Determination of composition of alginates by infrared spectroscopic method

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An infrared spectroscopic method for the determination of the composition of alginates has been elaborated. This method is based upon the determination of the ratio of absorbances of bands at 1320 and 1290 cm^{-1} (KBr technique, 1—2 mg of potassium alginate, analysis error ±3%), and 1125 and 1030 cm^{-1} (0.1—0.2 mg of potassium alginate, analysis error ±8%).

The properties of alginic acids as well as their selectivity of exchange reactions of metal cations depend on the ratio of D-mannuronic (M) and L-guluronic (G) acid units in the molecule of alginate [1]. To estimate the ratio M/G, a sufficiently precise, but quite laborious method has been elaborated [2]. Infrared spectroscopy has been employed for a rapid qualitative information on the composition of alginates [3]. The estimation of the ratio of absorbances at 787 and 808 cm^{-1} allowed to determine the M/G fraction within a 10% error [4].

The aim of our investigation was to determine the M/G ratio on the basis of infrared spectra applying the KBr technique, because films of alginates cannot be prepared in all the circumstances, and especially with low molecular fragments.

Examined were the infrared spectra of alginates with a high content of D-mannuronic acid (94% M, 6% G; $\overline{M}_w > 500\ 000$) and L-guluronic acid (91% G, 9% M; $\overline{M}_n = 8300$,

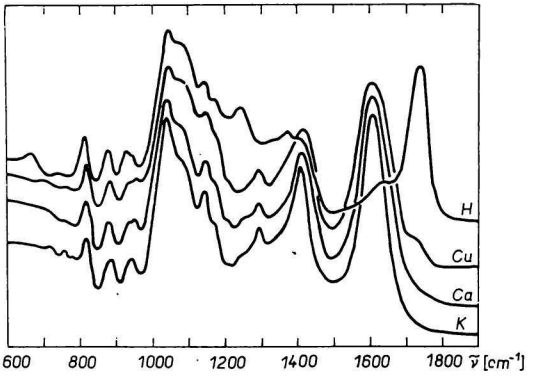

Fig. 1. Spectra of films of polymannuronic acid (H) and its salts (Cu, Ca, K).

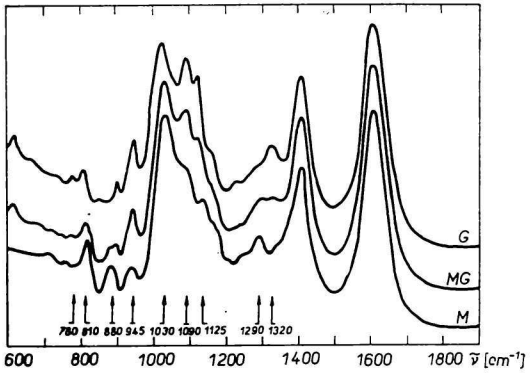

Fig. 2. Spectra of potassium alginates of various composition (KBr technique). G — 91% G, 9% M; MG — 48% G, 52% M; M — 6% G, 94% M.

$\overline{DP}$ = 47). We did not succeed in preparing convenient films from the polyguluronic acid. The effect of hydrogen atom exchange in carboxyl group for a metal cation upon infrared spectra was therefore investigated with polymannuronic acid only. Spectra of the same film of polymannuronic acid and its Cu, Ca, and K salts were measured without support [5], enabling thus to record also slight alterations in wavenumbers and intensities of bands involved (Fig. 1). The spectrum of polymannuronic acid markedly differs from those of its salts; spectra of its salts differ less from each other. Since tabletting of polyuronic acids with KBr results in the exchange of counter-ions [6], a part of alginate will be present in K form. Alginates should be therefore analyzed as K salts.

The spectra of potassium polymannuronate and polyguluronate markedly differ in the 750 to 1400 cm^{-1} region. We selected 9 various wavenumbers in the spectra (Fig. 2) at which the M/G ratio can be in principle determined from absorbance readings. Mixtures of various M and G content were prepared from the starting potassium alginates and the

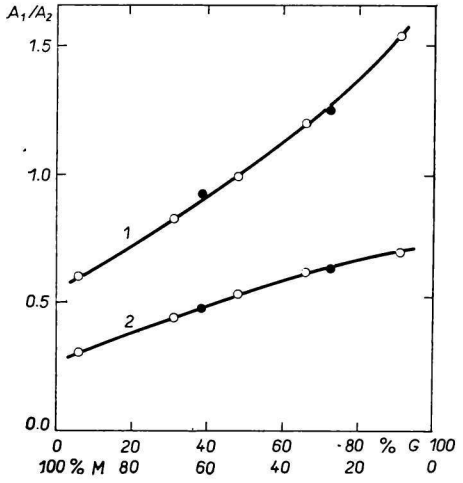

Fig. 3. Dependence of the A_1/A_2 absorbance ratio on the composition of alginates.
1. A_{1320}/A_{1290}; *2.* A_{1125}/A_{1030}.
○ Model mixtures; ● reference alginates.

relationship between absorbances A_1/A_2 of the following bands and the composition of alginates was put into a graph: A_{780}/A_{810}, A_{880}/A_{945}, A_{945}/A_{1030}, A_{1090}/A_{1030}, A_{1125}/A_{1030}, and A_{1320}/A_{1290}. Of those listed, the best result was found with A_{1320}/A_{1290}, having the mean quadratic error $\pm 3\%$ (Fig. 3). Similar result was obtained also with the A_{1125}/A_{1030} ratio; the error of analysis increased in this case to $\pm 8\%$ due to a less steeply descending calibration curve. Even though this pair of bands is suitable for spectral analysis because the high absorptivities of bands enable to take spectra with only 0.1—0.2 mg of alginate in the KBr pellet without lowering the determination accuracy.

Verification of this method by two samples of alginates of known M and G content [8] showed a sufficient accuracy for determination of the composition of alginic acids (Table 1).

Table 1

Spectral analysis of reference alginates

Alginate (Source)	Composition		Determined on the basis of			
	Chemical analysis		A_{1320}/A_{1290}		A_{1125}/A_{1030}	
	% G	% M	% G	% M	% G	% M
Laminaria hyperborea; stipes	72.5	27.5	71	29	69	31
Laminaria digitata	38.5	61.5	41	59	38	62

Experimental

The aqueous solution containing potassium alginate and KBr in a 1 : 200 ratio was freeze-dried [7]; pellets 12 mm in diameter were made of 150 mg of this mixture.

The preparation of a polymannuronic acid film was described earlier [5]. The spectra were taken with a 457 Perkin—Elmer spectrophotometer in the 600 to 1900 cm^{-1} range. Absorbances of bands were determined in the spectra by the method of base-line drawn through the absorption minima at 850 and 1500 cm^{-1}.

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