ICCP INTERLABORATORY EXERCISE ON THE APPLICATION OF MICRO SPECTRAL FLUORESCENCE MEASUREMENTS AS MATURITY PARAMETERS

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ABSTRACT - In the present study, comparative and reproducible spectral fluorescence measurements were obtained from an interlaboratorial analysis (round robin analysis) as an exercise of the Thermal Indices Working Group of Commission II (International Committee for Coal and Organic Petrography (ICCP)). In this work duplicates of a calibrated lamp source (certified by Laboratoire National d'Essais, Paris, France) were provided to the various laboratories. The spectral radiance B (λ) for each of these duplicates was determined and served for the determination of the relative correction function for each photo-optical system used. Once the correction function was established, fluorescence characteristics of four samples, rich in *Tasmanites*, representing a sequence of increasing maturation were determined by each laboratory. The spectral curves and comparison of λ max and Q values showed good agreement among laboratories for the low maturity samples. In contrast, results obtained from the sample representing the highest maturity level presented a significant scatter.

RESUMO - Este trabalho apresenta resultados de uma análise interlaboratorial (round robin analysis) realizada pelo Grupo de Trabalho de Indices Térmicos, da Comissão II, do Comitê Internacional de Petrografia Orgânica e de Carvão (ICCP). Neste trabalho foram obtidas medidas de fluorescência comparáveis e com reprodutibilidade entre diferentes laboratórios. Com este objetivo, uma duplicata de lâmpadas calibradas (certificadas pelo Laboratoire National d'Essais, Paris, France) foram enviadas aos vários laboratórios tendo servido para a obtenção da radiância espectral B'(λ) que tornou possível a determinação da função de correção relativa para cada sistema foto-ótico. Com a obtenção da função de correção, cada laboratório procedeu a análise de um conjunto de quatro amostras, ricas em tasmanáceas, que representam uma sequência com maturação crescente. Os resultados mostraram uma boa correlação entre as curvas espectrais, λ max e valores da razão Q entre os vários laboratórios para as amostras de baixa maturação. Por outro lado, os resultados obtidos para a amostra mais matura apresentaram uma dispersão significativa.

INTRODUCTION

Fluorescence microscopy has become an important tool in the evaluation of maturity and hydrocarbon generative potential of dispersed organic matter (DOM) based on the pioneering work by Jacob (1965), Ottenjann *et al.* (1975) and Gijzel (1981). Quantitative methods such as spectral fluorescence microscopy and derived parameters (Red/Green Quotient (Q) and λmax) are routinely used to define level of maturity in DOM, where vitrinite for maturity assessment is rare, absent or ambiguous (Thompson-Rizer and Woods, 1987; Pradier et al., 1988). However, to obtain comparative results among laboratories has been proven difficult in the past, related to the calculation of correction factors used for the various microscopes.

The working group on "Thermal Indices" within the ICCP (International Committee on Coal and Organic Petrology) conducted in 1995/96 and 1996/97 two interlaboratory exercises with the aim to improve the reproducibility and comparability of spectral fluorescence measurements by a) calculation of the relative correction functions using

a calibrated common lamp source (Baranger et al., 1991); and b) measurement of *Tasmanites* algae in a series of samples from the Toarcien of the Paris Basin, representing a 0.48 to 0.77 % vitrinite reflectance range (immature to moderately mature).

EXPERIMENTAL

In the present study the correction factors were obtained from a common calibrated lamp source (certified by the Laboratoire National d' Essais, Paris, France). By using the halogen lamps, with which the microscopes are commonly equipped, several types of errors may arise and therefore the correction calculation may be biased (Baranger et. al;, 1991).

The calibrated lamp source comes with a special device, which is screwed onto the microscope stage holder (Fig. 1). It consists basically of a quartz-iodine lamp (type Halostar, 35W-6V) illuminating a parallel-sided plane opalin glass, which diffuses according to Lambert' s Law, placed at a fixed distance of the lamp.

To obtain a perfect definition of the colour temperature of the lamp, and consequently to obtain the known spectral radiance B (λ) the lamp is connected to a 6 Volt low tension power supply providing a stabilized current of 6.0 A. Under these conditions the colour temperature only depends on current intensity and resistance of the lamp and not on the power supply tension.

