr & As. | x | ✓ | ✓ | ? | x |

Key

✓ Undesirable effect.

x No undesirable effect.

? Effect unknown.

## 5.2 Electrical cell

Previous workers studying ion migration or electrokinetics in wood used a variety of cells (sections 3.2, 3.5.1). All of these apparatuses suffered from one or more interfering effects, including:

unequal hydrostatic pressure across the wood; exposure of electrolytes to the atmosphere (leading to evaporation and contamination); leakage of electrolyte solution onto the surface of the wood (leading to short-circuiting of the current); excessive heating of the wood; disintegration of the electrodes; possible reactions between products of the electrode reaction and the wood; and possibly reactions between ions in the electrolytes and the cell itself (such as ion-exchange).

In this project the cell was designed to overcome all of the above problems, and - for the first time - to combine ion migration with electro-osmotic studies. Constant direct electric currents had to be passed through the cylinders of fresh green wood, by applying a potential difference across electrolyte solutions bathing both ends of the wood. In this way transference numbers of ions migrating into the electrolytes could be determined, and processes at the wood/solution and electrode/solution interfaces could be clearly distinguished.

5.2.1 Cell Design

Figures 5.4 and 5.5 and Plate 1 show a typical cell design. The following features were important components of the cell:

(a) Sovirel screw cap attachments (40 mm outer diameter, cat. no. 4701-43) with Sovirel silicon rubber O-rings (20 mm internal diameter, cat. no. 4701-26) stripped of their phenoplast covers were used to fit the wood into the glass electrode compartments (made from Sovirel screw joint glass cylinders 138 mm long x 26 mm internal diameter, cat. no. 4701-42). This unique part of the cell was crucial to making a watertight seal between the wood and the glass cell, without contaminating the wood, and it allowed repeated re-use of the cell.

(b) Horizontal orientation of the whole cell. In this way equal hydrostatic pressure was maintained across the wood.

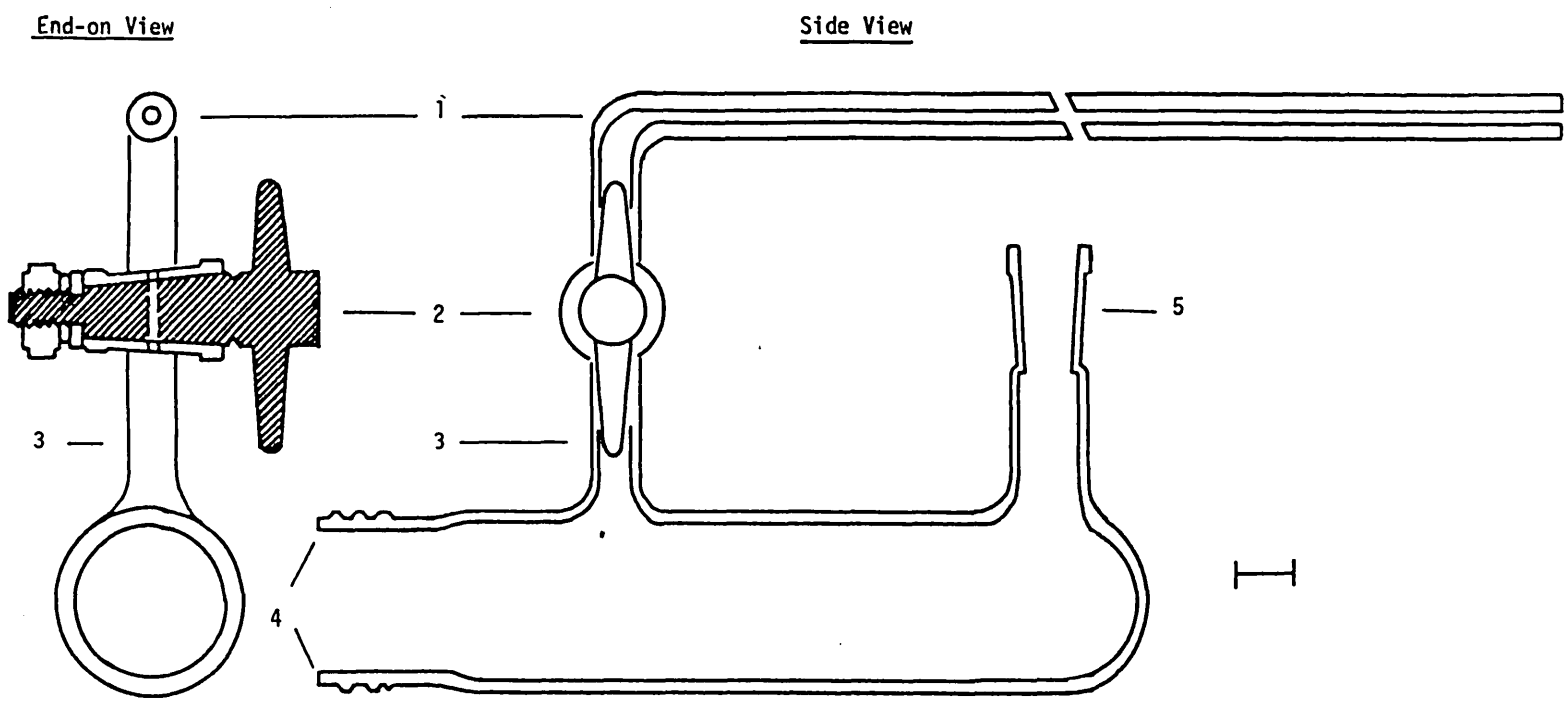
(c) Open-ended horizontal capillary tubes of known internal bore attached to each electrode compartment. This arrangement ensured equal hydrostatic pressure across the wood throughout an electrical run, and allowed changes in electrolyte volumes to be measured.

(d) Electrode ports (made from Quickfit 10/19 glass sockets) were provided for inserting electrodes at a finite distance from the wood, and also for filling and emptying the cell of electrolyte solution.

(e) Two-way taps attached to vertical tubes sealed to each electrode compartment facilitated the filling and emptying of the cell. 'Interflon' taps (made of Teflon keys and plain glass barrels, manufactured by George Springham Ltd., Temple Fields, Harlow, Essex) were employed to obviate the use of lubricant which might otherwise have spread to the surface of the electrodes or the wood.

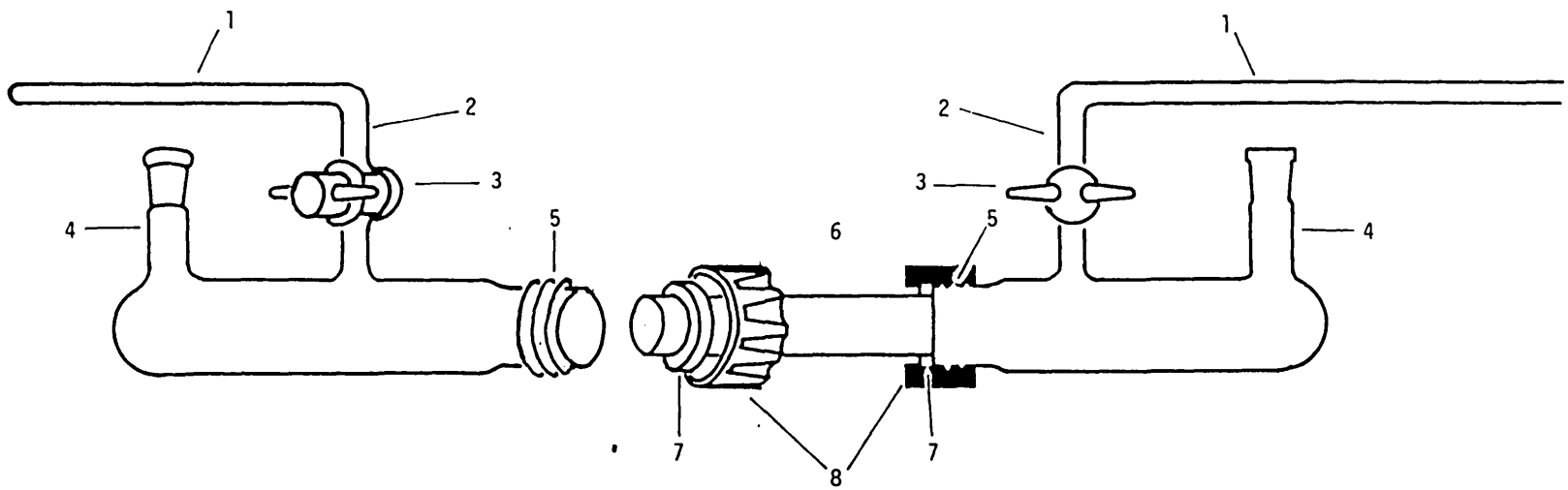
(f) Glass components were made of borosilicate (Pyrex) glass to minimise ion-leaching and cation-exchange with the electrolyte solutions.

FIGURE 5.4 Basic Electrical Cell: Electrode Compartment



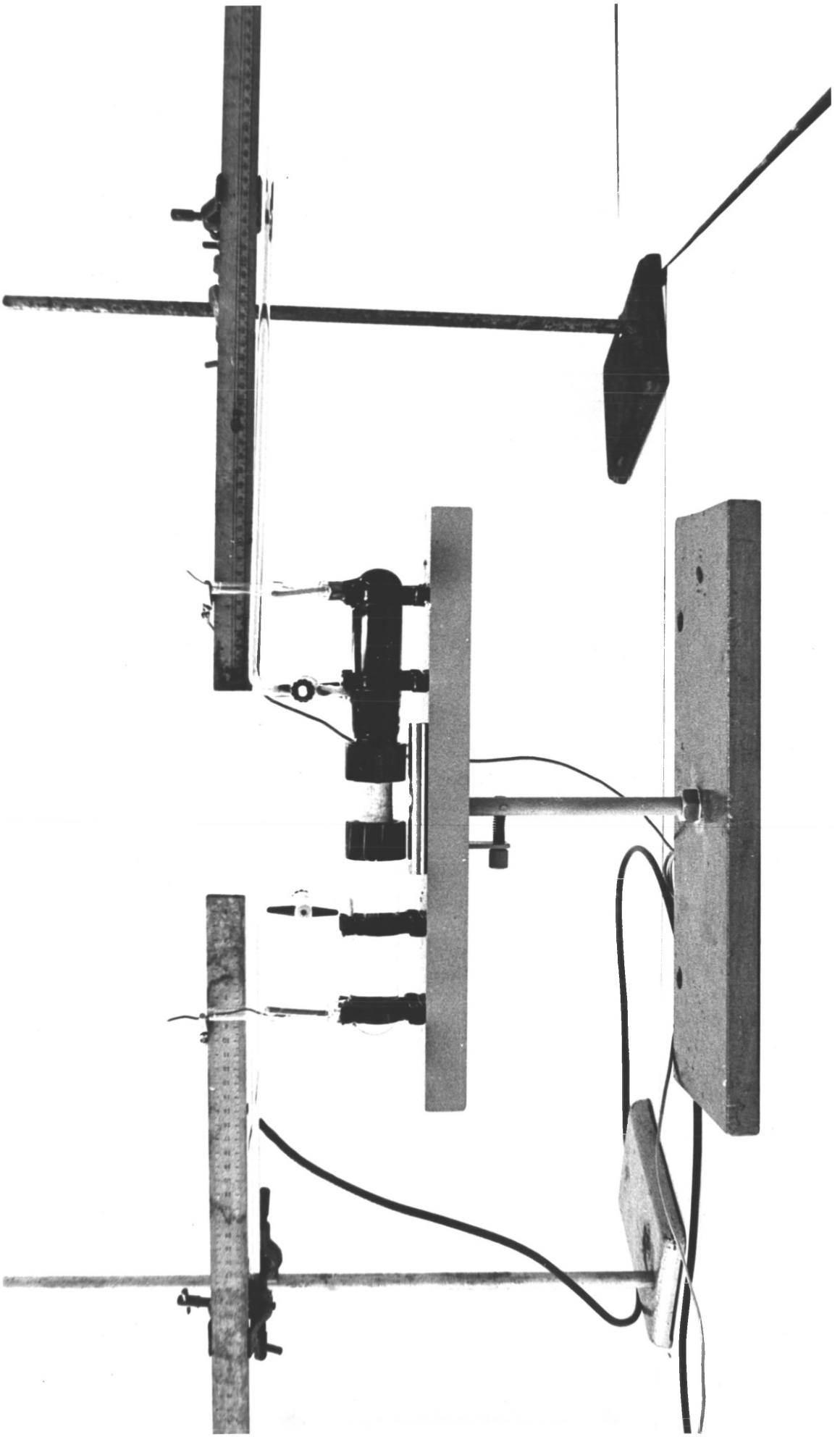

Key: (1) Capillary tube; (2) 2-way 'Interflon' tap (3) Vertical tube; (4) Screw-threaded joint; (5) Ground glass joint of electrode port. Bar represents 10 mm.

FIGURE 5.5 Basic Electrical Cell: Wood Fitted in Electrode Compartments (shown in exploded and cut-away views)




Key: (1) Capillary; (2) Vertical tube; (3) 2-way 'Interflon' tap; (4) Electrode port; (5) Screw-threaded joint; (6) Wood; (7) Silicon rubber O-ring; (8) Phenoplast cap.

PLATE 1 THE COMPLETE ELECTRICAL CELL



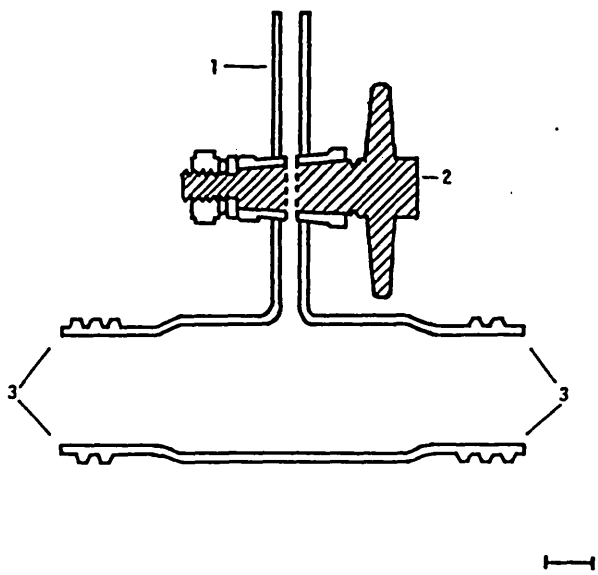
## 5.2.2 Modified cells

A range of cell modifications was used to suit particular electrical runs (Table 5.3 ). In addition, for electrical runs using two pieces of wood in series (referred to as ' double-wood runs') a middle compartment was added to the cell (Fig. 5.6).

TABLE 5.3 Modifications to Basic Cell Design

| Cell type | Modifications | Advantages |
|---|---|---|
| Mark I | 3-way tap in vertical tube, feeding capillary and extended vertical tube. | Withdrawal or filling of electrolyte solution through the extended vertical tube. |
| Mark II | Larger (80 $cm^3$) electrode compartment. | Larger volume of electrolyte solution for analysis of migrated ions. |
| Mark III | Extended (ca. 1 m long) capillary tube. | Measured larger changes in electrolyte volume during an electrical run. |
| Mark IV | Additional capillary (ca. 0.5 m long) fitted onto capillary of electrode compartment using plastic tube sleeving. | Ibid., and capillary less prone to breakage. |
| Mark V | Wider bore vertical tube (7 mm internal bore) and tap. | Vertical tube and capillary less prone to breakage. |

FIGURE 5.6 Middle Compartment, Used in 'Double-wood Runs'

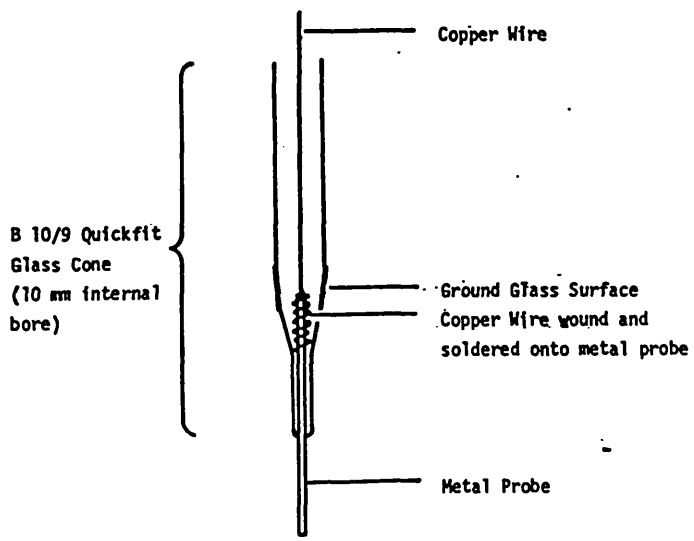



Key: (1) Vertical tube; (2) 2-way 'Interflon' tap;
(3) Screw-threaded joint. Bar represents 10 mm.

5.2.3 Electrodes

A variety of different electrodes was used according to the specific requirements of each electrical run. However, all the electrodes were designed to be placed easily in and out of the electrode compartments. Where volume changes of electrolytes were being measured, non-gassing electrodes were used. The basic electrode design is shown in Fig. 5.7, in which the glass holder was made from a Quickfit 10/19 cone. Each type of electrode will be described individually.

FIGURE 5.7 Basic Electrode Design




(i) Copper electrode. Approx. 50 mm of 1 mm diameter Specpure copper wire (Johnson Matthey, Reading, Berks.) was wound into a coil, and twisted and soldered onto ordinary copper wire. The coil was sealed into the glass cone with a small amount of Araldite glue.

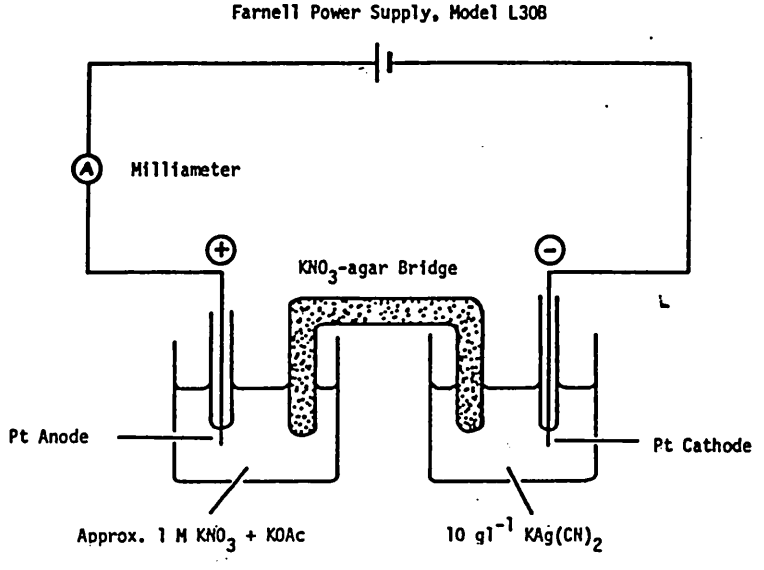
(ii) Silver electrode. In preliminary experiments silver electrodes, using Specpure silver wire, were made as for copper electrodes.

(iii) Platinum electrodes. About 20 mm of 100 $\mu$m thick platinum wire was twisted and soldered onto ordinary electrical copper wire, and the platinum fused into the Pyrex glass cone by careful heating. No copper protruded out of the glass into the solution.

(iv) Platinum/silver electrode. Platinum electrodes were soaked in concentrated nitric acid to remove surface deposits. After being rinsed well with distilled water, the electrodes were cathodised in $KAg(CN)_2$ solution (10 $gl^{-1}$) (Fig. 5.8) at a current of $\leq$2 mA to produce a smooth silver deposit. The plating was carried out in a fume cupboard. Acetate was added to the anolyte vessel (Fig. 5.8) to prevent the $H^+$ ions formed at the anode from migrating into the cyanide solution to produce HCN.

From the current I (in A) and the duration of plating (t in sec), the number of coulombs, C, passed was calculated from C = It. This information was needed when a chloride coat was subsequently applied, since not more than about half the silver can be chloridised anodically.

FIGURE 5.8 Silver-plating of Platinum Electrode

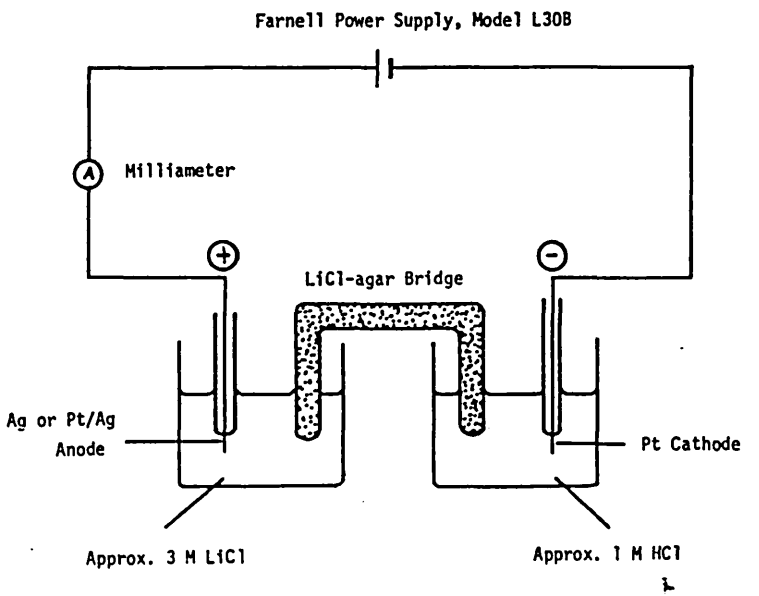



(v) Platinum/silver/silver chloride electrode. Previously used Pt/Ag/AgCl electrodes were first stripped of their old AgCl coating by dissolving it in sodium thiosulphate solution.

Before plating, electrodes were well washed with methanol (to remove grease) followed by distilled water. The silver was anodised in a concentrated chloride solution, such as 3 M LiCl. A platinum cathode was placed in a separate beaker connected by a chloride agar bridge (Fig. 5.9) to avoid contamination by $OH^-$ formed at the cathode. A current of 3 mA was passed using an L30B Farnell stabilised power source

for a known length of time. Not more than 75% of the total number of coulombs used in the chloridisation was passed in subsequent electrical run(s) before re-chloridising the electrode. Alternatively a clean Ag electrode was dipped into molten AgCl, heated in a crucible. On cooling, the silver chloride crystallised on the exposed silver. Electrodes made in this way were generally less satisfactory than those made by electroplating, cf. section 6.2.2 .

FIGURE 5.9 Chloridisation of an Ag or Pt/Ag Electrode

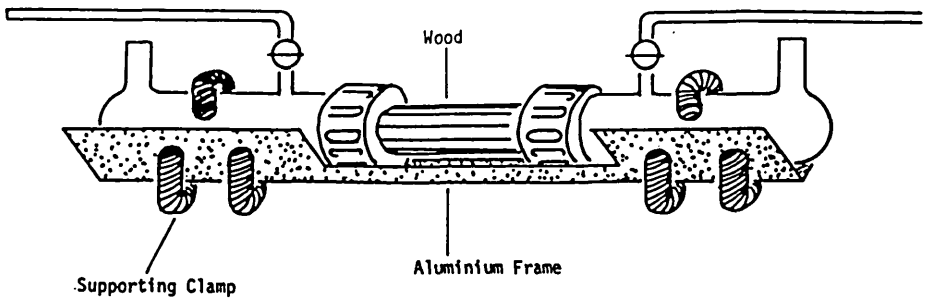



## 5.2.4 Supporting jigs for cell

Since the cells could not be satisfactorily held horizontally by clamping directly onto retort stands, two types of jig were developed for their support during electrical runs.

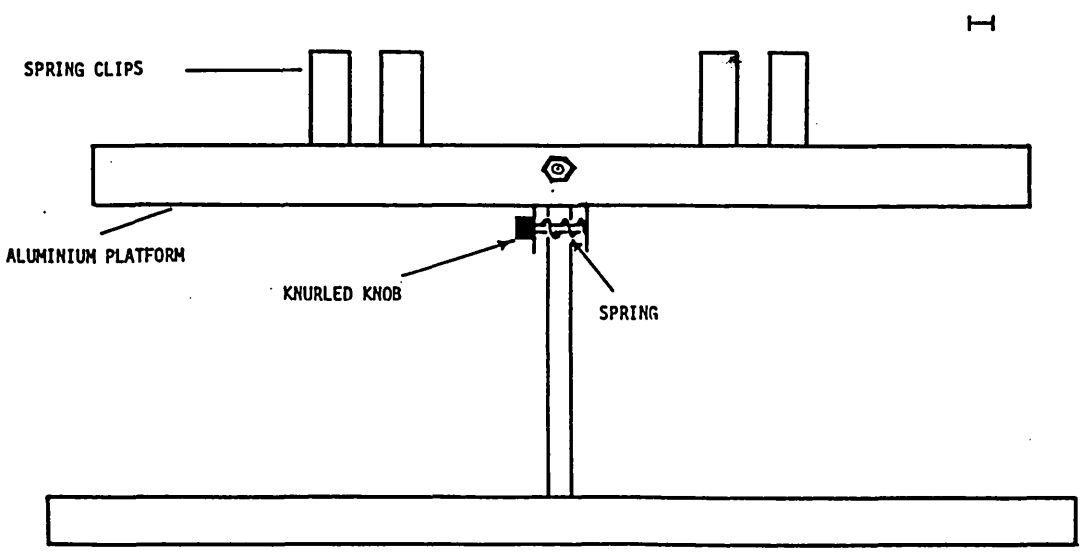
(a) Aluminium frame jig. Cells were held in an aluminium frame, which in turn was held by clamps attached to retort stands (Fig. 5.10). Spirit levels resting on top of and below the cell were used to adjust the jig to horizontal. However, this arrangement proved awkward, and jig (b) was later developed.

FIGURE 5.10 Aluminium Frame Jig, for Support of Electrical Cell




(b) Platform jig. An aluminium platform with adjustable horizontal hold was fixed onto a cast iron base, and strong spring clips screwed onto the platform (Fig. 5.11, Plate 1). The cell was held in these clips. The platform was made horizontal by adjusting the knurled knob and using a spirit level. Several settings in the platform allowed the spring clips to be moved into a variety of positions so that cells of different lengths could be accommodated. This jig design proved fairly satisfactory, although problems were encountered with mounting and removing the cells from their clips (cf. section 6.2.1)

FIGURE 5.11 Platform Jig, for Support of Electrical Cell



## 5.3 Electrical circuitry

A stable current was obtained using a constant current generator (Fig. 5.12) built in the Chemistry Department electrical workshop..The maximum output was 23 mA with interval settings of 0.05 mA. The generator was connected to 100 Ω or 1000 Ω standard resistors in series with the cell. A digital multimeter (Solartron 7045) was used in the voltmeter mode, and attached to the magenta terminals of the resistor. From the voltage, V, the current, I, was calculated by Ohm's law. The leads to the electrode terminals were attached by crocodile clips. The complete circuit - including cell - is shown in Plate 2.

Figure 5.12 Electric Circuitry of Constant Current Generator

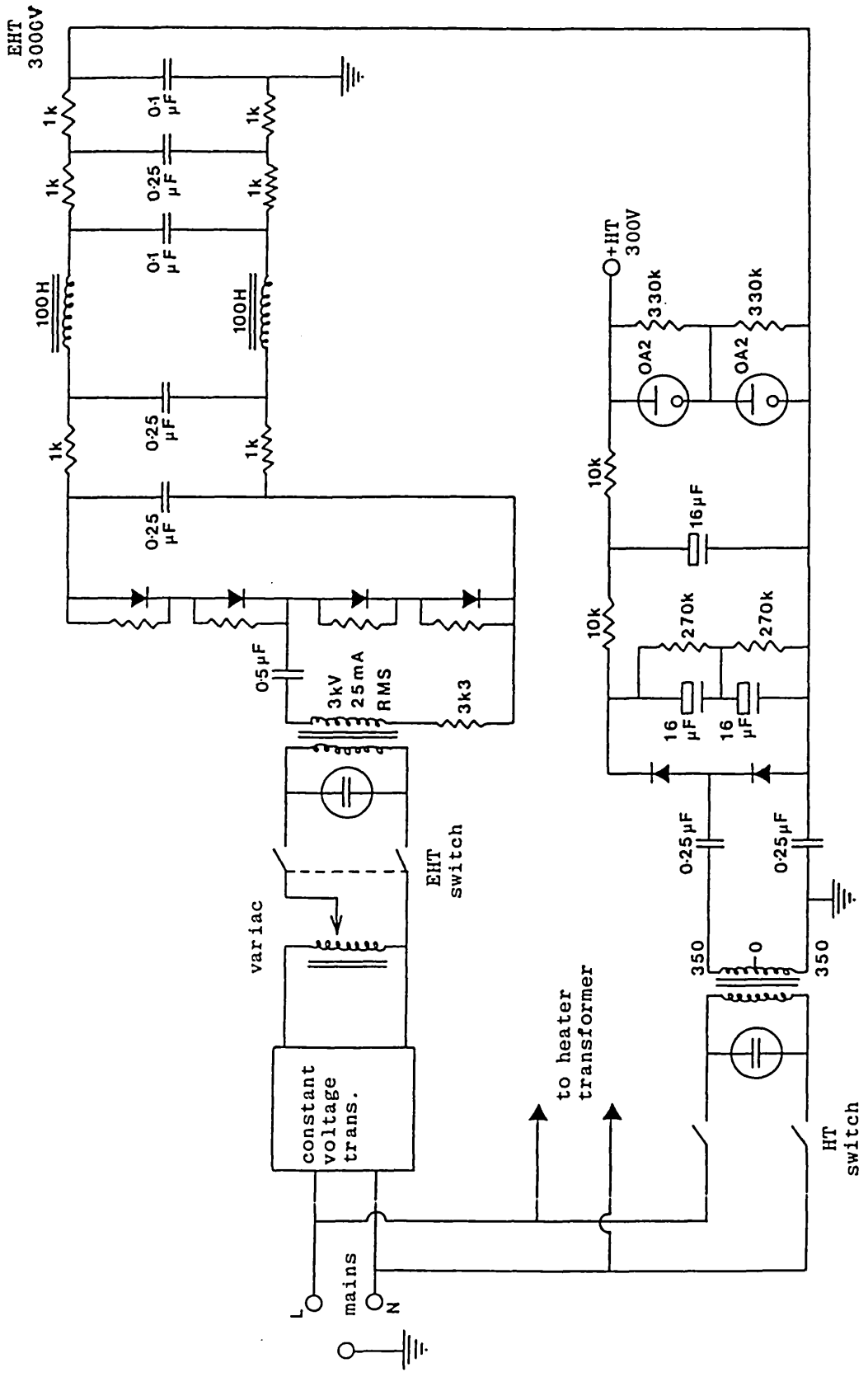
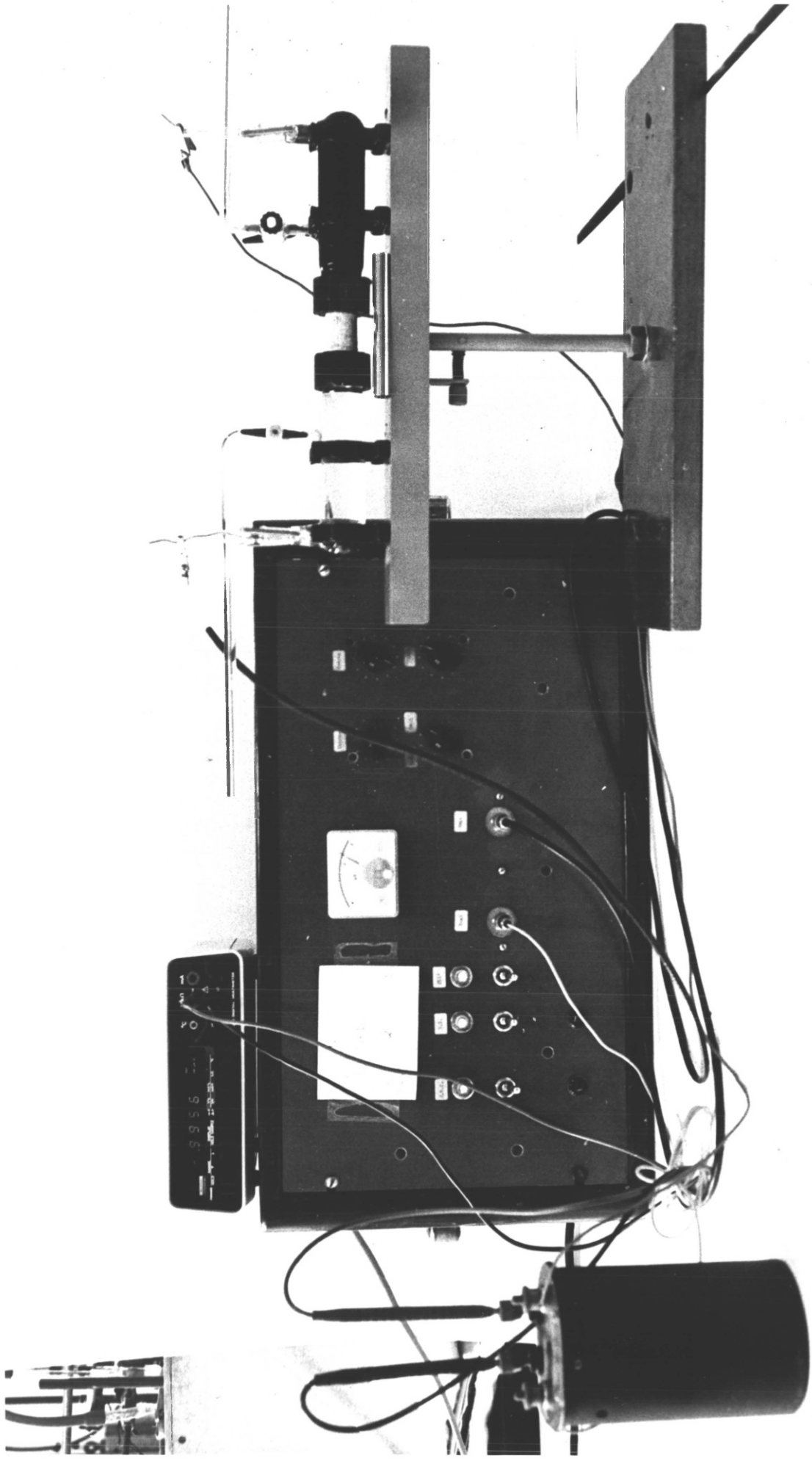


PLATE 2 ELECTRICAL APPARATUS AND CELL



## 5.4 Flushing techniques

A variety of techniques was used for 'flushing' samples of wood with various eluents.

### 5.4.1 Modified cell apparatus

A cell was assembled as for an electrical run, excluding the electrodes. A Pyrex glass tube (500 mm long x 6 mm internal bore) was fitted to a glass cone with a plastic sleeve inserted into the electrode port of one half cell, and supported by a retort stand and clamp. The tap of this half cell was closed, and eluent poured into the attached vertical tube. The eluted solution was collected in the opposite half cell.

### 5.4.2 Vertically-orientated apparatus

Open-ended Sovirel cylinders (cf. section 5.2.1) were fitted onto both ends of a wood sample using screw caps and silicon rubber O-rings. The complete apparatus was held vertically with retort stands and clamps, and eluent poured into the top tube. Eluted solution was then collected from the bottom tube in a measuring cylinder. In preliminary experiments the top tube was extended to a length of 1 m by fusing an additional piece of Pyrex glass tubing onto the original Sovirel cylinder. However, the hydrostatic pressure created when the modified cylinder was even partially filled forced solution past the sealing O-rings.

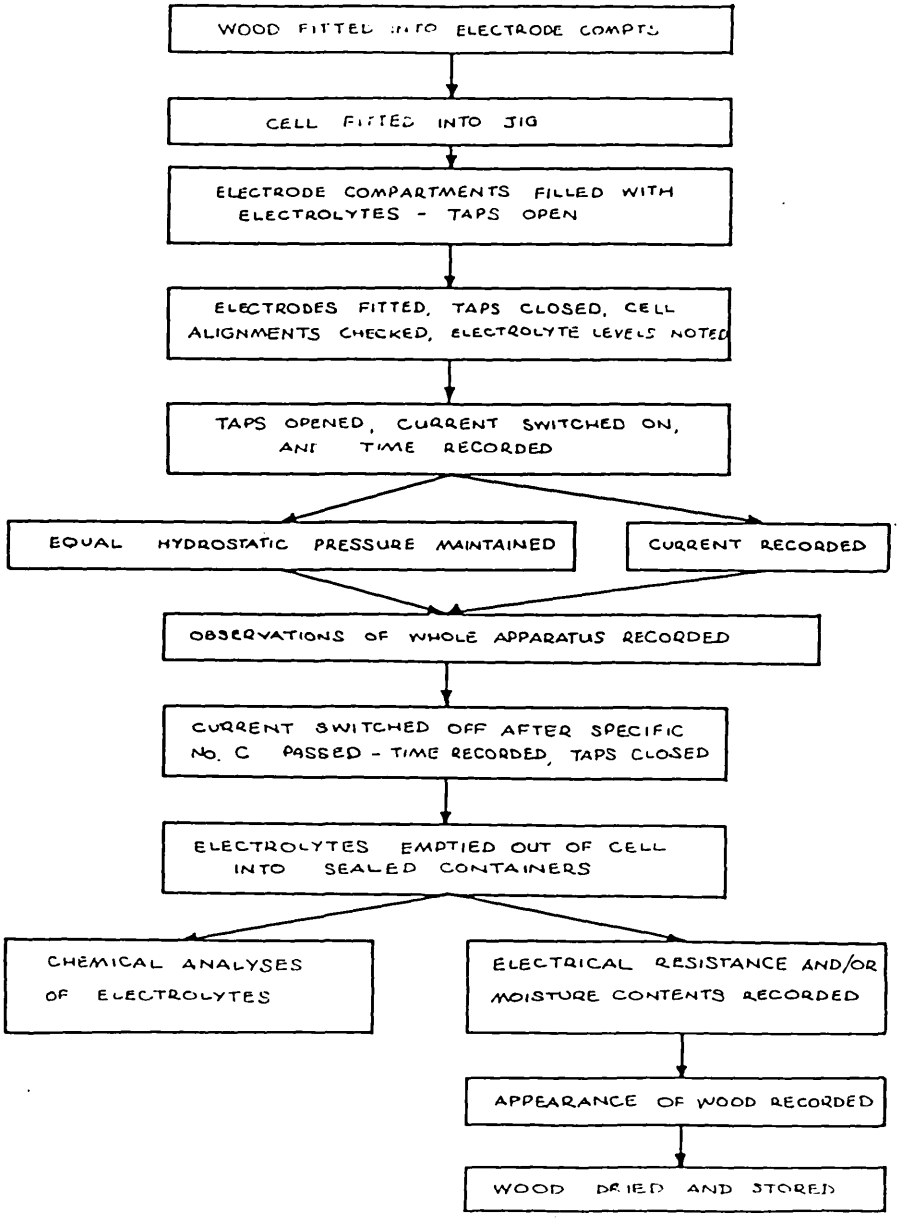
## 5.5 Electrolytes and standards

All the electrolytes used in flushings, electrical runs, and the standard solutions used in subsequent ion analyses were prepared from BDH 'AnalaR' grade compounds. Solutions were stored in plastic stoppered borosilicate volumetric flasks, which were soaked in distilled water when not in regular use. Where possible, flasks were reserved for specific ions at particular concentrations. This minimised leaching, ion-exchange, and contamination problems.

## 5.6 Experimental procedure

The general procedure for preparing and carrying out each electrical run is summarised in Fig. 5.13, and is now described step by step.

Figure 5.13 General Procedure for Preparing and Performing Electrical Runs



(i) The electrode compartments were stoppered and filled with chromic acid for 5-15 min, to remove surface contaminants. Taps and electrode ports were washed separately in chromic acid before the whole compartment was thoroughly washed in distilled water 6 times, and then soaked overnight in distilled water. The compartment was emptied and re-washed in distilled water another 6 times the following day, to leach out any acid which may have penetrated the glassware.

(ii) Cylinders of wood were unpacked from their polythene wrappers. If wood had been refrigerated after turning on the lathe, it was allowed to equilibrate in its polythene wrapper at room temperature for at least 2 h. In all cases the wood was handled with clean, disposable rubber gloves.

(iii) In some cases weight and/or electrical resistance measurements of the wood were determined.

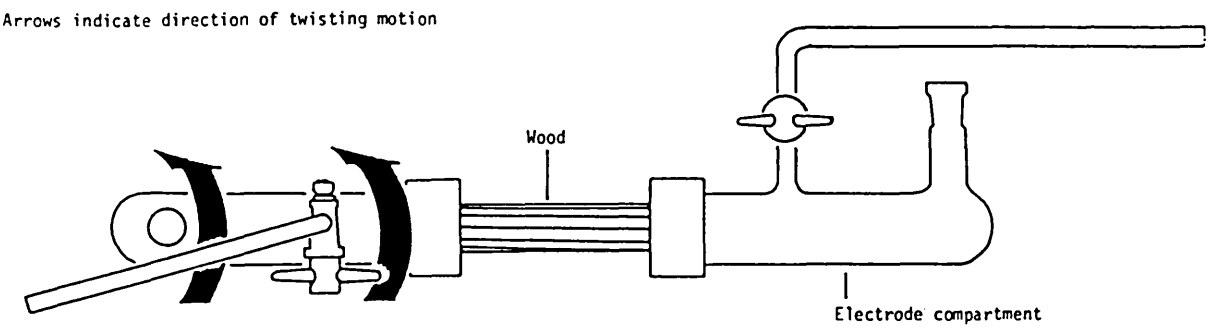
(iv) In flushing experiments the wood was treated as described in section 5.4 .

(v) The silicon rubber O-rings and phenoplast caps were washed in a dilute Teepol detergent solution, thoroughly rinsed with distilled water, and dried with Kleenex tissues. The O-rings were then slipped over each end of the wood sample, and carefully screwed into the screw cap using a clean, open-ended Sovirel screw-jointed glass cylinder. Care was taken not to force the O-ring too hard into the cap, since excessive force could shatter the glass cylinder. The glass cylinder was unscrewed again when stubborn resistance was offered by the O-ring, the wood sample twisted into a better position, and the cylinder re-screwed.

In preliminary runs the O-ring was sometimes too tight or loose in the cap; in the latter cases leaks occurred from the electrode compartments. To avoid these problems the wood was machined to more critical tolerances (cf. section 5.1.2).

(vi) The electrode compartments were then screwed into the phenoplast caps abutting onto the O-rings, to make a tight junction with the wood. By twisting one of the electrode compartments and its corresponding cap, the capillary tubes on both the electrode compartments were aligned parallel to each other (Fig. 5.14). It was not practicable to align the angle of the wood grain in any particular direction.

FIGURE 5.14 Aligning Capillary Tubes Parallel to Each Other




(vii) Next, the cell was clamped onto a jig (Fig. 5.10 or 5.11), and the cell aligned horizontal and at the same level using a spirit level.

