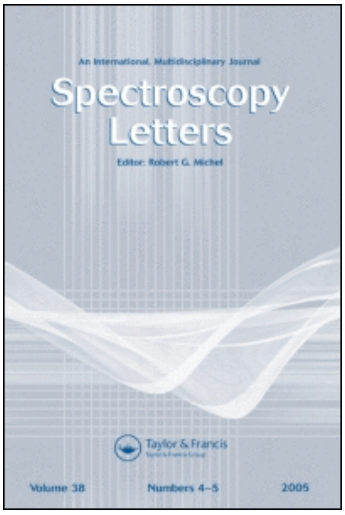

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Identification of Paper by Infrared Spectrometry

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IDENTIFICATION OF PAPER BY INFRARED SPECTROMETRY

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KEYWORDS : IR spectrometry, paper, identification

ABSTRACT

The possibilities offered by IR spectrometry for the characterization of paper samples were explored. Two aspects were considered : the content of inorganic matter and some of its structural features.

INTRODUCTION

Several very sensitive techniques, such as atomic absorption spectroscopy[1-3], neutron activation analysis[4-6] or X-ray

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fluorescence [7,8] have been used to determine the elements in paper. These methods allow today to set up the chemical " table" of any sample, an operation which has had an important outcome for sample identifications. Other methods, such as the thermogravimetric studies [9-12] and spark mass spectrometry [13], have also provided significant data for the characterization of such samples.

Owing to their complex composition, the paper samples have resisted identification by IR spectrometry. Although technical celluloses, which may make up to 99.5 % of the mass of paper, differ by their origin or by the preparation method (sulfite or sulfate method), the spectra do not reveal significant differences, which could permit an unambigous characterization of each kind of cellulose [14] For this reason, identification of paper samples still relies on the analysis of their inorganic and/or organic compounds. Several authors have carried out such analyses using the techniques of internal reflection [15-17] and of the KBr pellet [18,19] these techniques have provided both qualitative and qantitative estimations. To increase the IR transmittance of cellulose and paper samples, impregnation of the samples with solvents, followed by transmission measurements, was also proposed [20].

When the concentration of the inorganic part is low, or when this part consists of substances whose spectra do not show enough typical features, identification of paper by this method becomes difficult. In other cases, chemical changes occuring in the cellulosic material, caused by ageing, may introduce errors in identification.

In this work, we attempted to explore the possibilities offered by the IR spectrometry for the characterization of paper samples, both for determining the absolute content of inorganic matter and for evidencing its structural features.

EXPERIMENTAL

We analyzed a large number of paper samples for which we had data obtained by microscopic and thermal analysis. The samples were dispersed manually, homogeneized (during 10-15 min) with KBr in a ball vibrator, then pelleted. The optimum concentration was found to be of 3-5 mg of paper in 200 mg KBr. Attempts of first dispersing the paper in the vibrator produced pellets of very high transmittance, but the corresponding spectra suggested that some deterioration of the material occured.

Alternately the cellulosic material was first removed by ashing 100-200 mg samples at 450 $\pm$ 25°C during 24 hr and then pelleting the residues with KBr. The optimum ashing temperature was chosen on the basis of earlier thermogravimetric studies 9,10.

The influence of pH upon the mineral composition of technical celluloses was investigated by stirring during 1 hr various cellulose samples with a 0,1 % solution of $Al_2(SO_4)_3 \cdot 18\ H_2O$, followed by washing with water, drying and ashing at 450 $\pm$ 25°C.

The IR spectra were recorded on Jena-type Specord 75 IR (700-4600 cm^{-1}) and UR 10 (400-4000 cm^{-1}) spectrophotometers.