Obtaining comparative and reproducible spectral fluorescence measurements amongst laboratories using various microscope systems depends primarily on proper data correction. The correction function is specific for each equipment and depends on the photo-optical system transmission (i.e. lenses, emission and barrier filters, monochromator, sensitivity of the photomultiplier etc.). For determining the correction function a lamp with known spectral emission characteristics is generally used (Fig. 2) and the correction factors are determined for each wavelength from the ratio of the known spectral values to the measured values

($K(\lambda)= lo(\lambda)/l(\lambda)$). The known spectral values are expressed as arbitrary units and the measured values as apparatus units.

In the current exercise duplicates of the calibrated lamp source were provided to the various laboratories. The spectral radiance B (λ) for each of these duplicates was determined from the calibrated lamp source and served for the determination of the relative correction function of the photo-optical systems used. Once the correction functions were established, fluorescence characteristics of *Tasmanites* alginite were determined based on a minimum of 10 specimen measured per sample.

RESULTS AND DISCUSSION

In 1995/96 the initial exercise was to determine the relative correction factors for the various microscopes using a calibrated common lamp source (Fig. 3). The next step then was to apply these correction factors to the determination of spectral fluorescence characteristics of alginite (*Tasmanites*) in a shale sample from the Toarcien of the Paris Basin. Pellets prepared from the same sample were distributed to the laboratories and the resulting spectral characteristics are shown in Fig. 4. λmax and Q values derived from these curves (Fig. 5) show excellent comparability of the data set.

In 1996/97 a series of four "round robin" samples were distributed amongst the participating laboratories. The samples were chosen to represent variations in maturity levels in alginite (*tasmanites*) in shales from the Toarcian of the Paris Basin, France. Typical morphological characteristics of the *Tasmanites* alginite bodies and changes in fluorescence intensity and colours related to variations in maturity levels are presented in Plate 1. Vitrinite reflectance measurements reported by one laboratory indicate maturity levels from immature to moderately mature (0.48 - 0.77 % Rrandom). However, the reflectance levels of the samples may in fact be higher, because the sample material is rich in liptinite macerals, which are known

Lab #	Equipment	Sample 1				Sample 2				Sample 3				Sample 4			
		λmax	Q	Qmax	n	λmax	Q	Qmax	n	λmax	Q	Qmax	n	λmax	Q	Qmax	n
1	Leica MPV SP	535	0.53	1.06	12	540	0.70	1.13	10	590	1.34	1.53	12	635	1.44	1.54	6
2	Zeiss Axiophot MPM 400	530	0.48	1.03	10	530	0.57	1.11	10	610	1.04	1.39	10	740			9
3	Leitz MPV SP	565	0.80	1.23	15	580	0.99	1.33	15	590	1.39	1.52	15	625	1.43	1.49	5
4	Leitz MPV 3	515	0.44	1.05	-					535	0.74	1.13	-				
5	Leitz MPV 3	530	0.48	1.07	-					575	1.09	1.21	-				
6	Zeiss UMSP 50	526	0.44	1.08		554	0.70	1.23	15	584	1.24	1.49	16	644	1.52	1.64	7
7	Zeiss UMSP 50	535	0.70	1.05	8	565	0.89	1.14	7	630	1.14	1.24	6	700	2.74	1.53	2
8	Zeiss UMSP 50	538	0.57	1.08	10	554	0.76	1.11	10	614	1.48	1.23	10				
9	Zeiss Universal	530	0.63	1.13	-	565	0.81	1.23	-	620	1.35	1.49	-	620	1.26	1.53	-

Table 1: *Listing of fluorescence parameter determined by the various laboratories for samples 1 to 4. The table also shows the type of equipments which were used*

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to depress the level of vitrinite reflectance significantly.

Results of the spectral measurements (Table 1) were calculated from an average of 10 individual spectra and normalized for better comparison (Fig. 6). The spectral curves and comparison of λmax and Q values (Fig. 7) show good agreement among laboratories for the low maturity samples (Fig. 7 a, b, c). In contrast, results obtained from the sample representing the highest maturity level show a significant scatter in the shape of the spectral curves and derived spectral parameters (Figs. 7 d). The problems encountered by some laboratories in the analysis of this sample are most likely related to a) a significant decrease in fluorescence intensity of the alginite (see Plate 1), b) fewer measurable objects; and c) high background noise.