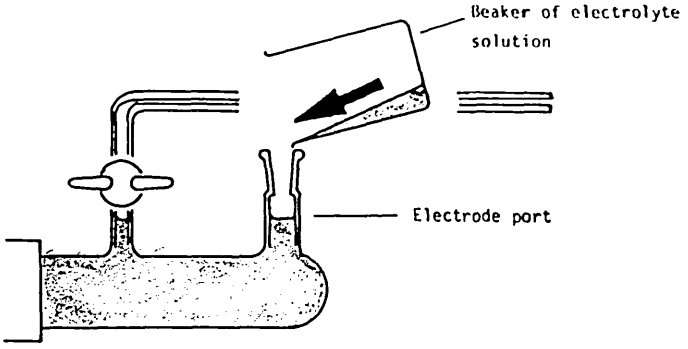
(viii) With the 2-way taps in the electrode compartments open, the latter were filled with their respective electrolytes through the electrode ports. Solution was then forced up into the capillary tubes to the desired extent by repeatedly plunging the electrodes into their respective ports, whilst opening and closing the 2-way taps to prevent solution dropping back out of the capillaries (Fig. 5.15). The electrodes were then placed in their ports.

(ix) The 2-way taps were closed, and electrical leads clipped onto their respective electrode terminals.

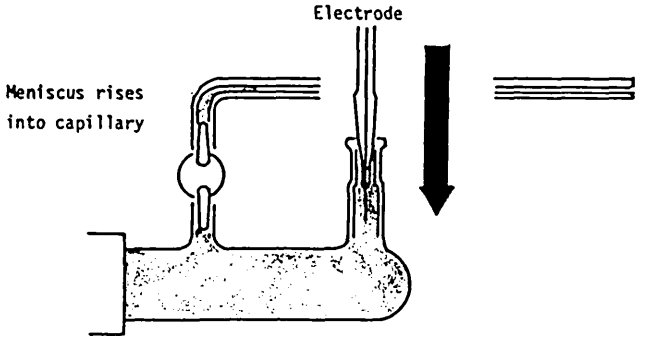
FIGURE 5.15 Filling of Electrode Compartment with Electrolyte Solution

Arrows indicate direction of motion

(a) Electrolyte solution poured into electrode compartment




(b) Electrode pushed into electrode port, forcing solution into capillary




(x) Electrical connections were checked on the standard resistor and digital multimeter, and the constant current generator (with the circuit on 'Dummy') switched on in the sequence: 'Filaments', 'High Tension', 'Extra High Tension'. At least 30 s was allowed between each part of the sequence to give the valves of the generator time to warm up sufficiently. The multimeter was then switched on.

(xi) Immediately before switching current through the cell, both taps were opened, and the position of the meniscus in each capillary marked with a felt-tipped pen. The time was noted, and the circuit switched from 'Dummy' to 'Live'.

(xii) During subsequent passage of current (10 mA, unless otherwise stated) through the cell, regular and frequent checks were made of the following:

the current (to check that it stayed constant to $\pm$ 0.01 mA); the distances of the menisci in their capillaries; the condition of the wood (appearance of surface moisture - 'sweating', surface discolouration, and so on); the seal between the wood and the electrode compartments (any failure was indicated by leakage of electrolytes from the inside of the phenoplast cap, along the wood surface); the appearance of the electrodes (such as gassing, leakage of electrolyte solution into the glass holder); the appearance of the electrolytes (e.g. colour, precipitation); and the condition of the electrode compartments (e.g. heating effects, cracking).

Electrical runs were abandoned if adverse conditions arose, such as: erratic current; excessive 'sweating' on the wood surface; leakage of solution from the electrode compartments; disintegration of an electrode (particularly copper anodes); unwanted gassing from an electrode.

(xiii) Incipient falls in menisci out of the capillary tubes into the vertical tubes, resulting in unequal hydrostatic pressure across the cell, were prevented by:

(a) using longer capillaries (as in the Mark III cell), and/or

(b) injecting fresh electrolyte into the respective capillary tube. This was done by means of a clean P.T.F.E. tube (1 mm outer diameter) attached to a clean disposable syringe, which were both filled with fresh electrolyte solution. During the injection it was important to close the 2-way tap in the electrode compartment in question, otherwise solution was forced through the wood into the opposite half of the cell where the meniscus was noticeably pushed forward. After the capillary was re-filled and the new meniscus position noted, the tap was re-opened.

(xiv) The run was continued until a pre-determined number of coulombs had been passed. The current was then turned off at the 'EHT' switch on the current generator, and the electrode compartment taps closed as quickly as possible.

(xv) In some cases the electrolyte solution temperatures were measured by removing the electrodes and inserting clean thermometers (accurate to $0.1^{o}C$) in each port. The thermometers were read after 2 min equilibration in the solutions.

(xvi) In removing the cell from the jig care was taken to keep it as near to horizontal as possible to avoid unnecessary disturbance. Both electrodes were placed in clean 25 $cm^3$ volumetric flasks filled with distilled water. The cell was then tipped approx. $180^{o}$ on its side, so that each electrode port dipped into a dry, labelled Pyrex boiling tube (200 x 32 mm), which was clamped onto a retort stand (the tubes had previously been cleaned and rinsed as described in step (i) ). The cell was gently shaken to break the surface tension across the openings, and the solutions poured out completely into the boiling tubes. The taps were then opened, the cell again tipped $180^{o}$ sideways, and the solutions in the capillaries collected. Odd drops remaining behind in the compartments were emptied out by gently tipping the cell end on by $90^{o}$ and sideways by $180^{o}$.

(xvii) The tops of the boiling tubes were carefully sealed with Gallenkamp 'Parafilm' sealing wax paper. The samples were then stored in a cool, shaded place before being analysed. Alternatively, samples sent by post for ion chromatography analysis were transferred to polythene 'Azlon' tubes (25 x 75 mm cat. no. 1530, from Scientific Supplies Ltd., London EC1R 5EB). The polythene tubes had been cleaned and rinsed in the same way as the silicon rubber O-rings and the phenoplast caps, and then soaked in distilled water for several days.

(xviii) The electrode compartments were unscrewed from their phenoplast caps and soaked in water before being thoroughly washed, as described in (i). The phenoplast caps and silicon rubber O-rings were slipped off the ends of the wood.

After its removal from the cell, the wood cylinder was immediately sketched. Colour changes, surface moisture patterns, or other physical changes were noted. Any resistance and/or weight measurements were also made. The wood samples were then left to dry slowly over the top of an oven.

## 5.7 Chemical analyses

### 5.7.1 Choice of analytical methods

The techniques for quantitative analyses of elements and ions needed to be:

(i) fairly rapid,
(ii) accurate, sensitive ($\mu$M level), and reproducible,
(iii) able to analyse mixtures of elements or ions, often against a relatively concentrated background electrolyte,
(iv) able to be performed on the instrumentation available.

The analytical techniques used are shown in Table 5.4 . However, the methods employed most were not always the most desirable. Thus, neutron activation analysis (NAA) is an accurate, non-destructible technique, capable of quantitatively determining a wide range of elements over a broad concentration range, and has been well proven in wood analyses (e.g. Langwig and Meyer, 1973 - section 1.6.3). Unfortunately the necessary instrumentation was not available for use in this project. In addition, argon- or helium plasma spectrometry (APS and HPS, respectively) are extremely useful analytical techniques (cf. section 5.7.4), but their availability at Imperial College was too limited for regular analyses. Radiochemical assay is accurate, non-destructive and inexpensive, but there was insufficient time to use it. In contrast, colorimetry involves a number of stages in the various procedures, and is neither rapid nor sensitive.

In all chemical analyses, samples were measured against blank solutions composed of background electrolyte(s) and/or reagents. Quantitative determinations were obtained by measuring samples against calibrated standard solutions.

The main analytical techniques used in this project will now be described.

TABLE 5.4 Methods Used for Chemical Analysis of Ashed Wood Samples and Electrolytes

| CATIONS | | | |
|---|---|---|---|
| Method | Operating Mode | Suitable Ions for Analysis | Problems |
| Flame photometry | - | $K^+$, $Na^+$, $Li^+$ | Interference between cations |
| pH meter | - | $H^+$ | - |
| Atomic Absorption Spectroscopy | Acetylene/air flame | Transition metals | Interference between cations at certain wavelengths |
| | Nitrous oxide/acetylene | $Ca^{2+}$, $Mg^{2+}$ | |
| Indole-phenol blue colorimetry | - | Ammonium compounds | Poor differentiation and sensitivity |
| Inductively-coupled Argon Plasma | - | Group II, Transition metals, Group III | - |
| Ion chromatography | Cation separator column | Group I, II cations, ammonium compds. (including low molecular wt. organic compds.) | Divalent cations bind to separator resin; interference from conc. background electrolyte. |
| Mass spectroscopy | - | High molecular wt. cations | Semi-quantitative only |
| ANIONS | | | |
| pH meter | - | $OH^-$ | - |
| Inductively-coupled Helium Plasma | - | $Cl^-$ | - |
| Ion chromatography | Anion separator colmn. | All common anions with $pK_a > 7$, low molecular wt. organic anions | $Cl^-$ dip; poor resolution between certain ion species under specific operating conditions; interference from conc.background electrolyte. |

### 5.7.2 Atomic absorption spectroscopy and flame emission

The same instrumentation can be used for AAS and flame emission (FE), and two models were employed - Instrumentation Laboratory Model 151, at Rentokil Ltd., and a Unicam SP90 at the Chemistry Department, Imperial College. The procedures for using both machines are given by their respective instruction manuals, and only features special to this project are described here.

AAS/FE analysis of the ashed wood samples proved difficult, as the high background level of acid in the samples frequently corroded the Teflon surface lining the inside of the burner head of the IL 151 (the Unicam SP90 was not used for these samples). The first sign of corrosion was indicated by erratic and irreproducible readings. This problem was only remedied by renewing the burner head.

Standards were frequently aspirated between sample analyses, to check for drifting of the base line. Checks were also made of:

constancy of gas and air pressures; colour of flame - particularly yellow flecks which indicated carbon deposits, that were removed by scraping the burner slit with a clean wire; rate of aspiration of solutions to test for blockages, which were removed by reversing the air flow through the aspirator jet (if this proved inadequate the aspirator was systematically dismantled to locate the obstacle).

Where concentrated background electrolytes (>50 mM) were present in the samples, solid deposits sometimes precipitated out of solution and fouled the aspirator system. This was avoided by prolonging the aspiration of distilled water between samples, to remove all possible deposits.

Interferences between different ions present in the samples were not encountered.

### 5.7.3 Flame photometry

An EEL flame photometer (Evans Electroselenium Ltd., Halstead, Essex) connected to an EEL 230 portable air compressor and mains gas supply was used in the Chemistry and Botany Departments at Imperial College. The manufacturer's instructions were followed.

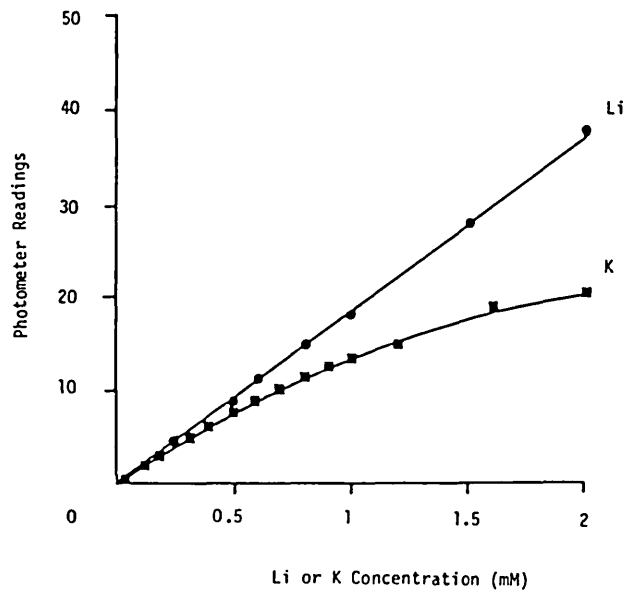
The problems encountered were generally similar to those for AAS/FE, viz.:

drifting baseline; fouling of the aspirator by solid deposits; carbonisation of the burner head slit.

In all these cases the remedies were the same as those described above.

Additional problems arose from interference of Li analysis by K in the same samples, although there is no report of such interference in the literature (e.g. Burriel-Marti, 1958). Reliable analysis of Li was achieved by calibrating combined Li and K standards (Fig. 5.16). By knowing the level of K in any one sample, the K interference could be accounted for.

FIGURE 5.16 K Interference in Li Analysis by Flame Photometry (Using Li Filter)




Other possible interferences between all permutations of Li, Na, Ca, and HCl were not found over the range of ionic concentrations encountered ($\mu$M to mM).

### 5.7.4 Argon- or helium plasma spectrometry

Instead of exciting atoms by burning in a flame, these inert gas plasma systems use radio-frequency induction to excite atoms, which are then drawn through an induction furnace in a flow of inert gas. The radiation from the resulting plasma is displaced by a plane grating monochromator with adjustable slits. A photomultiplier receives the light emitted, and the signals are displayed on a recorder. This system allows multi-element determinations to be made over wide concentration ranges. (Fassel and Kniseley, 1974a, b).

APS has proved to be immensely useful in analysis of metals, and more recently has been applied to determinations of Cu, Cr, and As in ashed wood samples (Ofori, 1977). The system has four major advantages over flame analyses:

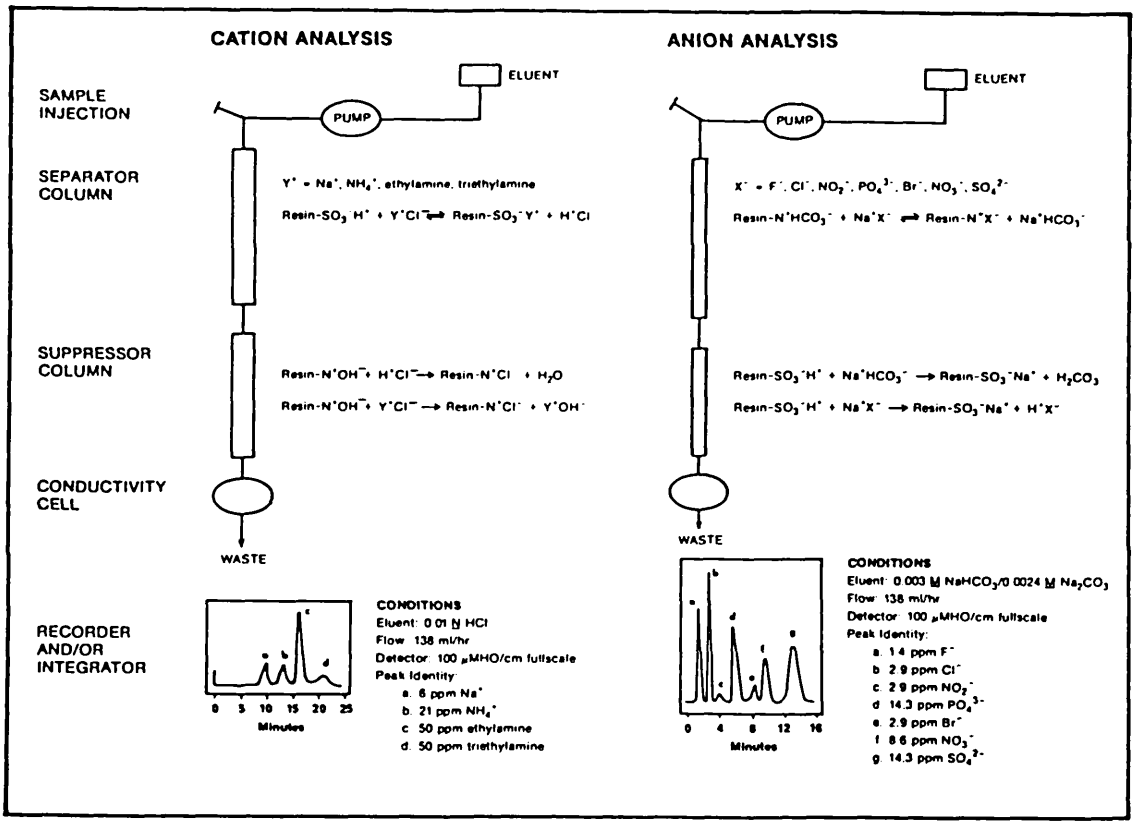
(a) low detection limits, in some cases down to ppb;
(b) more rapid analysis in routine determinations, as the plasma is not extinguished between different elemental analyses;
(c) simultaneous multi-element analyses;
(d) a slightly greater range of elements detected (e.g. analysis of halides by HPS - Alder, Jin and Snook, 1981);
(e) accuracy strictly compared to AAS is the same (Ofori, 1977), but as less dilution is required to stay within the linear concentration range of analysis overall accuracy is better.

### 5.7.5 Ion chromatography

Ion chromatography was performed on Dionex Model 10 instruments at Courtaulds Ltd., Coventry, at British Gas, London SW6, and at C.E.R.L., Leatherhead, Surrey. This is a relatively new analytical technique introduced into the U.K. by Dionex Corporation, and described by Small, Stevens and Bauman, 1975, and Small and Solc, 1976. It is based on ions in a sample solution exchanging with a strong acid or base exchange resin, packed onto beads inside column containers. The sample is washed through two exchange columns in series using an eluent solution (e.g. $NaHCO_3/Na_2CO_3$ for anion analysis) under pressure. The first column (either a cation or anion separator) separates the ions in the sample and eluent by exchanging them with protons on the column (Fig. 5.17). The second (suppressor)

column removes the background interference of the eluting ions, while converting sample species to a common, highly conductive form (Fig. 5.17). The sensor is a conductance cell. Typical cation and anion spectra of results are shown in Fig. 5.17 .

FIGURE 5.17 Scheme of Cation and Anion Analyses by Ion Chromatography




Because background eluent interference is eliminated, multiple ion analysis can be performed. Using an anion separating column, both inorganic anions and organic acids (mostly aliphatic) can be analysed. A cation separating column allows the determination of alkali metals, alkaline earths, alkylamines, and quaternary ammonium compounds. Ion chromatography fails for weakly dissociated species where $pK_a > \sim 7$; amphoteric species (e.g. amino acids); and species that undergo 'negative' chemistry on the suppressor column (e.g. transition metals, which bind to the ion-exchange resins).

The operating conditions are adequately described in the manufacturer's handbook. Briefly, eluent (3 mM $NaHCO_3$/ 2.4 mM $Na_2CO_3$ or 2.5 mM $Na_2B_4O_7$ for anions, and 5 mM HCl eluent for cations) was initially pumped through the columns on its own, until a stable readout appeared on the chart recorder - generally 1 to 2 h for the 3-10 $\mu$mho sensitivity used. The sample (1-3 $cm^3$) was then injected into the sample loop and pumped into the eluent stream whilst an electronic blip was simultaneously pressed. Each ion species was identified from the retention times, i.e. the distance on the chart from the injection blip to the peak position of the ion concerned (Fig. 5.17). The concentration of each ion was determined from the height of its peak above the base line. Ion chromatographers have not found it necessary to use the more usual chromatographic technique of calculating the area under each curve (R. Parker, pers. comm.).

A variety of problems was encountered with ion chromatography:

(a) A 'water dip' on the chart occurred when the background eluent in the sample was separated on the first column, resulting in a negative peak. With a $NaHCO_3/Na_2CO_3$ eluent for anion analysis, the water dip overlapped into the $Cl^-$ peak, so giving misleading results. This problem was overcome by adjusting the sample before injection with an equivalent concentration of eluent, to match its concentration in the eluent solution.

(b) Overlapping and masking ion peaks occurred when different ion species had similar retention times on the separator column. Better resolution was obtained by using more dilute eluent, giving longer separation times. Alternatively, the type of eluent was changed. In preliminary anion analyses - where 3 mM $NaHCO_3$/2.4 mM $Na_2CO_3$ eluent was generally used - two runs were made with 2.5 mM $Na_2B_4O_7$ eluent, as a safeguard against any peaks being hidden by the previous technique.

(c) Cations with valencies greater than 2 tend to bind tightly to both anion and cation separator columns, resulting in reduced exchange capacity and hence poorer resolution and accuracy. This problem arose with samples containing a background $CuSO_4$ electrolyte. By injecting samples through 'pre-columns' containing separator column resin, these contaminants were removed before they were injected into the separator itself.

(d) Peaks of ions with long retention times may appear in subsequent sample analyses if insufficient time has been allowed for their elution. In preliminary analyses samples were run for 1.5 h (the maximum reported retention time of any ion) to check that all ions in each sample had been eluted.

(e) In most electrolyte samples the concentration of the background anion - say, $SO_4^{2-}$ in $CuSO_4$ - was >1 mM. The resulting large peak for this ion could envelop other ion peaks, or even destabilise the separator column and lead to an erratic base line. This problem was best overcome by diluting samples with distilled water - if necessary with 2 or 3 different dilutions to 'catch' ions present at low concentrations.

5.7.6 Mass spectrometry

Samples analysed for organic acids by mass spectrometry were pre-treated as follows, to esterify any organic acids present:

(i) Samples (ca. 50 $cm^3$) were neutralised with NaOH.

(ii) The neutralised sample was repeatedly extracted with re-distilled ether using a separator funnel. The aqueous alkaline phase was retained and the (neutral) ether solution fraction discarded.

(iii) The alkaline phase was acidified with HCl and repeatedly extracted with re-distilled ether.

(iv) The extracted sample was evaporated down on a 'Buchi' apparatus to remove the ether, leaving a crystalline solid.

(v) The solid was taken up again in re-distilled ether, dried over solid $Na_2SO_4$, and filtered.

(vi) Distilled diazomethane was prepared according to the method of Vogel, 1951.

(vii) The solid sample was esterified by adding fresh distilled diazomethane using a fire-polished pipette, and the mixture evaporated down on a 'Buchi'.

(viii) The esterified sample was finally analysed on a mass spectrometer (Vacuum Generator 7070).

5.7.7 Ashing

The inorganic contents of wood can be analysed by oxidising off the organic constituents. This processing of ashing (cf. section 1.6.4) can be performed with oxidising chemicals (so-called 'wet ashing') - as used in this project - or by burning the wood in a crucible in a furnace (so-called 'dry-ashing').

Samples of wood were oven-dried at 101$^{o}$C for 48 h, and allowed to cool. While wearing disposable gloves, chips of wood were shaved off with chisels, and the chips milled into sawdust using a 'Moulinex' electric coffee grinder. Sawdust (0.4 g) was weighed out into a micro-Kjeldahl flask (25 cm$^3$) and placed inside a fume cupboard on a rack that could hold up to 6 flasks. A 10 cm$^3$ aliquot of hydrogen peroxide (30% w/v) plus 13.3% $H_2SO_4$ was carefully added to the sawdust from a calibrated dispenser. The flask was then gently warmed using a micro-burner until a vigorous effervescence started. The heat was then removed and the flask allowed to cool, when a clear solution settled out. Strong heat was next applied until white fumes were given off, and the flask allowed to cool for 2 min. Then 4-5 cm$^3$ peroxide solution were added with a teat pipette. Strong heat was re-applied until white fumes appeared again; this procedure was repeated 4 times so as to oxidise all organic matter of the wood completely.

After oxidisation, the flask was then allowed to cool to ambient temperature, and the ashed solution transferred to a 25 cm$^3$ Pyrex flask. The solution was made up to volume with distilled water washings from the Kjeldahl flask. However, the exothermic reaction between acid and water raised the temperature of the solution, and the flask was allowed to cool before re-making the volume. A blank solution was prepared following the same procedures, but without using a wood sample. The samples were then analysed by flame photometry.

5.7.8 Other analytical techniques

(a) Indole-phenol blue colorimetry

Determination of $NH_4^+$ by the indole-phenol colorimetric method (as described by Allen, 1974) proved satisfactory over a linear concentration range 10-80 $\mu$M $NH_4^+$. Optical densities of reacted samples were read at

625 nm on a Perkin-Elmer double beam spectrophotometer model 124.

(b) pH meter

The pH of samples was measured with a Cambridge pH meter, or Radiometer PHM 62 standard pH meter.

(c) Rubeanic acid stain for copper

Copper was detected *in situ* in the wood using rubeanic acid (dithio-oxamide) spot test reagent (manufactured by BDH). Wood samples were sprayed with 5% ammonium hydroxide solution sufficient to wet the wood. Dilute (approx. 1% w/v) rubeanic acid solution was then sprayed from about 50 mm onto the wood surface. Copper stained a blue-black-green colour.

## 5.8 Physical Analyses of wood

### 5.8.1 Weight and moisture content

Samples of wood about to be used in electrical runs were weighed in clean, dry glass beakers or disposable polystyrene weighing boats, to one decimal place. Clean gloves were worn, hand contact being avoided to prevent warming the wood.

The moisture content of wood samples was determined by oven-drying the weighed samples at 101$^{o}$C for 48 h. The samples were then allowed to cool before re-weighing to one decimal place. The % moisture content was calculated from the formula given in section 1.7 .

### 5.8.2 Electrical resistance

A variety of methods has been used by previous workers to measure the resistance of wood, from portable meters with copper wire probes (cf. section 3.6.3) to sophisticated cells containing gold electrodes connected to a high impedance bridge (Erickson, Schmitz and Gortner, 1937).

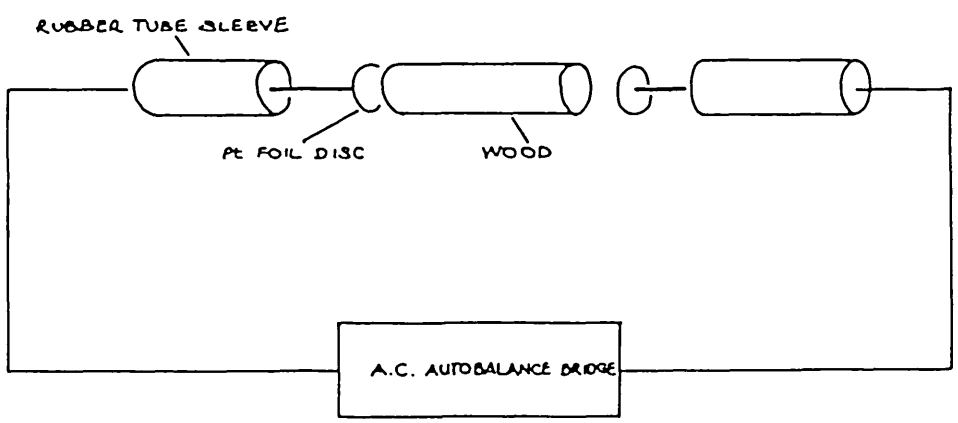
Preliminary measurements of d.c. electrical resistance were made in this project with an Avometer model 28723 battery-powered portable multimeter. The exposed metal tips of the insulated probes were cleaned in a dilute Teepol detergent solution, rinsed with distilled water, dried, and then

placed firmly across the ends of the wood sample. This method gave unsatisfactory results, as the resistance depended on the location of the metal probes on the surface of the wood ends, and how hard the probes were pressed on the wood. Also the meter itself could not be read with precision.

Similar problems were encountered using a high accuracy multimeter, Solartron 7045, in the resistance mode. Its probes were also connected to the electrodes fitted in a complete electrical cell containing electrolytes and wood, but irreproducible results were again obtained.

Better results were achieved with a high impedance a.c. autobalance bridge (Wayne Kerr model B905), used with circular platinum disc electrodes applied firmly to wood samples held in a retort clamp (Fig. 5.18). Individual wood samples were fixed in place and a drop of distilled water applied to both interfaces. Cleaned and dried Pt foil electrodes (shaped to match the surface area of the ends of the wood) were slipped into rubber tube sleeves, and these sleeves were clamped onto retort stands. By holding the supporting retorts in a fixed arrangement the pressure of the electrodes on the wood surface was reasonably constant from one sample to another. The average of 3 resistance readings made within 2 min of applying the electrodes to the wood was made and recorded.

Figure 5.18 Exploded Diagram of Electrical Measurement Apparatus, Using a High Impedance Bridge



## 5.9 Calculation of transference numbers

The number of moles, n, of an ion species, i, which had migrated out from the wood into an electrode compartment of volume V (in l) was calculated from

$$n = cV$$

where c is the molarity of the ion in the compartment. The transference number, $t_i$, of the ion was calculated from

$$t_i = \frac{n|z_i|}{f}$$

where $z_i$ is the algebraic charge number of the ion and f the number of faradays passed (i.e. coulombs/96487) (cf. equation 2.26).

## 5.10 Statistical analyses

The variability of data was expressed as confidence limits at the 0.95 level of probability. That is, the true mean of a population has a 95% probability of falling within these limits, and is calculated from

$$\bar{x} \pm 1.96\ s/\sqrt{n}$$

where $\bar{x}$ is the mean of a representative group from within the population, n the number of data points, and s is the standard deviation calculated from

$$s = \sqrt{\frac{\Sigma x^2 - (\Sigma x)^2/n}{n-1}}$$

Further details of these statistics are given by a number of authors, including Parker (1973).

# CHAPTER 6

# PRELIMINARY EXPERIMENTS

## 6.1 Microbial contamination and storage

### 6.1.1 Electrical effects of contamination

Samples of wood which became heavily contaminated with fungal growth (as described in section 6.1.2) after cutting on the lathe were compared in electrical runs to uncontaminated samples cut from the same tree.

TABLE 6.1 Comparison of Endogenous Cation Current of Infected and Uninfected Wood

50 mm long wood
Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.05 M $CuSO_4$

| Wood | Transference numbers | | |
|---|---|---|---|
| | $t_{K^+}$ | $t_{Na^+}$ | $t_{Mg^{2+}}$ |
| Uninfected | .192 | .036 | .092 |
| Infected | .096 | .024 | .082 |

The total endogenous cation current of the uninfected wood was somewhat greater than the infected wood (Table 6.1). This result was contrary to expectations from the literature, in which fungal decay considerably raises the levels of many inorganic elements (Safford, Shigo and Ashley, 1974). However, the wood used here, unlike that in previous studies, became infected *after* removal from the tree. Thus, ions sequestered by the fungi could not be replaced by ions translocated from other parts of the tree. Furthermore, the likely increase in cation-exchange capacity of the decaying wood (Kratzl and Stepnicka, 1955) could have retarded the migration of cations.

These results also indicate that the fungi did not 'leak' ions during passage of current, as reported by Hattori and Tamura (1939) (cf. section 3.7).

6.1.2 Storage of wood: Tree I

Several sticks of refrigerated wood from Tree I began to show signs of fungal contamination - particularly with colonies of a green mould - approx. 4 weeks after packing into polythene bags and storing in the refrigerators. The packages most affected had been stored furthest away from the refrigeration grill. The green mould was identified as *Trichoderma* spp. under a light microscope by Dr C. Clubbe, Department of Botany, Imperial College. Smaller colonies of an unspecified basidiomycete were also detected.

The extent of hyphal cell penetration into the wood was determined by extracting chips of wood from the core of the sticks, and plating them out onto sterile nutrient agar medium in a petri dish. After 2 weeks unidentified fungal hyphae were detected in several samples, indicating that infection had penetrated into the wood core. As a result, sticks of wood found with any sign of surface contamination were discarded.

As *Trichoderma* spp. can grow at temperatures as low as 2°C, and since the refrigerators only maintained temperatures between 4 to 7°C (when empty), the fungus was able to colonise the wood gradually (having presumably entered the polythene storage bags through unsealed gaps). The contamination problem was reduced in later wood supplies by:

(i) putting fewer sticks of wood into each polythene bag, to reduce the spread of any infection;
(ii) supporting the packages on the floor of the refrigerators on aluminium frames (cf. Fig. 5.10) to allow better ventilation;
(iii) packing the wood bags less densely to permit better ventilation;
(iv) irradiating the woods from Trees II, III, and IV with $\gamma$-irradiation before packing into the polythene bags (as described in section 5.1.3)

6.1.3 Storage of wood: All trees

The measures to prevent fungal infection of stored wood helped prolong its fresh-keeping (Table 6.2). The "durability" figures depend not only on the onset of fungal infection, but also on how quickly

the batch of wood was used. A heavy demand of wood could exhaust a particular supply before infection became widespread. The short durability of wood from Tree III may have resulted from felling it on a hot summer day, whilst the other trees were felled on cold winter days. More regular supplies of fresh wood could not be obtained because of the high cost of felling, cutting, and transportation.

TABLE 6.2 Durability of Refrigerated Wood

| Tree number | Date of Felling | γ-irradiation | Durability of wood |
|---|---|---|---|
| I | 13/ 3/78 | x | 21 weeks |
| II | 8/12/78 | ✓ | 57 weeks |
| III | 11/ 7/79 | ✓ | 14 weeks |
| IV | 22/ 1/80 | ✓ | 36 weeks |
| V | 7/11/80 | ✓ | not determined |

## 6.1.4 Electrical effects of γ-irradiation

Table 6.3 shows the result of passing 10 C through untreated and γ-irradiated wood from Tree II. There is clearly no significant difference in the transference numbers of endogenous $K^+$, $Ca^{2+}$, and $Cl^-$. This supports previous work which showed that radiation causes negligible changes in the electrical properties of wood (Brown, 1962, cited by Langwig and Meyer, 1973).

TABLE 6.3 Transference Numbers of Endogenous Ions of Untreated and γ-irradiated Wood

100 mm long wood from Tree II.
Ag/AgCl cathode in 0.25 mM HCl; Cu anode in 0.25 mM $CuSO_4$.

| Treatment | Transference numbers | | |
|---|---|---|---|
| | $t_{K^+}$ | $t_{Ca^{2+}}$ | $t_{Cl^-}$ |
| Untreated | .286 | .023 | .015 |
| γ-irradiated | .278 | .020 | .016 |

### 6.1.5 Electrical effects of cold storage

Sticks of wood that had been deep frozen at -10°C for 20 weeks were defrosted in a refrigerator for 48 h before being cut to size. Cut samples of both refrigerated and frozen wood were thermally equilibrated at room temperature before use.

Tables 6.4a and 6.4b show that there are no apparent differences in the migration of endo- or exogenous ions between refrigerated and deep frozen wood, even though frozen wood contained slightly more moisture (Appendix 4).

TABLE 6.4 Transference Numbers of Previously Refrigerated and Frozen Wood

(a) After Passing 36 C

100 mm long wood.
Pt electrodes in 0.054 M electrolytes.

| Wood storage | Transference numbers | |
|---|---|---|
| | $t_{K^+}$ | $t_{Cl^-}$ |
| Refrigerated | .329 | .032 |
| Frozen | .357 | .023 |

(b) After Passing 250 C

50 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.05 M $CuSO_4$.

| Wood storage | Transference numbers | |
|---|---|---|
| | $t_{K^+}$ | $t_{Cu^{2+}}$ |
| Refrigerated | .050 | .035 |
| Frozen | .024 | .037 |

## 6.2 Electrical cell problems

### 6.2.1 Electrode compartments

The electrode compartments were prone to breakages, particularly when screwing the cell together, or when the complete cell was clipped onto the platform jig. Breakages generally occurred at the junctions of the vertical tube with the electrode compartment, or with the capillary tube, where the glass had been weakened during glassblowing. Cell models using a one-way tap and wider bore tube (7 mm instead of 6 mm internal bore, as used in the Mark V cell) lessened this problem.

### 6.2.2 Electrodes

Disintegration or gassing problems occasionally occurred during high coulomb ($>100$C runs). Disintegration generally took place in Cu anodes at the top of the exposed Cu wire, so that the wire snapped off. In practice, 1 mm diameter Cu wire anodes did not pass more than 750 C without disintegrating.

Gassing of 'non-gassing' Ag/AgCl cathodes occurred as a result of the AgCl coating wearing away near the junction with the glass casing of the electrode. Once this had happened the underlying Ag began gassing:

$$H^+ + e^- \rightarrow \tfrac{1}{2}H_2$$

so decreasing the $H^+$ concentration. This problem was overcome in one of two ways. For low coulomb runs ($<50$ C), about 25% more coulombs were passed during electroplating of a cathode than were needed during a subsequent electrical run. However, for high coulomb runs it proved necessary to manufacture the Ag/AgCl cathodes by the molten dip method (section 5.2.3e). Its only drawback is that the AgCl coat is uneven and porous, and therefore liable to absorb some ions from the surrounding electrolyte.

Gassing also occasionally occurred on Ag anodes:

$$H_2O \rightarrow \tfrac{1}{2}O_2 + 2H^+ + 2e^-$$

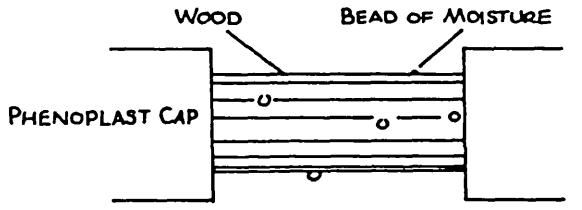
resulting in an increase in the $H^+$ concentration. This problem was overcome by using (non-gassing) Cu anodes.

### 6.2.3 Sweating of wood

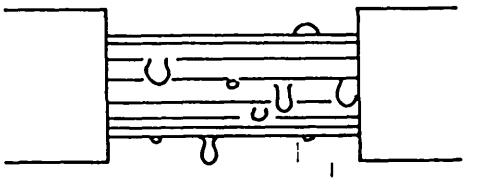
Colourless beads of moisture ('sweat') frequently appeared on the exposed surface of naked wood samples during electrical runs (Fig. 6.1a). The droplets gradually enlarged, particularly on the underside of the wood (Fig. 6.1b), until a continuous film of moisture was formed (Fig. 6.1c). Sweating tended to increase with larger numbers of coulombs, but there was no clear relationship with the original moisture content of the wood (Table 6.5).

FIGURE 6.1 Progression of 'Sweating' on Wood Surface During an Electrical Run

(a) First signs of sweating




(b) Solution begins to drip



(c) Continuous film of solution runs along underside of wood

Similar sweating was observed in the hydrostatic pressure experiments (section 6.2.5), becoming more extensive with increasing pressure. Thus, pressure alone may have caused the seepage of liquid, possibly by forcing out solution through the ray tissues.

TABLE 6.5 Effect of Wood Moisture Content on 'Sweating'

| Moisture content (%) | Degree of sweating (letters refer to Fig. 6.1) |
|---|---|
| 67 | a |
| 83 | None |
| 83 | None |
| 87 | a |
| 92 | b |
| 95 | b |
| 96 | a |
| 96 | a |
| 112 | b |
| 113 | a |
| 113 | b |
| 118 | c |
| 119 | b |
| 119 | a |
| 122 | c |
| 126 | a |
| 126 | b |
| 131 | c |
| 135 | b |

| Moisture content (%) | Degree of sweating (letters refer to Fig. 6.1) |
|---|---|
| 136 | b |
| 136 | c |
| 138 | c |
| 139 | b |
| 141 | c |
| 141 | a |
| 143 | b |
| 143 | c |
| 144 | b |
| 144 | a |
| 144 | b |
| 144 | c |
| 146 | c |
| 146 | b |
| 146 | c |
| 146 | b |
| 149 | None |
| 152 | c |
| 154 | b |

Sweating was partly overcome by preventing unequal hydrostatic pressure across the wood (cf. 6.2.5), but pressure arising from electro-osmotic flow (cf. chapter 10) was unavoidable. Sweating was therefore contained within a barrier applied over the wood surface. A number of materials was assessed for this purpose, including 'Clearasil' lacquer varnish, 'Teflon' spray, 'Clingfilm' cellophane, heat-shrinking plastic tubing (Radio Spares cat.no. 399-647), and paraffin wax. None of these proved satisfactory. However, 'Mobilcer R' provided an adequate barrier to seepage of liquid. It is a rubber-based emulsion which sets as a thin film over wet or dry wood. The emulsion had to be allowed to dry thoroughly on the wood to prevent the film of rubber being scratched off during the cell assembly.

In electrical runs, the Mobilcer R-coated wood showed no signs of sweating except at high numbers of coulombs ($>50$), and had no effect on the transference properties of the wood (Table 6.6).

TABLE 6.6 Electrical Effect of Coating Wood with Mobilcer R

100 mm long wood.
Pt/Ag/AgCl cathode in $Bu_4NI$; Cu anode in $CuSO_4$ anolyte.
10 C.

| Wood | Electrolyte concn. (mM) | $t_{K^+}$ | $t_{Na^+}$ |
|---|---|---|---|
| Uncoated | 25 | .188 | .012 |
| Mobilcer R-coated | 25 | .158 | .032 |
| Uncoated | 0.25 | .212 | .008 |
| Mobilcer R-coated | 0.25 | .208 | .012 |

### 6.2.4 Leakages

In some runs liquid leaked out at the cell/wood junction. This was often caused by insufficient tightening of the glass cell into the phenoplast cap, or by damaged O-rings. However, the leakage often occurred only - or at first - at the cathode compartment/wood junction. This became worse if the cathode tap was closed, and pressure arising from electro-osmosis may have been involved (cf. section 10.1.3). Leakages were also more prone over high coulomb (>500 C) runs.

### 6.2.5 Unequal hydrostatic pressure

Occasionally one or both electrode compartment menisci fell back out of their horizontal capillaries into the vertical tubes, largely resulting from electro-osmosis. To determine if the subsequent unequal hydrostatic pressure could interfere with the transference numbers of the wood, a run was made using a cell with an artificially raised pressure difference. This was done by fitting a vertical glass tube into a Mark II cathode compartment (containing a Pt/Ag/AgCl cathode in 0.05 M HCl), and filling the tube to 580 mm above the capillary level with the 0.05 M HCl electrolyte solution. The anode compartment contained 0.05 M $CuSO_4$ and a Cu anode, and the wood was 50 mm long. Both taps were closed during filling. When the current (10 mA) was passed, only the anode compartment tap was opened; the cathode tap was kept shut to prevent electrolyte solution simply flowing out through the capillary tube, and so rapidly reducing the hydrostatic pressure difference. Even so, the level of catholyte in the vertical tube fell

rapidly, whilst the volume of anolyte rose simultaneously (movement through the anode capillary was approx. 20 mm $s^{-1}$, or 1.6 $mm^3$ $s^{-1}$). The anode capillary was filled after 2 min, and began dripping; after 6 min the wood sweated excessively, and the run was abandoned after passing 4 C. It was clear that catholyte solution had been forced through the wood into the anode compartment by the pressure difference, and that such differences (even of smaller magnitude) had to be avoided.

In 'normal' runs, unequal hydrostatic pressure due to the anolyte meniscus falling out of its capillary tube only occurred when more than 50 C were passed. This problem was overcome by:

(i) holding the cell level in a horizontal jig, and
(ii) using longer capillary tubes, and/or,
(iii) injecting fresh electrolyte solution into the capillary tubes (cf. sections 5.2.2, 5.2.4, 5.6xiii).

The long capillary tubes contained the falls in anolyte levels during most runs over 250 C, but tended to break easily. Injecting fresh electrolyte was more convenient, and was used for most runs later on in the project.

## 6.3 Physical changes occurring during electrical runs

### 6.3.1 Current

The current deviated by $< \pm$ 0.5 mA during electrical runs, except when using oven-dried wood (see next sub-section).

### 6.3.2 Electrical resistance

Electrical resistance measurements by the a.c. method (cf. section 5.8.2) of 50 mm long wood samples were made before and after certain runs, as shown in Table 6.7.. In general, the electrical resistance of the wood fell by over 50% following passage of current. Although the initial resistance of the samples varied from 12 to 82 kΩ (excluding the oven-dried wood), the final values were remarkably similar after passing a wide range of coulombs. Diffusion alone cannot account for all of this, as the final resistance of the electrolyte-bathed control

was not as low as in the electrically-treated samples.