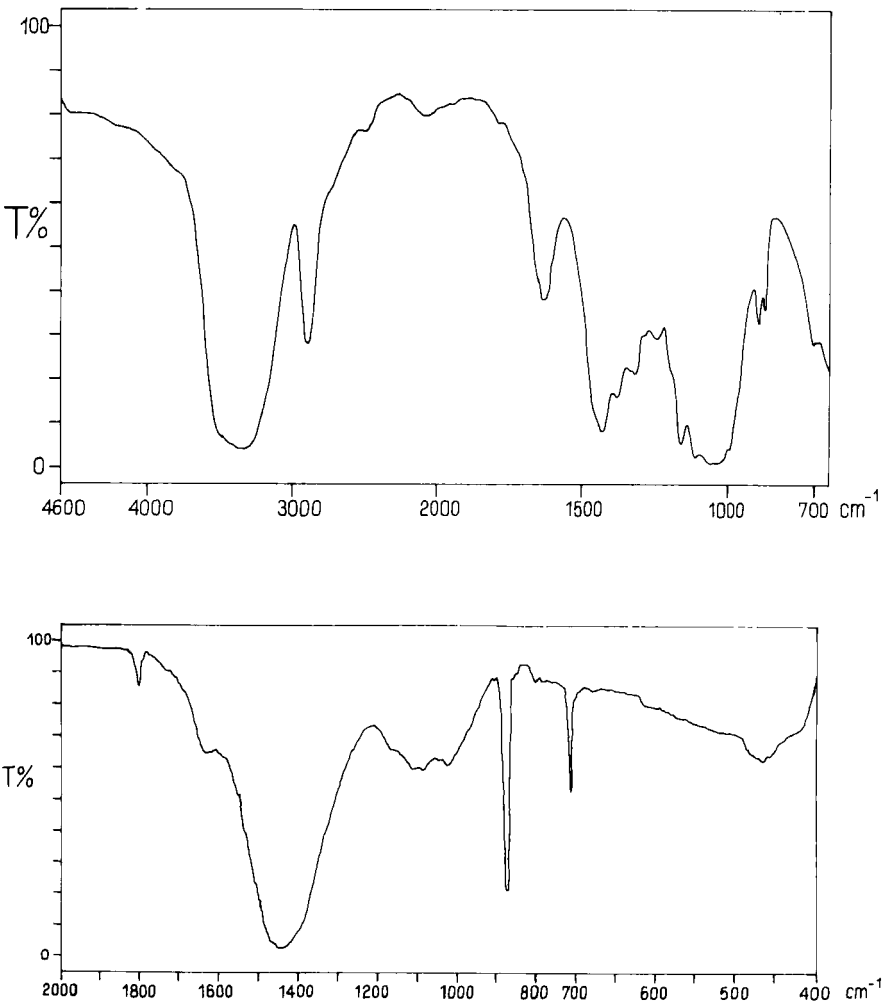

Figure 1. a) The IR spectra of a paper sample containing 7.2 % calcite (solid line)

b) The IR spectra of the ashing residue (dashed line)

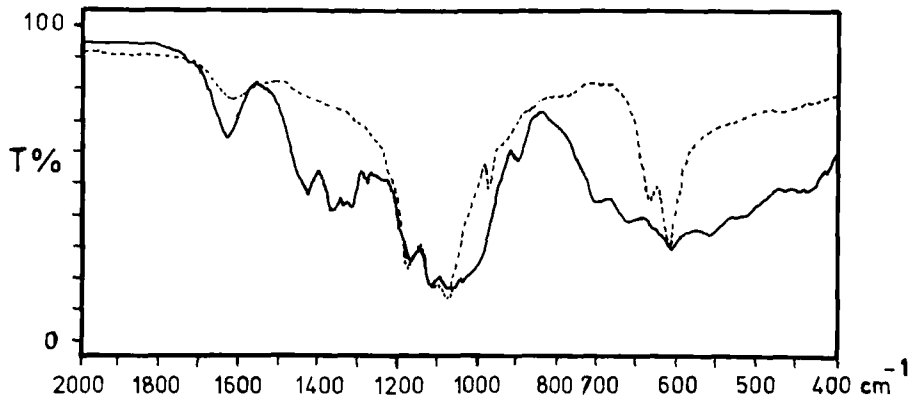

Figure 2. a) The IR spectra of a paper sample containing $BaSO_4$ (solid line)
b) The IR spectra of the ashing residue (dashed line)

RESULTS AND DISCUSSION

The spectra of paper samples containing various mineral materials are shown in Figures 1 to 6 and the typical absorption bands which are useful for their identification in paper are given in Table I. The spectra shows that the strong bands characteristic to cellulose are generally overlapped with bands of the minerals; this makes it difficult to identify the paper, especially when the constituents are present in low concentrations. However, some constituents induce typical changes in the spectra which allow to identify the mineral material present in the sample.