Averaged fluorescence parameters for the four samples are shown in Figure 8 in relation to vitrinite reflectances determined by one laboratory. Low λmax, Q and Qmax values correspond to low vitrinite reflectance values and vice versa .

CONCLUSIONS

From these results we can conclude: a) using a calibrated lamp source for the calculation of correction factors has reduced significantly the scatter of fluorescence data. The accuracy and repeatability of fluorescence spectra and derived parameters is comparable to that known to occur for vitrinite reflectance measurements; b) spectral curves and related fluorescence parameters obtained by the various laboratories were in good agreement for samples belonging to the immature to moderately mature stage; c) difficulties were encountered at the highest maturation level, where some laboratories reported erratic fluorescence spectra due to low fluorescence intensities.

Current activities of the "ICCP Thermal Indices" working group include the analysis of coal samples from Australia. The samples come from the same seam, but differ significantly in petrographic composition. The aim of this study is to determine the range of fluorescence properties of alginite in coals of same rank but different compositional characteristics.

With the analysis of more sample material over the next years, including the application of other optical and chemical maturity parameters, it is hoped to establish well-defined correlations amongst the various parameters.

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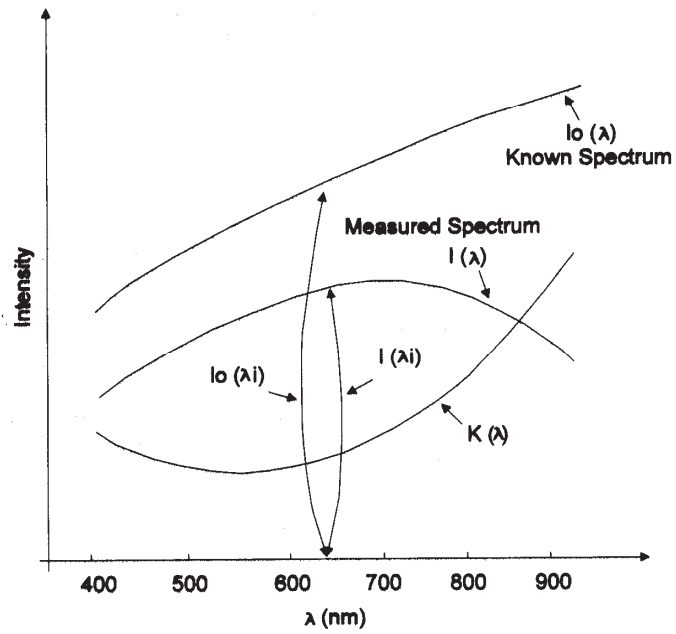
Fig. 2: Determination of correction factors. lo(λ)= known spectrum; l(λ); corrected spectrum= K((λ)= (lo((λ)/l((λ)
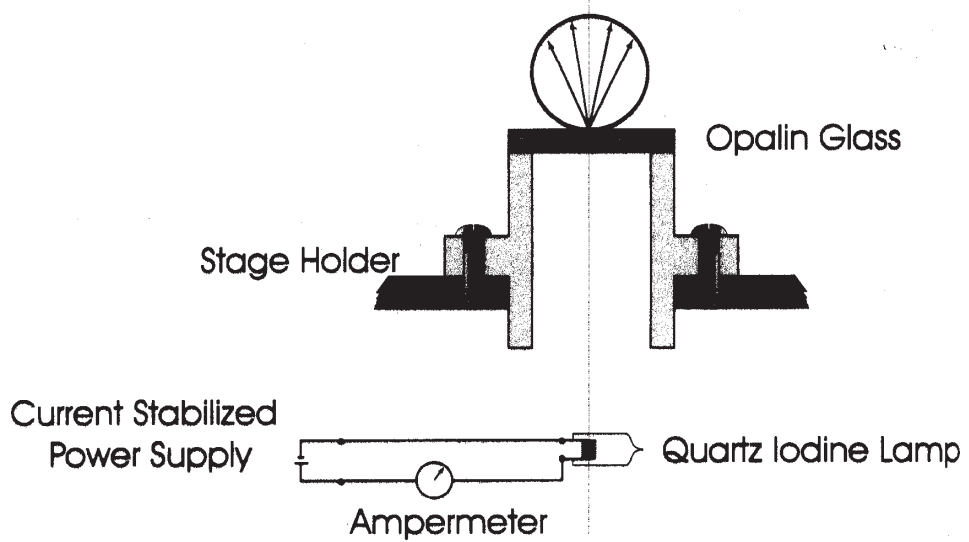