TABLE 6.7 Changes in Electrical Resistance of Wood Following Electrical Runs

Measurements were made with a Wayne Kerr a.c. autobalance model B905.
50 mm long wood.
Pt/Ag/AgCl cathode in various electrolytes; Cu anode in various electrolytes.

| Catholyte | Anolyte | No. of coulombs | Resistance (kΩ) | | |
|---|---|---|---|---|---|
| | | | Before | After | Δ |
| 0.05 M HCl | 0.025 M $K_2SO_4$ | 10 | 14 | 5 | -9 |
| | | 60 | 28 | 5 | -23 |
| | | 100 | 33 | 3 | -30 |
| | | 150 | 28 | 3 | -25 |
| 0.05 M HCl | 0.05 M $CuSO_4$ | 30[a] | 12 | 5 | -7 |
| | | 2.5[b] | 30 000 | 285 | -29 715 |
| | | 0[c] | 48 | 14 | -34 |
| 0.05 M $HClO_4$ | 0.05 M $CuSO_4$ | 150 | 27 | 5 | -22 |
| | | 150[d] | 82 | 14 | -68 |
| | | 500 | 15 | 3 | -12 |

Key: a contaminated wood (see section 6.1.1).
b oven-dried wood.
c control: no current passed (wood in cell for 15 000 s, equivalent to a 150 C run at 10 mA).
d 100 mm long wood.

The greater resistances of the 100 mm wood sample reflect its longer length (equation 2.4). The dramatic fall in resistance of the oven-dried wood illustrates the clear effect of increasing moisture content (cf. section 3.1.1). The original resistance of the wood heavily contaminated with fungi was not as low as expected from previous workers, who distinguished decaying wood from sound wood solely by electrical resistance measurements (Shigo and Shigo, 1974).

### 6.3.3 Temperature

The ambient temperature for all runs varied between 20-25°C. For most runs only small temperature changes ($\Delta T < 1^{o}C$) occurred in the bathing electrolytes. These could often be accounted for by variations in ambient temperature during runs, particularly those longer than 1000 s, as indicated in a control experiment in which no current was passed

(cf. section 6.4.3). However, marked temperature changes did occur - particularly in the anolytes - when using dilute (0.25 mM) electrolytes, where $\Delta$ T was 3 to 9$^{o}$C; transversely- compared to longitudinally-orientated wood when the temperature was about 1.5$^{o}$C higher; and oven-dried wood where $\Delta T$ was $>5^{o}C$.

All the temperature rises resulted from Joule heating, as discussed in section 2.1.1 . Similar temperature changes in wood have been recorded by other workers (cf. section 3.4.2) - Ito (1960a,b ) reported higher temperatures near the anode than near the cathode, probably caused by the rising resistance of the solution around the anode and anode-facing parts of the wood, which Ito also recorded (Fig. 3.12).

### 6.3.4 Weight

Changes in the wet weight of wood after passage of current were measured by weighing the wood before ($w_1$) and immediately after passing current ($w_2$), and expressing any weight change as a percentage:

$$\Delta w = (w_2-w_1)/w_2 \times 100$$

Varying numbers of coulombs were passed through separate 50 mm long wood samples, using Pt/Ag/AgCl cathodes in 0.05 M HCl, and Cu anodes in 0.05 M $CuSO_4$. In addition, one sample of wood was hydraulically flushed with 0.025 M $Li_2SO_4$ solution, using the vertical flushing apparatus described in section 5.4b, and weighed both before and after flushing, and after passing current.

The wet weight of all wood samples increased slightly after passing electricity (Table 6.8a). It is not clear why increasing numbers of coulombs attenuated the rise in weight. However, the weight increased much more on flushing the wood with electrolyte solution, subsequent passage of current resulting in negligible change in weight (Table 6.8b). Thus, the increase in wet weight of wood was probably caused by saturation of the void spaces in the wood with solution. The hydraulic pressure during flushing probably displaced more air trapped in the wood tissues, than the gradual replacement during electrical runs.

TABLE 6.8 Change in Wet Weight of Wood Following Passage of Current

ΔW is % weight change following each run, after passing a specific number of coulombs or flushing with electrolyte solution.

(a) Unflushed Wood

| No. of Coulombs | ΔW (%) |
|---|---|
| 10 | +2.05 |
| 30 | +1.95 |
| 60 | +0.92 |
| 100 | +0.53 |
| 500 | +0.04 |

(b) Flushed Wood

| Treatment | ΔW (%) |
|---|---|
| Flushed with $Li_2SO_4$ soln. | +6.00 |
| Ibid., and 30 C passed | +0.01 |

## 6.3.5 Colour and precipitate formation

Wood samples only changed colour with certain electrodes or electrolytes (Table 6.9). The turquoise-green colouration caused by $Cu^{2+}$ ions on the ends and lengths of the wood samples occurred with Cu anodes and $CuSO_4$ electrolytes, and to a lesser extent with $CuSO_4$ flushing. This staining was more intense near the top of the end surfaces when Cu anodes were used (Fig. 6.2 A, B). Furthermore, intense turquoise specks were randomly distributed over the same end surfaces (Fig. 6.2 A, B), and light microscopy showed that these flecks corresponded to dissected resin ducts. In high coulomb runs (> 250 C) where $Cu^{2+}$ passed from anode to cathode compartments, faint speckling could also be seen at the cathode face of the wood (Fig. 6.2C). Dissected wood samples showed copper precipitates in the longitudinal resin ducts (Fig. 6.3) (cf. Petri, 1921; Schwarz, 1928b), confirming that $Cu^{2+}$ ions can migrate through the wood via these ducts.

Rubeanic acid staining showed that copper was also carried through longitudinal tracheids (and ray tissues), and that the tracheid pathway

may be faster than through the resin ducts . . The staining was uneven and patchy in transverse section, and could only be partly related to the external surface green streaks. Both early- and latewood contained copper, although it was not clear if they carried equal quantities (Fig. 6.3).

TABLE 6.9 Occurrence of Discolouration of Wood with Various Electrolytes and Anodes After Passing Current

| Catholyte | Discolouration |
|---|---|
| HCl | - |
| LiCl | - |
| NaCl | - |
| KCl | - |
| $HClO_4$ | - |
| $Li_2SO_4$ | - |
| $Na_2CO_3$ | Faint yellow-green |
| Na borate | - |
| Na laurylsulphate | - |
| $KNO_3$ | - |
| $AgNO_3$ | Purple-brown |
| $NH_4(CO_3)$ | - |
| $CdI_2$ | - |
| $Bu_4NCl$ | - |
| $Bu_4NI$ | - |

| Cathode | Discolouration |
|---|---|
| Ag | - |
| Ag/AgCl | - |
| Pt/Ag/AgCl | - |
| Pt | - |

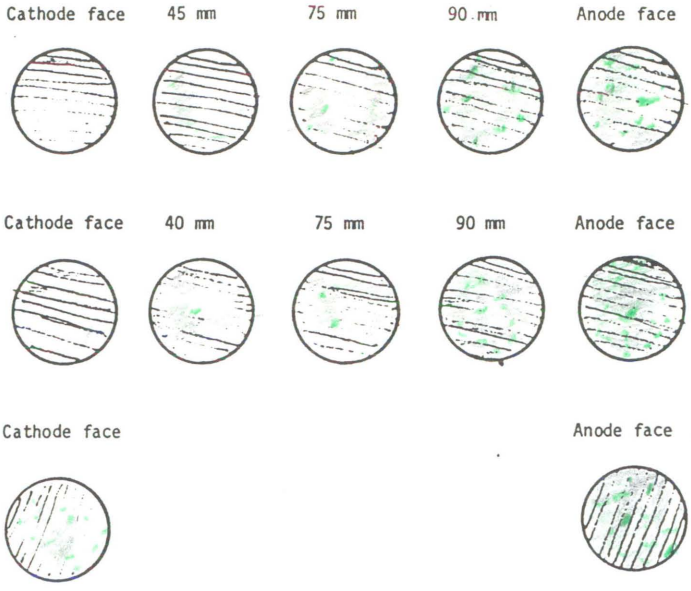
| Anolyte | Discolouration |
|---|---|
| HCl | - |
| $Li_2SO_4$ | Faint yellow-green |
| $Na_2CO_3$ | - |
| $KNO_3$ | - |
| KI | - |
| $NH_4(CO_3)$ | - |
| $AgNO_3$ | Purple-brown |
| $CuSO_4$ | Green-blue |
| CTAB* | - |

| Anode | Discolouration |
|---|---|
| Cu | Green-blue |
| Ag | Purple-grey |
| Pt | - |

* Cetyltrimethylammonium bromide

Figure 6.2 Transverse Sections Through Electrically-treated, Rubeanic-stained Wood Samples

All runs: Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.05 M $CuSO_4$.
(A) 100 mm long wood; 10 C passed.
(B) 100 mm long wood; 60 C passed.
(C) 50 mm long wood; 250 C passed.




Lengths (given in mm) are distances of sections from their respective cathode faces.

FIGURE 6.3 Longitudinal Section Through Rubeanic-stained Wood Sample

50 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M $HClO_4$; Cu anode in 0.05 M $CuSO_4$.
10 C passed.

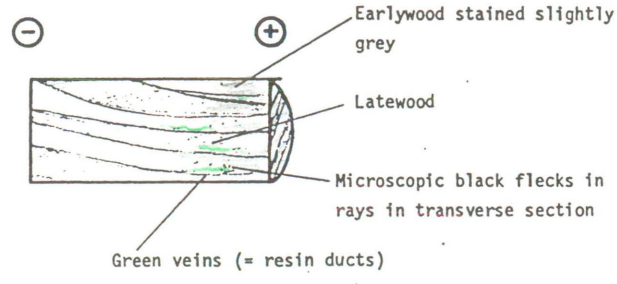
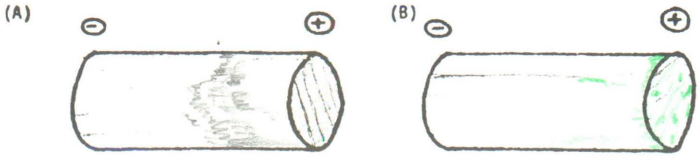



FIGURE 6.4 Surface View of Silver- and Copper-Impregnated Wood Samples

(A) 50 mm long wood.
Ag/AgCl cathode in 0.05 M HCl; Ag anode in 0.05 M $KNO_3$.
35 C passed.
(B) 50 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.05 M $CuSO_4$.
45 C passed.



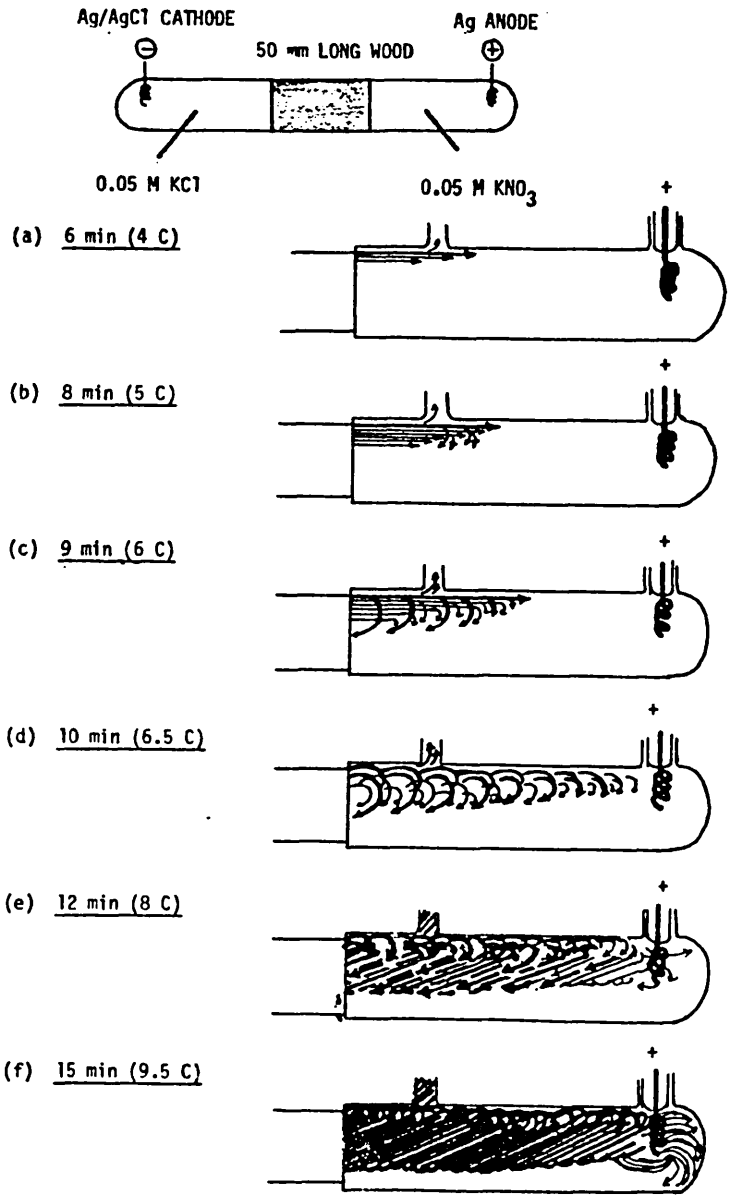
$Ag^+$ discolouration of the wood was more irregular than that of $Cu^{2+}$, but both cations passed along the length of the wood surface as irregular streaks during electrical runs (Fig. 6.4 ). Their intensity increased during the runs, although they were often patchy or truncated and therefore difficult to follow. Furthermore, tests for copper in the beads of surface sweat (section 6.2.3), using rubeanic acid-soaked strips of filter paper, showed that copper-containing droplets could precede the advancing copper streaks. Thus the streaks were a poor indicator of the migration of $Cu^{2+}$ through the interior of the wood. Fainter streaks also occurred during hydraulic flushing with $CuSO_4$ solution, so this surface discolouration is not solely an electrical phenomenon. However, when current was passed through $CuSO_4$-flushed wood (using a Pt/Ag/AgCl cathode in 0.05 M HCl, and Ag anode in 0.025 M $Li_2SO_4$), the $Cu^{2+}$ ions migrated into the cathode compartments (cf. section 9.5), but without causing the speckling pattern on the cathode face of the wood. Thus, the pathway of $Cu^{2+}$ transport may differ between hydraulically flushed and electrically treated woods.

Similar blue-green discolouration of pine sapwood using $CuSO_4$ anolyte solution was reported by Bechhold and Heymann (1927), who also found that the colour was more intense towards the anode. Similarly, Schwarz (1928b) and Muraoka (1929) reported blue-green discolouration of wood using a $CuSO_4$ anolyte, and Langwig and Meyer (1973) described a turquoise-green coating on the wood surface directly pressed onto a Cu anode. However, the sharp boundary of migrating copper shown by Muraoka (Fig. 3.7) for Japanese cedar wood, and by Stalker (pers. comm.) for *Pinus sylvestris* (Chapter 4) was not found here.

There was no change in the colour of electrolytes during electrical runs, except for those using $Ag^+$-containing anolytes. In these, silver halide precipitates were seen after passing 3 to 12 C. The precipitate usually appeared as tubular shaped streams of greyish material, gradually passing from the wood/anolyte interface towards the anode (Fig. 6.5). The streaming began from the apex of the wood interface (Fig. 6.5a), later also forming lower down the interface (Fig. 6.5b). As the streams advanced towards the anode, many particles reversed direction back towards the wood (Fig. 6.5c), apparently drawn into the centre of the wood face (Fig. 6.5d). With further precipitation this streaming

pattern became more distinct (Fig. 6.5e), until a dense 'plate' of precipitate formed midway along the length of the anode compartment (Fig. 6.5f ). Eventually the precipitate sheet diffused into the rest of the anolyte, forming an homogenous cloud.

FIGURE 65 Progression of Halide Precipitate 'Streaming' into Anode Compartment




As the endogenous halide current consists largely of $Cl^-$ ions (Chapter 7), the precipitate is mainly AgCl. The pattern of streaming indicates that the $Cl^-$ current passes preferentially through the top of the wood, so following the path of least electrical resistance between the cathode and anode. The diameters of the streaming 'tubes'

were larger than the diameter of any of the wood cells, so that the precipitate probably formed around irregular points of the wood surface (caused by machining on the lathe). The angle of the precipitate streams and plate matched that of the wood grain to a remarkable degree, so that the precipitate may have been a visible extension of the current inside the wood, i.e. the current passes along the grain. Similar patterns of streaming passed from wood samples containing both sap- and heartwood, whether the heartwood was orientated across the top, bottom, or sides of the wood cylinder. This suggests that current passes through sap- and heartwood without preference.

The reversal of the precipitate stream back towards the wood may have been caused by electro-osmotic flow from anode to cathode compartments (cf. chapter 10), dragging the silver halide with it. Interestingly, the anode interface of the wood became densely stained with this precipitate, but there was only slight (ca. 1 mm deep) penetration into the wood interior.

Varying the type of cathodes (Ag or Ag/AgCl), catholytes (LiCl, KCl, $AgNO_3$, or $KNO_3$), or anolytes ($KNO_3$ or $CuSO_4$) did not affect the streaming, provided an Ag anode was used. Chloride-containing catholytes resulted in more intense and prolonged precipitation once the endogenous $Cl^-$ ions had migrated through the wood, although the respective rates of exo- and endogenous $Cl^-$ ion migration could not be distinguished.

With wood whose endogenous $Cl^-$ had been removed by flushing with 0.05 M $CuSO_4$, only diffuse precipitation occurred after passing over 130 C (using a Pt/Ag/AgCl cathode in 0.05 M HCl, and Ag anode in 0.025 M $Li_2SO_4$). This suggests that exogenous $Cl^-$ migration is retarded in $CuSO_4$-saturated wood, probably because here the anion current was carried largely by the $SO_4^{2-}$ ions.

Streaming was also absent when 0.05 M NaCl catholyte and 0.2 mM $AgNO_3$ anolyte were used with 100 mm long wood. Instead, the anolyte and anode-facing portion of the wood turned black-brown, characteristic of $AgNO_3$ staining. As the run progressed the blackish discolouration advanced along the surface of the wood towards the cathode, forming an irregular boundary. After the passage of about 70 C a clear purple-grey

ring became distinguishable in front of the blackish boundary, about half-way along the wood. The anolyte became extremely hot, whereas the catholyte stayed cool. This phenomenon indicated that the $Ag^+$ ions migrating from anode to cathode compartments precipitated with $Cl^-$ ions migrating in the opposite direction.

## 6.4 Experimental variables and errors

### 6.4.1 Trees

Slight variations in the ash and moisture contents of wood taken from logs 0.2 - 0.4 m and 0.4 - 0.6 m above ground level in Tree I (Appendices 1 and 2) point to a longitudinal gradient in these properties within the sapwood of a single tree. Smaller variations were found in the moisture contents of wood from Trees II and III (Appendix 3).

Similarly, previous workers have found that the site of the tree, time of year of felling, and location of the wood within the tree significantly affect the levels of inorganic constituents of wood samples (cf. sections 1.6.3, 1.6.4). The type of wood may also affect its cation-exchangeability (section 1.7.3).

Such variations in ion- and to a lesser extent moisture - contents probably account for the variations in the endogenous ion transference numbers of wood from different trees (Table 6.10) and from within the same tree (Table 6.11).

TABLE 6.10 Variation in Endogenous Ion Current of Wood From Different Trees

50 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl, Cu anode in 0.05 M $CuSO_4$.

| Tree Number | No. of Coulombs | $t_{K^+}$ |
|---|---|---|
| II | 10 | .172 |
| III | 10 | .270 |
| | 60 | .216 |
| | 100 | .160 |
| IV | 10 | .162 |
| | 60 | .051 |
| | 100 | .042 |

TABLE 6.11 Variation in Endogenous Ion Current From Different Wood Samples Within a Tree

100 mm long wood of Tree IV.
Pt/Ag/AgCl cathode in 0.25 mM HCl, Cu anode in 0.25 mM $CuSO_4$.
10 C passed.

| Location of Wood in Log | $t_{K^+}$ | $t_{Ca^{2+}}$ |
|---|---|---|
| 'Top' | .224 | .110 |
| 'Middle' | .347 | .113 |
| 'Bottom' | .278 | .117 |

## 6.4.2 Storage and lathe work

It is possible that infected wood was not always detected, since fungal growth (i.e. coloured fruiting bodies) may not have been manifested on the wood surface (cf. sections 6.1.2 and 6.1.3). Slight microbial contamination could also have occurred during the cutting of the wood.

Moisture loss may have taken place during storage (Appendix 4), and before the Mobilcer R coating had been applied and set.

Despite careful cutting procedures, it was difficult to obtain a completely horizontal grain throughout longitudinally-orientated wood samples.

## 6.4.3 Electrical runs

The assembly, operation and dismantling of electrical runs involved a number of experimental uncertainties. The main ones were:

(a) The angle of the grain across the ends of the wood - relative to the cell - varied considerably from run to run.
(b) Small portions of wood samples inevitably protruded from their rubber O-rings into the bathing electrolyte, thereby increasing the interface area of the wood.
(c) Electrolyte solution was forced into the wood during fitting of the electrodes (cf. section 5.6viii).

(d) The ambient temperature varied over a 5°C range with or between different runs (cf. section 6.3.3).

(e) Electrolytes diffused into or out of the wood before and after an electrical run.

The contribution of each of these factors towards experimental variability was probably small. The diffusion of ions out of the wood was determined by control experiments in which the cell was assembled as usual, but no current was passed. Table 6.12 shows that the relative effect was only slight in both short- and long-duration controls, as compared to equivalent electrical runs. The extent of possible ionic diffusion into or within the wood was not determined.

TABLE 6.12 Effect of Diffusion on Ion Movement

Cells filled with electrolytes and fitted with Pt/Ag/AgCl 'cathodes' and Cu 'anodes'.

| Treatment | Endogenous ion concn. in 'catholyte' (μM) | |
|---|---|---|
| | $K^+$ | $Ca^{2+}$ |
| No current, 100 mm long wood, 0.05 M HCl 'catholyte', 0.025 M $Li_2SO_4$ 'anolyte', 1000 s duration. 65 $cm^3$ 'catholyte' volume | 15 | 20 |
| 10 C. Experimental set-up ibid. | 210 | 92 |
| No current, 50 mm long wood, 0.05 M HCl 'catholyte', 0.05 M $CuSO_4$ 'anolyte', 15 000 s duration. 80 $cm^3$ 'catholyte' volume. | <10 | <5 |
| 150 C. Experimental set-up ibid. | 3980 | 85 |

# CHAPTER 7

# IDENTIFICATION OF ENDOGENOUS IONIC CURREN CARRIERS

## 7.1 Introduction

Endogenous ionic current carriers were identified by analysing the electrolyte solutions bathing the ends of a wood sample after passing current. Once these migrating ions had been identified and their concentrations determined, then their transference numbers ($t_{ion}^{wood}$) could be calculated.

In order to detect all the possible ions migrating from the wood, a variety of electrodes and electrolytes was used. For example, non-gassing Ag/AgCl electrodes avoided pH changes in the surrounding electrolytes, resulting from gassing at the electrodes:

Cathode reaction: $H^+ + e^- \rightarrow \frac{1}{2}H_2$ (g) Turns electrolyte alkaline

Anode reaction: $H_2O \rightarrow \frac{1}{2}O_2$ (g) $+ 2H^+ + 2e^-$

$OH^- \rightarrow \frac{1}{2}O_2$ (g) $+ H^+ + 2e^-$

} Turns electrolyte acidic

Thus, any pH changes that occurred in the solutions after the passage of electricity must have resulted from respective $H^+$ or $OH^-$ migration from the wood.

It was also important in these identification experiments to prevent exogenous, electrolyte ions passing through the entire length of the wood, from one electrode compartment to the other. If this did occur, migrating endo- and exogenous ions would have become mixed together in the same electrolyte solution. This could be avoided by passing only a small number of coulombs, say $<5$. On the other hand, sufficient quantities of migrating ions were needed for reliable analysis of the electrolyte to be made. A compromise was reached in practice, whereby roughly half the wood was exhausted of its current-carrying ions. The number of coulombs required for this purpose was estimated as follows.

Since the levels of the inorganic *elements* (but not the *ions*) in the wood was known from the ashing experiments and from data in the literature (Appendix 1, section 1.6.4), the total salt concentration in the wood was estimated as 0.05 moles in 1000 $cm^3$ (= 0.05 M). The volume of a cylinder of wood 50 mm long x 22 mm diameter is

$$= 5.0 \times \pi (1.1)^2 \text{ cm}^3 = 19.0 \text{ cm}^3$$

Estimated quantity of salt in a wood sample is

$$= (0.05/1000) \times 19.0 \approx 0.000\ 95 \text{ moles}$$

The passage of all these endogenous ions (if assumed to be monovalent) across a plane would require 0.000 95 faradays, or 0.000 95 x 96487 = 92 C. So to exhaust half the total endogenous ions needs 46 C. More electricity would actually be needed, since some of the ions (e.g. $Ca^{2+}$, $Mg^{2+}$, $SO_4^{2-}$) are divalent. However, cations and anions will migrate to their respective electrodes, so that the above figure is an overestimate. Moreover, exogenous ions in the bathing electrolytes may migrate more rapidly through the wood, and overtake the endogenous ions before less than half the wood has been exhausted.

It must also be emphasised that this estimate is based on the total inorganic element content of the wood. Much of the mineral constituents of the wood are likely to be covalently bonded into the structure of the wood itself (section 1.6.4), and therefore incapable of passing current. The conductivity of wood may also vary within a sample, so that one particular tissue may conduct current more readily than another.

Despite these uncertaintities, this calculation of 46 coulombs provided an order-of-magnitude estimate. In practice, varying numbers of coulombs were passed until the migration of both endo- and exogenous ions was better understood (cf. chapters 8 and 9).

In these early experiments, the bathing electrolytes were matched as far as possible to the likely endogenous electrolytes. Thus, $Cl^-$ and $NO_3^-$ catholytes and $K^+$ anolytes were chosen to match the presumed large amounts of these endogenous ions (as found from ashing studies - see Appendix 1). Similarly, 0.05 M electrolyte was used to match the

theoretical concentration of total endogenous electrolytes. In this way it was hoped to create a crude electrochemical replica of the wood in the electrode compartments.

## 7.2 Results

The following results are based on the changes in ionic composition of 0.05 M electrolytes after passing a known number of coulombs through longitudinally-grained, 50 mm long x 22 mm diameter wood samples at room temperature.

The pH was measured with a Cambridge pH meter. pH values were converted to $H^+$ concentrations by taking the effective activity coefficient as unity, i.e.

$$pH = -\log_{10}[H^+]$$

The $OH^-$ ion concentration was evaluated from the ionic product of water, $K_w$, by the equation

$$[H^+][OH^-] = K_w = 1.0 \times 10^{-14}$$

In nearly all the catholytes analysed there was a negligible change in $H^+$ concentration (Table 7.1). The marked increases in pH in some runs

TABLE 7.1 Possible Migration of Endogenous $H^+$ with Varying Numbers of Coulombs

pH measurements were made on 0.05 M LiCl or KCl catholytes, from electrical runs using Ag/AgCl cathode, Ag anode, and 0.05 M KI or $KNO_3$ anolytes.

| Catholyte (0.05 M) | No. of coulombs | pH of catholyte | | | $\Delta[H^+]$ ($\mu$M) | wood $t_{H^+}$ |
|---|---|---|---|---|---|---|
| | | Before run | After run | $\Delta$ | | |
| LiCl | 1 | 6.05 | 6.05 | 0 | 0 | 0 |
| | 6 | 6.05 | 6.12 | +0.07 | -0.1 | - |
| | 14 | 6.05 | 6.47 | +0.42 | -0.5 | - |
| | 24 | 6.05 | 6.20 | +0.15 | -0.2 | - |
| KCl | 9.5 | 6.35 | 7.10 | +0.75 | -0.4 | - |
| | 19 | 6.35 | 5.50 | -0.85 | +2.7 | 0.001 |
| | 27 | 6.35 | 10.30 | +3.95 | ng | - |
| | 37 | 6.35 | 6.40 | +0.05 | -0.05 | - |
| | 38 | 6.35 | 8.15 | +1.8 | -0.5 | - |

Key: ng Negligible (< 0.1 $\mu$M)

were attributable to gassing at the cathode, resulting from erosion of the AgCl coat on the outside of the electrode. This exposed the Ag beneath, leading to the liberation of hydrogen and an excess of $OH^-$ (as described in the previous sub-section). In only one run did the catholyte pH decrease. This led to a very small $H^+$ concentration and a correspondingly small $H^+$ transference number.

In nearly all the anolytes analysed there was negligible change in pH, and therefore $OH^-$ concentration (Table 7.2). In only one run, the first in the table, was there an appreciable pH change, which could be interpreted as a small amount of $OH^-$ transfer from cathode to anode compartments (as a result of gassing on the cathode). Taking the evidence on the whole, however, endogenous $OH^-$ can be ruled out as a significant current carrier in the wood.

TABLE 7.2 Possible Migration of Endogenous $OH^-$ with Varying Numbers of Coulombs

pH measurements were made on 0.05 M KI or $KNO_3$ anolytes, from similar or identical electrical runs to those described in Table 7.1 .

| Anolyte (0.05 M) | No. of coulombs | pH of anolyte | | | $\Delta [OH^-]$ ($\mu$M) | wood $t_{OH^-}$ |
|---|---|---|---|---|---|---|
| | | Before run | After run | $\Delta$ | | |
| KI | 5 | 6.50 | 9.42 | +2.92 | +260 | .033 |
| | 12.5 | 6.50 | 6.47 | -0.03 | - | - |
| $KNO_3$ | 4 | 6.0 | 6.0 | 0 | 0 | - |
| | 9 | 6.0 | 4.8 | -1.2 | $\ll$-1.0 | - |
| | 19 | 6.0 | 6.5 | +0.5 | $\ll$+1.0 | ng |
| | 27 | 6.0 | 6.0 | 0 | 0 | - |
| | 37 | 6.0 | 6.05 | +0.05 | $\ll$+1.0 | ng |
| | 44 | 5.5 | 5.4 | -0.1 | $\ll$-1.0 | - |

Key: ng Negligible ($t^{wood}_{ion} < 0.001$)

The concentrations of migrating endogenous cations are shown in Table 7.3, and migrating endogenous anions in Table 7.4 . The limited volume (65 $cm^3$) of each electrolyte sample prevented a direct comparison of different analytical techniques. For example, the levels of alkali metals found from flame photometery and from ion chromatography cannot be directly compared, as different catholyte samples were used for each method of analysis.

TABLE 7.3 Migration of Endogenous Cations (other than $H^+$)

Analyses of endogenous cations in cathode compartments were based on runs using a variety of electrodes and electrolytes (0.05 M): Ag or Ag/AgCl cathodes in $Na_2CO_3$, $KNO_3$, HCl, $NH_4CO_3$ or $Li_2SO_4$; Ag or Cu anodes in $Na_2CO_3$, $KNO_3$, $CuSO_4$ or $Li_2SO_4$.

| Method of analysis | Average no. of coulombs | Endogenous cation | Average concn. ($\mu$M) | Average transference no. | No. of replicates |
|---|---|---|---|---|---|
| Flame photometry | 19 ± 5 | $K^+$ | 629 ± 288 | .30 ± .14 | 6 |
| | | $Na^+$ | 154 ± 77 | .10 ± .04 | |
| | | $Li^+$ | n.d. | - | |
| APS | 37 ± 1 | $Ca^{2+}$ | 32 ± 6 | .011 ± .002 | 5 |
| | | $Mg^{2+}$ | 39 ± 24 | .013 ± .008 | |
| | | Pb | n.d. | - | |
| | | Sn | n.d. | - | |
| | | $Cu^{2+}$ | n.d. | - | |
| | | Co | n.d. | - | |
| | | $Zn^{2+}$ | n.d. | - | |
| | | $Mn^{2+}$ | n.d. | - | |
| | | Fe | n.d. | - | |
| | | Cr | n.d. | - | |
| | | Al | n.d. | - | |
| AAS/FE | 43 ± 13 | $Mn^{2+}$ | 18 ± 5 | .004 ± .002 | 20 |
| | | $Cu^{2+}$ | 1 | .001 | |
| | | $Zn^{2+}$ | 1 | .001 | |
| | | Fe | 1 | .001 | |
| IC | 9 ± 1 | $K^+$ | 329 ± 113 | .21 ± .14 | 5 |
| | | $Na^+$ | 23 ± 6 | .015 ± .004 | |
| | | $NH_4^+$ | 5 ± 5 | .001 ± .001 | |
| | | Organic acids | n.d. | - | |
| M.Sp. | 36 ± 1 | Organic acids | n.d. | - | 3 |
| Colorimetry | 37 ± 1 | $NH_4^+$ | 12. ± 5 | .004 ± .002 | 4 |

Key:
APS Argon Plasma Spectrometry
AAS Atomic Absorption Spectroscopy
FE Flame Emission
IC Ion Chromatography
M.Sp. Mass Spectrometry

n.d. not detected
± confidence limits

TABLE 7.4 Migration of Endogenous Anions (other than $OH^-$)

Analyses of endogenous anions (by anion chromatography) in anode compartments were based on runs using Pt electrodes, and 0.05 M $Na_2CO_3$ electrolytes.

| No. of coulombs | Endogenous anion | Average concn. (μM) | Average transference no. | No. of replicates |
|---|---|---|---|---|
| 18 | $Cl^-$ | 45 | .016 | - |
| | $H_2PO_4^-$ | 14 | .005 | |
| | $NO_3^-$ | 14 | .005 | |
| | $Br^-$ | 5 | .002 | |
| | $SO_4^{2-}$ | 26 | .018 | |
| 36 | $Cl^-$ | 126 ± 25 | .023 ± .002 | 5 |
| | $H_2PO_4^-$ | 50 ± 36 | .009 ± .009 | |
| | $NO_3^-$ | 50 ± 30 | .009 ± .005 | |
| | $Br^-$ | 10 ± 6 | .002 ± .001 | |
| | $SO_4^{2-}$ | 103 ± 25 | .035 ± .009 | |

(± confidence limits)

These results should also only be regarded as an initial estimate of the relative level of migrating ions, since the experimental parameters often varied from one sample to another. Nevertheless, comparison of the transference numbers of the various ions gives a useful indication of the relative contribution each ion makes to current-carrying. Thus, assuming all experimental parameters equal, the order of current-carrying of each cation species is:

$$K^+ \gg Na^+ > Ca^{2+},\ Mg^{2+} > Mn^{2+} > NH_4^+$$

In contrast, the total anion current is considerably less than that of the cations (Table 7.4). The levels of particular anions also varied considerably - as indicated by the relatively large confidence limits in the 5-replicate, 36-coulomb analyses. The relative proportions of current carried by each anion species was not consistent, but roughly fell into the following order:

$$Cl^-,\ SO_4^{2-} > H_2PO_4^-,\ NO_3^- > Br^-$$

In some anolytes $H_2PO_4^-$, $NO_3^-$ and $Br^-$ were each absent, so that their overall contribution to carrying current was highly variable. No organic or any other inorganic migrating anions were detected in the anolytes by mass spectrometry or ion chromatography.

## 7.3 Discussion

The combined results of these experiments show that the endogenous ion current largely comprises several ions, in the order:

$$K^+ \gg Na^+ > Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}$$

Thus, the bulk of this current is carried by $K^+$, and compared to the cations the migrating anions are relatively insignificant. This order of current-carrying only marginally reflects the levels of each corresponding element in the wood ash (cf. Appendix 1, section 1.6.3):

$$K, Ca \gg Mg \gg Na > Mn > Cu, Cr, Fe$$

Although the levels of $Cl^-$, $SO_4^{2-}$, and other anions in the wood are not known, they are likely to be present at no more than trace concentrations (cf. section 1.6.3).

A disproportionately large current is carried by the monovalent, rather than the divalent cations, even though each divalent ion carries twice the electrical charge of a monovalent ion. This indicates that $Ca^{2+}$ and $Mg^{2+}$ are held more tightly to the wood. It is also interesting that the trace elements Cu, Cr and Fe take no part in the electrical conduction. This suggests that these cations or elements are bound even more tightly within the wood, possibly cementing the cell wall layers together (cf. section 1.6.3).

The considerable increase in levels of all ions with increasing numbers of coulombs indicates that the range of coulombs passed had not completely exhausted the wood. However, the combined transference numbers of all endogenous ions in any one electrical run were relatively small (about 0.3). This could be explained if the remaining 70% of the current was carried by exogenous ions which entered the wood from the electrode chamber being analysed, e.g. by anions such as $Cl^-$ moving into the wood from the catholyte solution, and by cations such as $K^+$ migrating into the wood from the anode compartment. This migration is a reflection of the high concentration (0.05 M) of exogenous ions in the bathing electrolytes, compared with the concentrations produced by the endogenous ions - of the order of 1 mM. This suggests that the concentration of labile ions in the wood is much less than the levels of elements found in the wood ash.

The removal of a fraction of the ash content of wood by passing d.c. electricity agrees with previous workers, although the migrating ion species in their experiments were largely undetermined (cf. section 3.2.1). Thus, Bechhold and Heymann (1928) found that the ash content of samples of pine sapwood - of comparable size to those used here - fell from 0.31% to 0.02% by passing about 45 000 C. Thus, most endogenous minerals can eventually be electrically removed from wood with sufficiently high numbers of coulombs, but a small fraction remains immobile. Although these workers also reported rapid changes in pH in both electrode compartments, these were probably caused solely by the electrode reactions at their graphite electrodes.

There was no indication here that organic material migrated. The apparent changes in various organic constituents of Japanese cedar wood (*Cryptomeria japonica*) found by Muraoka (1929) are highly suspect (see section 3.2.1). Nevertheless, the passage of organic matter was implicated in Bechhold and Heymann's observation of brown discolouration of liquid in the cathode compartment. They found this liquid contained (unspecified) reducing substances, but no tannin (which would be expected to give a brown discolouration). Even more intriguing, the intensity of the brown colour began to fade as soon as the impregnating material had completely passed out into the cathode compartment. This suggests that the colouration was a property of the endogenous ion current, or that electrolytic reduction of the material occurred at the cathode, with no more new material coming along to maintain the colour. In contrast, Schwarz (1928a, b, c) found brown or yellow-brown discolouration generally only occurred in the anolyte. Although Schwarz's apparatus differed from Bechhold and Heymann's (compare Figs. 3.2, 3.3), these conflicting observations are difficult to reconcile. The migration of xylan to the anode was reported by Petri (1921) and Herzner (1932), but is suspect as both workers failed to present methods of analyses or supporting data.

The migration of endogenous $K^+$ and $Na^+$ ions found by Langwig and Meyer (1973) in wood of three species of jungle trees agrees with findings given here. The relatively large $Cl^-$ and $Br^-$ current also detected by these workers reflects the unusually high concentrations of both anions in the woods they studied. It is interesting that the other

elements - Ca, Mo, Mn, Si, S, V, Al - detected in these three tropical woods by Langwig and Meyer (1973) remained immobile under the electrical field. This immobility was particularly notable for Mn, which was present in unusually large concentrations (up to 106 ppm), and which was also found to be immobile here. The possible causes of the difference in migration between mono- and divalent cations is discussed further in Chapter 11.

# CHAPTER 8

# PHYSICAL FACTORS AFFECTING CURRENT

## 8.1 Number of coulombs

The endogenous cation current generally fell sharply with increasing numbers of coulombs (Figs. 8.1 to 8.8), becoming completely exhausted between 60 and 100 C, although $K^+$ migrated more rapidly than $Ca^{2+}$ (Figs. 8.1, 8.3, 8.5). The transference numbers show that $K^+$ is the major endogenous ion carrier over small numbers of coulombs ($< 10$), but with longer runs the $Ca^{2+}$ migration becomes larger. An apparent peak in $t_{Ca}2+$ in wood from Tree IV (Figs. 8.2, 8.4) may have simply arisen from variations between different pieces of wood.

With exogenous $Li^+$ or $Cu^{2+}$ cations, a lag phase occurred before they completely migrated through the wood (Figs. 8.1 to 8.6). This lag did not appear with exogenous $K^+$ migration, as exo- and endogenous $K^+$ ions became mixed together (Figs. 8.7, 8.8). Nevertheless, both $K^+$ and $Li^+$ clearly migrated more rapidly through the wood than $Cu^{2+}$ ions - $Li^+$ migrating into the catholyte after 10 to 30 C, whereas $Cu^{2+}$ only migrated out after about 60 C. Thus, monovalent cations have a higher ion-constituent mobility through wood than this divalent cation. Once the endogenous cations had completely migrated, $t_{Cu}2+$ rose linearly. However, a steady state was not reached even after passing 750 C (Fig. 8.2), and this may reflect the opening up of further passages for $Cu^{2+}$ migration through the wood tissues (cf. section 6.3.5).

FIGURE 8.1 Concentration of Cations Migrating into Cathode Compartment with Increasing Numbers of Coulombs: $CuSO_4$ Anolyte

50 mm long wood, Tree IV.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.05 M $CuSO_4$.

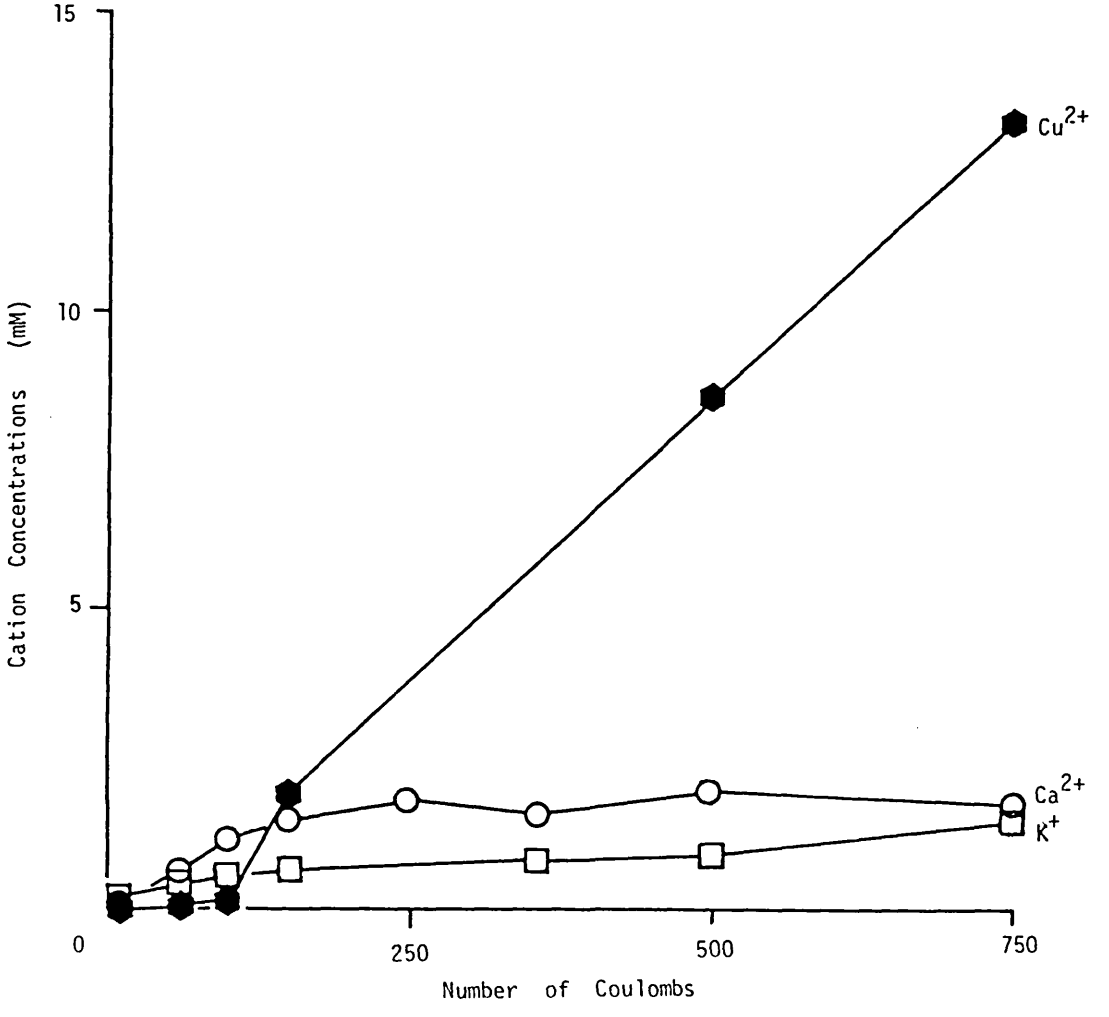


FIGURE 8.2 Transference Numbers of Cations Migrating into Cathode Compartment with Increasing Numbers of Coulombs: $CuSO_4$ Anolyte

Same experimental details as Fig. 8.1.