Thus, the absorbance ratio for the 1430 and 1370 cm^{-1} bands in the spectrum of samples of paper containing calcite

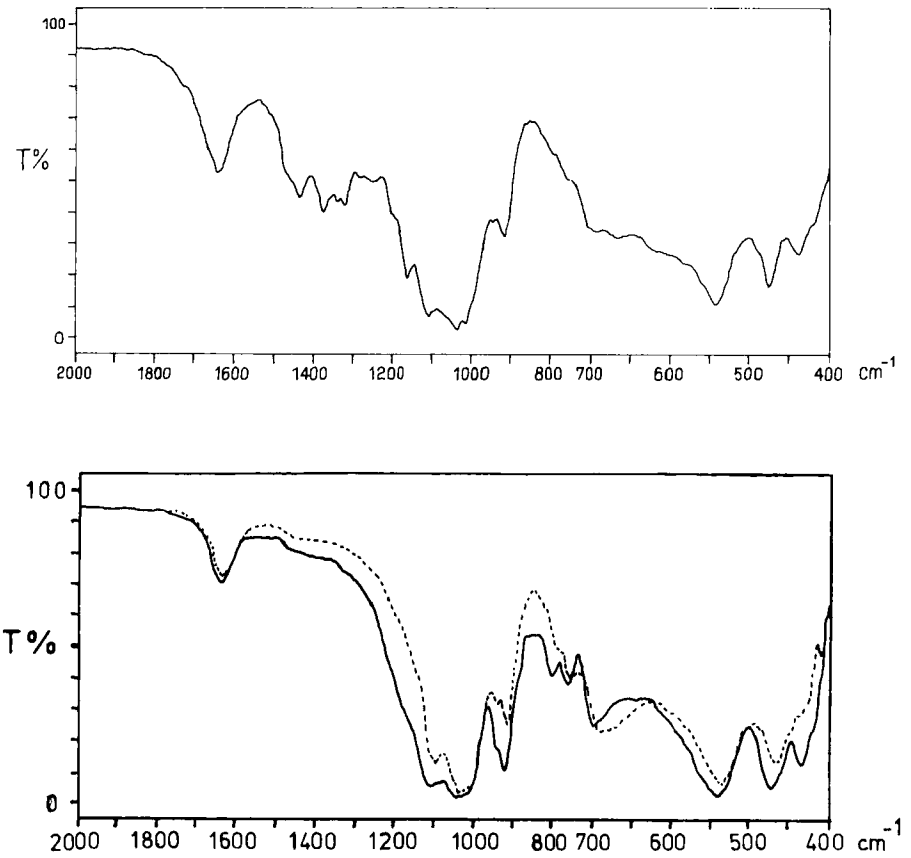

Figure 3. a) The IR spectra of a paper sample containing 14.3 % kaolinite

b) The IR spectra of the ashing residue of two kaolinite containing samples

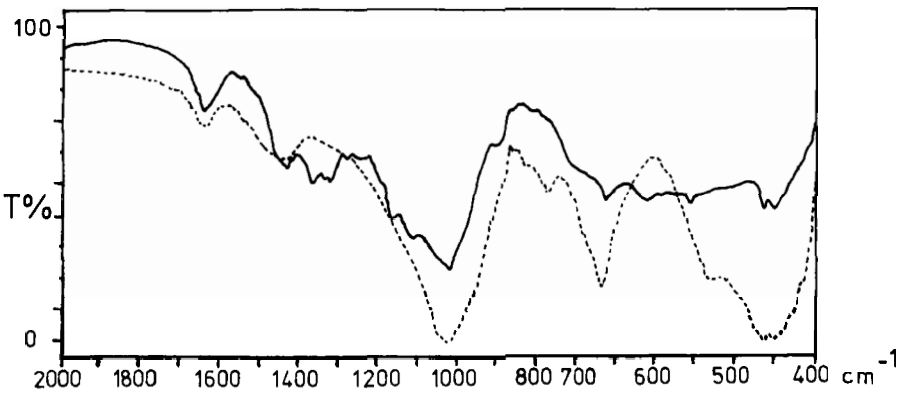

Figure 4. a) The IR spectra of a paper sample containing 4.8 % talcum (solid line)

b) The IR spectra of the ashing residue (dashed line)

(Fig. 1), representing bending modes of the CH_2 groups, increases significantly compared to the value of 0.887 ± 4 % determined for a large number of analyzed samples of technical cellulose. The increased value of this ratio may be accounted for by the important contribution of the 1435 cm^{-1} band (representing the CO_3^{2-} groups in calcite). In some cases, the value of this ratio may also provide quantitative information. The samples of paper containing calcite have in their spectra and additional, strong band at 877 cm^{-1} and two weaker bands at 712 and 1800 cm^{-1}, which turned out to be useful for the identification of this component.