Fig. 1: Schematic diagram of stage holder and calibrated lamp source used in the experiments
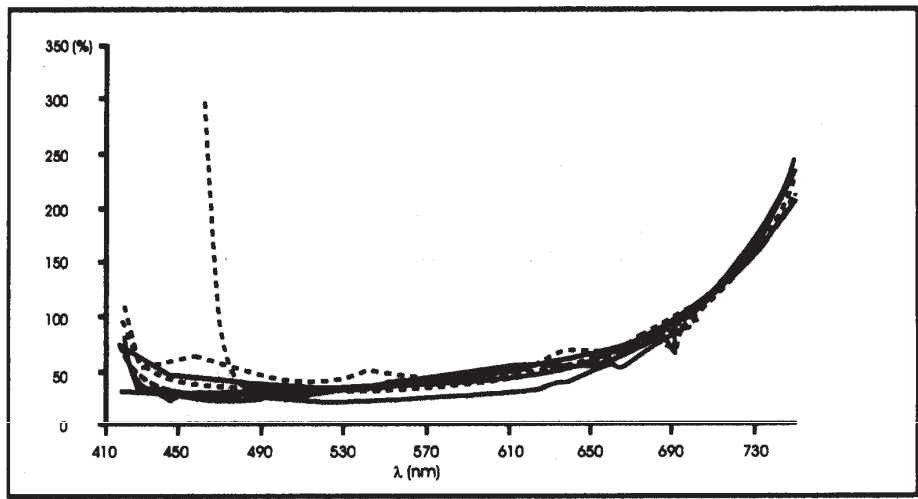
Fig. 3: Relative correction curves determined by the laboratories using calibrated common lamp sources
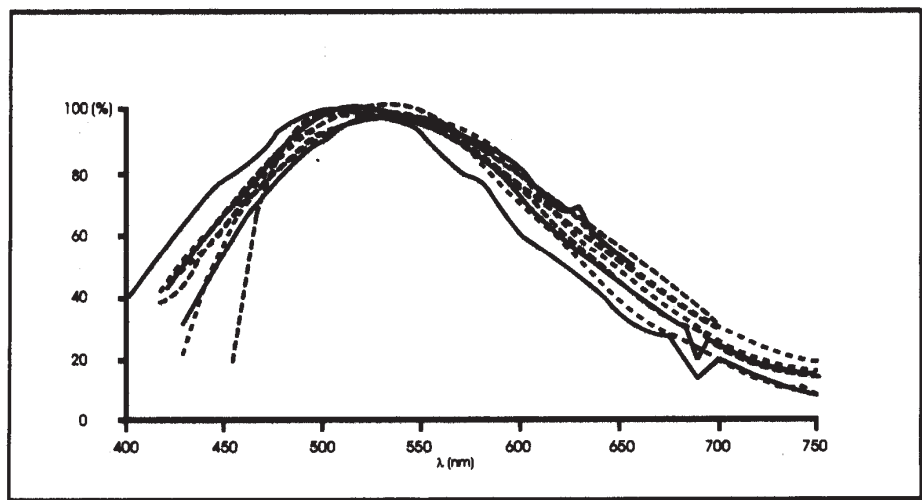