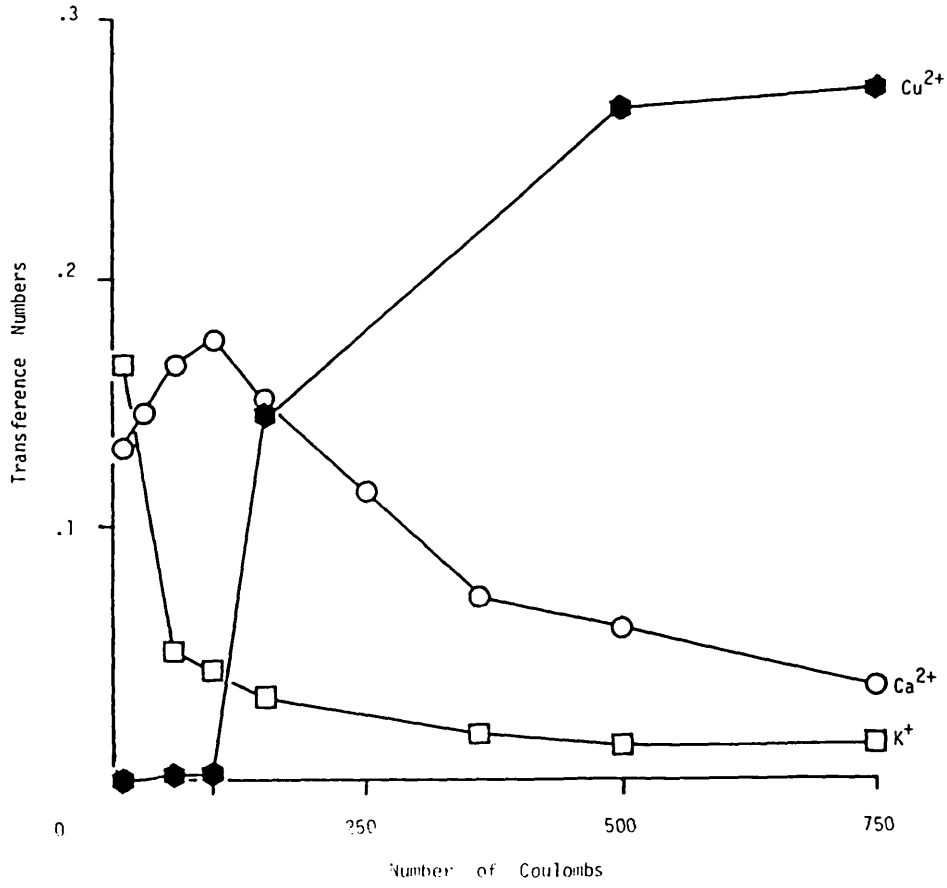


FIGURE 8.3 Migration of Cations Through Wood: Concentration of Cations

50 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.05 M $CuSO_4$.

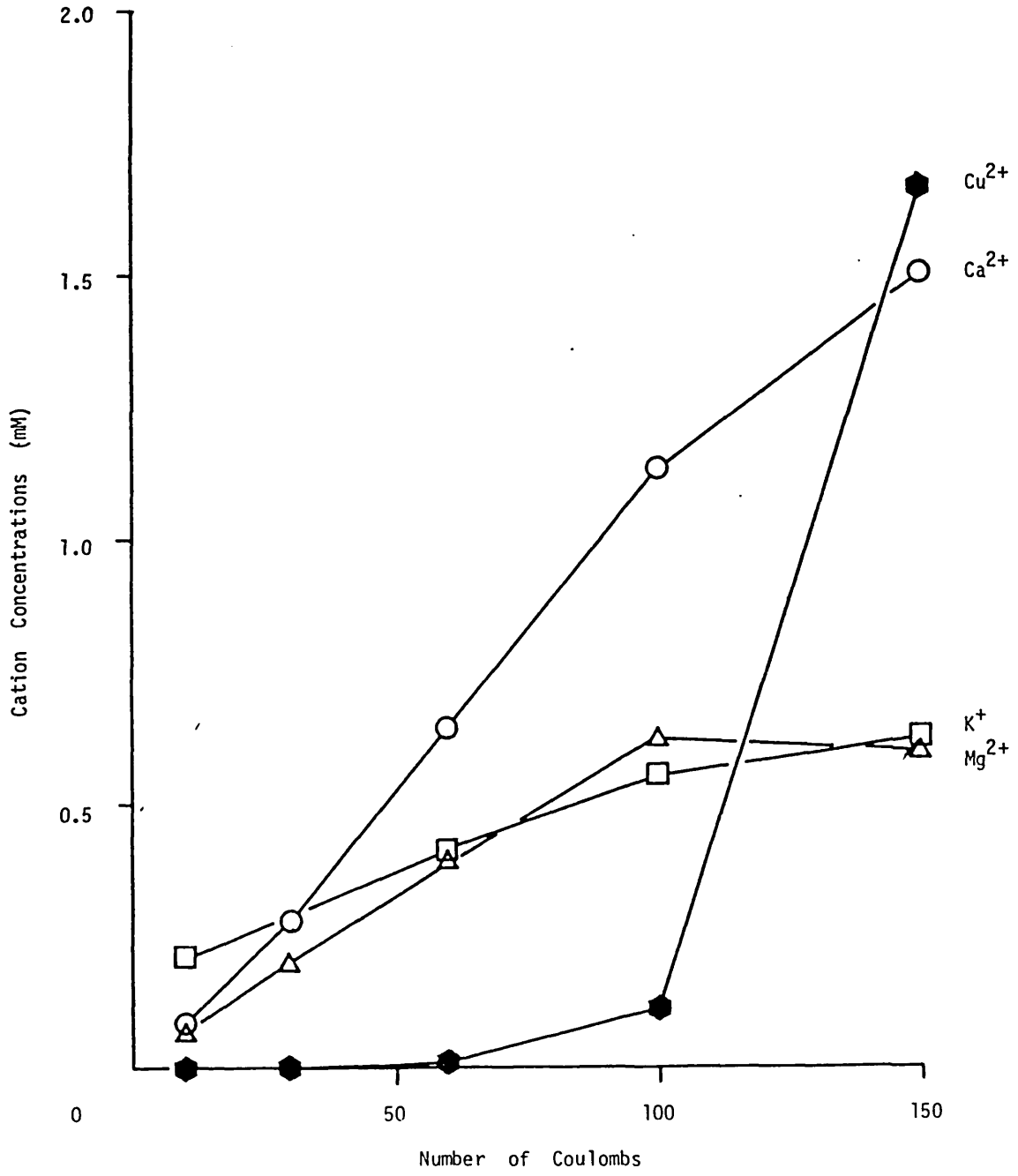


FIGURE 8.4 Migration of Cations Through Wood: Transference Numbers

50 mm long wood.

Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.05 M $CuSO_4$.

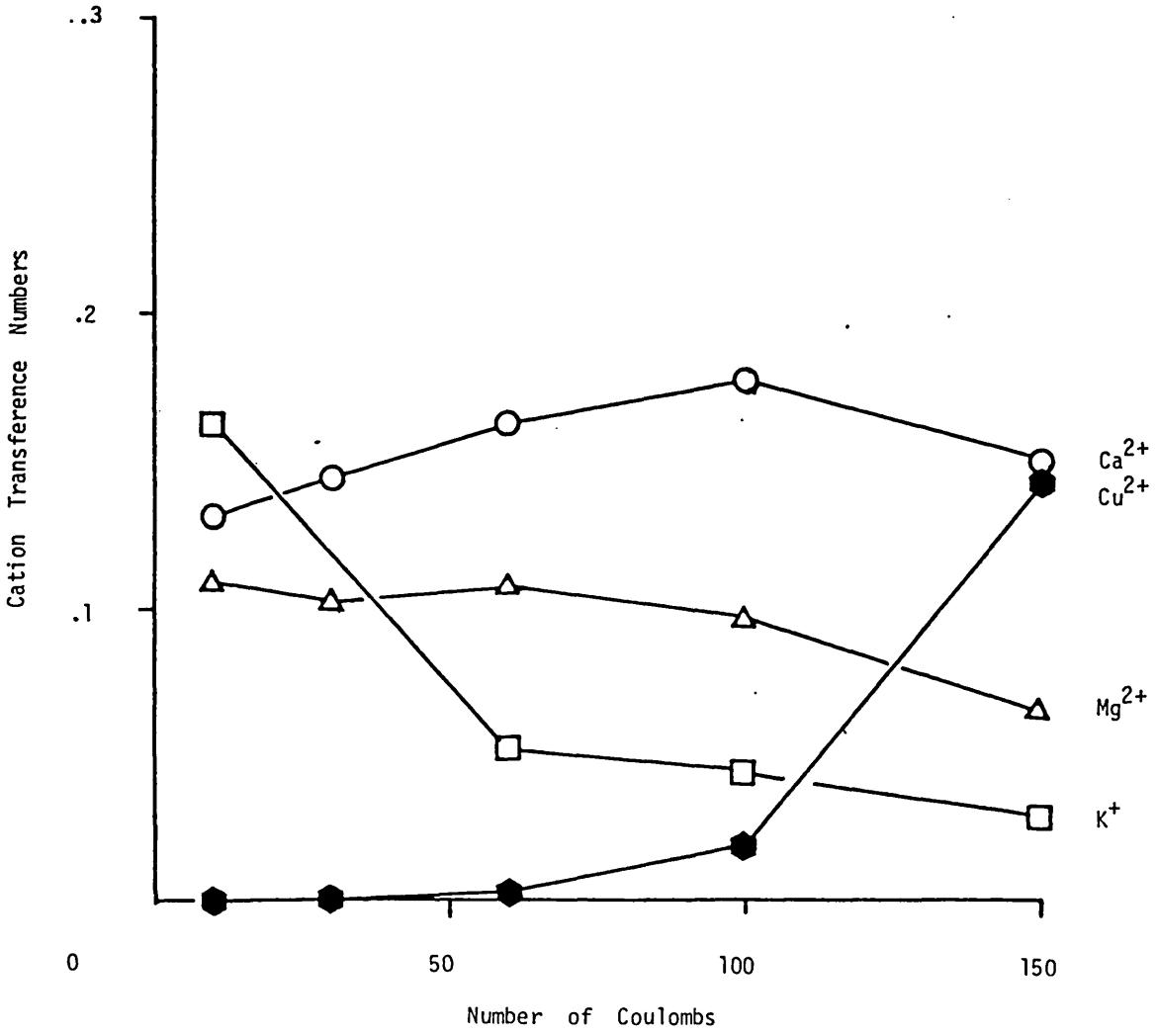


FIGURE 8.5 Migration of Cations with Increasing Numbers of Coulombs: $Li_2SO_4$ Anolyte

50 mm long wood, Tree IV.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.025 M $Li_2SO_4$.

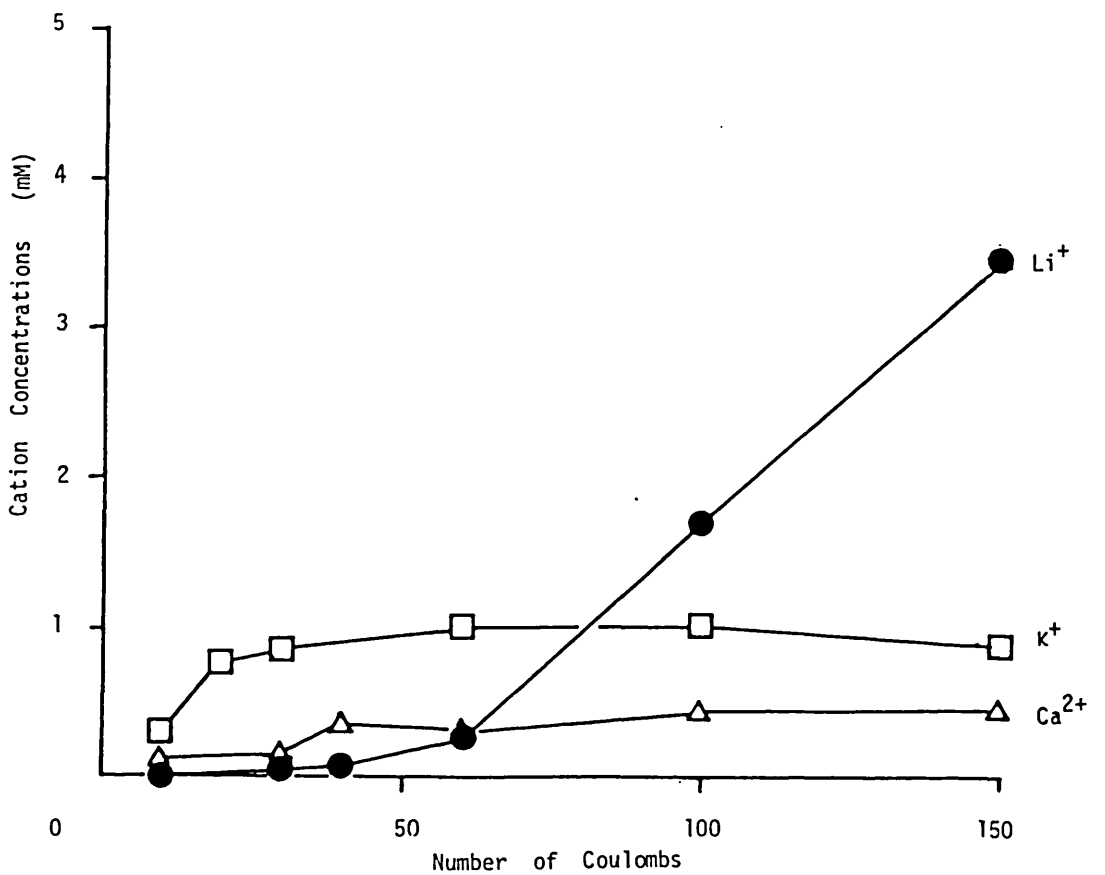


FIGURE 8.6 Migration of Cations with Increasing Numbers of Coulombs: $Li_2SO_4$ Anolyte

50 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.025 M $Li_2SO_4$.

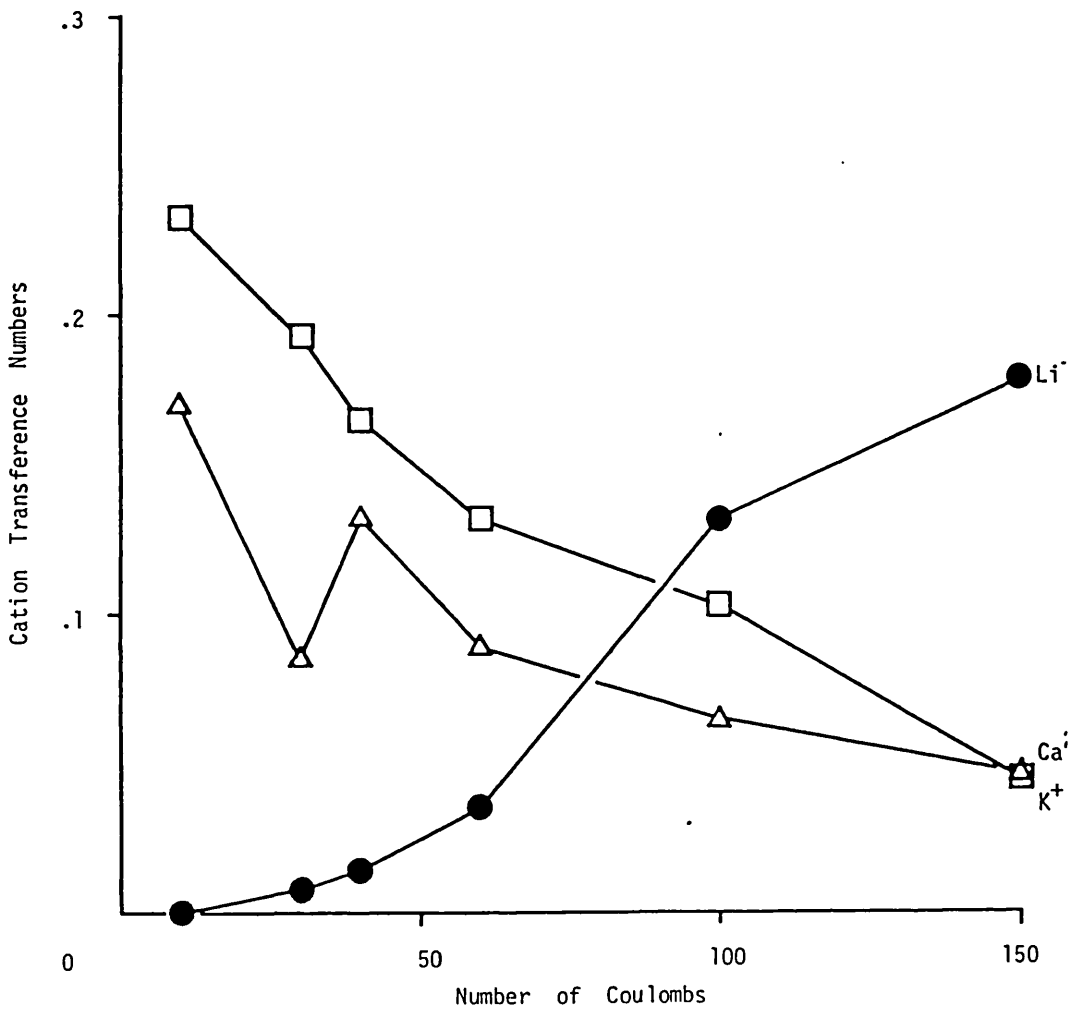


FIGURE 8.7 Migration of Cations with Increasing Numbers of Coulombs: $K_2SO_4$ Anolyte

50 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.025 M $K_2SO_4$.

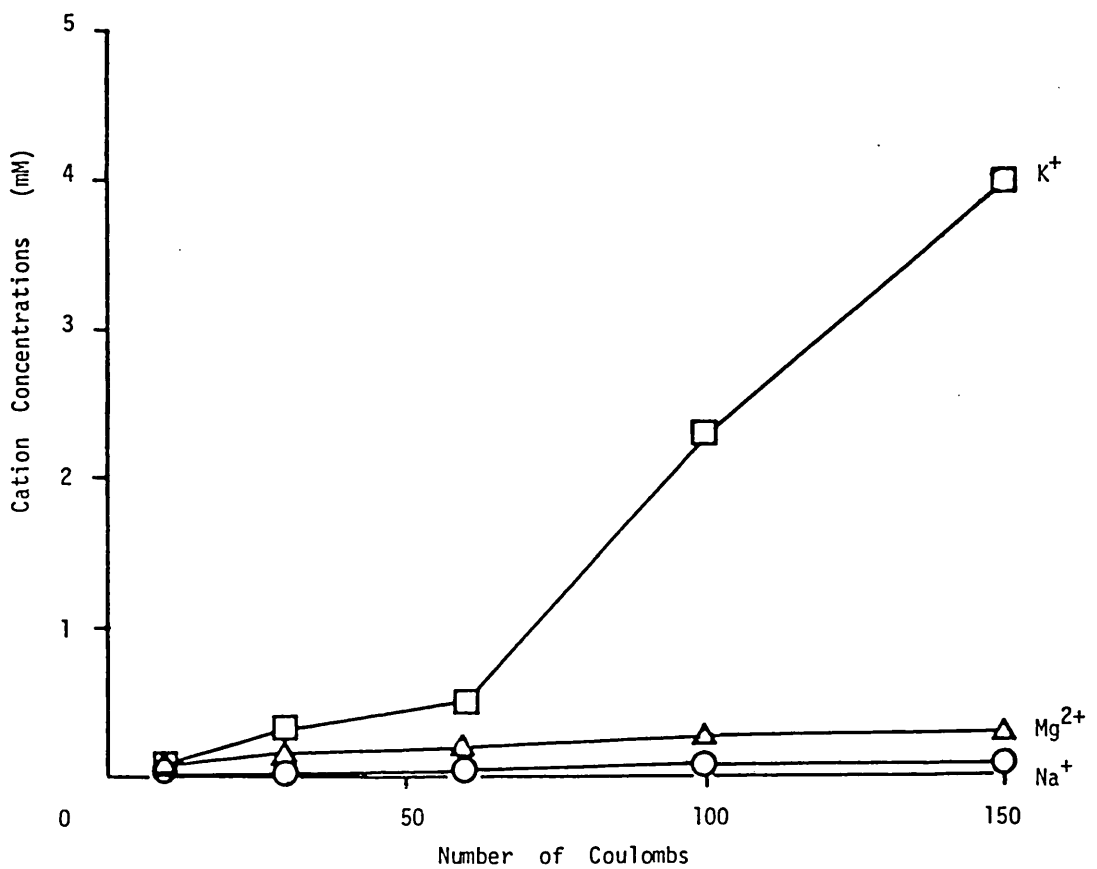
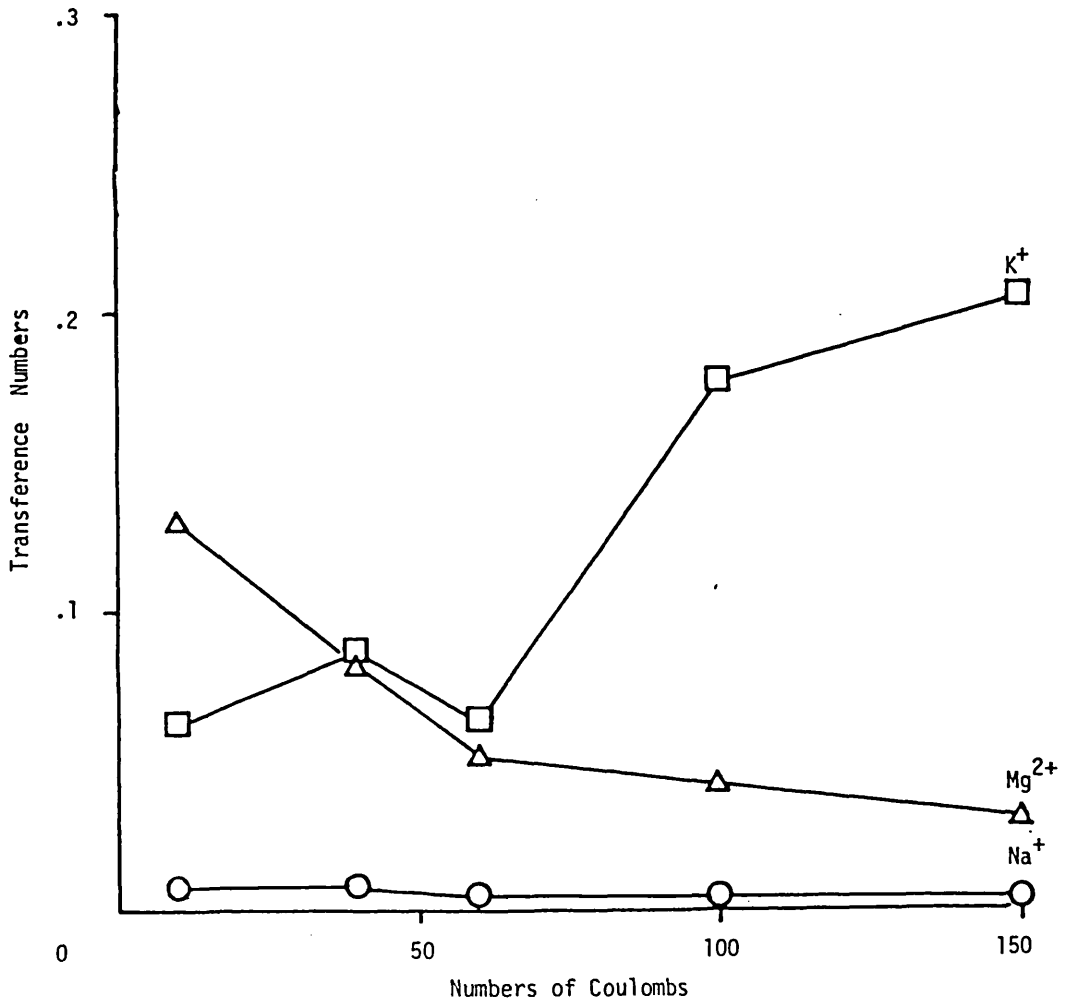


FIGURE 8.8 Migration of Cations with Increasing Numbers of Coulombs: 0.025 M $K_2SO_4$

50 mm long wood.

Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.025 M $K_2SO_4$



The small endogenous anion current was apparently carried solely by $Cl^-$ ions (Fig 8.9), although $SO_4^{2-}$ migration known to occur (cf. chapter 7) could not be determined in the runs using $CuSO_4$ anolyte. The exogenous $Cl^-$ current also appeared to be negligible, even when 750 C were passed (Fig. 8.10). In contrast, exogenous $Cl^-$ migration was much greater in runs using anolytes other than $CuSO_4$ (cf. section 6.3.5 and Table 8.1). It is possible that the migrating $Cu^{2+}$ and $Cl^-$ ions associated together as $CuCl^+$ both in the wood and in the electrolyte solutions, and would therefore have been undetected by anion chromatography.

FIGURE 8.9 Migration of $Cl^-$ Ions Into Anode Compartment with Increasing Number of Coulombs: $Cl^-$ Concentration

50 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.05 M $CuSO_4$.

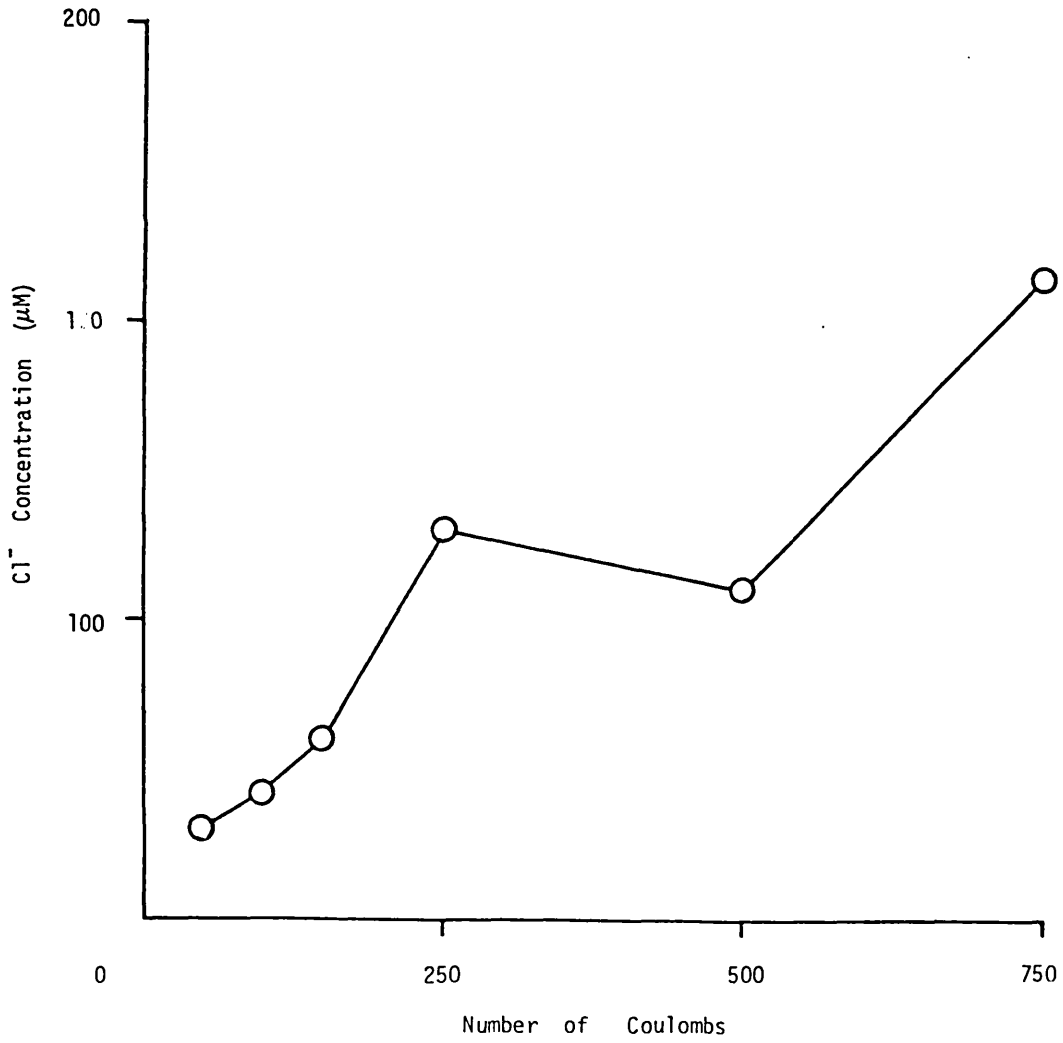


FIGURE 8.10 Migration of $Cl^-$ Ions Into Anode Compartment With Increasing Number of Coulombs: Transference Numbers

50 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.05 M $CuSO_4$.

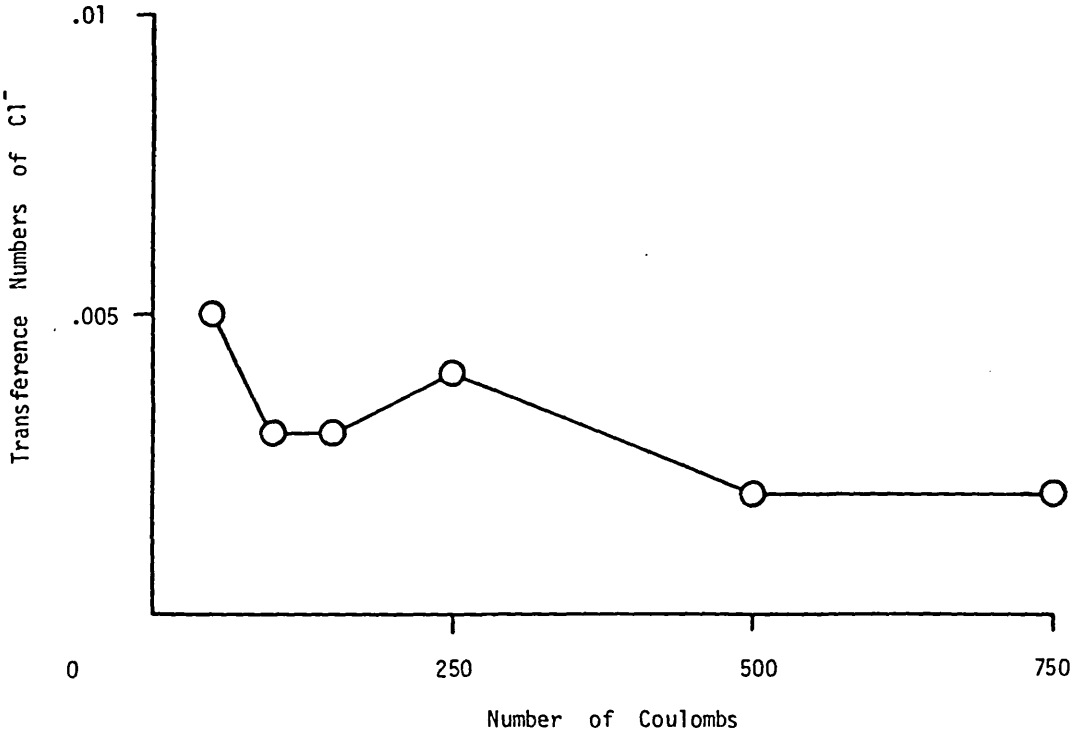


TABLE 8.1 Migration of $Cl^-$ Using Different Anolytes

50 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in two different anolytes.

| Anolyte Solution | No. of Coulombs | $t_{Cl^-}$ |
|---|---|---|
| 0.05 M $CuSO_4$ | 150 | .003 |
| 0.025 M $Li_2SO_4$ | 150 | .533 |

## 8.2 Current intensity

At the higher currents $t_{Ca}2+$ was always smaller than in the 10 mA runs, whereas the $t_K+$ values were greater (Table 8.2). There is no clear pattern for the sum of the two transference numbers. It is possible that $Ca^{2+}$ binds more strongly than $K^+$ to negatively charged sites in the wood, resulting in slower dissociation. Thus, with longer runs (i.e. smaller currents) $Ca^{2+}$ migration is promoted.

TABLE 8.2 Effect of Different Currents on Endogenous Ionic Migration

50 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.05 M $CuSO_4$.

| No. of Coulombs | Current (mA) | Transference Numbers | | |
|---|---|---|---|---|
| | | $t_K+$ | $t_{Ca}2+$ | $t_K+ + t_{Ca}2+$ |
| 20 | 10 | .156 | .262 | .418 |
| | 20 | .270 | .170 | .440 |
| 60 | 10 | .051 | .163 | .214 |
| | 25 | .107 | .011 | .118 |
| 100 | 10 | .160 | .286 | .446 |
| | 20 | .170 | .154 | .324 |

## 8.3 Closed cathode compartment

The possible effects of electro-osmosis on ion migration - such as dragging the ions along with the flow of water - was tested by carrying out experiments with the tap in the cathode compartment closed throughout the runs.

There were no significant differences between cation transference numbers in open or closed compartments (Table 8.3), so that electro-osmosis has no apparent effect on ionic migration.

TABLE 8.3 Effect of Closed Cathode Compartment on Cation Migration

50 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in $CuSO_4$.

| No. of coulombs | Cathode Compartment | Cation Transference Numbers | | | |
|---|---|---|---|---|---|
| | | $t_{Cu^{2+}}$ | $t_{K^+}$ | $t_{Ca^{2+}}$ | $t_{Cu^{2+}} + t_{K^+} + t_{Ca^{2+}}$ |
| 10 | Open | 0 | .106 | .096 | .202 |
| | Closed | 0 | .100 | .077 | .177 |
| 150 | Open | .143 | .032 | .150 | .325 |
| | Closed | .172 | .028 | .154 | .354 |

## 8.4 Length of wood

The effects of the length of wood on ion migration were studied using 50 and 100 mm samples.

The endogenous $K^+$ migration became exhausted more rapidly in the shorter sample (Fig. 8.11), as expected from the smaller reservoir of $K^+$ in the wood. However, there was little difference in the $Ca^{2+}$ current between both lengths of wood (at least over 150 C) (Fig. 8.12), probably reflecting the slower migration of this cation through wood.

The characteristic lag phase before exogenous $Li^+$ and $Cu^{2+}$ ions completed migration through the wood was distinctly greater in the longer wood (Figs. 8.13, 8.14).

FIGURE 8.11 Migration of Endogenous $K^+$ Through Wood of Different Lengths

50 mm or 100 mm long wood.

Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.05 M $CuSO_4$ or 0.025 M $Li_2SO_4$.

Bars represent confidence limits based on 4 replicates

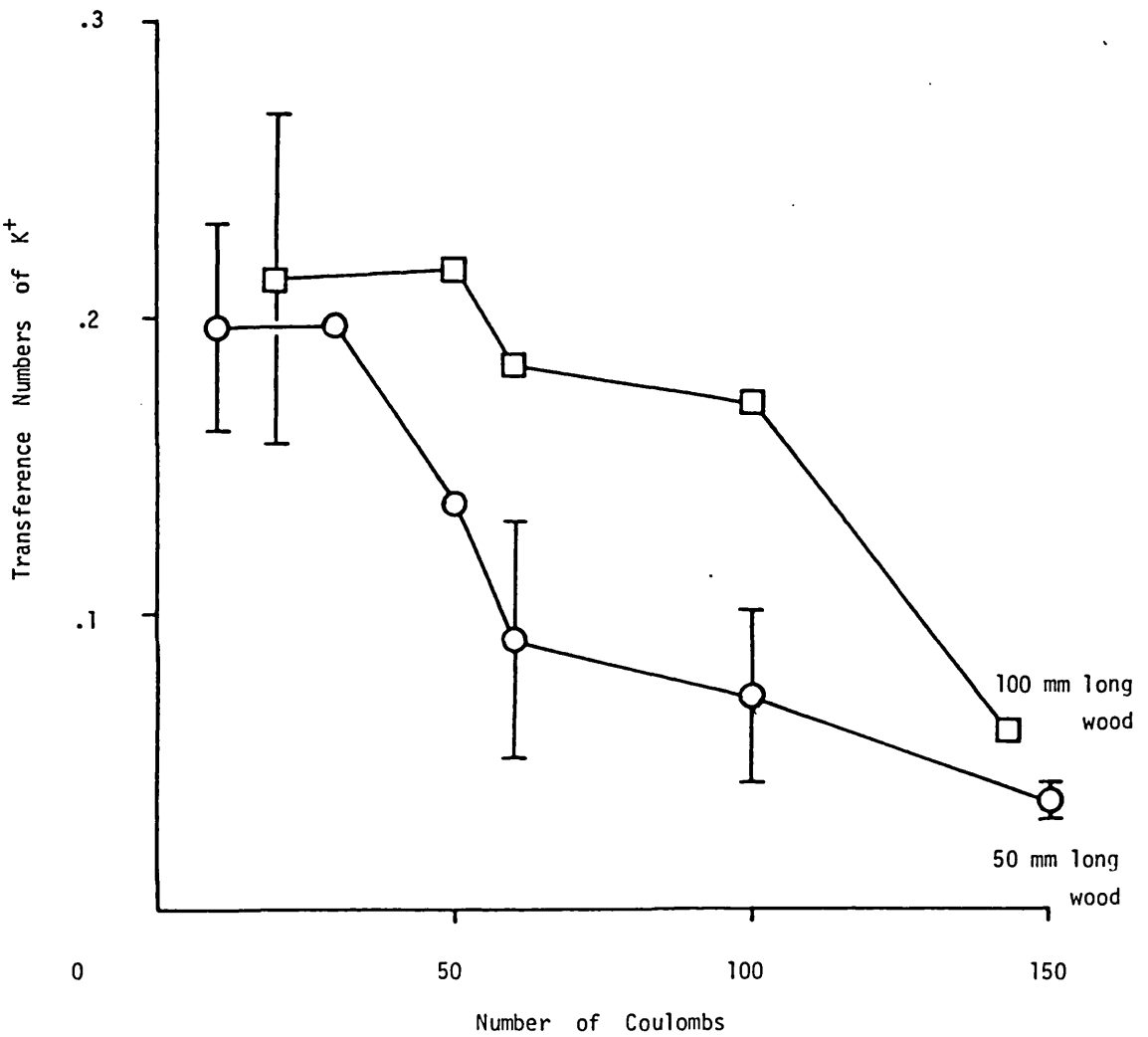


FIGURE 8.12 Migration of Endogenous $Ca^{2+}$ Through Wood of Different Lengths

50 mm or 100 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.05 M $CuSO_4$ or 0.025 M $Li_2SO_4$.
Bars represent confidence limits based on 4 replicates

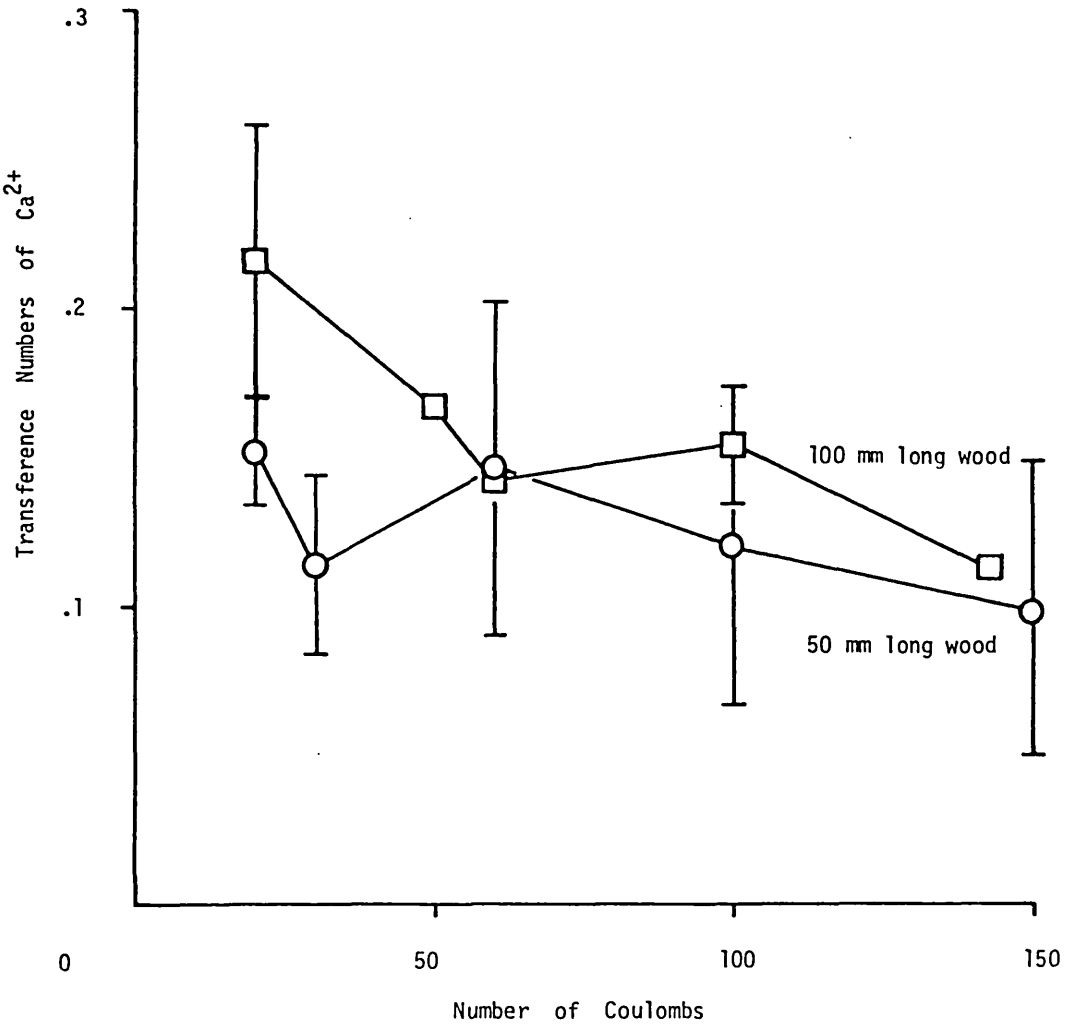


FIGURE 8.13 Migration of Exogenous $Li^+$ Through Wood of Different Lengths

50 mm or 100 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.025 M $Li_2SO_4$.

