## Conclusion

The Benesch and Mangelsdorf method for the determination of ammonia has only the advantage of a somewhat shorter reaction time, if compared with the Koroleff method, modified by Grasshoff and Johannsen (1972). There are, however, a number of disadvantages, such as a tedious procedure, less sensitivity and a strong salt error which is in disagreement with the findings of Benesch and Mangelsdorf (1972), who stated that there is no salt error.

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# A rapid semiquantitative screening procedure for lignin in marine sediments

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Lignin in marine sediments can be rapidly identified under the microscope after reaction with 1,3,5-trihydroxybenzene in alcoholic hydrochloric acid. This reaction serves to screen samples for subsequent quantitative determination by alkaline nitrobenzene oxidation.

Alkaline nitrobenzene oxidation of samples to produce vanillin and syringaldehyde, extraction of products and subsequent gas chromatographic determination of the characteristic aldehydes has been used for the determination of lignin in marine sediments and particulate matter on filters (Pocklington and MacGregor, 1973). Due to the length of time required to complete this procedure (ca 4 man-hours per sample) and the fact that many samples have no detectable lignin, a need became apparent for a simple semiquantitative method for identifying samples containing lignin within the range of detectability (0·02–360 mg lignin/g sample) of the quantitative method.

Due to the great difficulty in extracting lignin from wood and wood-fibre bearing materials, an *in situ* spot test based upon the Wiesner colour reaction (Wiesner, 1878) was developed. The reaction has universal applicability to all lignins, although it may be weak or even absent in lignins containing high amounts of syringyl propane units, i.e. certain hardwoods, (Sarkanen and Ludwig, 1971).

## Procedure

An Ekman grab was used to obtain surface sediment samples which were placed in plastic bags and subsequently deep-frozen. A freeze drier (Virtis Co., Gardiner, N.Y., Model USM-15) was used to dry samples without subjecting them to heat. Sediment samples were then ground to pass a 24-mesh sieve (0·707 mm diameter).

Approximately 10 mg of sediment was placed on a glass microscope slide, preferably one with a well, and smeared with 2 or 3 drops of reagent. The test reagent is prepared by addition of 9 ml concentrated hydrochloric acid to 1 ml of a 10% solution of 1,3,5-trihydroxybenzene in methanol (Feigl, 1960). It must be stored in the dark. The reagent reacts with

Table 1. Results of screening procedure on previously analyzed samples

| Sample | Before test | After test | Lignin[1] mg/g | Semi-quantitative[2] Value |
|---|---|---|---|---|
| *Lignum vitae* (powdered hardwood) | yellow powder | Entirely dark reddish-violet | 181·0 | A |
| Corner Brook Harbour 101/72 (sediment taken adjacent to pulp mill) | brown fibrous fluff | Mainly large patches of reddish-violet fibres | 41·3 | A |
| (near Harbour mouth) 102/72 | grey dusty powder | Isolated spots of reddish-violet | 1·46 | B |
| Esquiman Channel 024/72 (sediment) | brown sandy powder | 1 or 2 minute fibres per slide | 0·94 | B |
| Anticosti Island 034/72 (sediment) | brown sandy powder | A few isolated small spots | 1·63 | B |
| St. Lawrence Estuary 053/72 (sediment) | brown sandy powder | Isolated spots of reddish-violet. Largely brown slurry | 1·22 | B |
| Upper Saguenay River 056/72 (sediment) | light brown sandy powder | Reddish-violet fibres seen throughout. Less than 101/72. More than 102/72 | 9·04 | A |
| Lower Saguenay River 060/72 (sediment) | light brown sandy powder | Much like 102/72. Isolated spots of reddish-violet | 1·93 | B |

[1] By method of Pocklington and MacGregor (1973); means of replicate determinations

[2]

| Category | Appearance | Semiquantitative value (mg lignin/g sediment) |
|---|---|---|
| A | Much colour, detectable with naked eye | > 5·0 |
| B | Colour detectable under the microscope | 0·005–5·0 |
| C | Undetectable | < 0·005 |

the coniferaldehyde groups in lignin (Adler and Ellmer, 1948), forming a purple cationic chromophore. The development of the purple colouration is taken as positive evidence for the presence of lignin in the sample.

The smeared samples were then examined microscopically (Heerburg Model M5-32236) at magnification 125x and if no indication of lignin was given (absence of purple colouration), again at 250x with the aid of a high intensity white light source (Hammond Microscope Transformer, Model 20-D; Philips Holland light bulb, 13347W, 6 volts, 15 watts). Some gravelly sediments containing rose-coloured quartz presented something of a problem because of the similarity in colour but careful observation before smearing showed the texture of this and of the coloured lignified material to be quite different. Evaluation was easier with some samples after they had been allowed to dry out on the microscope slide.

Using standards made from lignin-free mud and finely ground White Pine (*Pinus strobus*) wood (W/W), a semiquantitative colour scale was created to evaluate samples to be screened upon some of which a quantitative determination of lignin by the method of Pocklington and MacGregor (1973) had been performed. All samples receiving an A or B grade were then determined quantitatively and the analytical results compared with the screening test (Table 1). One set of standards and samples was evaluated by two outside observers and excellent reproducibility of interpretation was established.

## Results and discussion

Whereas the quantitative determination of one sample for lignin requires approximately four man-hours, the semiquantitative method described here can be completed in one minute. The method is dependable and does not require chemical modification of the analyte before analysis unless lignin sulphonic acid is suspected. In this case prior treatment with alkali is required (Adler, Björkqvist and Häggroth, 1948). Of 64 sediment samples checked by the semiquantitative method, 39 were also determined by the quantitative method. The quantitative results were found to support the results of the semiquantitative colour test in all cases, except for sediment samples 028/73 and 026/73 where lignin was indicated on 1 out of 4 slides but not found in the quantitative determination with double replicates. We infer from this that the limit of detectability, currently 0·005 mg lignin/g sediment might be lowered by screening multiple replicates. Work is proceeding on the application of this test to material retained on filters.

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