Fig. 4: Spectral fluorescence curves determined for Tasmanites *alginite from the Toarcian of the Paris Basin, France (1995/96 exercise)*
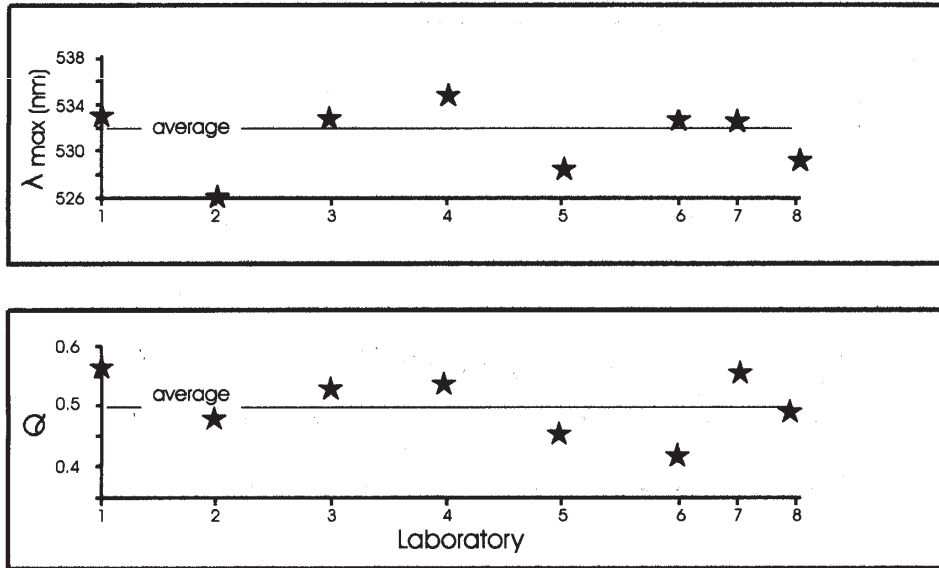
Fig. 5: *Comparison of lambda max and Q (Red/Green Quotient) values derived from the spectral curves shown in Fig. 4. (Solid lines indicate mean values)*
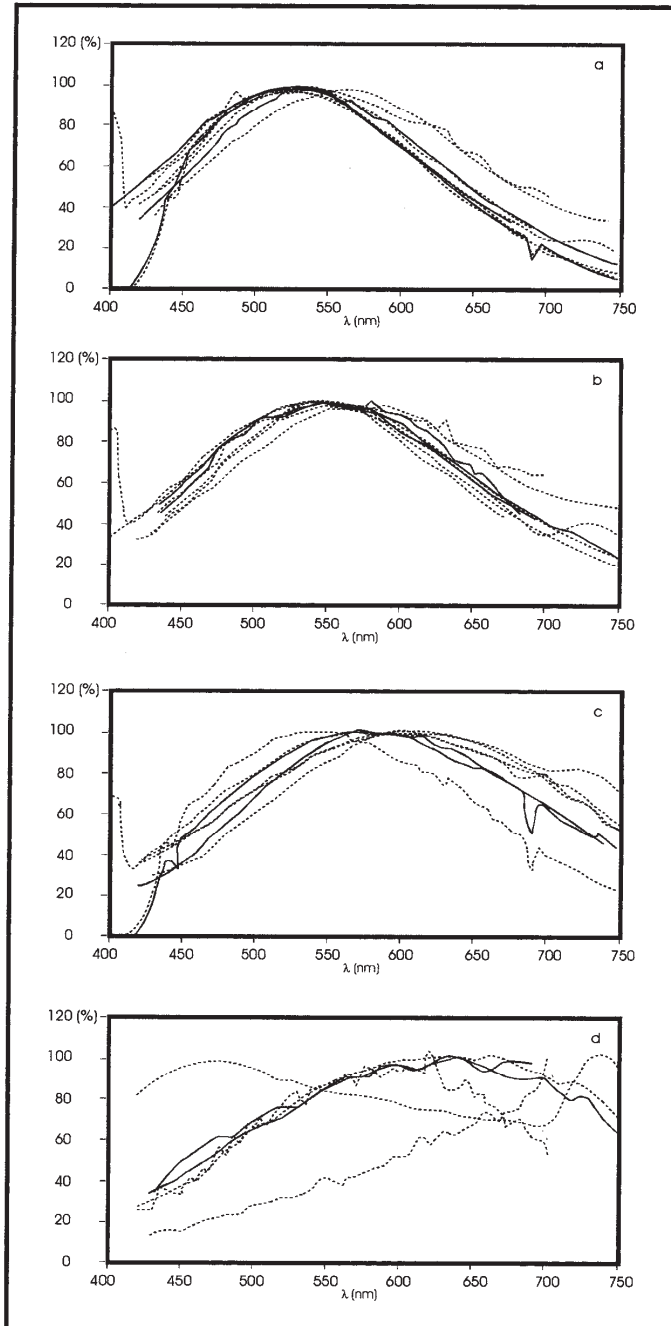