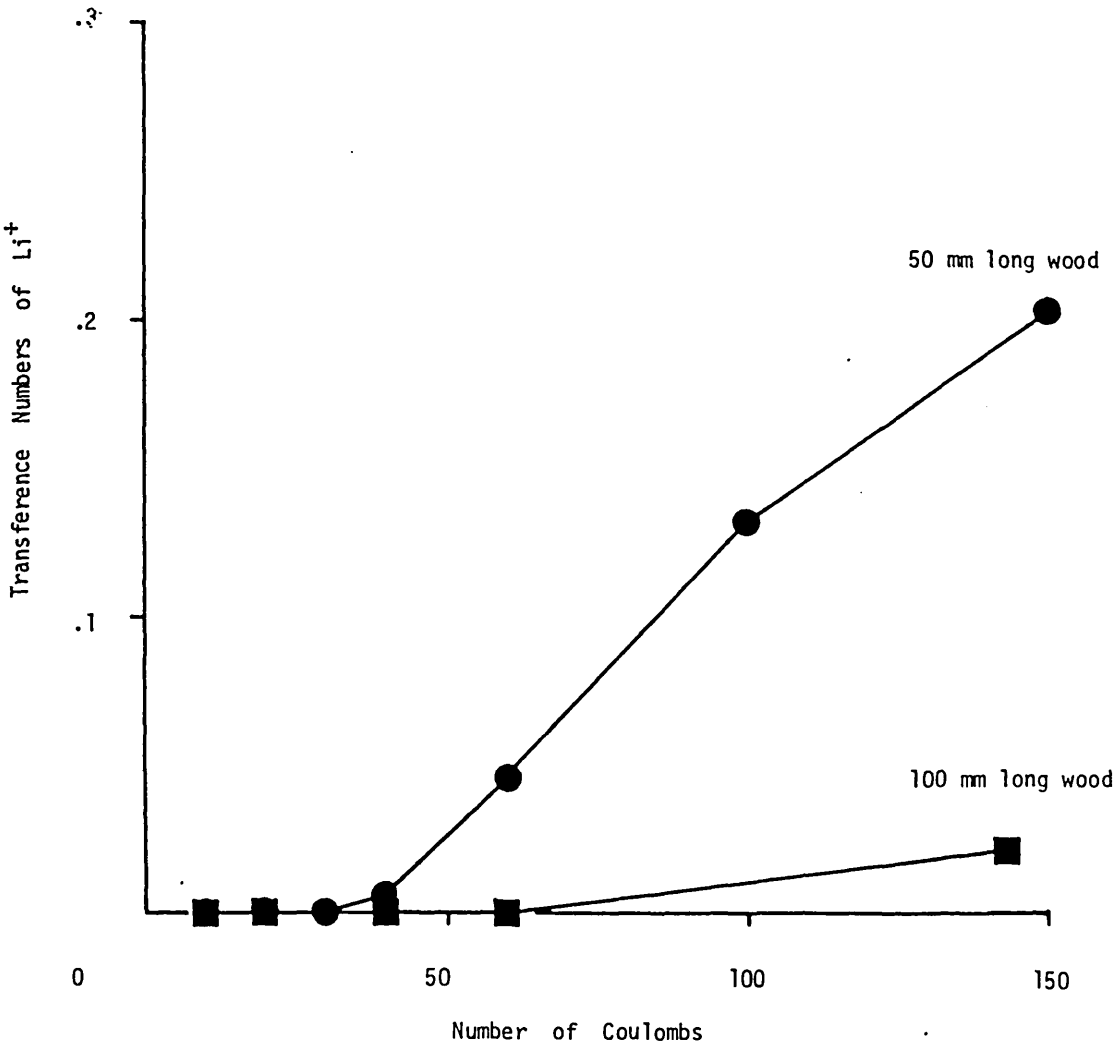
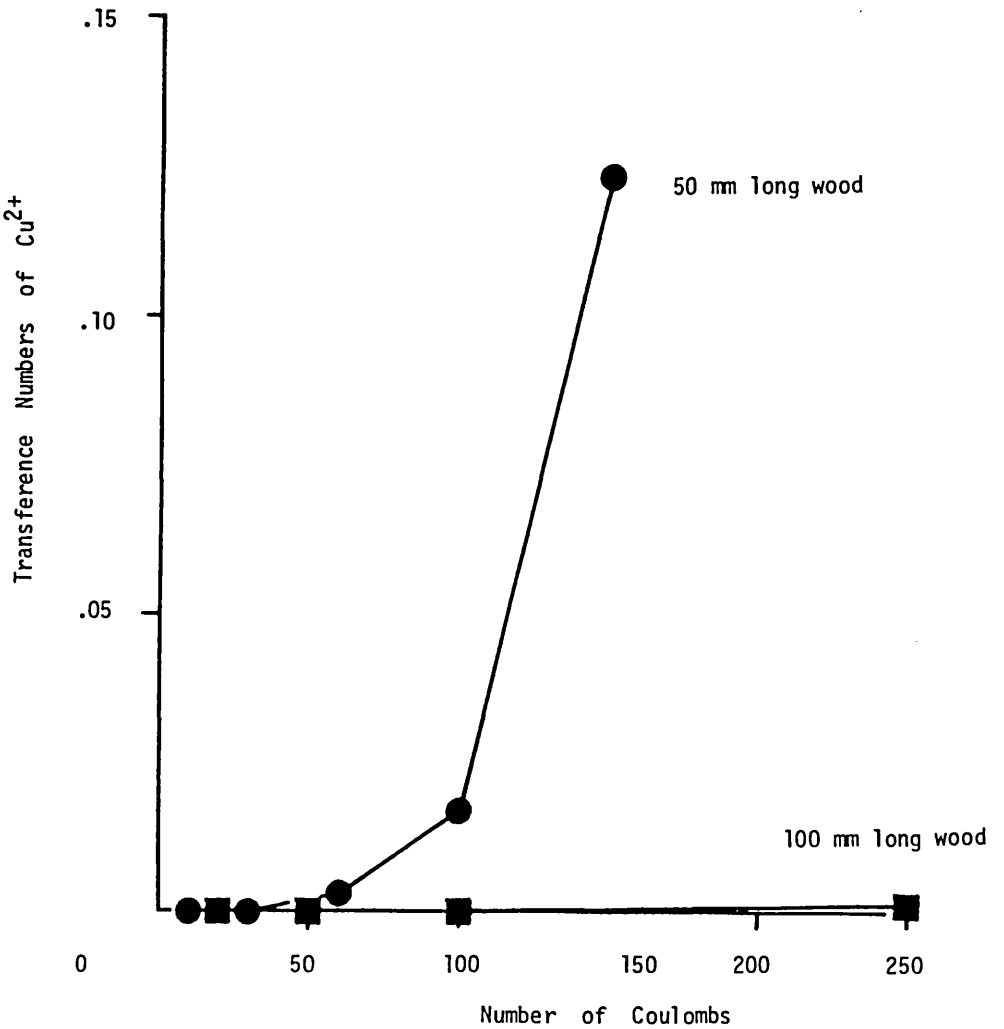


FIGURE 8.14 Migration of Exogenous $Cu^{2+}$ Through Different Lengths of Wood

50 mm or 100 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.05 M $CuSO_4$.



## 8.5 Grain orientation of wood

The effect of grain orientation on ion migration was studied using transversely- and longitudinally-orientated wood (cf. section 5.1.2).

There were no really significant differences in the endogenous ion currents between both orientations of wood (Tables 8.4, 8.5).

TABLE 8.4 Comparison of Endogenous Ion Migration in Transversely- or Longitudinally-orientated Wood

100 mm long wood.
Pt/Ag/AgCl cathode in 0.1 M HCl; Cu anode in 0.1 M $CuSO_4$.
10 C. $t_{ion}$ ± confidence limits.

| Grain Orientation | No. of Replicates | Cation Transference Numbers | |
|---|---|---|---|
| | | $t_{K^+}$ | $t_{Na^+}$ |
| Transverse | 4 | .154 ± .004 | .009 ± .007 |
| Longitudinal | 2 | .127 ± .061 | .008 ± .001 |

TABLE 8.5 Comparison of Endogenous Ion Migration in Transversely- or Longitudinally-grained Wood

100 mm long wood.
Pt/Ag/AgCl cathode in 0.25 mM $Bu_4NI$; Cu anode in 0.25 mM $CuSO_4$.
10 C. $t_{ion}$ ± confidence limits.

| Grain Orientation | No. of Replicates | Cation Transference Numbers | | | |
|---|---|---|---|---|---|
| | | $t_{K^+}$ | $t_{Na^+}$ | $t_{Ca^{2+}}$ | $t_{Cl^-}$ |
| Transverse | 2 | .243 ± .002 | .028 ± .002 | .100 ± 0 | .041 ± .004 |
| Longitudinal | 4 | .211 ± .011 | .009 ± .003 | .099 ± .030 | .016 ± .002 |

## 8.6 Moisture content of wood

An attempt to pass electrical current through dry wood failed (cf. section 6.3.3). Instead, the effect of moisture content of the wood on ion migration was studied using green wood.

Within the range of moisture studied, there was no significant effect of moisture content on the endogenous cation transference numbers (Table 8.6). Since this range of moisture contents largely covers the values found in most samples (cf. Table 6.5, Appendices 2, 3, 4), moisture was not a significant factor in this project.

TABLE 8.6 Endogenous Ion Migration in Wood of Different Moisture Contents

100 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.05 M $CuSO_4$.
10 C.

| Moisture Contents (%) | Cation Transference Numbers $t_{K^+}$ | $t_{Na^+}$ |
|---|---|---|
| 86 | .198 | .010 |
| 113 | .172 | .021 |
| 141 | .172 | .013 |

## 8.7 Discussion

The greatest physical effect on the electrical transport of ions in the wood was the number of coulombs of electricity passed. This is expected since $t_{ion}$ is numerically equal to the net number of moles of an ion transferred for every $|z_i|$ faradays passed (cf. section 2.3.1). This effect had not been shown by previous workers, as they had not used a constant current. Furthermore, by changing other experimental parameters with runs of varying duration, they were not able to detect the coulomb effect. Although current intensity was studied by Petri (1921), he only recorded the colour changes in the wood tissues resulting from impregnation with $CuSO_4$.

The virtual complete removal of the ash content of wood by passing electricity, reported by Bechhold and Heymann (1927) and Schwarz (1928b, c) was partially confirmed here (cf. section 3.2.1), although various inorganic elements such as Mn did not migrate (cf. chapter 7). Also these workers had passed considerably greater numbers of coulombs, when in fact only about 100 C are needed to remove most labile endogenous ions in samples of similar size to theirs.

The proportions of current carried through wood by exogenous anions and cations have not been compared before. Results here indicate that the transference numbers of exogenous anions are probably larger than that of the total cations, unless significant ion association effects occur, e.g. between $Cu^{2+}$ and $Cl^-$ ions.

Both the coulomb and wood length studies clearly showed that divalent cations migrated more slowly than monovalent ones. Again, previous workers had not been able to show this. Petri (1921) passed different cations through wood samples, but he varied the experimental conditions in each run, making comparisons difficult. Duran et al. (1978) found that $Cu^{2+}$ ions migrated more slowly than As anions passing in the opposite direction. Their data also indicate that $Na^+$ migrated more readily than $Cu^{2+}$, although they did not comment on this. Comparison of the endogenous ion currents measured by Langwig and Meyer (1973) using the same Venezuelan jungle tree species as used by Duran et al. - in which $K^+$, $Na^+$, $Cl^-$ , and $Br^-$ were found to be the major current

carriers - also shows that monovalent cation migration is greater than for $Cu^{2+}$.

Although current passes more readily along than across the grain (cf. section 3.1.4), the relative ionic contributions were remarkably similar. This may indicate that in both cases the ions migrate through comparable pathways, even though the larger number of pit-apertures across the grain is thought to result in the higher electrical resistance (cf. section 3.1.4) and Joule heating of transversely-orientated wood (section 6.3.3).

The absence of any moisture content effect on ion migration (except for dried wood) agrees with the relatively small changes in electrical conductivity of wood with moisture contents above 30% (fibre saturation point) (cf. section 3.1.1). However, the wood samples rapidly absorbed solution during electrical runs (cf. section 6.2.3).

Electro-osmosis had no effect on ion migration. Previous workers claimed that the electro-osmotic flow dragged inorganic and organic material along with it (Petri, 1921; Schwarz, 1928a, b, c; Bechhold and Heymann, 1927; Herzner, 1932). As a result, they claimed that the greater the rate of electro-osmosis, the larger the quantity of material carried out of the wood. However, evidence here and further on in section 10.1.3 shows that ion migration and electro-osmosis are effectively independent of each other. The earlier work in the literature, though, suffered from variations in moisture loss, hydrostatic pressure, leakages, and other interfering factors which were often beyond control.

# CHAPTER 9

# CHEMICAL FACTORS AFFECTING CURRENT

## 9.1 Electrolyte concentration

Endogenous $K^+$ and $Cl^-$ migration rises markedly as the HCl catholytes and $CuSO_4$ anolytes, respectively, become more dilute (Figs. 9.1, 9.2). This shows that the transference number of the exogenous ion of opposite charge ($Cl^-$, $Cu^{2+}$, respectively) rises as its concentration rises ($t_i$ rises with $c_i$ - see equation 2.26). Similar results were obtained using different concentrations of $Bu_4NI$ (Table 9.1). In other words, as the endogenous ions migrate out, the exogenous bathing electrolyte ions migrate in. The more concentrated the electrolyte ions, and also the greater their mobility, the larger the current-carrying contribution in the wood will be.

FIGURE 9.1 Effect of Electrolyte Concentration on Endogenous Ion Migration

50 mm long wood.
Pt/Ag/AgCl cathode in HCl; Cu anode in $CuSO_4$.
Confidence limits shown as bars, representing 4 replicates.

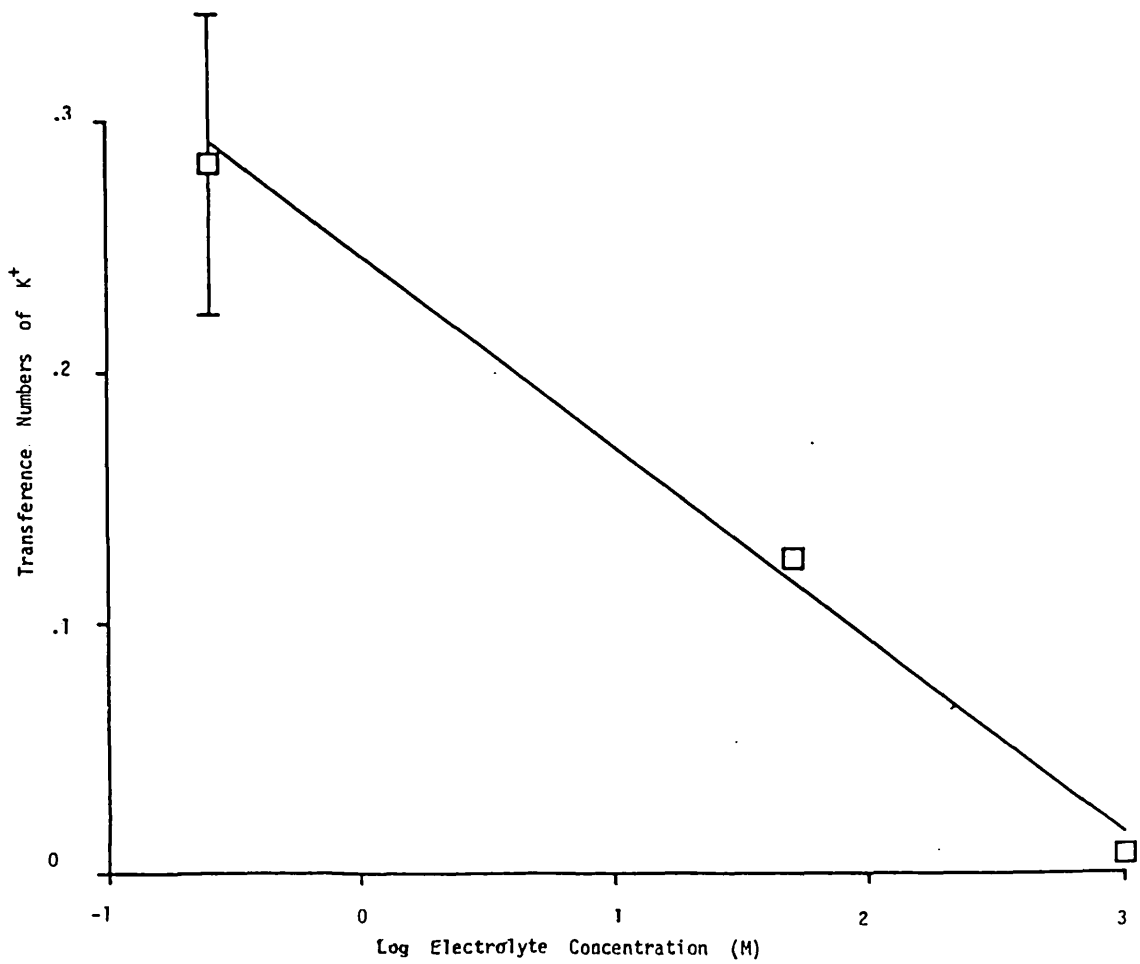


FIGURE 9.2 Effect of Electrolyte Concentration on Endogenous Ion Migration

50 mm long wood.
Pt/Ag/AgCl cathode in HCl; Cu anode in $CuSO_4$.
Confidence limits shown as bars, representing 4 replicates.

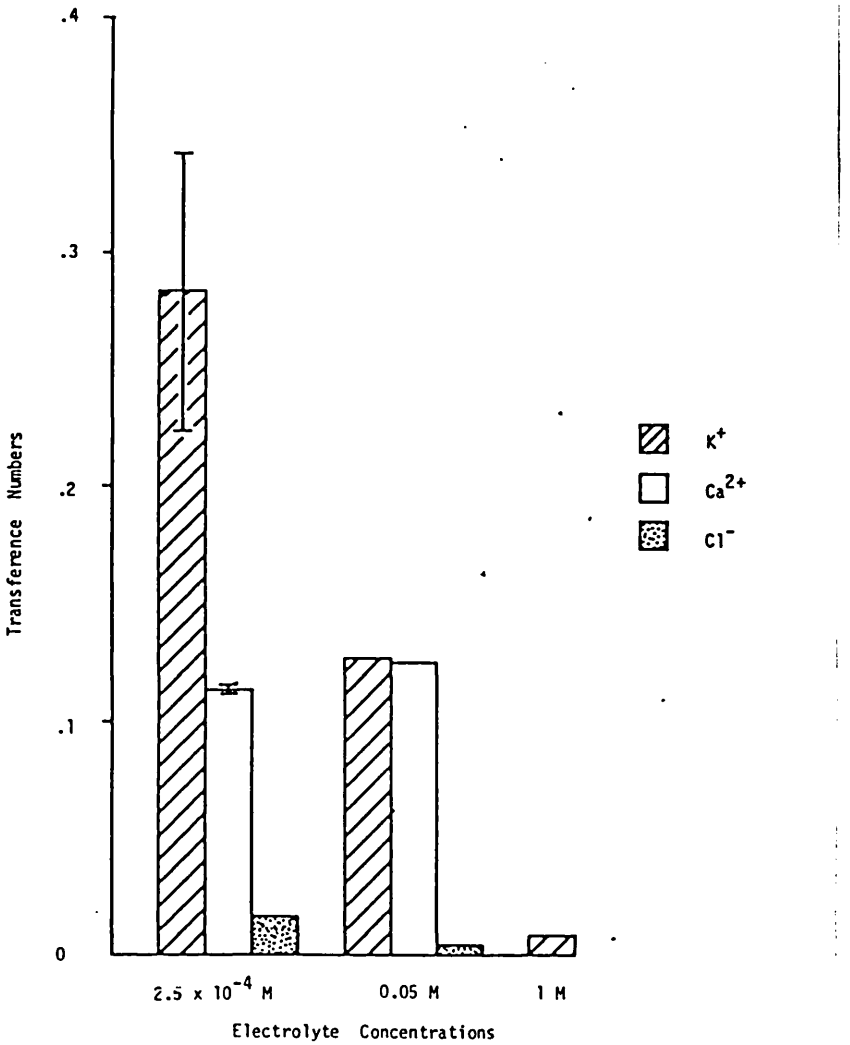



TABLE 9.1 Effect of Electrolyte Concentration on Endogenous Ion Migration: $Bu_4NI$

100 mm long wood
Pt/Ag/AgCl cathode in $Bu_4NI$; Cu anode in $CuSO_4$.
10 C. $t_{ion}$ ± confidence limits.

| Electrolyte Concentration mM | Cation Transference Numbers | | No. of Replicates |
|---|---|---|---|
| | $t_{K^+}$ | $t_{Na^+}$ | |
| 0.25 | .211 ± .011 | .009 ± .003 | 4 |
| 25 | .169 ± .005 | .057 ± .018 | 3 |

## 9.2 Catholyte species

Exogenous ions in the bathing electrolytes carry a large part of the current through the wood (cf. chapter 7). The effects of different exogenous ions were studied at the catholyte/wood interface using different catholyte species.

### 9.2.1 HCl, $HClO_4$

The $ClO_4^-$ anion migrates less fast in water than the $Cl^-$ anion ($\lambda(ClO_4^-)$ = 67.4 $cm^2\ \Omega^{-1}\ mol^{-1}$ at 25°C, $\lambda(Cl^-)$ = 76.4 $cm^2\ \Omega^{-1}\ mol^{-1}$, Robinson and Stokes, 1955). Endogenous cation current-carrying would therefore be expected to be larger. However, there were no apparent differences in monovalent cation migration between HCl or $HClO_4$ catholytes, but the differences in $t_{Mg^{2+}}$ were less clear (Table 9.2)

TABLE 9.2 Effect of HCl and $HClO_4$ Catholytes on Endogenous Cation Migration

Pt/Ag/AgCl cathode in 0.05 M HCl or $HClO_4$; Cu anode in 0.05 M $CuSO_4$.

| Length of Wood (mm) | No. of Coulombs | Catholyte Species | Cation Transference Numbers | | |
|---|---|---|---|---|---|
| | | | $t_{K^+}$ | $t_{Na^+}$ | $t_{Mg^{2+}}$ |
| 50 | 150 | HCl | .029 | .066 | n.d |
| | | $HClO_4$ | .018 | .080 | .004 |
| 100 | 150 | HCl | .060 | .155 | .042 |
| | 143 | $HClO_4$ | .082 | .132 | .006 |

n.d. not determined

### 9.2.2 $Bu_4NI$ (Tetrabutylammonium Iodide)

If electrolytes diffuse into the wood before and during an electrical run they will be able to conduct current. To test for this, $Bu_4NI$ catholyte was used, as the tetrabutylammonium cation, $Bu_4N^+$, has both a low diffusion coefficient and low ion-constituent mobility (i.e. it moves slowly by diffusion or by electrical conduction).

Endogenous cation migration using HCl or $Bu_4NI$ catholytes was almost indistinguishable (Table 9.3). Thus, it is unlikely that ions in the catholyte diffuse into the wood - with the anions subsequently migrating through it while the cations migrate out again under the action of the electric field.

TABLE 9.3 Effect of HCl and $Bu_4NI$ Catholytes on Endogenous Cation Migration

100 mm long wood.
Pt/Ag/AgCl cathode in 0.25 mM catholytes; Cu anode in $CuSO_4$.
10 C. $t_{ion}$ ± confidence limits, based on 4 replicates.

| Catholyte | Cation Transference Numbers | |
|---|---|---|
| | $t_{K^+}$ | $t_{Na^+}$ |
| HCl | .238 ± .021 | .030 ± .009 |
| $Bu_4NI$ | .211 ± .011 | .009 ± .003 |

### 9.2.3 Sodium laurylsulphate

To determine the effect of exogenous anion migration through the wood on the endogenous cation current, sodium laurylsulphate catholyte was used. The large laurylsulphate anion, $C_{12}H_{25}OSO_3^-$, has a low ion-constituent mobility, and should therefore migrate very slowly through the wood. A small number of coulombs (10 C) was passed through a long (100 mm) wood sample, to prevent exogenous $Cu^{2+}$ ions in the anolyte from migrating completely through the wood (cf. section 9.2), into the catholyte.

There was an appreciable increase in $t_{K^+}$ on substituting laurylsulphate for chloride anions in the catholyte (Table 9.4). Thus, exogenous anion migration into the wood significantly affects the endogenous cation current.

TABLE 9.4 Effect of Sodium Laurylsulphate Catholyte on Endogenous Cation Migration

100 mm long wood.
Pt/Ag/AgCl cathode in 0.25 mM HCl or Sodium laurylsulphate; Cu anode in 0.25 mM $CuSO_4$.
10 C. $t_{ion}$ ± confidence limits.

| Catholyte Species | Replicates | $t_{K^+}$ |
|---|---|---|
| HCl | 4 | .238 ± .021 |
| Sodium laurylsulphate | 3 | .318 ± .033 |

## 9.3 Anolyte species

Migration of exogenous cations through the wood was investigated by determining the number of coulombs required for complete migration into the cathode compartment.

Between 10 to 30 C were required to pass $Li^+$ completely through the wood, whereas $Cu^{2+}$ migrated through after about 50 C (Figs 9.3, 9.4). The corresponding number of coulombs for $K^+$ could not be determined, as exo- and endogenous $K^+$ currents could not be distinguished. Assuming that the endogenous $K^+$ current had been completely exhausted after 60 C (cf. section 8.1), then exogenous $K^+$ migrated out faster than $Li^+$. This would be expected, as hydrated $K^+$ ions have a much higher ionic mobility in water than hydrated ions (Robinson and Stokes, 1955). In contrast, $Cu^{2+}$ ion migration was much slower, probably due to ion-pair formation with counter-migrating $Cl^-$ ions (cf. section 9.1).

FIGURE 9.3 Migration of Exogenous (Anolyte) Cations Through Wood: Concentration of Cations in Catholyte

50 mm long wood.

Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.05 M $CuSO_4$ or 0.025 M $Li_2SO_4$ or 0.025 M $K_2SO_4$.

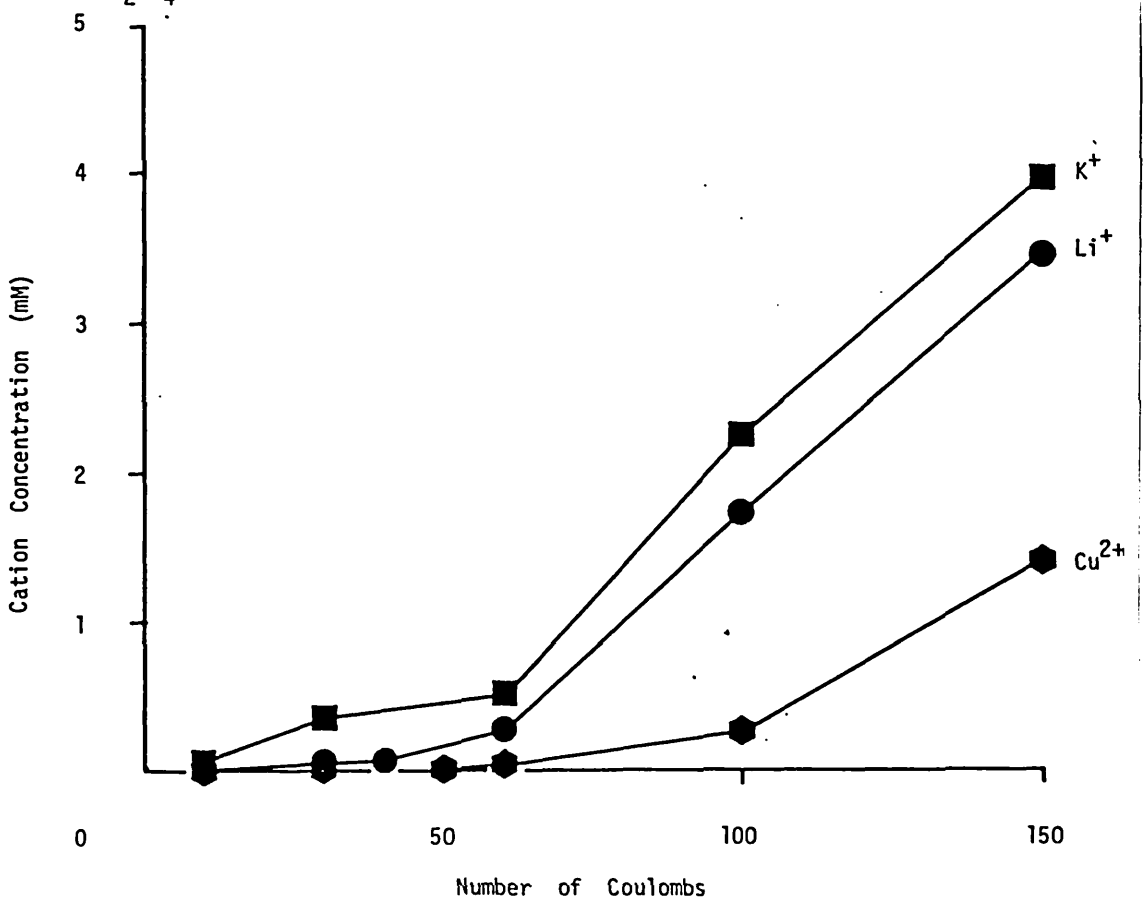
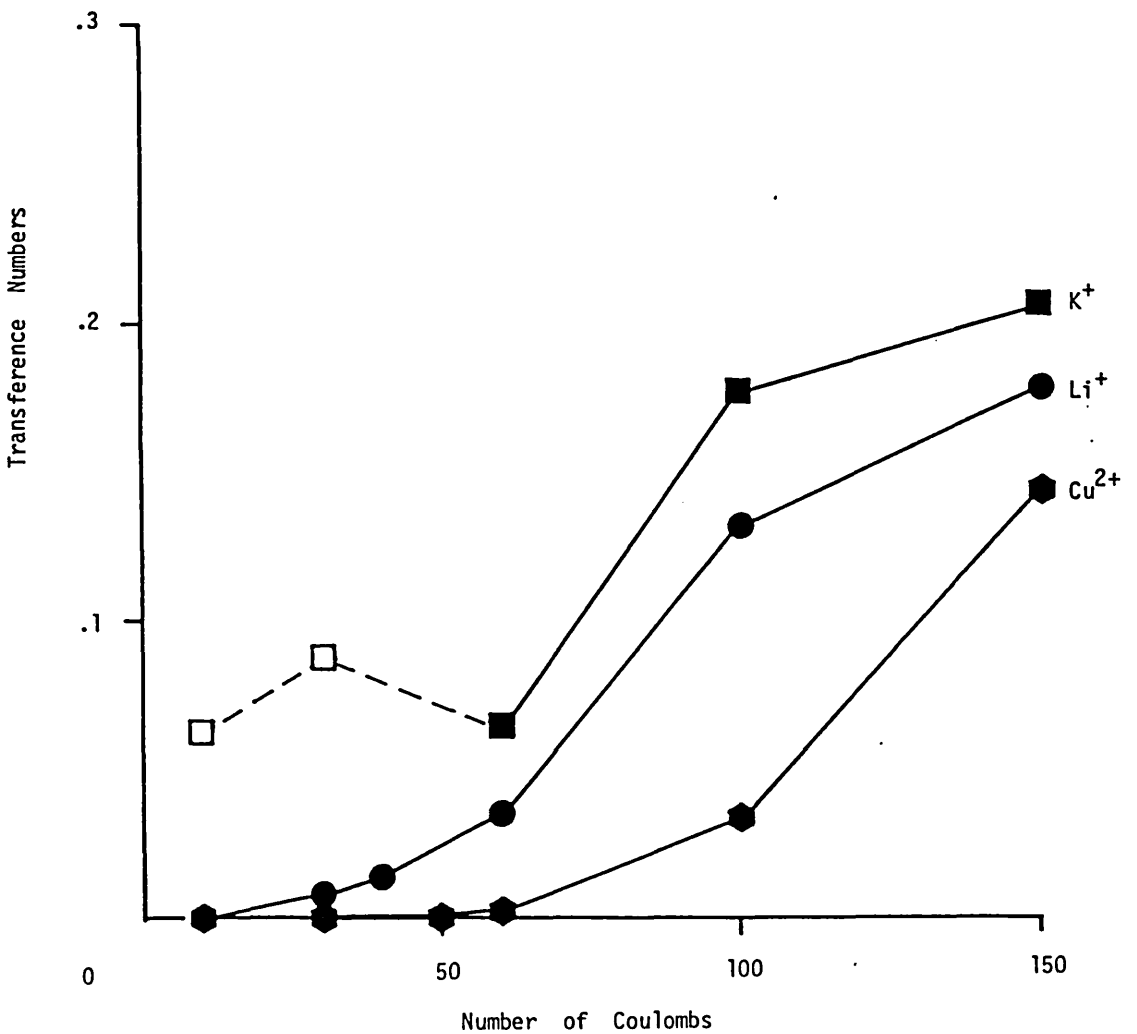


FIGURE 9.4 Migration of Exogenous (Anolyte) Cations Through Wood: Cation Transference Numbers

50 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.05 M $CuSO_4$ or 0.025 M $Li_2SO_4$ or 0.025 M $K_2SO_4$.

— □ — Endogenous $K^+$ Current



## 9.4 Double wood runs

The transference numbers determined so far depended on endogenous ions migrating out of the wood and exogenous ions migrating in. An attempt was now made to determine the transference numbers of the endogenous ions alone, without participation by catholyte or anolyte ions. For this a new 'double wood' cell was devised, containing a middle compartment (cf. section 5.2.2) held between two wood samples and their respective electrode compartments. The following factors had to be taken into account:

(a) The ions in the middle compartment electrolyte solution had to differ from the major endogenous current carriers, to distinguish between endo- and exogenous ionic currents.

(b) The ionic concentration of the middle electrolyte roughly matched the total exchangeable endogenous ion concentration, to help prevent concentration gradient effects (e.g. osmotic water flow).

(c) The middle electrolyte was chosen to avoid interactions between it and the endogenous ions (e.g. precipitation).

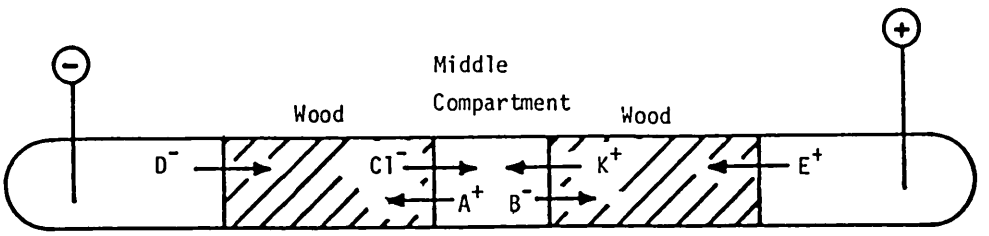
(d) The ions in the middle electrolyte had to migrate readily into the wood, so that the endogenous ions completely replaced them.

(e) The ions in the catholyte and anion solutions were prevented from migrating into the middle compartment by using slow migrating species and long (100 mm) wood.

(f) Sufficient coulombs were passed to ensure the complete replacement of original electrolyte in the middle compartment (as for point d), by endogenous ions migrating from the two wood samples.

The ideal system for these runs is shown in Fig. 9.5 . Sodium perchlorate solution ($NaClO_4$) largely fulfilled the criteria for the middle electrolyte, and sodium laurylsulphate and cetyltrimethylammonium bromide (CTAB) were used as the catholyte and anolyte solutions, respectively. Both the laurylsulphate anion (ion $D^-$ in Fig. 9.5) and cetyltrimethylammonium cation ($[CH_3(CH_2)_{15}](CH_3)_3N^+$)(ion $E^+$) migrate slowly.

FIGURE 9.5 Theory of Double Wood Runs




Middle compartment electrolyte ions $A^+B^-$ (i.e. $NaClO_4$) readily migrate into the wood, and are replaced by the endogenous ions (represented by $Cl^-$ and $K^+$), which can be analysed for after the run. Ions $D^-$ and $E^+$ in the catholyte and anolyte solutions migrate too slowly through the long wood samples to penetrate the middle compartment.

The number of coulombs needed to replace the $NaClO_4$ solution with endogenous ions was calculated as follows. The number of moles, n, of $NaClO_4$ solution of molarity c in the middle compartment of volume V (in l) is

$$n = cV \qquad (9.1)$$

With 1 mM $NaClO_4$, and a middle compartment of 45 $cm^3$

$$n = (1 \times 10^{-3})(45/1000) = 45 \times 10^{-6} \text{ moles} \qquad (9.2)$$

1 faraday transfers approx. ½ mole of each ion in each direction. Under ideal conditions X coulombs are needed to remove these ions, where

$$X = (96\,500)(45 \times 10^{-6}/\tfrac{1}{2}) \simeq 10 \text{ C} \qquad (9.3)$$

In practice, the conditions at the wood/electrolyte solution are unlikely to be ideal because of mixing between $Na^+$ and $ClO_4^-$ ions and endogenous ions emerging from the wood. So in practice between 5 and 50 C were passed.

pH measurements were made using a Radiometer PHM62 meter.

Based on the elution results of the flushing experiments (cf. section 9.5.1), 1 or 5 mM $NaClO_4$ was considered a good simulation of the total exchangeable ionic concentration of the wood. The results of several double wood runs are shown in Figs. 9.6 to 9.10.

The level of endogenous cations migrating into the middle compartment was relatively low (Fig. 9.6) and their transference numbers small (Fig. 9.7). The endogenous $K^+$ and $Ca^{2+}$ transference numbers declined as more electricity was passed, while that of the cetyltrimethylammonium cations rose. Much of the current in the 'anodic' wood sample must therefore have been carried by exogenous $ClO_4^-$ ions. The $Na^+$ ions from the $NaClO_4$ electrolyte rapidly migrated out of the wood towards the cathode.

FIGURE 9.6 Cation Migration into Middle Compartment with Increasing Number of Coulombs: Ionic Concentrations

1 mM $NaClO_4$ original electrolyte in middle compartment.

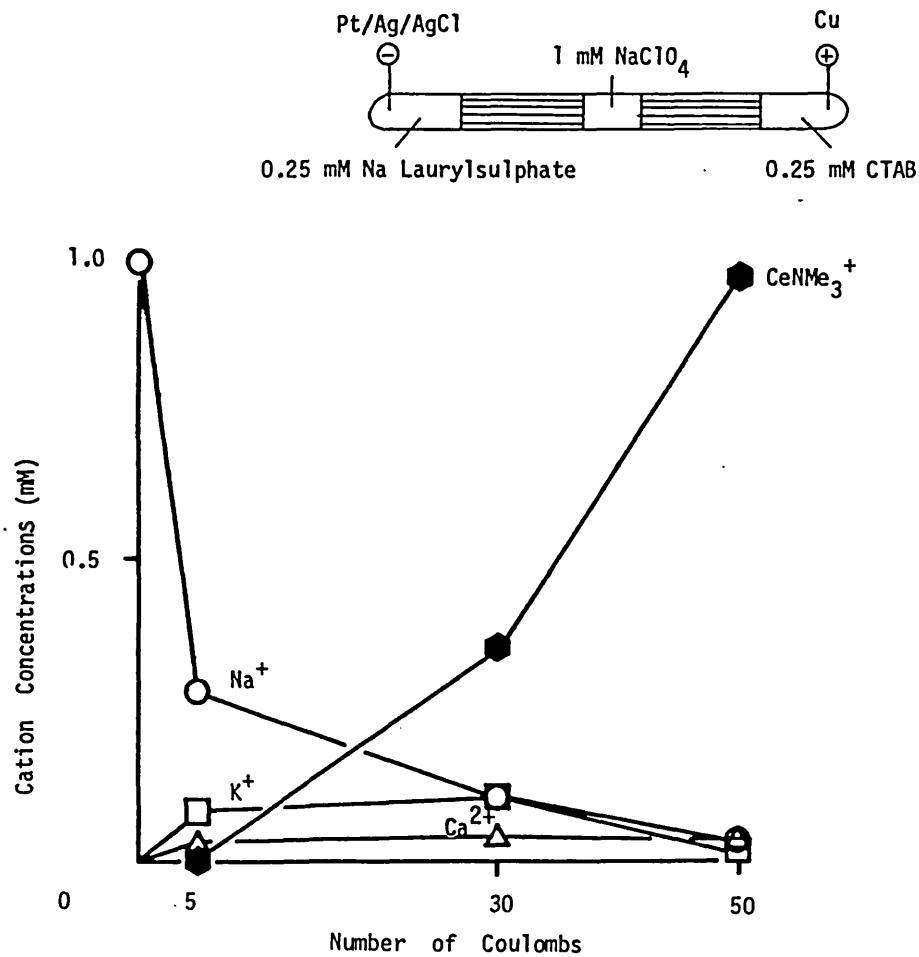
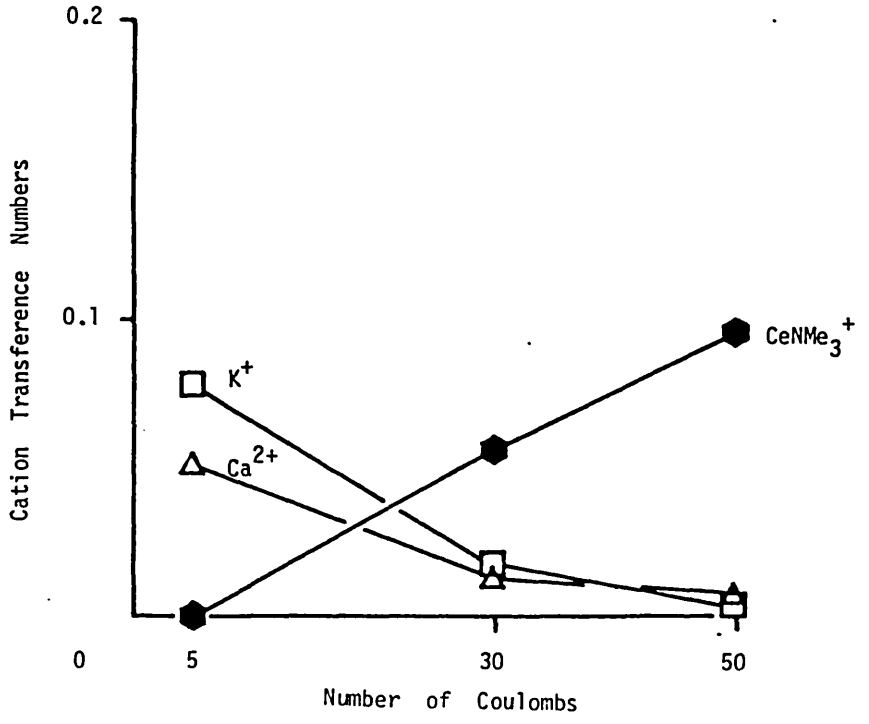


FIGURE 9.7 Cation Migration into Middle Compartment with Increasing Number of Coulombs: Transference Numbers

Experimental parameters as for Fig. 9.6



The endogenous anion contribution from the 'cathodic' wood sample was also low, mainly consisting of $SO_4^{2-}$ ions at low numbers of coulombs (Figs. 9.8, 9.9, also Table 9.6) and of $Cl^-$ ions at higher numbers of coulombs (Figs. 9.8, 9.9). The absence of $SO_4^{2-}$ ion migration at higher numbers of coulombs may be due to its being rapidly exhausted. If exogenous laurylsulphate anions had caused the initially high $t_{SO_4^{2-}}$, then it would have been sustained with increasing coulombs.