The typical bands of calcite become extremely sharp and strong in the spectrum of the ashing residue (Fig. 1). This

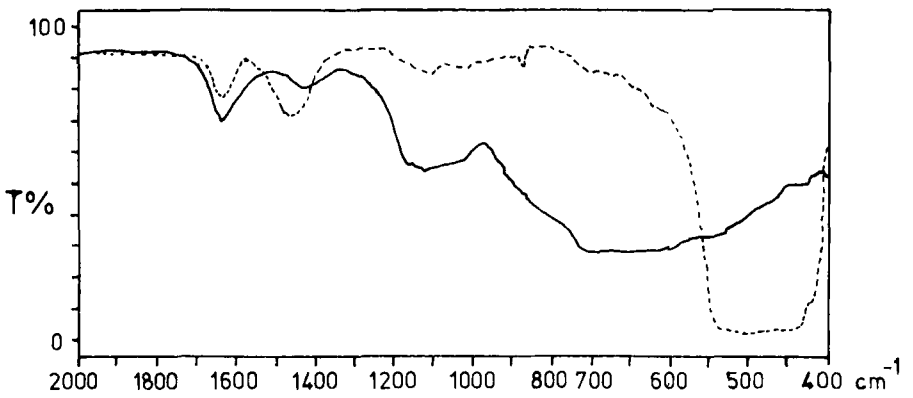

Figure 5. a) The IR spectra of the ashing residue of a paper sample containing TiO_2 (solid line)
b) The IR spectra of ashing residue of a paper sample containing ZnO (dashed line)

technique, however laborious, can give valuable information when the paper samples contain other components beside the mineral components usually accompanying calcite.

Inasmuch as $BaSO_4$ is concerned Figure 2 reveals its typical bands at 610 and 1084 cm^{-1} , which may be used for identification. If barium sulfate is present in concentrations higher than 3 %, the value of the A_{1115}/A_{1060} ration increases significantly as compared to the value in pure celluloses, due to the overlap of the bands in the region 1000-1100 cm^{-1} with the strong bands representing the modes of the OH groups of cellulose.