Fig. 6: *Spectral fluorescence curves representing increasing level of maturity (a-d), based on* Tasmanite *alginite from the Toarcian of the Paris Basin, France (1996/97 exercise)*
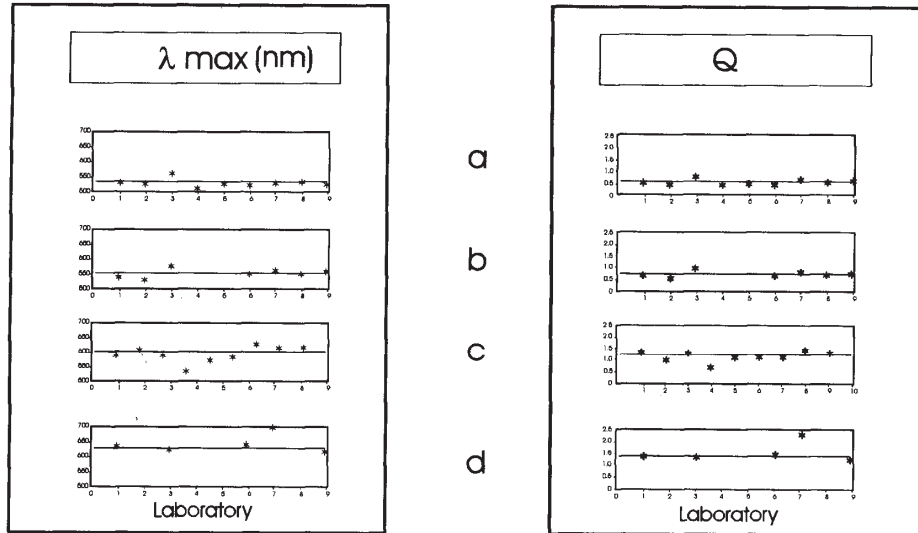
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Fig. 7: λmax and Q values for Tasminites alginite obtained by the various laboratories, based on the spectral fluorescence curves shown in Figure 6. Solid lines indicate mean values
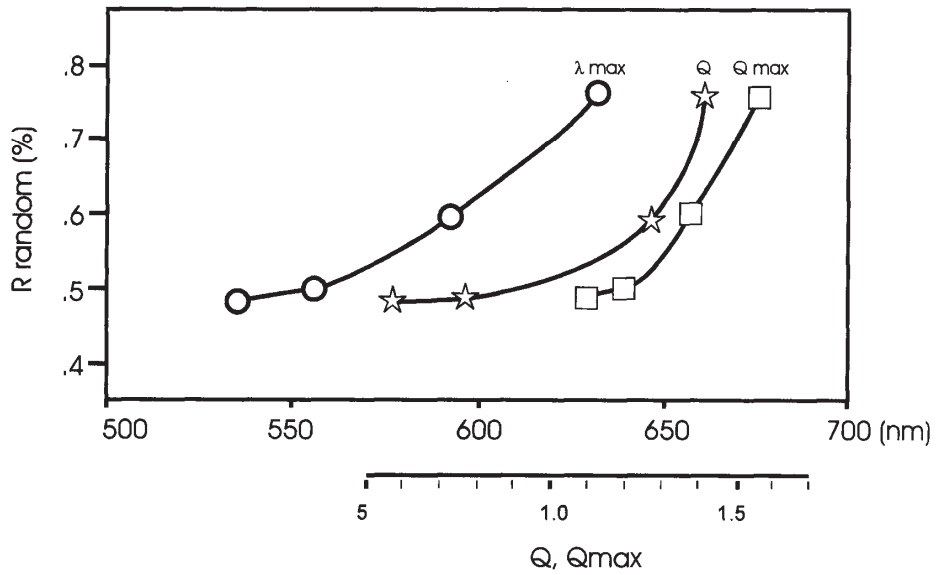