FIGURE 9.8 Anion Migration into Middle Compartment with Increasing Number of Coulombs: Ionic Concentrations

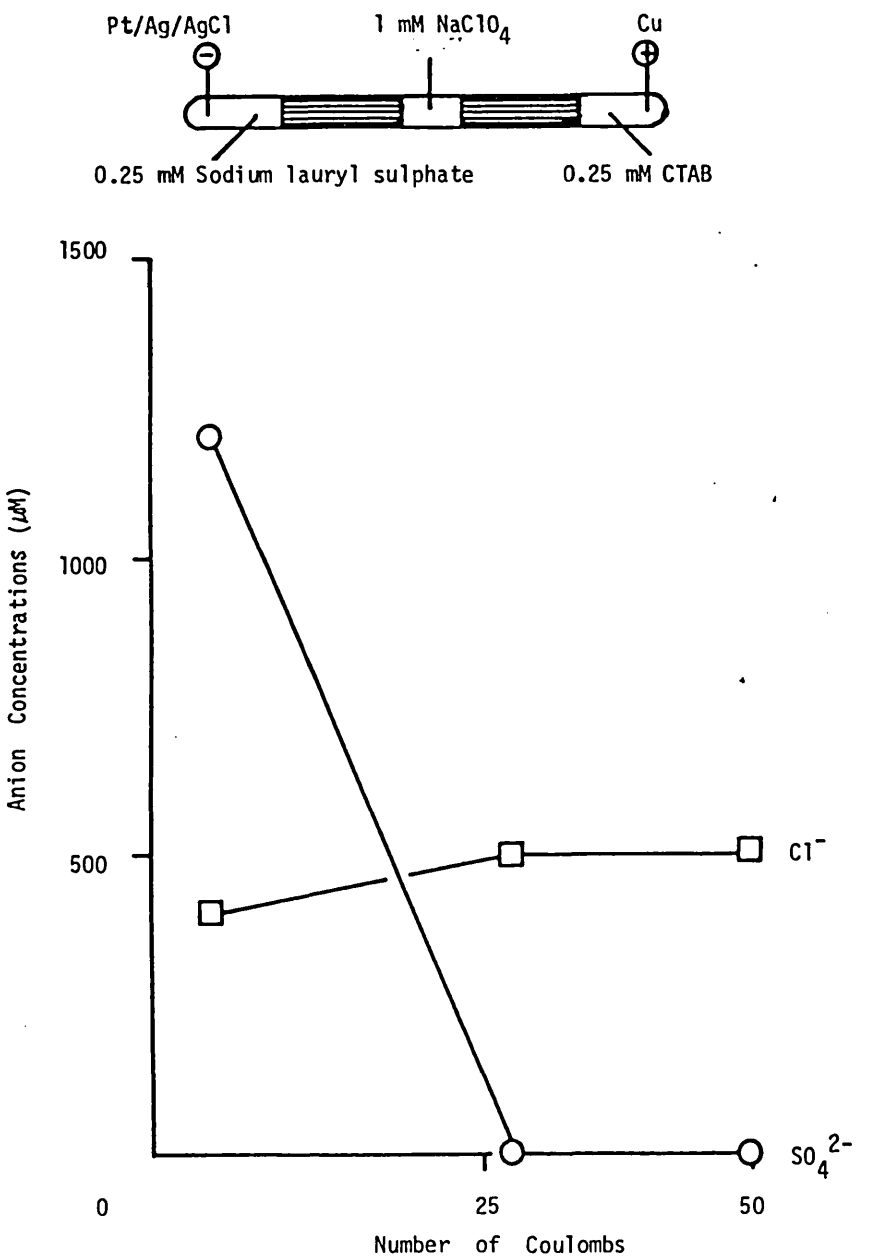
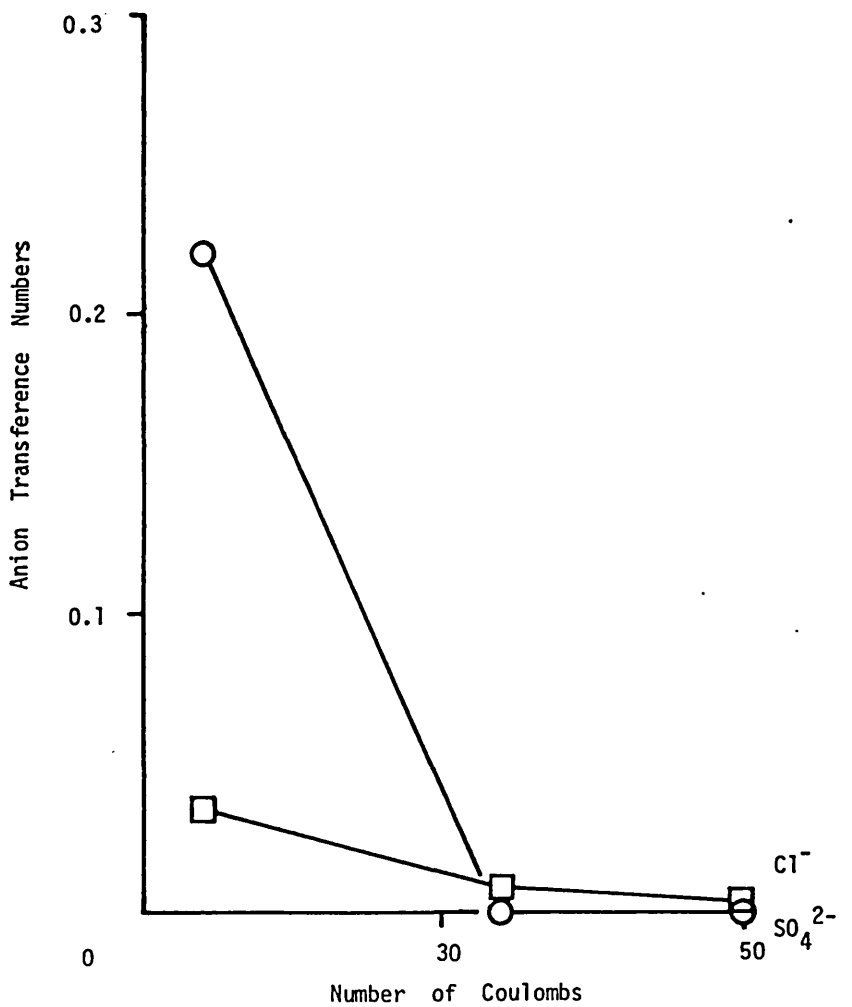


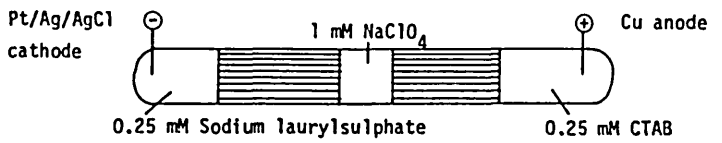
FIGURE 9.9 Anion Migration into Middle Compartment: Transference Numbers

Experimental parameters as for Fig. 9.8



The pH of the middle compartment electrolyte varied somewhat in an apparently random way (Table 9.5), but the changes in $H^+$ and $OH^-$ ion concentrations were negligible. Other anions were not detected in significant quantities (Table 9.6); divalent cations other than $Ca^{2+}$ were not tested for. All these results show that the current in the wood was still largely carried by exogenous ions from the middle or electrode compartments, even if these possessed low ion-consititùent mobilities. Thus, the cation current was carried by $Na^+$ through 'cathodic' wood samples, and $CTA^+$ through 'anodic' samples; the anion current was presumably carried by laurylsulphate anions through 'cathodic' wood samples, and $ClO_4^-$ ions through the 'anodic' samples.

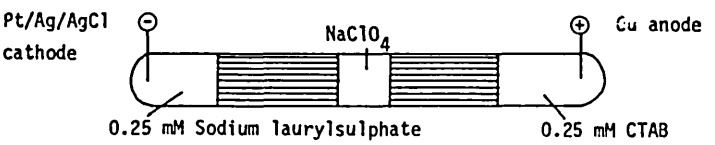
TABLE 9.5 Double Wood Runs: pH Changes in Middle Electrolytes




| No. of Coulombs | pH Before Run | pH After Run | Δ pH | $[H^+]$ |
|---|---|---|---|---|
| 5 | 5.70 | 4.36 | -1.34 | ng |
| 30 | 5.70 | 6.28 | +0.58 | ng |
| 50 | 5.70 | 7.51 | +1.81 | ng |

ng negligible ($<1 \times 10^{-4}$ M)

TABLE 9.6 Double Wood Runs: Ion Migration into Middle Compartment, Using Different Electrolyte Concentrations




5 C passed.

| Middle Electrolyte Concn. (mM) | Ion Concentrations (μM) | | | | Transference Numbers | | |
|---|---|---|---|---|---|---|---|
| | $Na^+$ | $K^+$ | $Cl^-$ | $SO_4^{2-}$ | $t_{K^+}$ | $t_{Cl^-}$ | $t_{SO_4^{2-}}$ |
| 1 | 280 | 80 | 37 | 110 | .077 | .035 | .211 |
| 5 | 3800 | 65 | 22 | 74 | .062 | .021 | .142 |

Cation analysis of the cathode compartment supports this idea, since unusually high levels of $Na^+$ migrated out (Figs. 9.10, 9.11). In contrast, $K^+$ and $Ca^{2+}$ migration into the catholyte showed the familiar pattern previously found from single wood runs (cf. section 8.1).

FIGURE 9.10 Cation Migration into Cathode Compartment: Ionic Concentrations

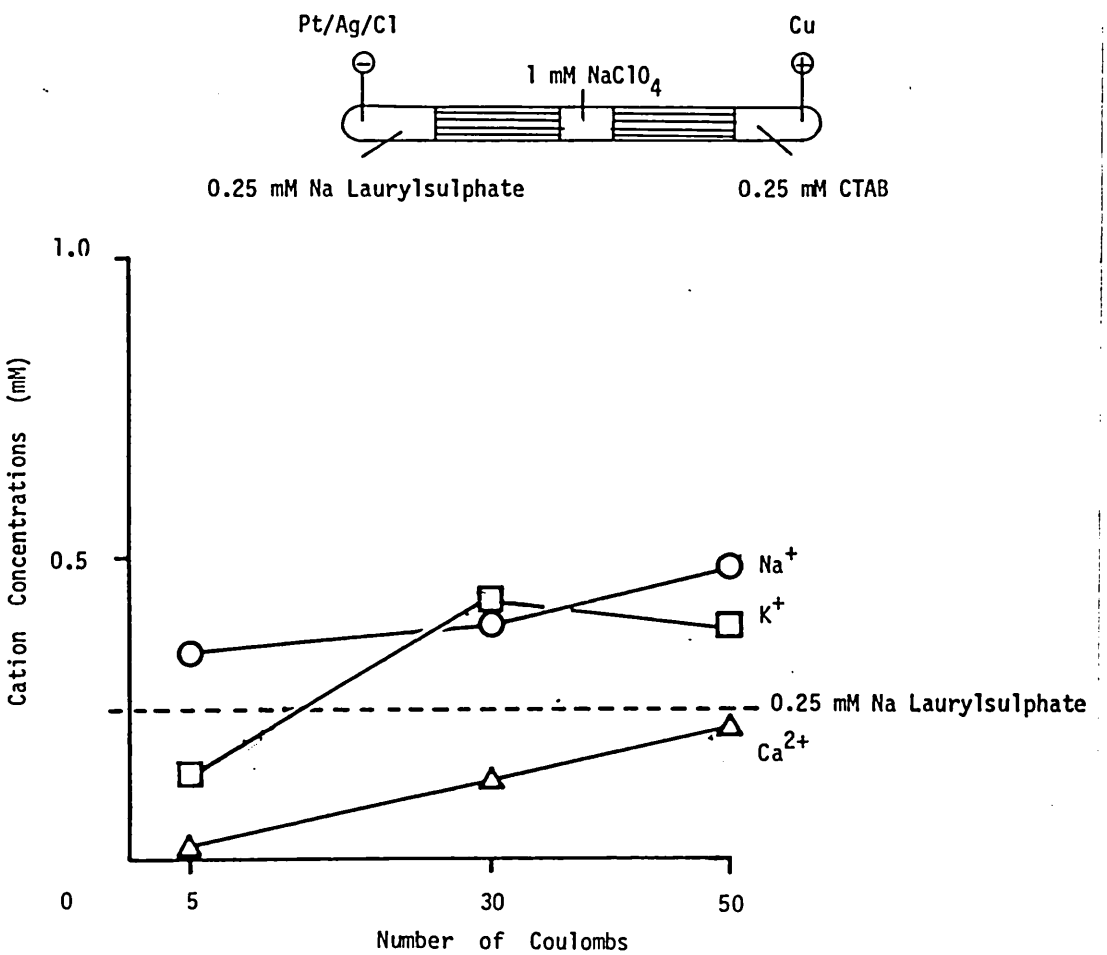
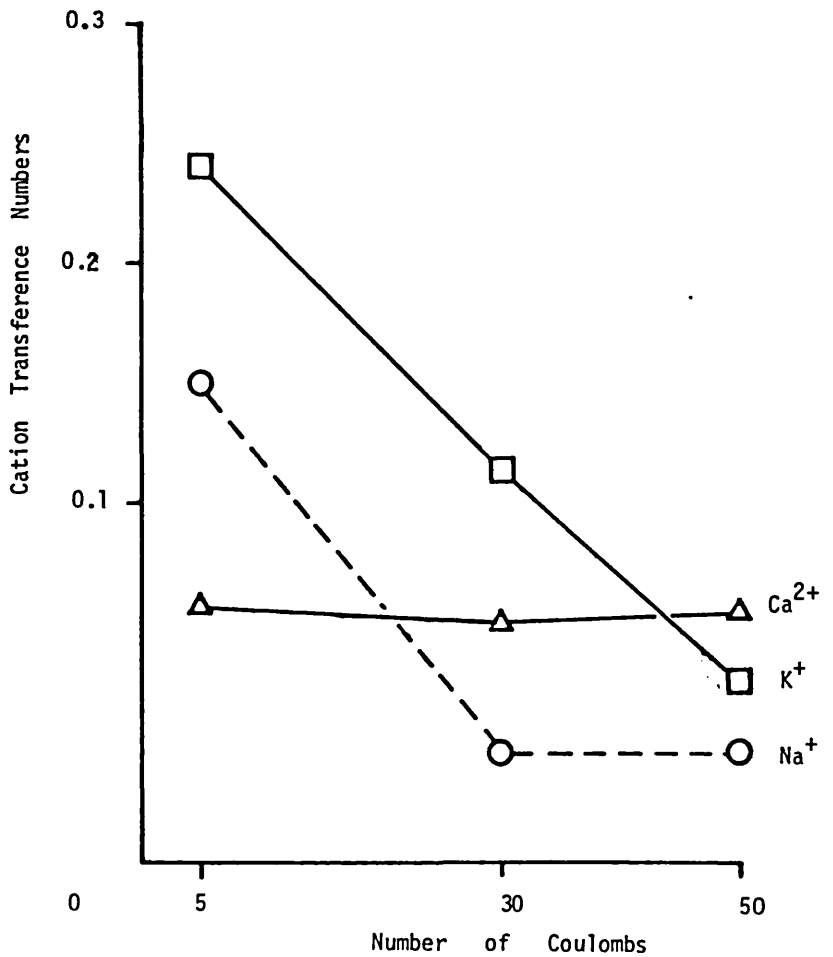


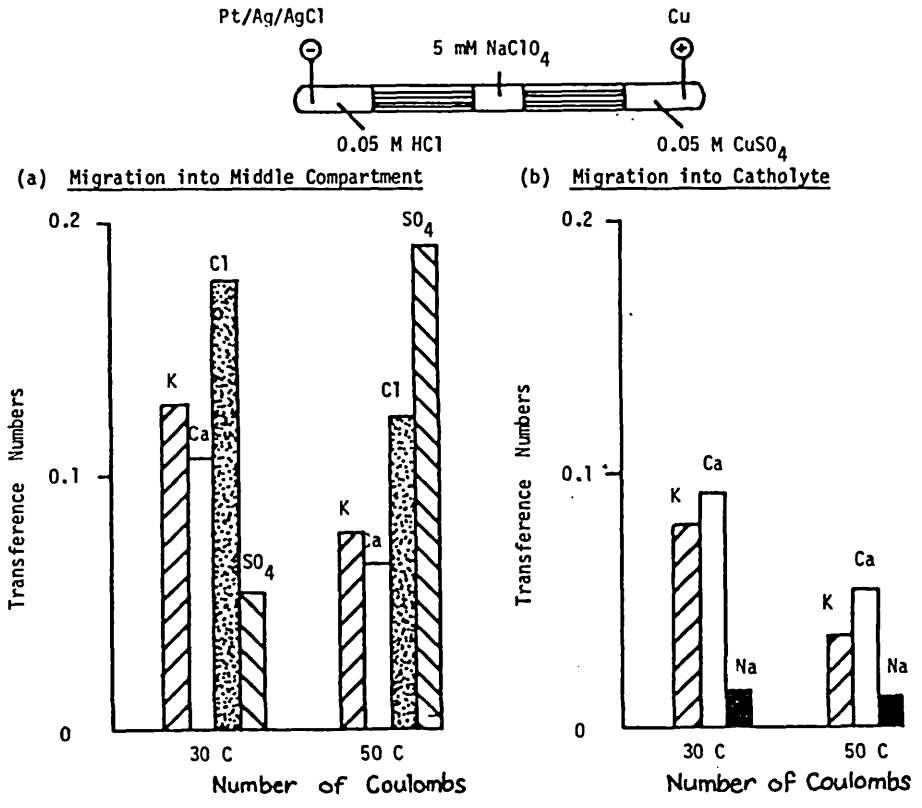
FIGURE 9.11 Cation Migration into Cathode Compartment: Transference Numbers

Experimental parameters as for Fig. 9.10



The pattern of migration into or out of the middle compartment did not alter much when a more concentrated electrolyte was used (5 mM instead of 1 mM $NaClO_4$), although endogenous ion transference numbers were smaller (Table 9.6). When the electrode compartment electrolytes were changed to 0.05 M HCl catholyte and 0.05 M anolyte a large $Cl^-$ migration resulted, caused by $Cl^-$ migrating from the catholyte solution (Fig. 9.12)

FIGURE 9.12 Ion Migration with HCl Catholyte, $CuSO_4$ Anolyte



## 9.5 Flushing experiments

### 9.5.1 Nature of eluted species

A variety of elution techniques and solutions was used for flushing 50 mm long wood samples (cf. section 5.4); each experiment was performed with a fresh sample of wood, and several runs were replicated. Eluted solutions were analysed by FE, AAS, and anion chromatography.

Eluted solutions passing out of the wood had a faint yellow-brown colour to begin with, but this colouration faded with further elution There were no significant differences between eluted solutions using different pressures, but slightly higher levels of ions were eluted using the 'vertical' rather than 'horizontal' flushing technique. (Fig. 9.13). Also, the levels of $K^+$ ions eluted with electrolyte solutions were greater than with distilled water (Fig. 9.14).

FIGURE 9.13 Concentration of Eluted Ions Using Different Flushing Pressures and Techniques

80 $cm^3$ 0.05 M $CuSO_4$ elution.
nd = not determined.
Bars represent confidence limits based on 5 replicates.

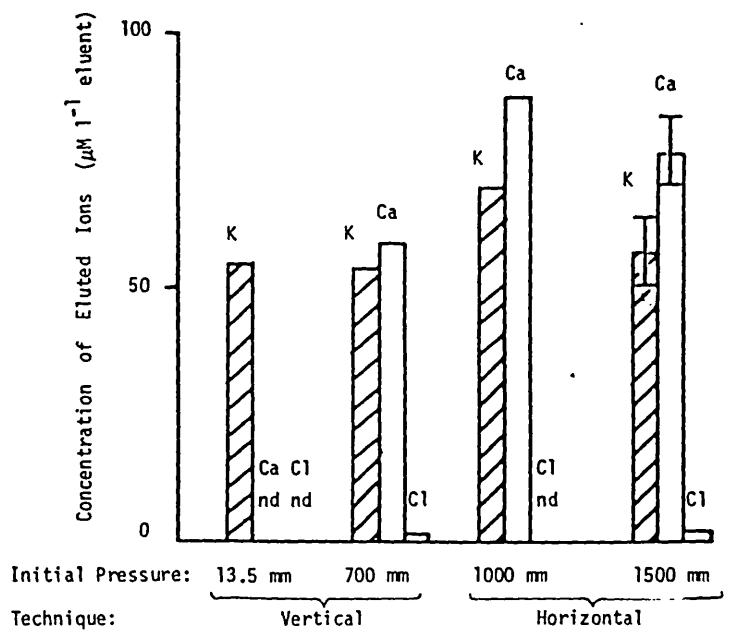
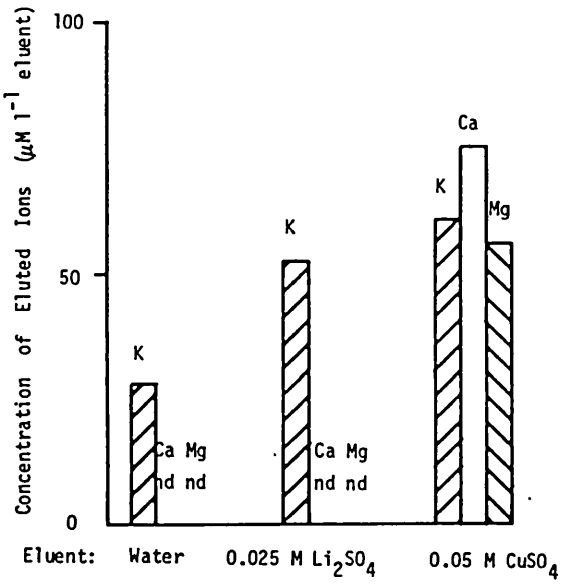


FIGURE 9.14 Concentration of Eluted Ions Using Different Elutant Solutions

80 $cm^3$ eluent, vertical or horizontal arrangement, 13.5/700/1000/1500 mm pressures.
nd = not determined.




The total levels of anions eluted with $CuSO_4$ were extremely low (Table 9.7) - although it was not possible to determine endogenous $SO_4^{2-}$ ions - whereas the eluted cation concentrations were considerably larger (Fig. 9.13).

TABLE 9.7 Flushing Experiments: Levels of Endogenous Anions Eluted by 0.05 M $CuSO_4$

50 mm long wood.

| Flushing Technique | Anion Concentrations ($\mu M\ l^{-1}$) | |
|---|---|---|
| | $Cl^-$ | $NO_3^-$ |
| Horizontal, 1.5 m pressure | 2 | 1 |
| | 3 | 1 |
| | 2 | n.d. |
| Vertical, 0.7 m pressure | 1 | n.d. |

n.d. not determined

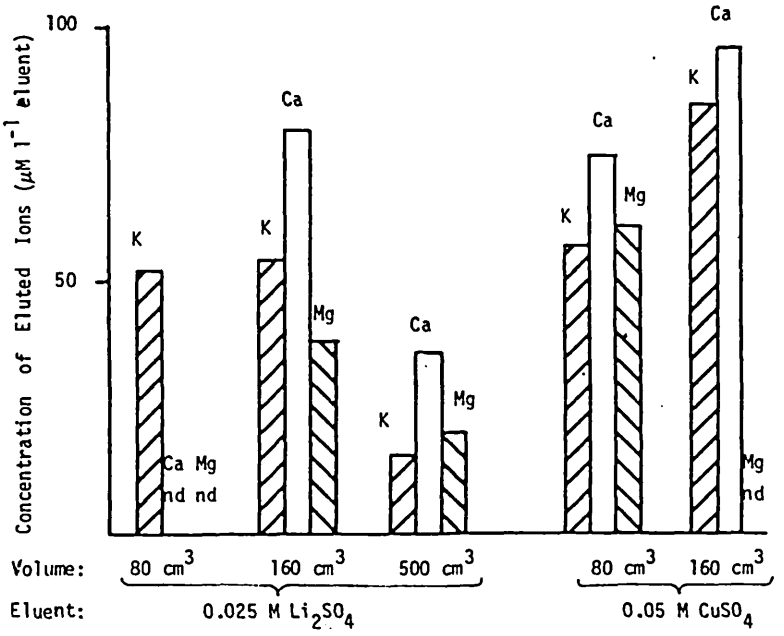
The order of eluted ions was

$$Ca^{2+} \gg K^{+} > Mg^{2+} \gg Cl^{-},\ NO_3^{-}$$

and reflected their order of current-carrying (cf. section 7.3). The total number of moles (concentration x volume eluted - equation 9.1) of cations eluted increased with larger volumes of elution, but stayed roughly the same between 160 and 500 $cm^3$ $Li_2SO_4$ elution (Fig. 9.15). The cation content of the wood 'flushable' with 0.025 M $Li_2SO_4$ therefore becomes exhausted with approx. 160 $cm^3$ elution. But even more cations were eluted by 0.05 M $CuSO_4$.

FIGURE 9.15 Concentrations of Eluted Ions Using Different Eluents: Range of Volumes of Eluant Solutions

Vertical or horizontal elution arrangement.
nd = not determined.

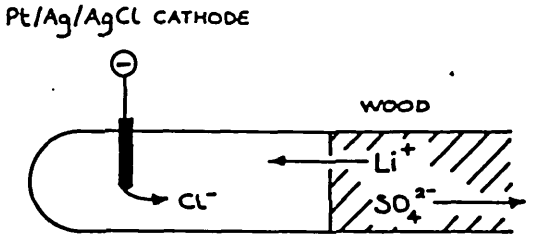



These results indicate that the wood contains both water- and cation-exchangeable cations - i.e. the wood behaves as a cation-exchanger. The greater selectivity of wood for divalent cations is shown by the larger concentration of cations eluted by $CuSO_4$. There is no evidence that the wood has any anion-exchange capacity.

## 9.5.2 Electrical effect of flushing

A number of electrical runs was performed with wood whose endogenous ions had been flushed out with a solution of a binary electrolyte. These experiments allowed an easier determination of the ratio of current carried through the wood by cations and anions (Fig. 9.16).

FIGURE 9.16 Theory of Runs Using Electrolyte-Flushed Wood



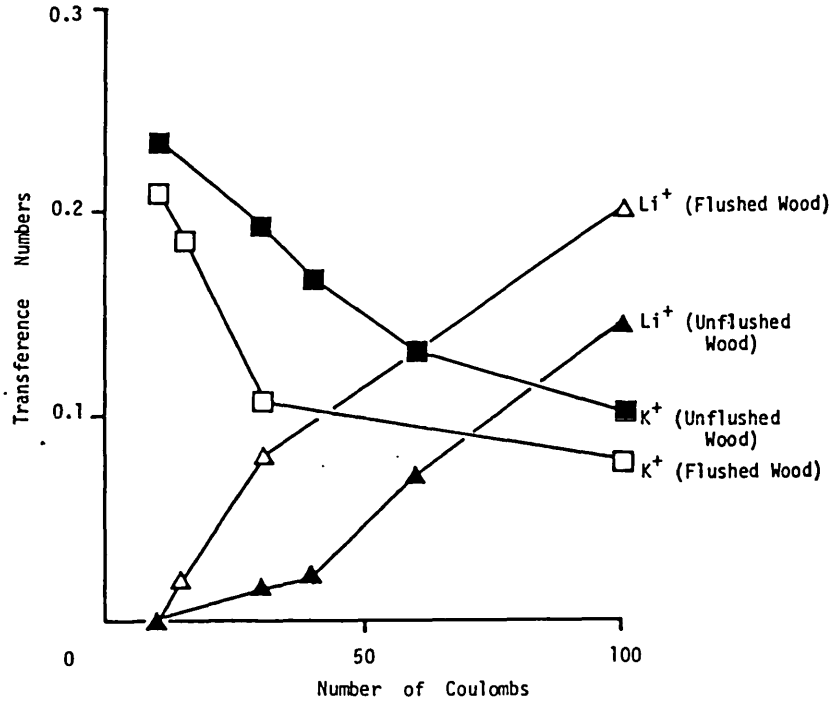

Wood flushed with $Li_2SO_4$.
At the cathode: $AgCl + e^- \rightarrow Ag + Cl^-$
Per faraday, the catholyte:
gains 1 mole $Cl^-$ from the electrode reaction
loses $t_{Cl^-}$ mole $Cl^-$ from migration
} net gain $(1-t_{Cl^-}) = t_{Li^+}$ mol $Cl^-$
gains $t_{Li^+}$ mole $Li^+$ from migration
Thus the net gain is $t_{Li^+}$ mole of LiCl.
If $t_{Li^+} = 1$, then the current at the wood/catholyte interface is carried entirely by cations, but if $t_{Li^+} < 1$, then the current-carrying must also involve anions.

9.5.2 (i) Water-flushed wood

Cation migration through water-flushed wood followed the same pattern as unflushed wood - endogenous $K^+$ and $Ca^{2+}$ transference numbers fell as those from the exogenous $Li^+$ or $Cu^{2+}$ ions rose with increasing numbers of coulombs (Fig. 9.17). However, the endogenous ion current was smaller, and the exogenous one correspondingly larger in the flushed wood. Clearly these reflect the removal of the water-exchangeable cations by flushing.

FIGURE 9.17 Comparison of Cation Migration Between Unflushed and Water-Flushed Wood

50 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl, Cu anode in 0.025 M $Li_2SO_4$.



### 9.5.2 (ii) Electrolyte-flushed wood

The size and pattern of cation migration was radically changed by flushing with $Li_2SO_4$ or $CuSO_4$ solutions (Figs. 9.18, 9.19, respectively). The endogenous cation current was virtually absent as a result of the previous cation-exchange during flushing. Exogenous cation migration from anode to cathode compartments was also retarded. Instead, almost all the cations initially carried across the catholyte/wood interface were the exogenous 'flushed' $Li^+$ or $Cu^{2+}$ ions. The corresponding $t_{Li}+$ and $t_{Cu}2+$ were relatively large but still $< .5$ (the largest values were $t_{Li}+ = .425$, and $t_{Cu}2+ = .437$ after passing 30 C through $Li^+$- or $Cu^{2+}$-flushed wood, respectively). Thus, cations only carry around 40% of the current across the catholyte/wood interface. The remainder must be attributed to anion migration from the catholyte solution.

The $Cl^-$ transference number into the anolyte was extremely large for water-flushed wood (Table 9.8), because exogenous $Cl^-$ ions from the HCl catholyte migrated completely through the wood. A similar phenomenon occurred in the longer 150 C run with unflushed wood. In contrast, $Cl^-$ migration in wood saturated with $SO_4^{2-}$ ions ($CuSO_4$-flushed wood) was far slower, presumably because the $SO_4^{2-}$ ions carried the bulk of the anion current.

TABLE 9.8 Flushing Experiments: $Cl^-$ Migration in Unflushed, Water- and $CuSO_4$-flushed Wood

50 mm long wood, flushed with 0.05 M $CuSO_4$ (1.5 m horizontal, or 0.7 m vertical pressure). Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.05 M $CuSO_4$ or 0.025 M $Li_2SO_4$ .

| Flushing Treatment | Anolyte | No. of Coulombs | $t_{Cl^-}$ |
|---|---|---|---|
| Unflushed | 0.05 M $CuSO_4$ | 10 | .004 |
| | | 10 | .003 |
| | | 30 | .004 |
| | 0.025 M $Li_2SO_4$ | 150 | .533 |
| Water-flushed | 0.025 M $Li_2SO_4$ | 10 | .286 |
| | | 100 | .479 |
| $CuSO_4$-flushed | 0.05 M $CuSO_4$ | 30 | .008 |

However the data in Table 9.8 were taken from both horizontally- and vertically-flushed wood samples, and the differences in these two treatments may have interfered in the interpretation of the data. Nevertheless, the results do indicate order-of-magnitude differences in $t_{ion}$ between water- and $CuSO_4$-flushed wood.

FIGURE 9.18 Cation Migration in Wood Flushed with 0.025 M $Li_2SO_4$

50 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.05 M $CuSO_4$.

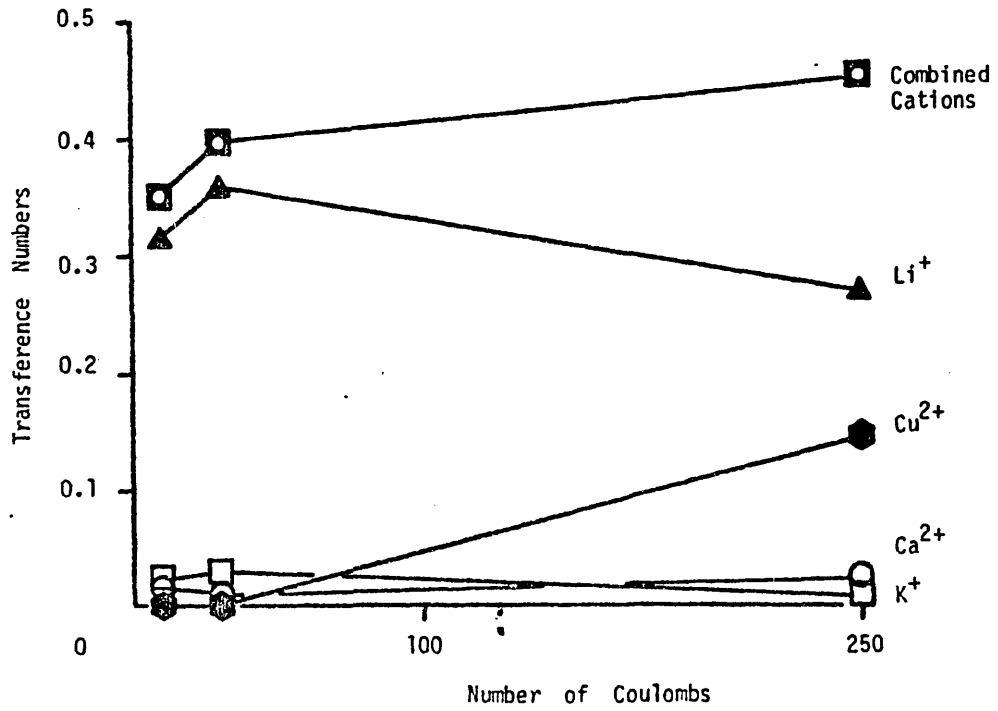
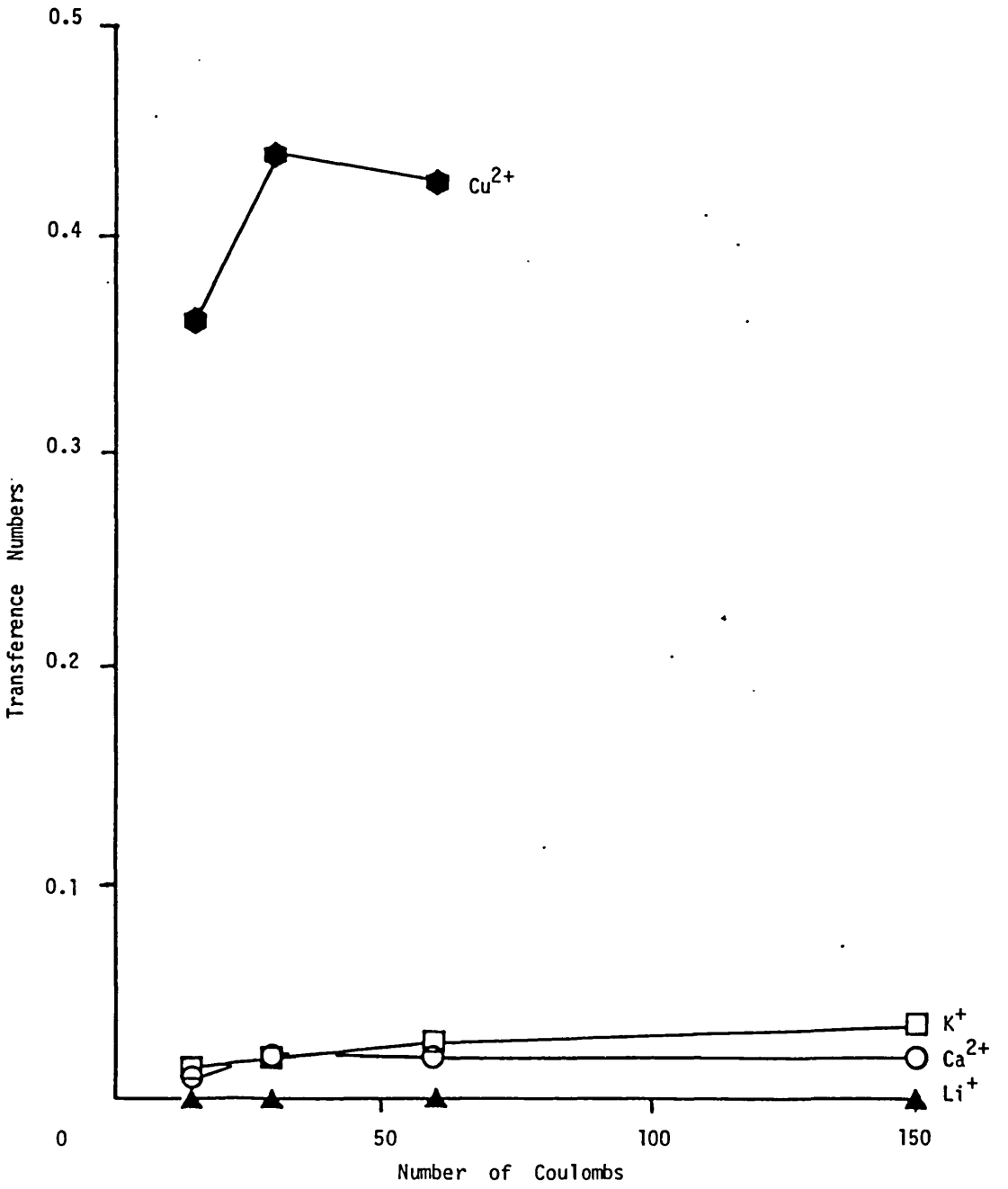


FIGURE 9.19 Cation Migration in Wood Flushed with 0.05 M $CuSO_4$

50 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.05 M $CuSO_4$.



## 9.6 Discussion

The evidence for current being carried through the wood by exogenous ions is shown by:

(a) the fall in the endogenous ion transference numbers with increasing bathing electrolyte concentration;

(b) the fall in the endogenous ion transference numbers with bathing electrolytes containing 'fast' migrating ions, such as monovalent cations;

(c) the low endogenous $t_{ion}$ values in the double wood runs;

(d) the large transference numbers of exogenous ions introduced into the wood by flushing.

However, a complete transference number (t = 1) was not found, as a complete analysis of all ions - particularly exogenous ones - was not performed for any single run.

There has been no previous comparison of exo- and endogenous ionic transference numbers in wood. Langwig and Meyer (1973) in their studies of endogenous ion migration in Venezuelan wood species found that $Cu^{2+}$ ions liberated from the Cu anode migrated into the wood, but the transference numbers of various ions could not be determined (cf. section 3.2.1).

The flushing experiments agree with previous reports that wood behaves as a cation-exchanger (cf. section 1.7.3). Although the cation-exchange capacity was not determined here, the results show for the first time that the order of eluted ions matches the order of endogenous ion current-carriers. Furthermore, a proportion of the $K^+$ ions (at least) are water-exchangeable - i.e. leachable by water - and the remainder are cation-exchangeable. Bechhold and Heymann (1927) found that $Cu^{2+}$ migrated more slowly through partly, than completely, de-ashed wood, suggesting that endogenous ions impede exogenous ion migration. In this project, $Li^+$ migrated more rapidly in the order: water-flushed, unflushed, $CuSO_4$-flushed wood, indicating that cations present in the wood impede the migration of other cations. This suggests that cation migration proceeds by cation-exchange.

The marked increase in exogenous anion transference numbers with water-flushed - rather than $CuSO_4$-flushed - wood indicates that $Cl^-$ ions associate with $Cu^{2+}$ as $CuCl^+$ ions, so masking the $Cl^-$ current. Alternatively, $Cl^-$ took a longer time to migrate in wood saturated with $CuSO_4$ as $SO_4^{2-}$ migrated out first.

# CHAPTER 10

# ELECTRO-OSMOSIS

## 10.1 Physical factors

### 10.1.1 Effect of electrical current

The volume of catholytes rose and those of the anolytes fell linearly with increasing numbers of coulombs. In blank, control experiments - where no current was passed - both electrolyte levels fell, albeit at different rates (Fig. 10.1, 10.2). When current was switched on, the fall in anolyte levels accelerated, while the catholyte levels were reversed (Fig. 10.3), although the extent of the volume changes, $V_e$, varied considerably between different runs. Thus, $\Delta V_e$ was caused by non-electrical (i.e. diffusion) and by electrical (i.e. electro-osmotic) means. Note that the diameter of the capillary meniscus (2 mm) was the same for all these and other runs described in this chapter.

FIGURE 10.1 Changes in Electrolyte Volume With or Without Current: Short Duration Runs

100 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.025 M $Li_2SO_4$ (electrodes used without current in non-electrical runs).
Data for each treatment taken from single runs.

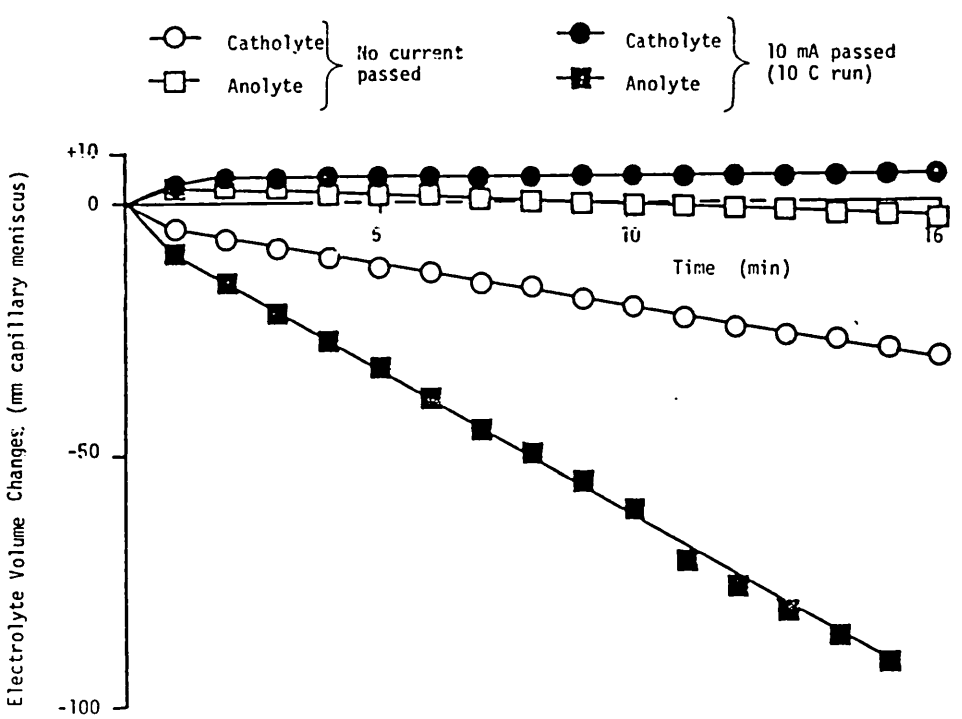


FIGURE 10.2 Changes in Electrolyte Volume With or Without Current: Long Duration Runs

100 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.05 M $CuSO_4$.
Data for each treatment taken from single runs.