Identification of kaolinite is favoured by the fact that this component is usually found in paper in high concentrations. The band located at 918 cm^{-1}, characteristic to the Si-O... Al bond, is sufficiently intense to overlap the 900 cm^{-1} band of cellulose

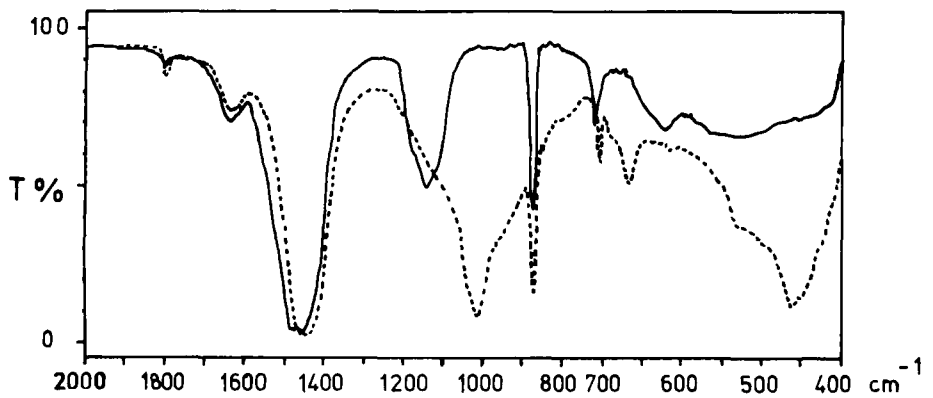

Figure 6. a) The IR spectra of the ashing residue of a sulfate-type cellulose (solid line)
b) The IR spectra of the ashing residue of a sulfite-type cellulose (dashed line)

which only appears as a shoulder (Fig. 3 a). The spectrum of two ashing residues (Fig. 3 b) shows also some structural peculiarities of kaolinite. Thus, differences in the intensity of the bands located at 795 and 445 cm^{-1} and modification of the aspect of the spectrum in the 650-700 cm^{-1} region were noticed. Some differences also occured in the region of the bending modes of the H-O... Al bonds (900-950 cm^{-1}).

The spectra of paper samples provide sufficient data for the identification of talcum, even when this component's concentration is low (Fig. 4). The strong absorption bands of talcum located at 1020 and 1050 cm^{-1} (due to bending of the Si-O... Mg bond) causes a change in the aspect of the spectrum of cellulose. The strong band at 1020 cm^{-1} appears distinctly outlined in the spectrum of the ashing residue (Fig. 4).

TABLE I

Typical absorption bands of some mineral materials present in paper samples[x)]

Mineral material	Typical bands (cm^{-1})	Notes
Calcite	877, 712, 1435, 1800	The ratio A_{1430}/A_{1370}= 0.887 indicates presence of calcite in the sample;
Barium sulfate	614, 1084, 1120, 1179	Identification possible for concentrations higher than 3 %;
Kaolinite	435, 470, 537, 755, 790, 918, 940, 3735	The 435, 790 and 918 cm^{-1} bands are sensitive to structural modifications ;
Talcum	450-465, 1020, 1050	The far IR region allows identification for very lov concentrations;
Metal oxides (TiO_2, ZnO)	400-700	

x) The table includes only those bands of the inorganic components which proved useful for the determination of the nature of paper samples.

As concerns the possibility of identifying metal oxides in paper samples, distinctions between samples containing TiO_2 and ZnO (in the 400-700 cm^{-1} region) only become apparent in the spectra of the ashing residues (Fig. 5).

Since analysis of the ashing residues helps in most cases the sample identification, the inorganic content of the technical celluloses was also investigated. The analyzed technical celluloses, prepared by the sulfite and the sulfate methods, had ashing residues of 0.2 - 0.8 %. The corresponding spectra (Fig. 6) reveal that most of the residue consists of calcium carbonate. For pH values specific to the process of paper gluing, the concentration of calcium carbonate decreases well below the sensitivity limits of IR spectroscopy and does therefore not affect adversely paper identification.

Problems may be encounteres for papers with low mineral filling prepared from sulfite-type celluloses which are richer in insoluble silicates, these silicates forming an important fraction of the ashing residue.

CONCLUSIONS

The results show that IR spectrometry , though less sensitive than other methods may still provide useful data on the nature and structural features of some inorganic components of paper samples.

Analysis of the ashing residues is useful when samples of low mineral content are considered and when the need arises to distinguish among samples of similar composition.

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