Fig. 8: Averaged fluorescence parameters obtained from Tasmanites alginite plotted versus vitrinite reflectance
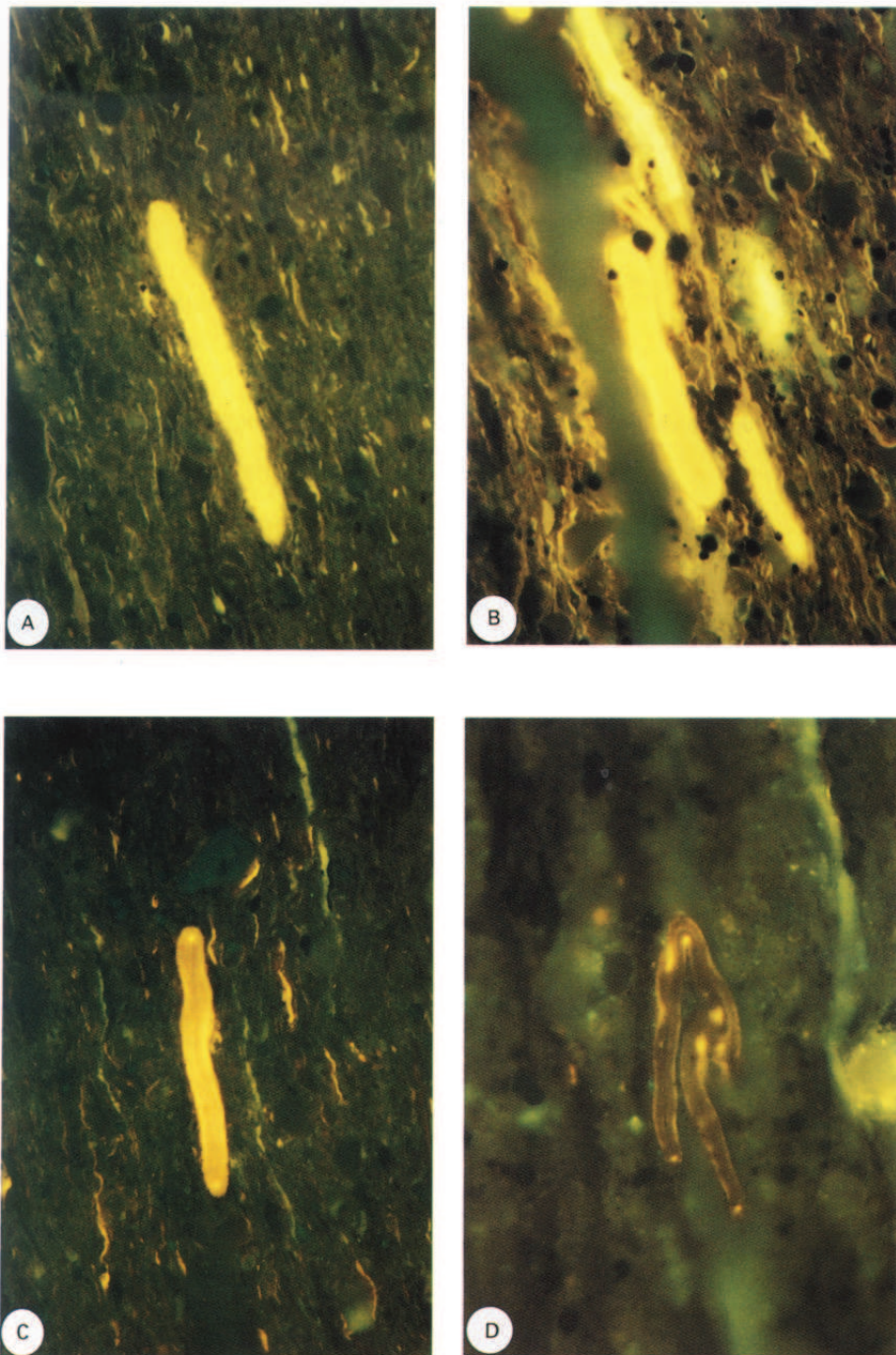
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Plate 1: *Examples of* Tasmanites *used for the determination of spectral fluorescence characteristics. Note the change from intense yellow in sample A and B (immature) to yellowish-brown and brown in samples C and D (moderately mature). Length of long axis of micrographs= approx imately 0.22 mm..*