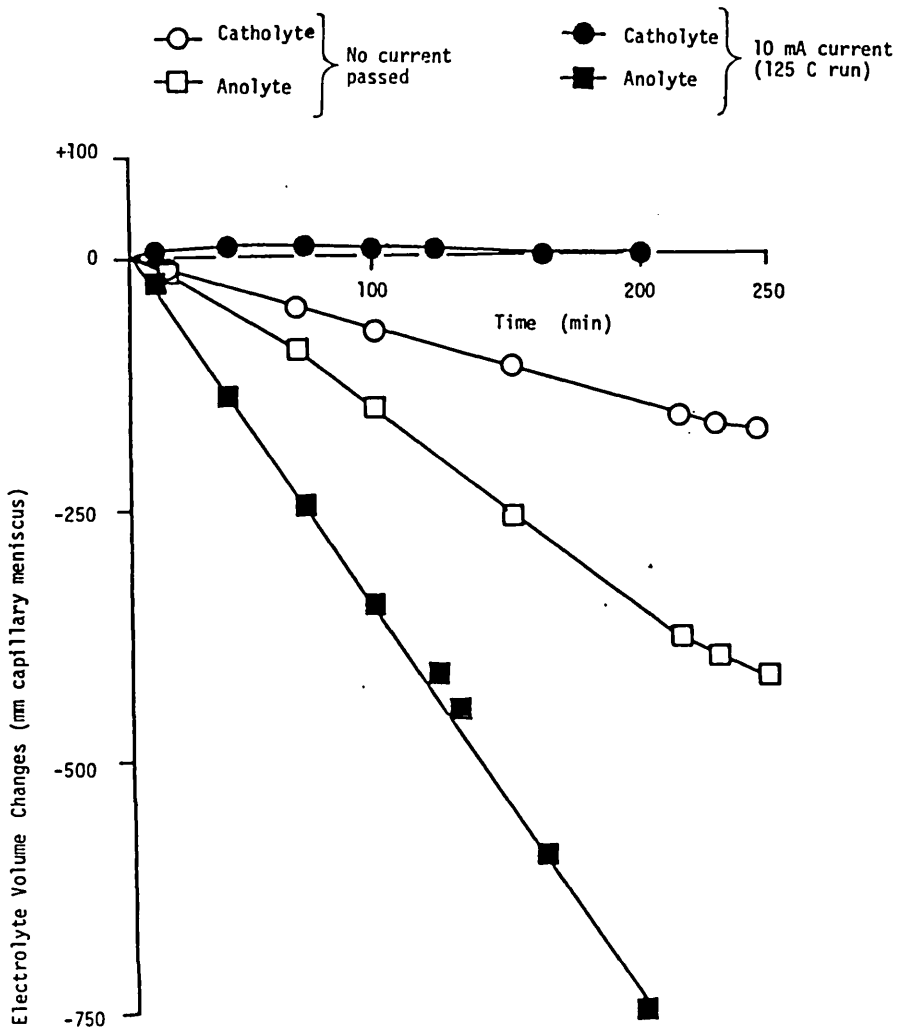
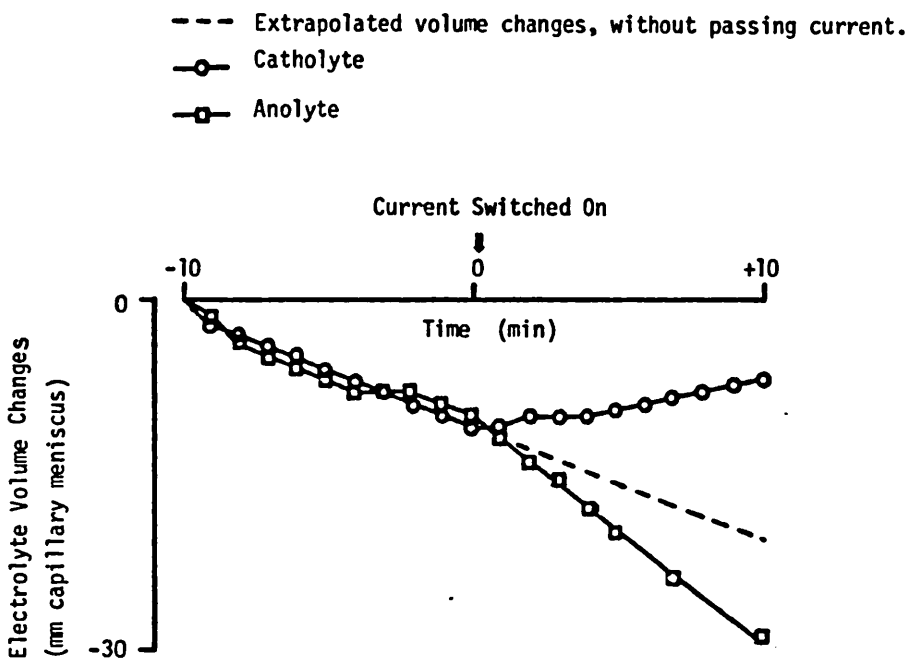


FIGURE 10.3 Electrolyte Volume Changes Before and After Passing Current

100 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.025 M $Li_2SO_4$.
10 mA current.



## 10.1.2 Current

The velocity of liquid flow $dV_e/dt$ markedly increased with greater currents (Figs. 10.4, 10.5). This would be expected with electro-osmosis, whose rate of flow is proportional to the applied potential gradient (cf. section 2.5). However, $\Delta V_e$ did not markedly differ between runs of different currents but same numbers of coulombs (Fig. 10.5). This would also be expected from the theory of electro-osmosis (equations 2.45 to 2.48, inclusive).

**FIGURE 10.4** Electrolyte Volume Changes Using Different Currents: Passing 250 C

Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.05 M $CuSO_4$.
Data for each treatment taken from single runs.

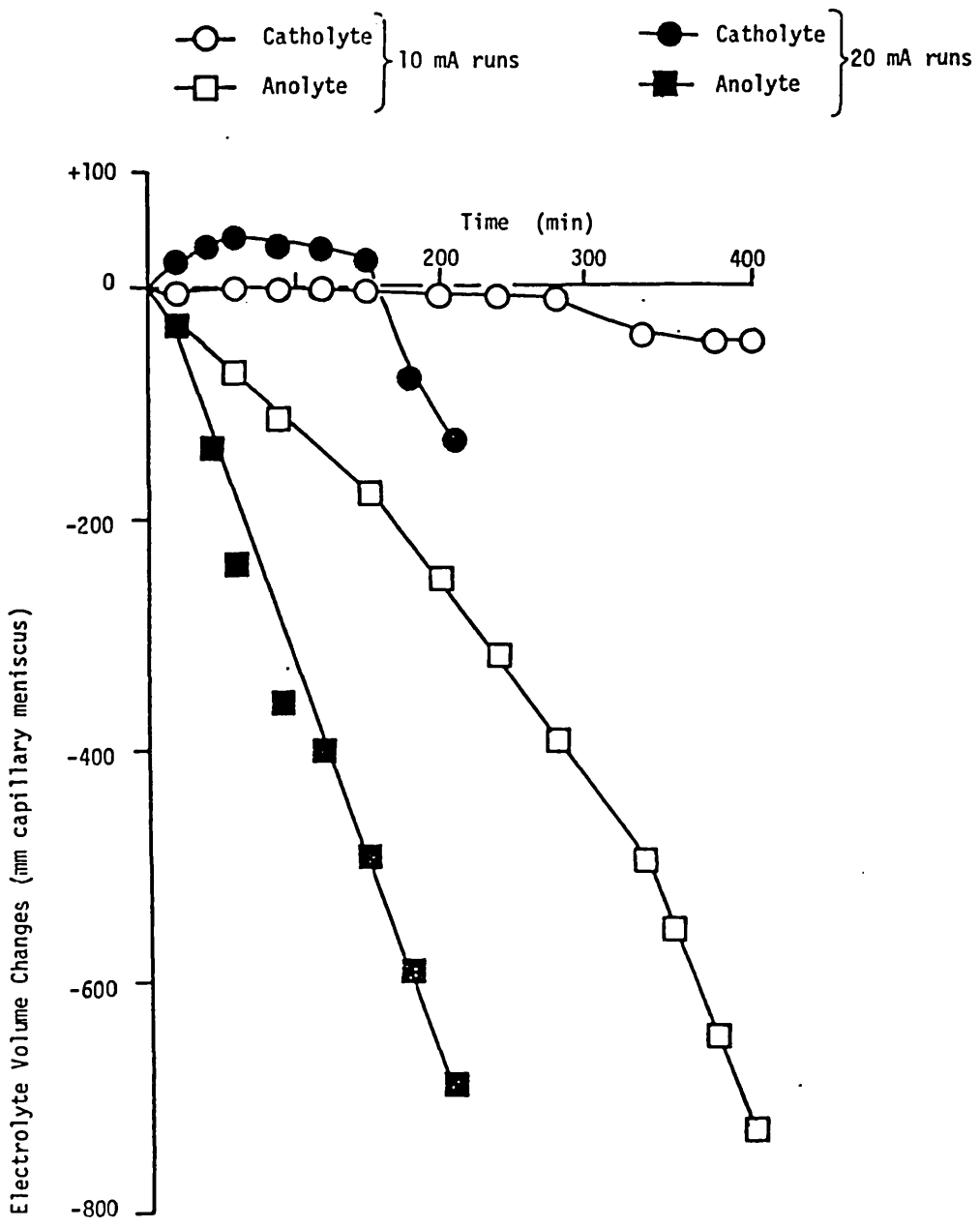
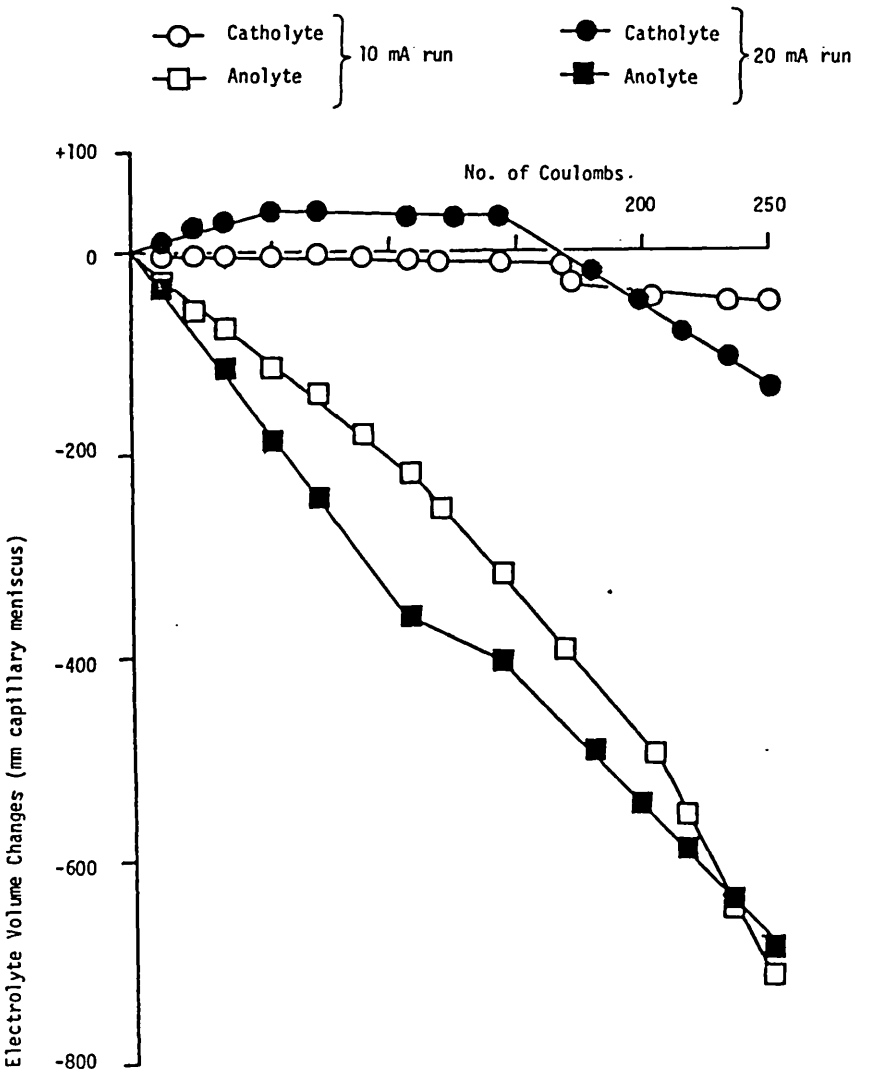


FIGURE 10.5 Electrolyte Volume Changes Using Different Currents

50 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.05 M $CuSO_4$.
Data for each treatment taken from single runs.



### 10.1.3 Closed cathode compartment

The fall in anolyte volume did not change when the cathode compartment was kept closed during a run (Figs. 10.6, 10.7). Thus, electro-osmotic flow out of the anode compartment occurs irrespective of the flow into the catholyte. Isolated beads of moisture broke through the Mobilcer R barrier on the wood during runs using closed cathode compartments, thereby releasing the electro-osmotic pressure.

FIGURE 10.6 Change in Anolyte Volume with Cathode Compartment Open or Closed: 10 C Run

50 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.05 M $CuSO_4$.
Data for each treatment taken from single runs.

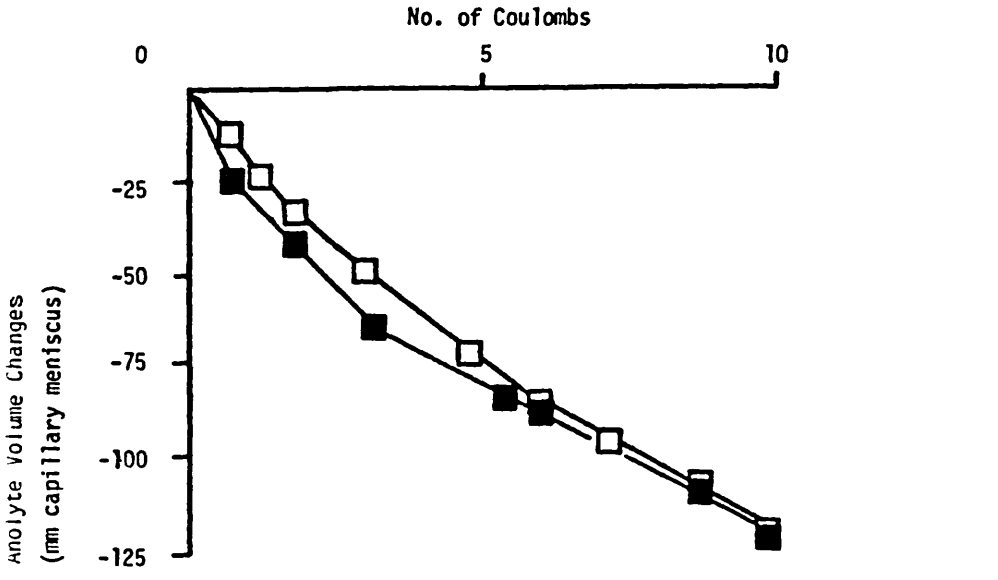
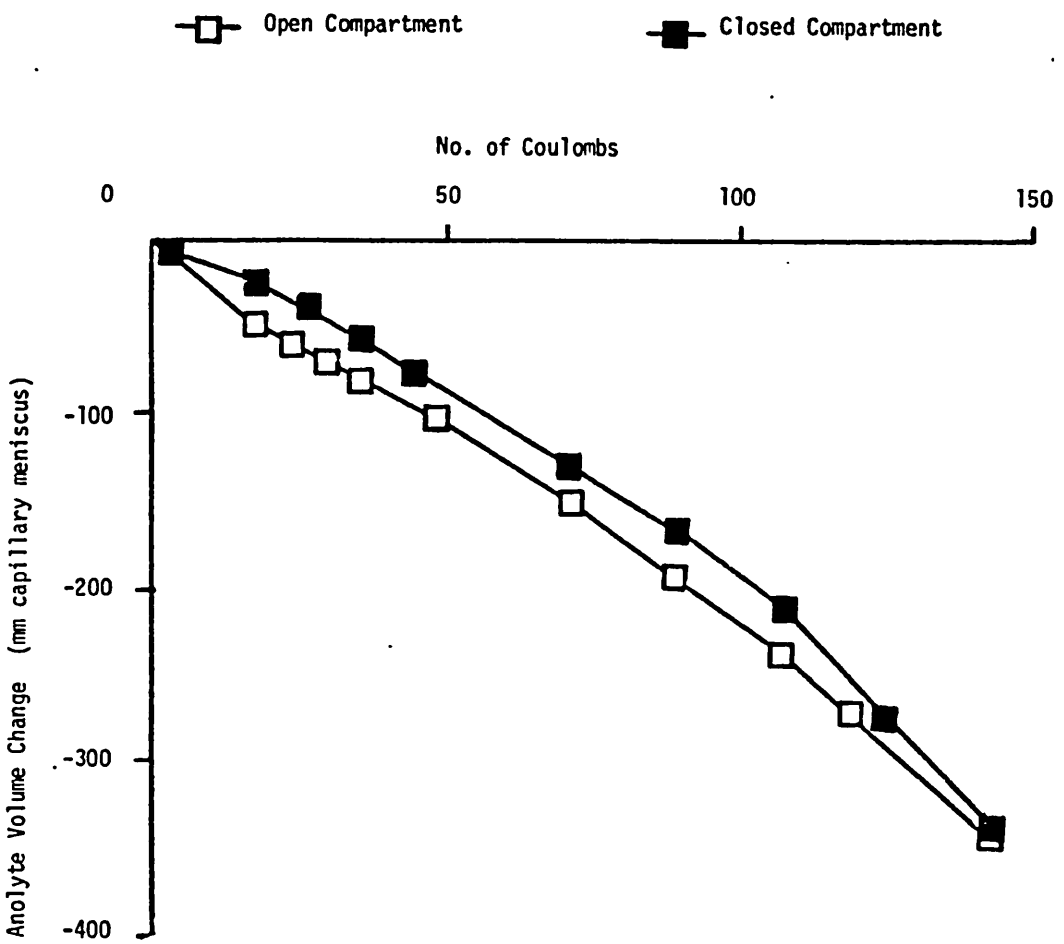


FIGURE 10.7 Change in Anolyte Volume with Cathode Compartment Open or Closed: 125 C Run

Experimental details as for Fig. 10.6



### 10.1.4 Length of wood

Larger $\Delta V_e$ occurred with longer lengths of wood (Figs. 10.8, 10.9), although wide variations occurred between different runs. This greater electro-osmotic flow is probably related to the larger potential gradient across the long wood samples, as shown by their electrical resistances (cf. section 6.3.2).

FIGURE 10.8 Electrolyte Volume Changes Using Different Lengths of Wood.

Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.05 M $CuSO_4$.
Data for each treatment taken from single runs.

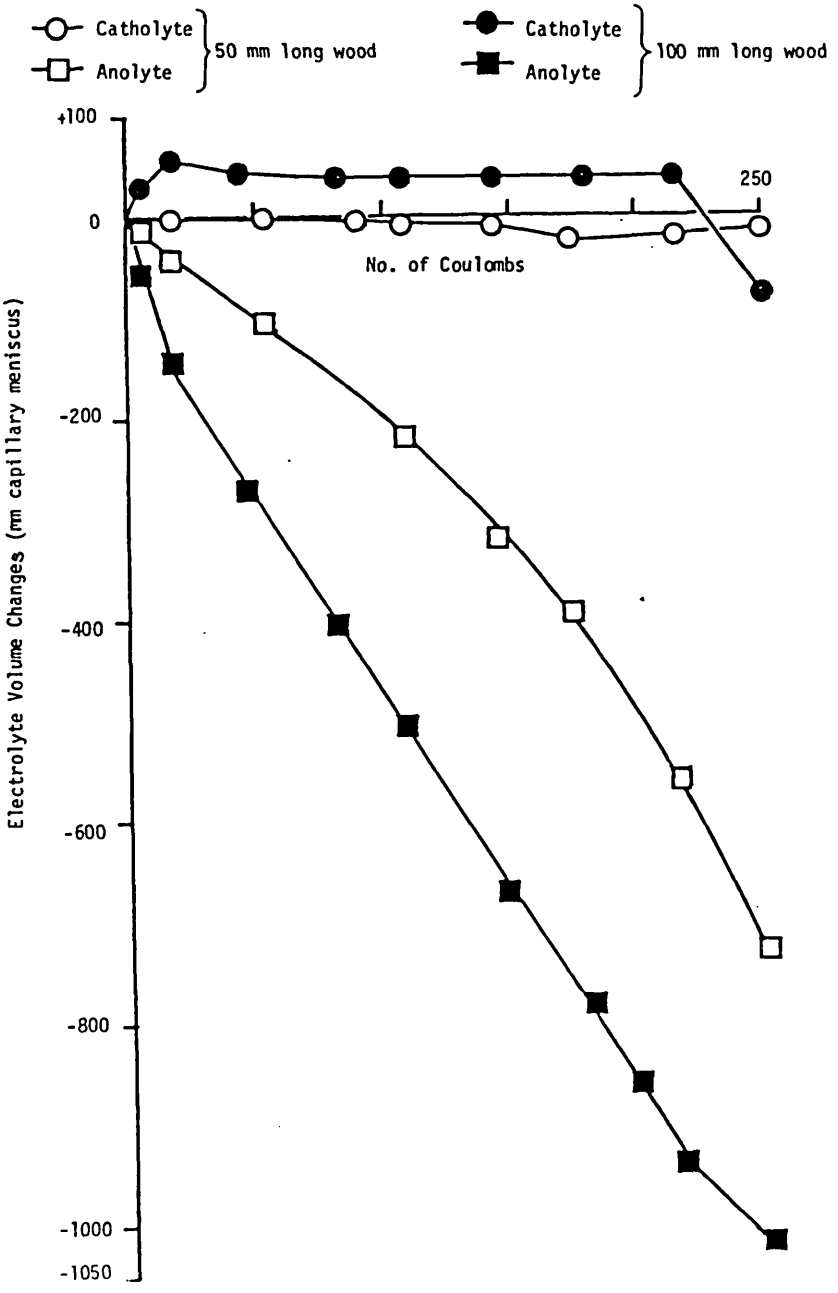
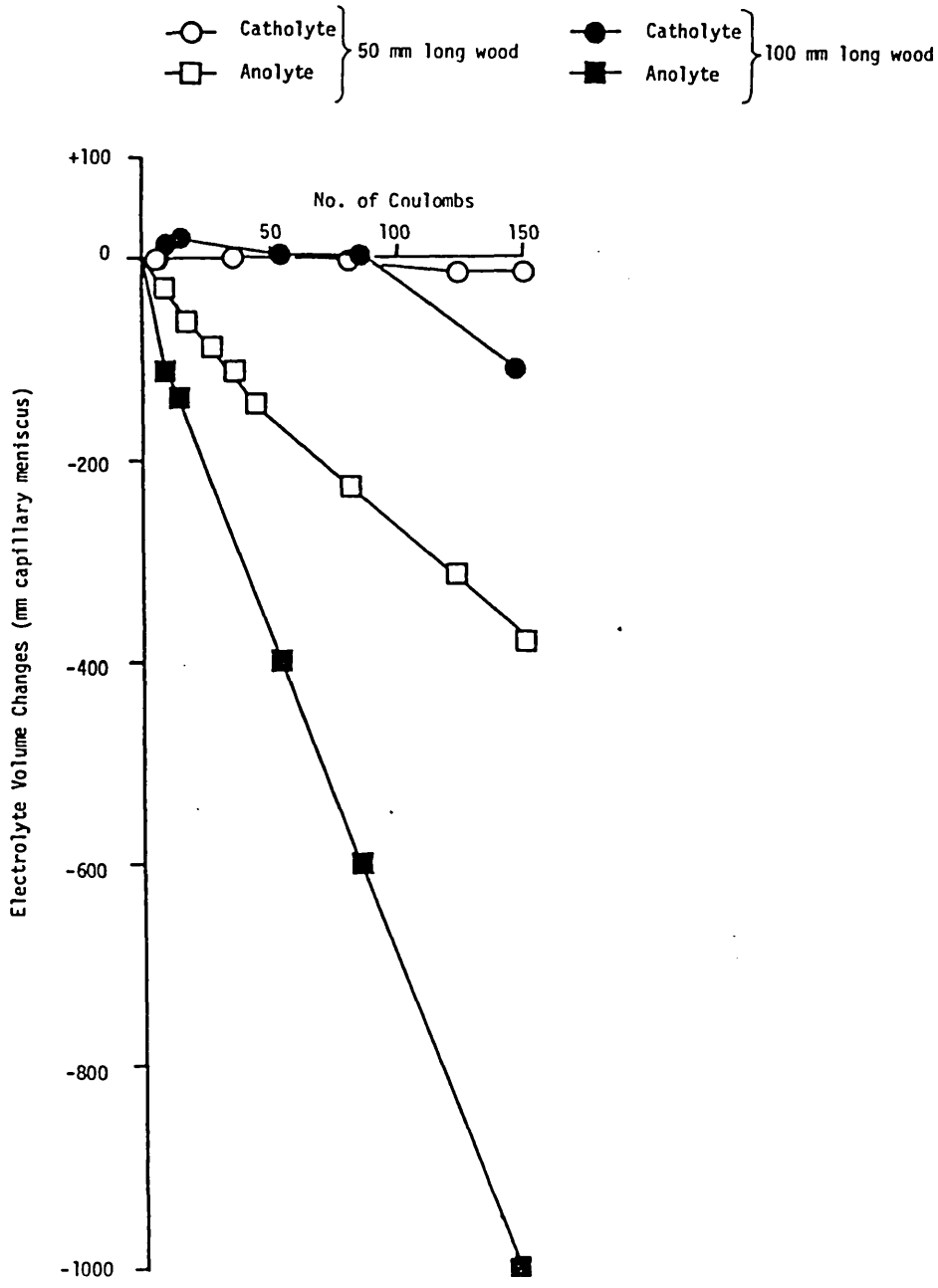


FIGURE 10.9 Electrolyte Volume Changes Using Different Lengths of Wood

Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.025 M $Li_2SO_4$
Data for each treatment taken from single runs.



## 10.1.5 Grain orientation

So far all runs had been made with longitudinally-orientated wood, and a comparison was now made with transversely-orientated samples. Large increases in the volumes of both catholyte and anolyte occurred using transversely-orientated wood placed between 0.25 mM electrolytes, whereas the volumes fell with longitudinally-orientated wood (Fig. 10.10). This probably arose from the larger potential gradient across the grain of the wood produced by its greater electrical resistance (cf. section 3.1.4). However, using more concentrated electrolyte solutions (0.1 M) in the two electrode compartments, the pattern of volume changes was comparable to that with longitudinally-orientated wood (Fig. 10.11, cf. 0.05 M electrolytes, Fig. 10.2). The wide variations from run to run in volume changes should also be noted.

FIGURE 10.10 Electrolyte Volume Changes Using Longitudinally- or Transversely-Orientated Wood

100 mm long wood.
Pt/Ag/AgCl cathode in 0.25 mM $Bu_4NI$; Cu anode in 0.25 mM $CuSO_4$.
2 replicates per treatment.

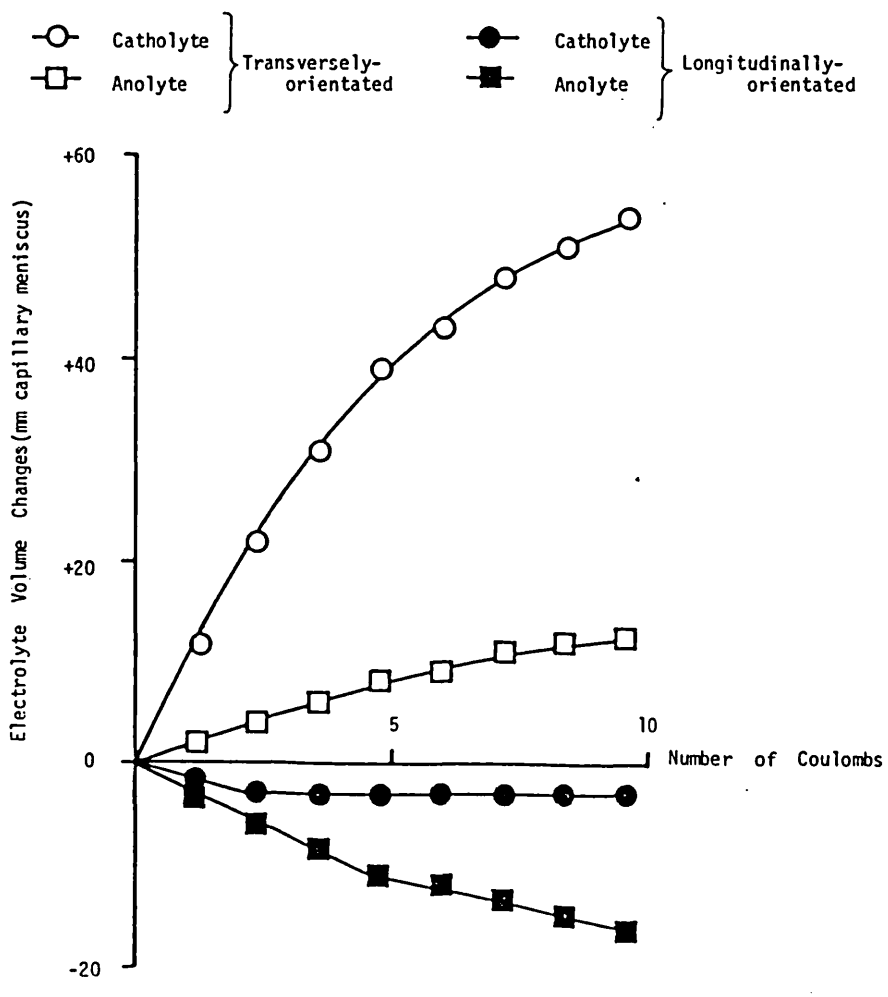
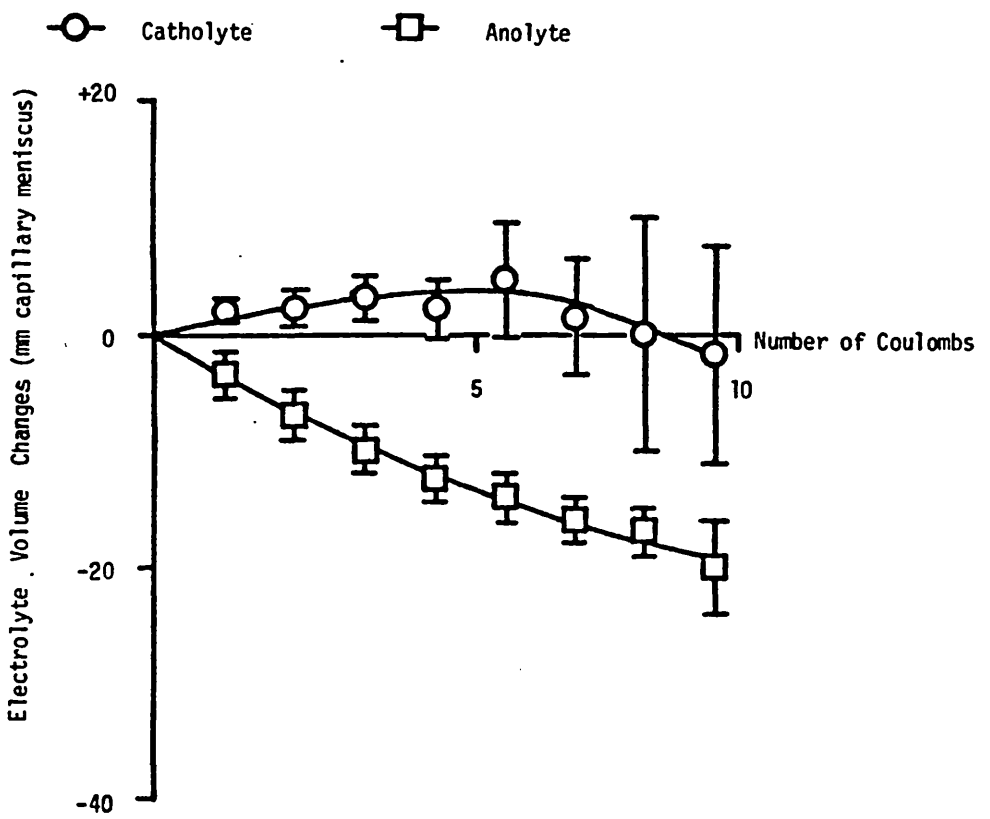


FIGURE 10.11 Electrolyte Volume Changes Using Transversely-Orientated Wood

100 mm long wood.
Pt/Ag/AgCl cathode in 0.1 M HCl; Cu anode in 0.1 M $CuSO_4$.
Confidence limits shown as bars, representing 4 replicates.

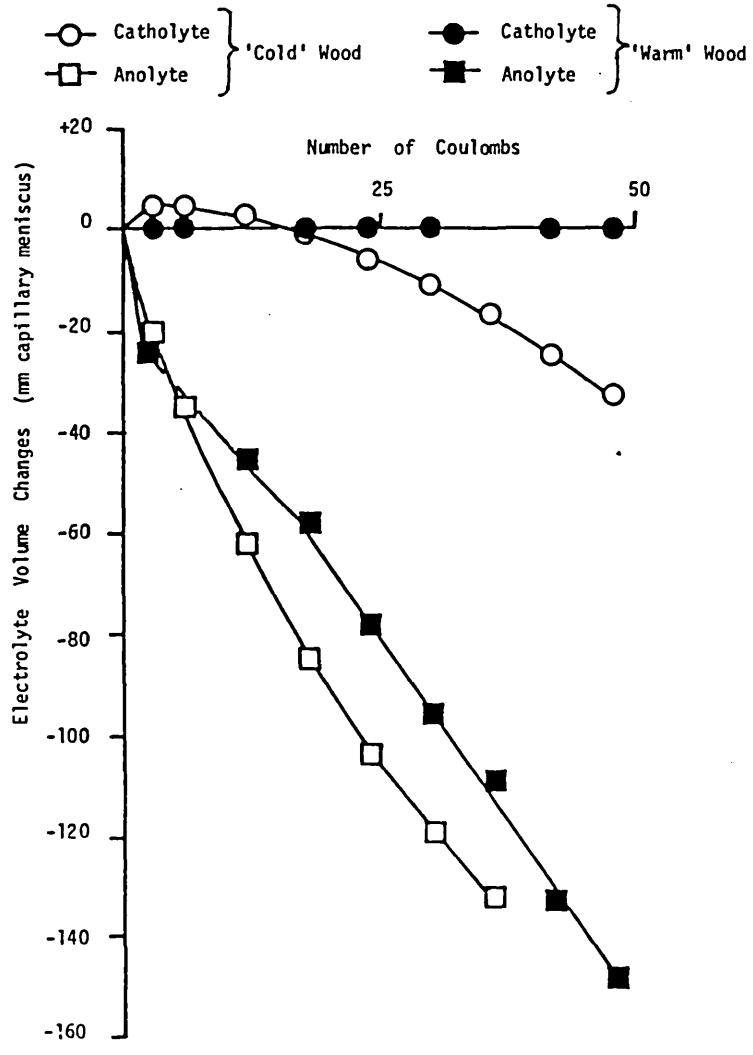


### 10.1.6 Temperature of wood

The temperature of the wood had a slight effect on $\Delta V_e$ (Fig. 10.12). The volume changes of electrolytes using 'cold' wood were apparently attenuated, but the anomalous initial rise and then fall of the catholyte using 'cold' wood may have been due to the inherent variability of the wood samples.

FIGURE 10.12 Electrolyte Volume Changes Using 'Cold' or 'Warm' Wood

50 mm long wood, used either 'cold' directly from refrigeration, or 'warm' after leaving at room temperature for 2 h.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.025 M $Li_2SO_4$.
Data taken from single runs.



Small changes in the temperatures of the solutions during electrical runs had little effect on $\Delta V_e$ values (Fig. 10.13, 10.14), except where Joule heating arose. With dilute (0.25 mM) $Bu_4NI$ catholyte and $CuSO_4$ anolyte (Fig. 10.15), or with dry wood (cf. section 6.3.3) runs, the volume of the anolyte rose. One effect of Joule heating can be estimated as follows. Suppose the electrolyte temperature rises from 20 to 25°C, then the density, D, of the water decreases from 0.9982 to 0.9971 g $cm^3$ ($\Delta D$ = -0.0011 g $cm^3$). Thus $\Delta V_e$ in an electrode compartment of volume 80 $cm^3$ will be

$$\Delta V_e = \frac{80 \times 0.9982}{0.9971} - 80 = 0.088 \text{ cm}^3$$

This will produce a rise, l, in a capillary meniscus of radius r equal to

$$l = \Delta V_e / \pi r^2 = (0.088/0.03) = 2.9 \text{ cm} = 29 \text{ mm}$$

The wood sample itself is also likely to swell as it becomes warmer, and contribute further to the rise in the capillary. Thus, an appreciable rise in temperature can by itself affect $\Delta V_e$, and this should be taken into account in interpreting results.

FIGURE 10.13 Electrolyte Volume and Temperature Changes: Catholytes

50 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.025 M $Li_2SO_4$.
Data taken from several runs.

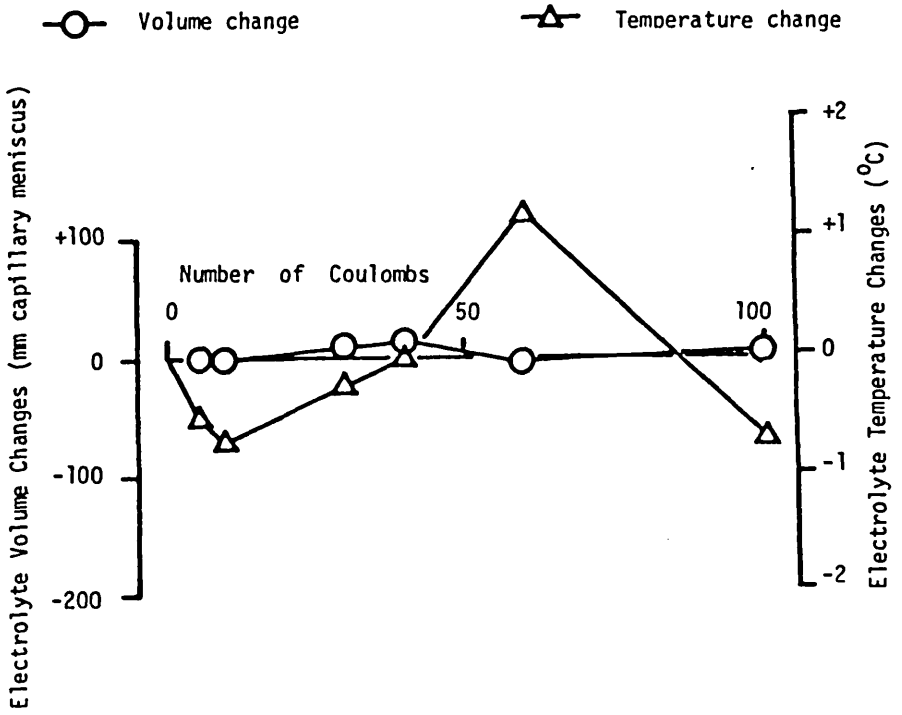
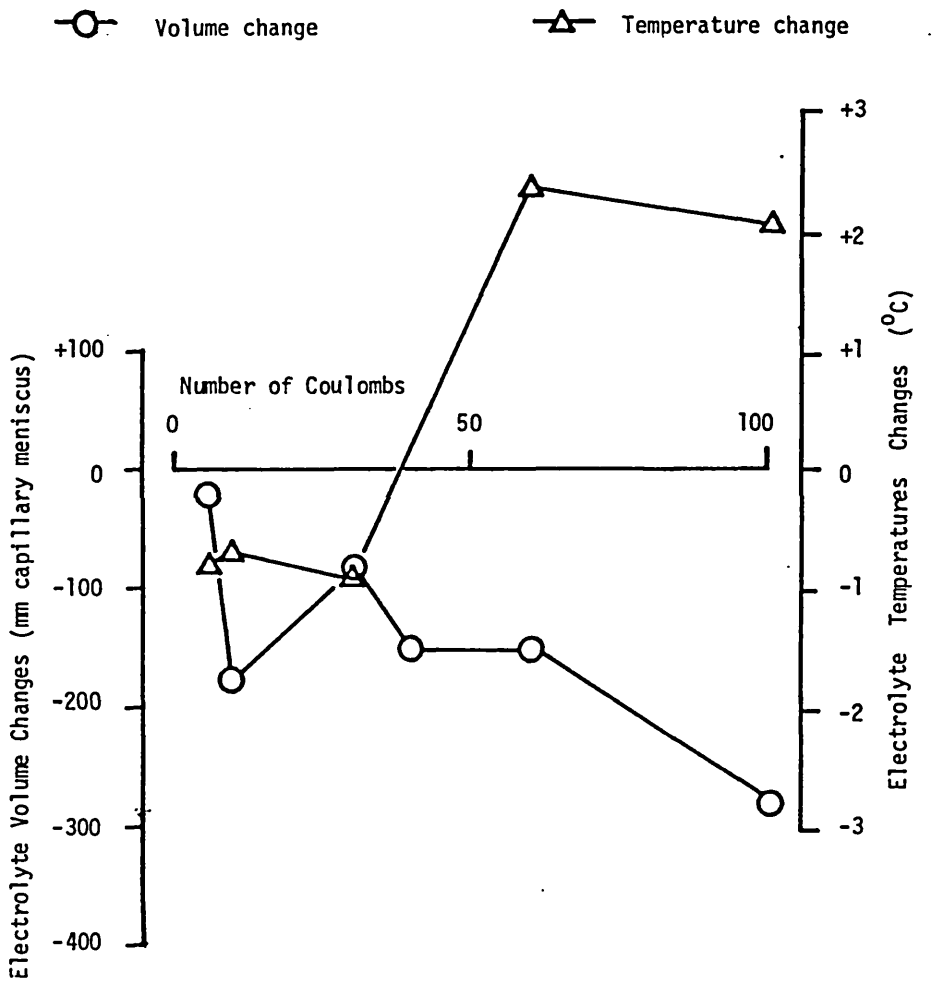


FIGURE 10.14 Electrolyte Volume and Temperature Changes: Anolytes

Same experimental conditions as in Fig. 10.13



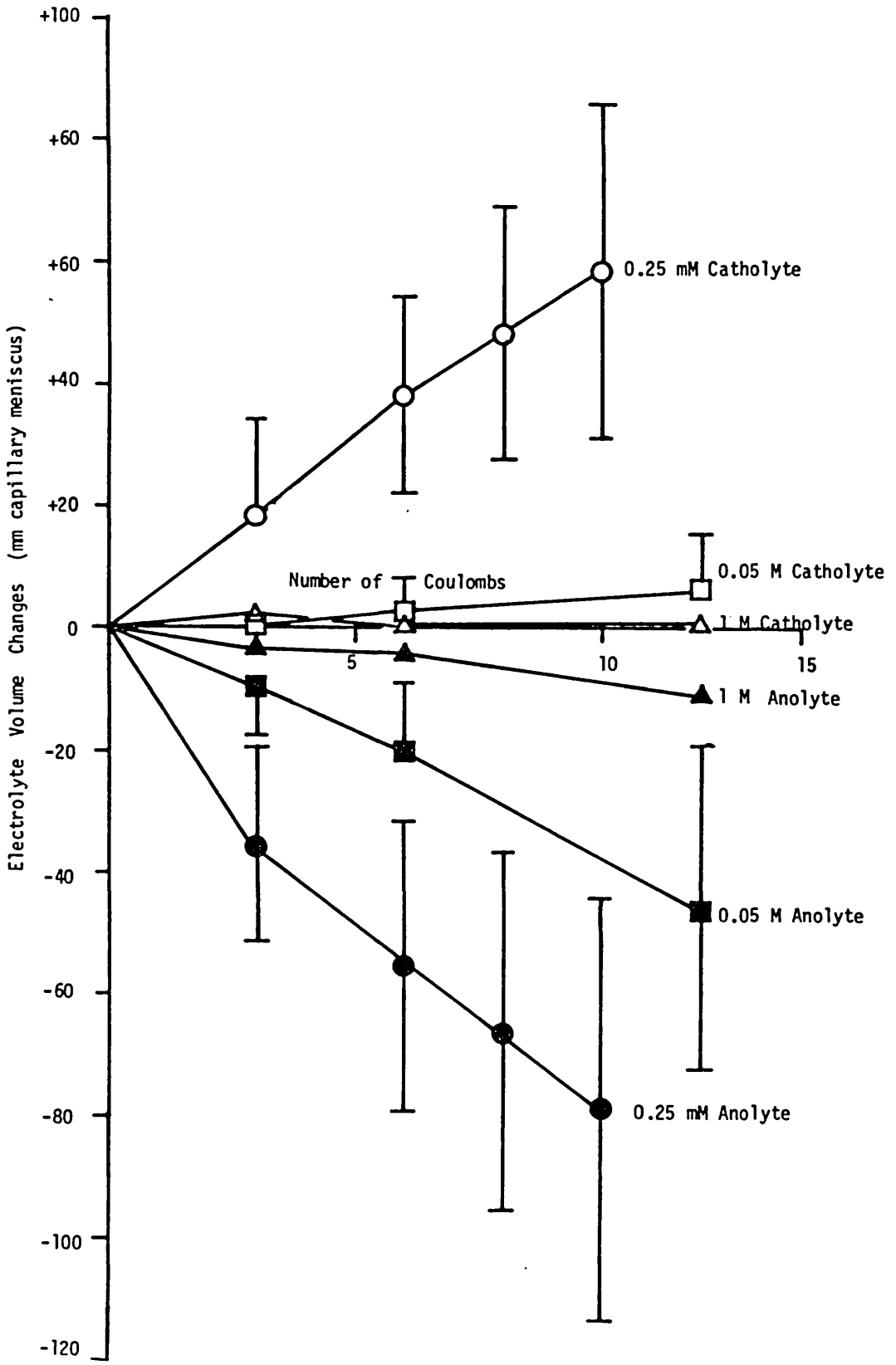
## 10.2 Chemical factors

### 10.2.1 Electrolyte concentrations

$\Delta V_e$ markedly increased using more dilute solutions, although wide variations occurred within each treatment (Fig. 10.15). This concentration effect probably arose from the greater potential gradient across the cell with dilute electrolyte solutions. However, it may also be related to a fall in pH with the most dilute HCl solution (cf. section 3.3), as electro-osmosis increases with increasing dissociation of fixed carboxyl groups, and hence zeta potential in the wood.

FIGURE 10.15 Electrolyte Volume Changes Using Different Electrolyte Concentrations

50 mm long wood.
Pt/Ag/AgCl cathode in HCl; Cu anode in $CuSO_4$ anolyte.
Bars represent confidence limits based on 4 replicates.

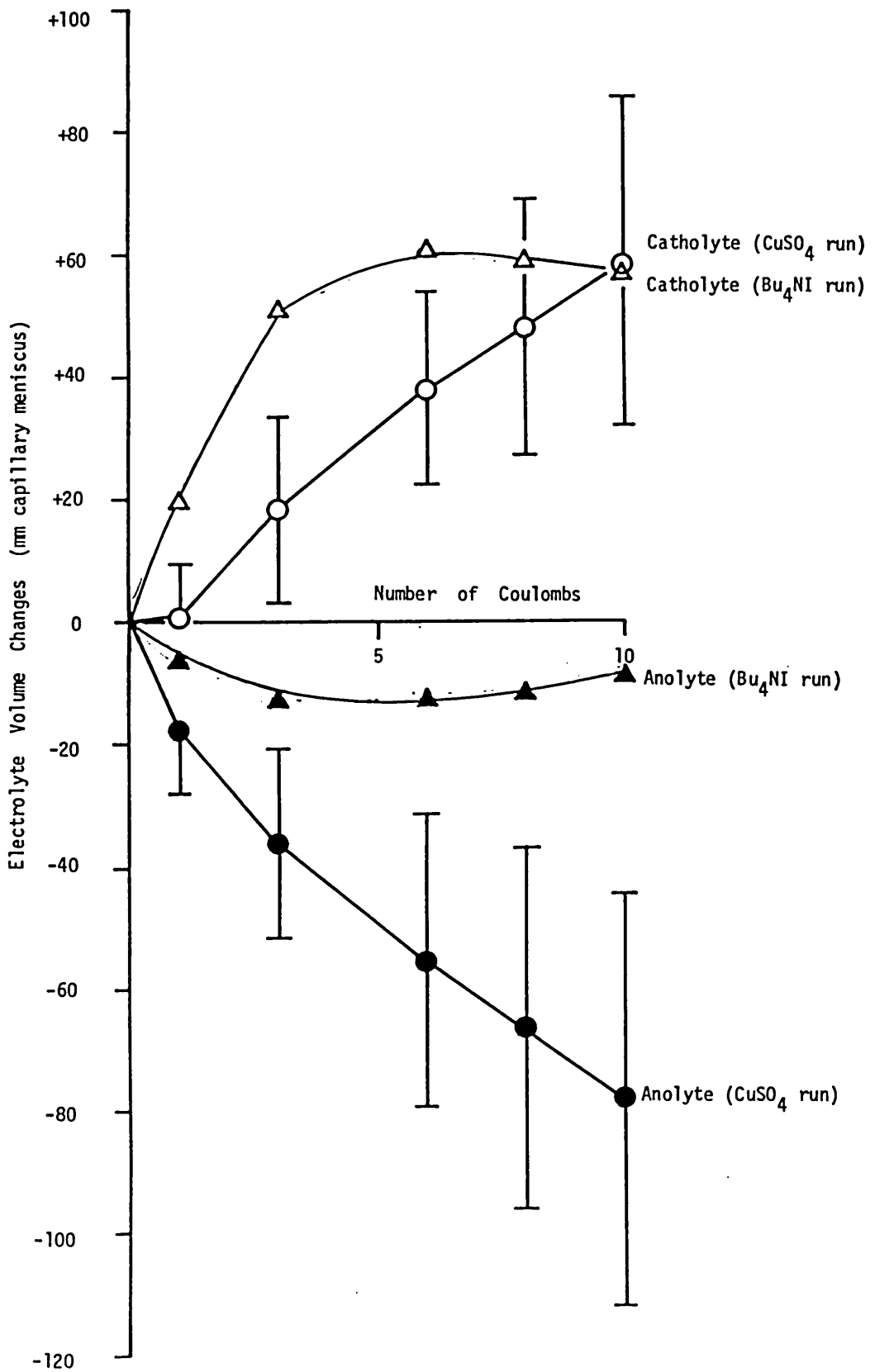


### 10.2.2 Catholyte species

With $Bu_4NI$ catholyte the rise in catholyte volume was larger, but the fall in anolyte smaller than that using HCl catholyte (Fig. 10.16). This was probably caused by a greater Joule heating effect (cf. section 10.1.6): the $Bu_4NI$ solution has much lower conductance (higher resistance) than the HCl solution (cf. section 9.2). The rise in anolyte volume above 6 C supports the idea that the electrolytes had become considerably heated. The larger pH of the $Bu_4NI$ solution may also have increased electro-osmosis, for reasons given in the previous sub-section.

FIGURE 10.16 Electrolyte Volume Changes Using $Bu_4NI$ or HCl Catholytes

100 mm long wood.
Pt/Ag/AgCl cathode in 0.25 mM catholyte; Cu anode in 0.25 mM $CuSO_4$.
Bars represent confidence limits based on 4 replicates.



### 10.2.3 Anolyte species

Using 0.05 M HCl catholyte throughout, the slight fall in catholyte and larger fall in anolyte volumes was virtually identical using $Li^+$- or $K^+$- containing anolytes (Figs. 10.17, 10.18). In contrast, the fall in the $Cu^{2+}$-containing anolyte was greater, and the corresponding catholyte rose, albeit with considerably wider variations. This distinction between mono- and divalent cation-containing anolytes may reflect the slower migration of $Cu^{2+}$ ions through the wood (cf. section 9.4), resulting in a larger potential gradient and producing a larger electro-osmotic flow.

FIGURE 10.17 Electrolyte Volume Changes Using Different Anolyte Species: Catholyte Volumes

50 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in various anolytes.
Bars represent confidence limits based on 4 replicates.

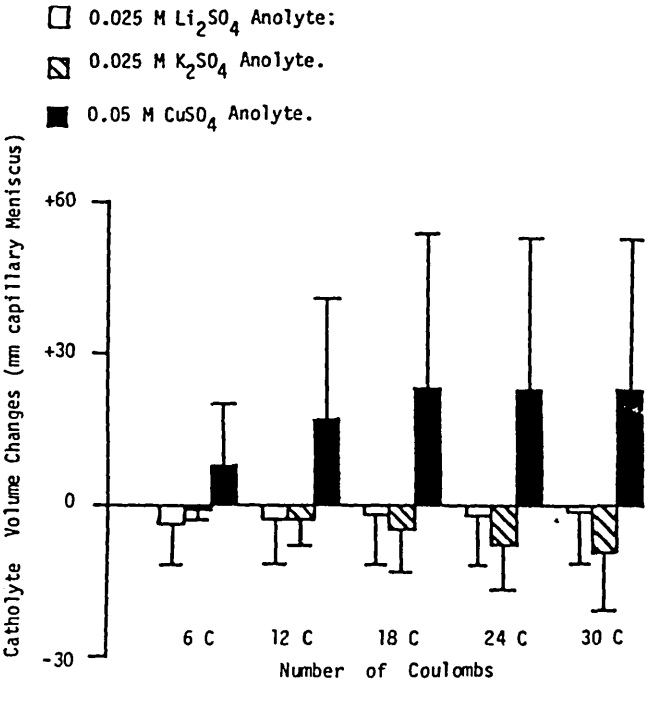
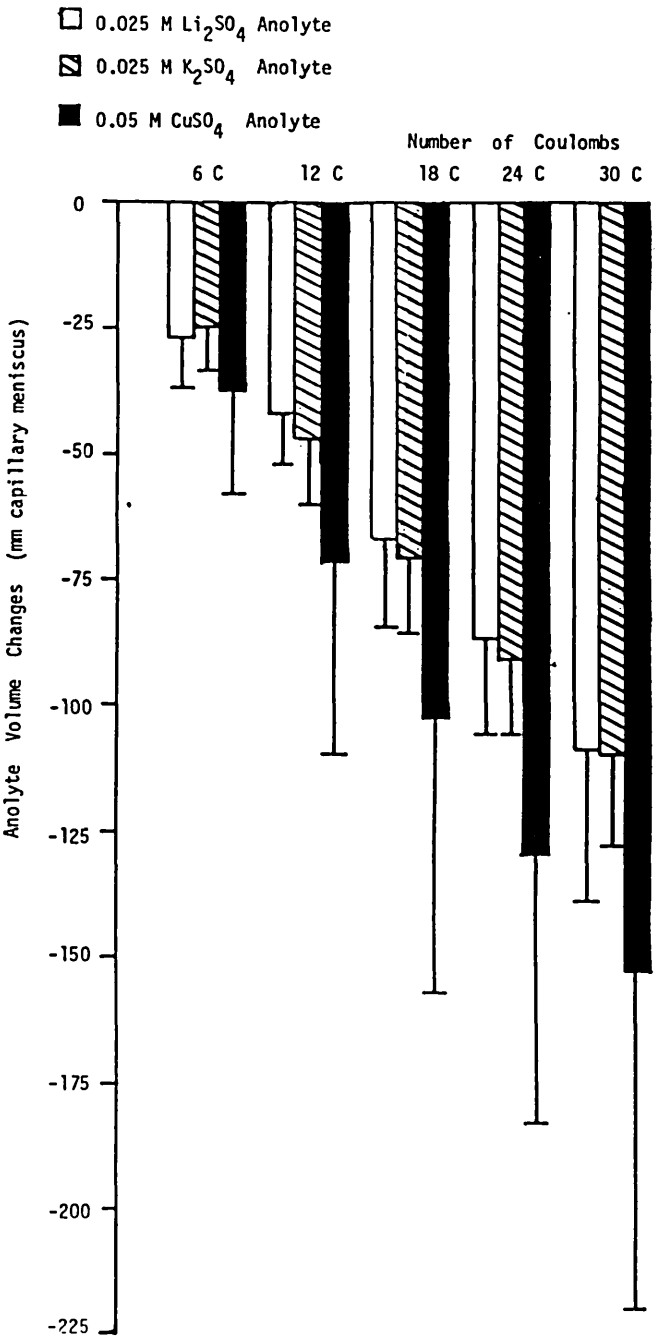


FIGURE 10.18 Electrolyte Volume Changes Using Different Anolyte Species: Anolyte Volumes

Same conditions as for Fig.10.17



10.2.4 Flushed wood

The patterns and degrees of electro-osmosis were very similar for unflushed and salt solution-flushed wood (Figs. 10.19, 10.20). However, the solution volume changes using 0.025 M $Li_2SO_4$ anolyte and wood flushed with distilled water were larger than those found in any other run. This will have been due to the high electrical resistance of the wood saturated with distilled water, and the equivalent large potential gradient through it.

What is puzzling, though, is why similarly large electrolyte volume changes across water-flushed wood were not recorded for runs using 0.05 M $CuSO_4$ anolyte (instead of $Li_2SO_4$), as the slower migration of $Cu^{2+}$ through the wood should have resulted in an even larger potential gradient across the wood.

FIGURE 10.19 Electrolyte Volume Changes in Flushed and Unflushed Wood: Passing $Li^+$

50 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.025 M $Li_2SO_4$.

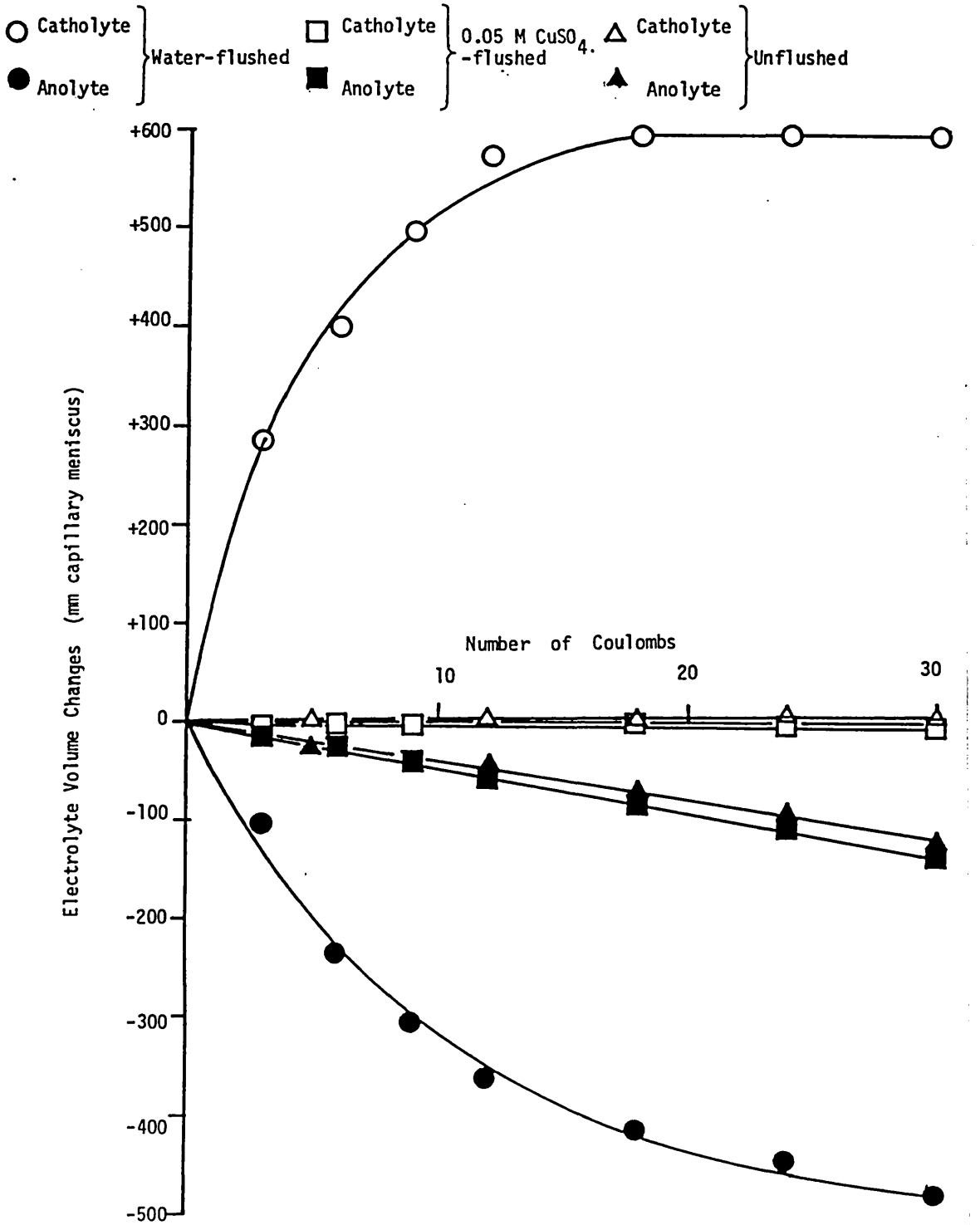
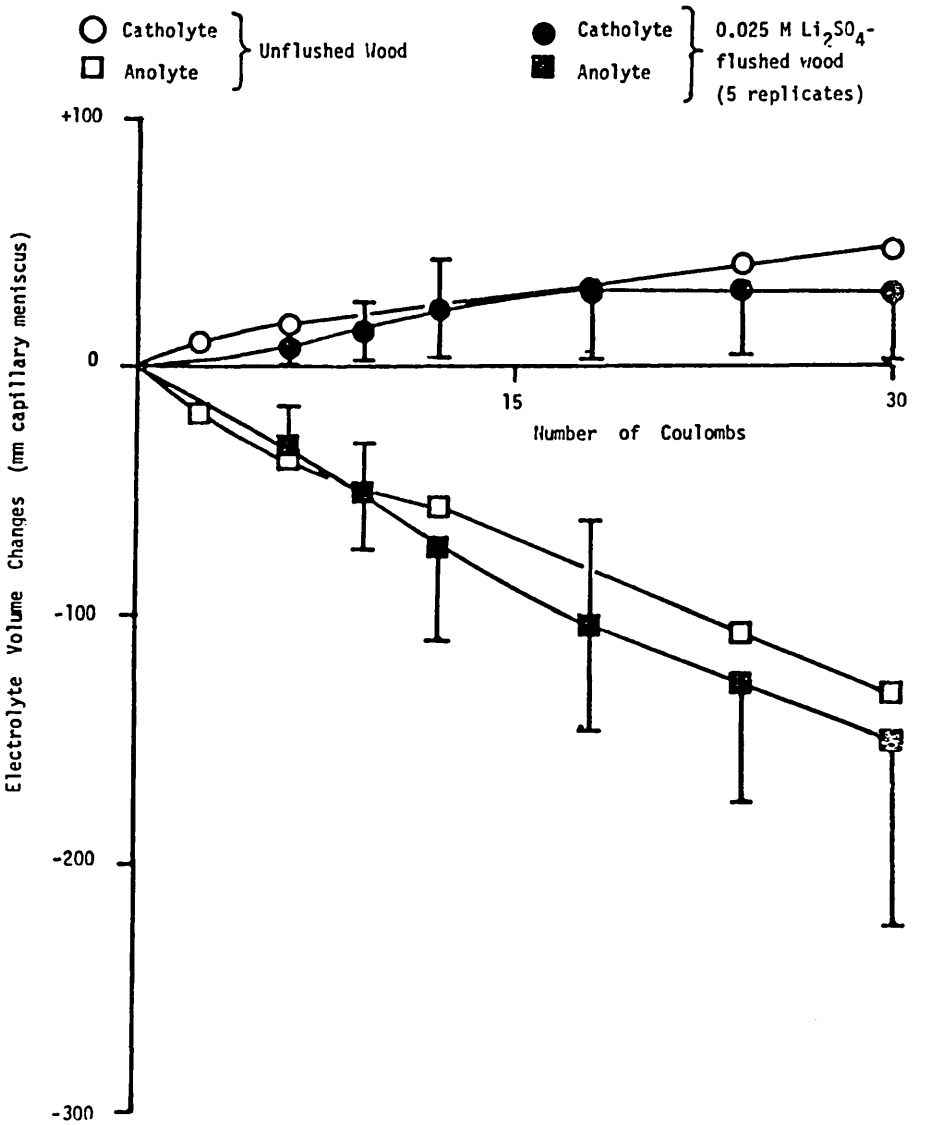


FIGURE 10.20 Electrolyte Volume Changes in Flushed and Unflushed Wood: Passing $Cu^{2+}$ Through $Li^{+}$-Flushed Wood

50 mm long wood.
Pt/Ag/AgCl cathode in 0.05 M HCl; Cu anode in 0.05 M $CuSO_4$.
Bars represent confidence limits based on 5 replicates.



## 10.3 Discussion

Passage of electrical current through the wood caused variable changes in the volume of the electrolyte solutions bathing in the wood. Electro-osmosis can account for most, if not all, of these volume changes, since:

(a) solution flowed from anode to cathode, as found by previous workers (Petri, 1921; Stamm, 1926; Bechhold and Heymann, 1927; Schwarz, 1982; Ito, 1960a);

(b) the rate of change of $V_e$ was closely related to the current (cf. section 2.5);

(c) $\Delta V_e$ was also related to factors affecting the potential gradient across the wood, such as the orientation of the wood and the electrolyte concentration in it.

However, other effects must also be considered:

(a) Temperature changes arising from Joule heating, and to a lesser extent in the surroundings, affect $\Delta V_e$, but in most cases the electro-osmotic effect is far greater.

(b) Migration of hydrated ions could account for part of $\Delta V_e$. However, $\Delta V_e$ is roughly the same for runs using $Li^+$- or $K^+$-containing anolytes (Figs. 10.17, 10.18), yet the ionic hydration number (i.e. number of water molecules per ion) of $Li^+$ = 2.8, and of $K^+$ = 0.9 (Robinson and Stokes, 1955). Ionic hydration therefore probably has an insignificant effect on $\Delta V_e$. (Also, the volume of electro-osmotic flow is far greater than any water that might be attached to the known amounts of ions migrating through the wood).

(c) Diffusion of water under a moisture gradient clearly effects $\Delta V_e$ by attenuating the rise in catholyte and increasing the fall in anolyte (cf. Fig. 10.3). The water will be retained by the wood owing to its increasing concentration of salts also entering by diffusion. The extent of diffusion is extremely variable (Figs. 10.1-10.3), and so its effect

was not known for all the runs. The $\Delta V_e$ value due to electro-osmosis alone cannot therefore be stated. This factor may well account for the variability in flow between experiments carried out under the same conditions.

(d) Osmosis may also affect $\Delta V_e$, according to the osmotic potential of electrolytes within and outside the wood. This agrees with Christensen and Williams (1951), who found that blocks of *Eucalyptus obliqua* behaved as a semi-permeable membrane. As a result, the water lodges in those regions of the wood with highest salt contents (ref. also to Christensen (1951b)).

Despite the wide variations in $\Delta V_e$, the catholyte level generally remained static or rose over the first 30°C, while the anolyte fell linearly to a far greater extent. The excess solution that passed into the wood - but not into the cathode compartment - presumably saturated the void spaces in the wood and/or evaporated through any breaks in the Mobilcer R coating. As discussed for diffusion, the wood will hold increasing levels of water as the concentration of salts in the wood rises, at least during electrical runs where migrating exogenous ions raised the salt concentration of the wood. This may help explain the sudden halt in the rise in catholyte volume, as an osmotic flow counters the electro-osmotic flow. However, over large numbers of coulombs (>250 C), or with a closed cathode compartment, sweating and leakages became increasingly noticeable (cf. sections 6.2.3, 6.2.4), and probably resulted from the flow of anolyte solution into the wood. The reason for the halt in catholyte $V_e$ with increasing numbers of C is not clear, but may be partly due to the decrease in potential gradient across the wood as exogenous electrolytes migrated through it. It is interesting that Bechhold and Heymann (1927) also found that the electro-osmotic velocity fell during electrical impregnation of wood with $CuSO_4$ (cf. section 3.5).

Lastly, it is worth emphasising the results of the runs using a closed compartment, showing that ionic migration and electro-osmosis were independent factors resulting from passing electricity through wood. This has never been previously shown.

# CHAPTER 11

# GENERAL DISCUSSION

## 11.1 Nature and Mechanism of Ion Migration

This has been the first study to distinguish between the migration of exo- and endogenous ions in wood. By careful design many extraneous factors were avoided - short-circuiting, unequal hydrostatic pressure, contamination - and others minimised (such as the interfering effects of electrode reactions and Joule heating). The present study was also the first to use constant current, rather than constant potential, and so enabled ionic transference numbers to be determined at the bathing electrolyte/wood interfaces.

The endogenous current was found to be carried by ions in the rough order $K^+$, $Ca^{2+} > Mg^{2+} > Na^+ > NH_4^+$, $Cl^-$, $SO_4^{2-}$. No contributions to carrying current were made by $H^+$ or $OH^-$ ions. However, both the transference numbers of the various species and their sum were highly variable. This may have arisen partly from experimental errors (cf. sections 6.4.2, 6.4.3), but more probably reflects the inherent variations between wood from the same or different trees (cf. section 6.4.1). Such differences are due at least partly to the variability of ion content (cf. sections 1.6.3, 6.4.1) and cation-exchange capacity (cf. section 1.7.3).

The results clearly show that cations are the major endogenous current carriers. Of these, $K^+$ and $Ca^{2+}$ ions transported the bulk of endogenous current, with $Ca^{2+}$ possessing a lower ion-constituent mobility (ie. slower migration) than $K^+$. Langwig and Meyer (1973), though, found that both endogenous cations and *anions* carried current through three Venezuelan wood species, reflecting the unusually high levels of anions in these species (cf. section 3.2.1). They also showed that Mn and a wide range of trace elements play no part in carrying current, agreeing with results here. These elements are probably too strongly bound to the cell walls of the wood to migrate in the electrical field (cf. section 1.6.3).

Migration of cations probably involves cation-exchange, since:

(a) the relative proportions of electrolyte-exchangeable cations matches the order of current-carrying;
(b) electrolyte-flushed wood possesses virtually no endogenous ion current, whereas water-flushing only partially depletes this current;
(c) divalent cations migrate slower than monovalent ones (cf. sections 1.7.1, 2.4);
(d) exogenous cation migration is in the order water-flushed $>$ unflushed $>$ $CuSO_4$-flushed wood.

The cation-exchange sites may well be negatively-charged carboxyl groups attached to uronic acids in the cell walls (cf. section 1.7). The migration of cations could be imagined as a 'hopping' process from one carboxyl group to another. Clearly, endogenous divalent cations occupying these groups will impede the migration of exogenous cations. As these divalent cations are removed from the wood they are replaced by the exogenous cations.

The rates of migration of different exogenous ions have not been distinguished in the literature. In this study the exogenous cations $Li^+$ and $Na^+$ were found to have higher ion-constituent mobilities than $Cu^{2+}$. This must be largely attributed to the association of ion species with each other (eg. $Cu^{2+}$ and $Cl^-$) and, more important, of the $Cu^{2+}$ ions with carboxyl groups in the wood.

However, less attention has been paid to exogenous anion migration in this study (and similarly with previous workers), although it clearly plays a major role in carrying current. It is not known whether the migration of divalent anions is slower than that of monovalent anions, but the AgCl precipitate streaming phenomenon (cf. section 6.3.5) and HCl catholyte/$Li_2SO_4$ anolyte runs indicate that $Cl^-$ migration is as rapid or more so than monovalent cation migration. Schwarz's (1928a) finding that $CrO_4^{2-}$ anions migrated faster than $Pb^{2+}$ (by determining where in the wood the two ions precipitated) could be used for other ions (although this was not possible with $Ag^+$ and $Cl^-$ ions used here). As mentioned in section 9.6, across the cathode face of the wood much of

the current must have been carried by exogenous anions. Less current was carried by large and slow exogenous anions, such as laurylsulphate. Clearly, more information on anion mobility could be obtained by using radioactively labelled ions. Cation and anion migration may actually interact with each other, as in the association of $Cu^{2+}$ and $Cl^{-}$ ions in the wood.

The transport of ions in the electrical runs was due almost entirely to electrical migration. Zero-current control runs produced relatively little ionic diffusion; similarly, diffusion of exogenous electrolyte ions prior to an electrical run was insignificant, as shown with slow ($Bu_4N^{+}$) and fast ($H^{+}$) catholyte ions (cf. section 9.2.2). Convection of electrolytes by a 'wick' action - solution being drawn into the wood by evaporation from the wood surface - was not found (Table 6.6: comparison of uncoated and Mobilcer R-coated wood samples).

Electro-osmosis had no effect on ion migration, in contrast to previous reports (Petri, 1921; Bechhold and Heymann, 1927; Schwarz, 1928b,c; Muraoka, 1929). This may be because in this project ionic migration and electro-osmosis could be measured simultaneously. Previous workers may have mistaken hydrostatic pressure effects for electro-osmosis; such effects would have substantially affected ion migration by forcing exogenous ions into the wood (cf. section 6.2.5) and eluting endogenous ions (cf. section 9.5.1). Significantly, brown-yellow discolouration of bathing electrolyte solutions was only found here when the wood was hydrostatically flushed, whereas many other workers observed such discolouration during electrical runs (cf. section 7.3).

## 11.2 Pathways of Ion Migration

The larger Joule heating occurring with transversely-orientated wood indicates that ions migrate preferentially along, rather than across, the grain. The streaming of silver chloride precipitates (section 6.3.5) and light microscopy support his. Nevertheless, the rays also carry copper, even when current was passed along the grain, showing that radial and longitudinal conduction occur simultaneously (assuming that the copper had not diffused into the rays after the current was switched off). This might explain the presence of copper in beads of moisture ('sweat') on the exposed wood surface; presumably it had passed through

pit-pairs from longitudinal tracheids to ray tissues.

Although copper was found in resin ducts, and in early- and latewood tracheids, the main pathway for ion migration is not clear. Resin ducts can carry large proportions of exogenous current, as shown by the heavy deposits of copper in them. However, light microscopy of rubeanic acid-stained wood samples showed that copper migration through the tracheids may be more rapid. Some tracheids, though, conducted faster than others, giving rise to a patchy impregnation with $CuSO_4$. In contrast, past workers, using greater numbers of coulombs (of the order of thousands) and more concentrated electrolyte solutions, found that copper is generally distributed homogeneously throughout most wood tissues by electrical impregnation. Petri (1921) found no distinction between early- and latewood, or sap- and heartwood, although discolouration tended to develop from the inside of wood samples outwards. Bechhold & Heymann (1927) merely differentiated between the greater copper content of sap- than heartwood. Schwarz (1928a) found $Pb^{2+}$ and $CrO_4^{2-}$ ions had migrated homogeneously in wood samples. Muraoka's (1929) illustrations indicate homogeneous impregnation with $CuSO_4$ solutions.

The only high magnification ( > x 500) microscopic observation of electrically impregnated wood, by Petri (1921), showed that copper homogeneously penetrated all secondary cell wall layers.

However, the cell lumina and open pit apertures are important channels for ion migration because of their low electrical resistance (Stamm, 1967; Siau, 1971). Since diffusion through wood is similar in many respects to electrical migration (cf. section 11.3), evidence from diffusion studies of the anisotropic behaviour of wood again bears out the significance of cell lumina and pit apertures (cf. sections 1.9.1 and 1.9.2). Stamm (1946) used diffusion measurement as a corollary to his investigations of the capillary structure of softwoods, and indeed regarded diffusion as analogous to the flow of current through a resistance network. He considered diffusion in all directions in softwoods is dependent largely on the communicating pits, but Christensen (1951b) indicated that current could also be carried through cell wall capillaries.

At the wood tissue level, adsorption studies (characterised by the ion-exchange properties of wood) suggest that migrating ions (particularly cations) would pass more easily through sap- than heartwood, through late- more easily than through earlywood, and through lignified tissues than living parenchyma cells (Klein and Bauch, 1977; Klein, 1978).

Further studies could be made to determine the amounts of metals at tissue level using SEM-EDAX (scanning electron microscopy with energy dispersive analyses of X-rays), and at the cell wall level using TEM-EDAX (transmission electron microscopy). Thus the commercial possibilities of electrical impregnation could be assessed against other, conventional, treatments, in which poor penetration of salt preservatives in certain tissues and/or cell wall layers can occur in many species of wood (e.g. Levy and Greaves, 1978).

## 11.3 Diffusion

The behaviour of ions migrating electrically through wood reflects many properties of their diffusion behaviour:

(a) Diffusion coefficients, D, of ions are generally inversely proportional to their limiting ionic conductances (which also represent their ionic mobilities). In other words, D decreases with increasing ionic radius (i.e. size of ion) (Christensen, 1951b; Bains and Kumar, 1979).

(b) Diffusing cations exchange with other, fixed cations which are held on negatively-charged sites on the cell walls of the wood (Christensen, 1951b). However, previous wood researchers such as Christensen do not seem to have fully appreciated the role of cation-exchange in diffusion, whereas many plant physiologists have paid close attention to this phenomenon in ion transport (which partly involves diffusion) in living plants (e.g. Van de Geijn and Petit, 1979).

(c) Divalent ions generally diffuse slower than monovalent ones, due to their larger electrostatic surface charge. Thus, a larger activation energy is needed by divalent ions to diffuse past a potential barrier such as a cation-exchange site (Christensen, 1951b).

(d) pH affects the diffusion of cations by controlling the dissociation of acid groups (such as -COOH) on the cell walls. Thus, low pH represses the dissociation of these groups, and so reduces the resistance to diffusing ions (Christensen, 1951b).

Given these striking similarities between diffusion and electrical migration of ions, it seems reasonable to predict features of migration not investigated in this project. For example, electrical migration would be expected to:

(a) increase with rising temperature (Christensen, 1951b; Kumar and Purushotham, 1972; Bains and Kumar, 1979);

(b) be affected by the anisotropic nature of wood, as discussed previously in section 11.2

## 11.4 Electro-osmosis

Both the cation-exchange capacity and direction of electro-osmosis (anode to cathode) show that wood is negatively charged with respect to water, confirming previous reports based on electrokinetic data (cf. section 1.9). The negative zeta potential probably originates from the ionised carboxyl groups on cell walls of the wood. The zeta potential falls as exogenous cations bind to these groups, and this reduces the rate of electro-osmosis. Thus the ion-constituent mobility and cation-exchangeability of different cation species will affect electro-osmotic flow.

The decrease in potential gradient across the wood samples during runs, as exogenous ions migrated into the wood, also decreased the rate of electro-osmosis. This contrasts with the increase in resistance,

particularly towards the anode found by Ito (1960a,b- cf. section 3.4.1), who applied electrodes *directly* onto the wood surface.

The pathway of electro-osmotic flow through the wood is likely to be largely longitudinal, following the channels of least electrical and mechanical resistance. Hence many of the factors affecting the porosity of wood will be expected to influence electro-osmosis, e.g. pit aperture aspiration, air bubbles in cell lumina, and so on (cf. section 1.10).

## 11.5 Wood Preservation

Little evidence was found here that electrical impregnation has any advantages over conventional preservation treatments (cf. section 1.11). Although high magnification ( $>$ x 100) microscopy was not undertaken (to determine copper impregnation of cell walls - cf. section 11.2), high numbers of coulombs ( $>$ 100), and hence energy, are clearly required to penetrate all tissues with a *relatively small (19cm$^3$) wood sample*.

However, previous workers showed that electrical impregnation offered better penetration of heartwood, and also across the grain, than conventional pressure techniques (e.g. Petri, 1921; Bechhold & Heymann, 1927). They also claimed that electrically-treated wood was mechanically stronger and, more significantly, less prone to microbial decay. Similar claims were also made in many potential industrial techniques (cf. section 3.6), and may be due to the removal of endogenous ions during electrical treatment. Since wood-decaying micro-organisms require various elements in the wood for their nutrition (e.g. Cartwright and Findlay, 1958), the absence of labile ions (such as K, Ca, Mg, etc) may retard microbial growth and development. In addition, passing an electric current may also kill micro-organisms *in situ*, as electricity has been reported to kill bacteria *in vitro* (Rowley, 1972) as well as fungi already living in wood (Hattori and Tamura, 1939).

Perhaps the feature of this project most relevant to wood preservation is the cation-exchange capacity of wood. This clearly affects the migration and diffusion of cations, and further investigation of it should improve the understanding of the fixation and leaching of salt preservative solutions. Areas of particular interest are the effects of fungal decay, the affinity of different cation species for fixed carboxyl groups, and the variation of the pH of preservative solutions inside the wood (cf. sections 1.7.3 and 2.4).

One commercial application could be in passing relatively weak currents ( $\mu$A), in conjunction with diffusion or pressure/vacuum treatment of wood, in which penetration of all tissues is required (including treatment of timbers in service). For example, further studies could determine the migration of ions through heartwood, spruce wood, and many hardwood species, all of which are difficult to treat owing to their poor permeability (e.g. Siau, 1971). Hardwoods may behave very differently to softwoods under an applied d.c. field (Petri, 1921). Moreover, little is yet known about the migration of commercially useful anions, such as chromate or borate, which might be passed electrically into wood.

However, in any commercial electrical treatment the capital and manual overheads may offset any practical advantages of the preservation. One possible way of cutting costs could be to encourage natural fixation and preservation of timbers in service (cf. section 1.11.4). Here the wood might be chemically treated to increase its cation-exchange capacity, and then wrapped in a preservative-soaked material, such as copper-impregnated cloth. The timber could then exchange its cations with the copper over a long duration in the ground.

The *deleterious* effects of ion migration should also be noted in:

(a) the decay of wood around dissimilar metals or metal electrodes fixed onto salt-soaked wood (cf. section 3.7);

(b) using wood containing excess salt preservative solution for carrying uninsulated electrical installations (cf. section 3.1.3);

(c) d.c. resistance meter measurements of moisture or decay in wood (cf. section 3.5.3).

The commercial prospects for drying wood using d.c. electricity seem unattractive because of the migration of ions, resulting in high electrical resistances as the ions pass out of the wood. Increasing resistance also results from falling moisture content (cf. section 3.1.1).

## 11.6 Relevance to the Living Tree

Wood *in vivo* and *in vitro* show similar cation-exchange properties (cf. section 1.7.3), so that wood in the living tree might react in a similar way to applied electric potentials. However, metabolic effects in the living parenchyma tissue would also be expected (cf. section 3.6), resulting in unknown reactions.

Nevertheless, ion migration under an applied d.c. electric field could radically alter the physiology of the whole tree, as has been shown for a wide variety of whole plant systems (e.g. Pohl, 1977; Ellis and Turner, 1978) and single plant cell systems (e.g. Jaffe and Nuccitelli, 1977). The applications of d.c. (and also a.c.) electricity to living systems are likely to be wide ranging and quite spectacular, as illustrated by astonishing success in bone regeneration (e.g. Bassett *et al*, 1974).

# A P P E N D I C E S

## APPENDIX 1 ASH CONTENT OF SAPWOOD FROM TREE I

10 replicates per log.

Lower log 0.2 to 0.4 m above ground level; Upper log 0.4 to 0.6 m above ground level.

| Element | Concentrations (ppm) | | |
|---|---|---|---|
| | Lower Log | Upper Log | Mean of both logs |
| Ca | 512 | 587 | 549 |
| K | 530 | 416 | 473 |
| Mg | 134 | 144 | 139 |
| Na | 24 | 26 | 22 |
| Mn | 6 | 6 | 6 |
| Cu | 4 | 7 | 5.5 |
| Cr | 3 | 5 | 4 |
| Fe | 2 | 4 | 3 |
| Pb | 0.05 | 0.05 | 0.05 |

APPENDIX 2 MOISTURE CONTENTS OF WOOD FROM TREE I

10 replicates per log. Averages ± confidence limits.
Lower log 0.2 to 0.4 m above ground level; Upper log 0.4 to 0.6 m above ground level.

| Log | Average moisture content (%) |
|---|---|
| Lower | 112 ± 26 |
| Upper | 129 ± 3 |

APPENDIX 3 MOISTURE CONTENTS OF WOOD FROM TREES I, II and III

10 replicates per tree. Averages ± confidence limits.

| Tree Number | Average Moisture Content (%) |
|---|---|
| I | 122 ± 12 |
| II | 142 ± 11 |
| III | 140 ± 5 |

APPENDIX 4 MOISTURE CONTENTS OF 20 WEEK OLD REFRIGERATED OR FROZEN WOOD

5 replicates per storage treatment. Averages ± confidence limits.

| Storage | Average Moisture Content (%) |
|---|---|
| Refrigerated | 120 ± 12 |
| Frozen | 134 ± 14 |

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# CORRECTION PAGE

With Reference to Page 112

The confidence limits are

$$\pm t\, s/\sqrt{n}$$

t is a statistic whose numerical values were calculated by R.A. Fisher. For the 95% confidence range

$$t = 1.96$$

for an infinite number of samples, but is larger for small samples. Numerical tables are given in standard texts. In the present thesis, however, all confidence limits were calculated with t = 1.96

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