A NEW METHOD FOR THE CHARACTERISATION AND CLASSIFICATION OF THE INFRARED TRANSMISSION PROPERTIES OF MATERIALS WITH HIGH MOLECULAR WEIGHT OR COMPLICATED COMPOSITION USING THE PRIMA METHOD (PATTERN RECOGNITION BY INDEPENDENT MULTICATEGORY ANALYSIS)

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Abstract

In the present work multicomponent systems, in most cases natural samples were investigated with the purpose of identification, or determination of the chemical structure of the constituents. IR spectra of the samples were evaluated using the PRIMA (Pattern Recognition by Independent Multicategory Analysis) pattern recognition method.

In the present report the application of the method to the identification of concrete additives, to the investigation of the degree of cross linking of dextran-based gel filters, and to studies on the chemical structure and composition of humic acids and tobacco plant parts is described.

In some of the above cases the IR band positions are identical for all the samples, so new data, the relative absorbances calculated for some selected bands, have been introduced to quantitatively characterize the spectra.

The method described is very simple and has proved to be very efficient in solving the problems outhived.

The infrared (IR) spectrum of a mixture is a physical property which depends on the composition of the mixture and on the chemical structure of the individual constituents. The traditional or computerized evaluation of IR spectra is based on the positions of transmission minima (absorption maxima) and intensities referred to unit sample mass. The latter is obtained as the absorbance calculated using the base line method or as the integral absorbance divided by the sample mass.

Our task has very often been to study multicomponent systems containing complicated constituents with the purpose of identification or investigation of changes in the composition. In the majority of cases the IR

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spectra of samples did not show significant differences, since in some cases the constituents were the same and the samples differed only by the ratio of the components, while in other cases the constituents differed in structure but the differences were small, and the bands of the identical groups appeared at the same wavelengths. In such cases only slight differences in band shapes and band intensities could be observed. However, part of these differences may be due to weighing errors, sample inhomogeneities, and differences in particle size, etc. On the other hand, integral absorbances are difficult to calculate, and there are only few modern instruments which provide integral intensity data directly.

Our experience collected during the past few years have shown [1, 2] that by determining the absorbances for the bands of the important groups in the sample, and expressing these absorbances as per cent of the sum of the absorbances, characteristic values, the so called relative absorbances can be obtained which are independent of the sample weight. These values are characteristic of the sample just like band positions and band intensities referred to unit mass.

Using these characteristic IR data and the PRIMA method we have succeeded in identifiing several samples with complicated structure or composed of many constituents provided that so called "training samples" of known composition were available. Even if such samples were not available, samples could be grouped into classes and by this the composition changes brought about by the effect of changes in different factors could be observed.

In this paper some examples of the application of the method are presented. The details of the analyses have been described in separate papers. The analytical problems included in this paper are as follows: identification of concrete additives, determination of the degree of cross-linking of dextrane-based gel filters, structural studies on humic acids of different origin, and investigation of the chemical processes taking place in various parts of a tobacco plant during its life.

In the first two cases we had training samples by means of which unknown samples were identified whereas in the other two cases compounds of different origin but with similar chemical composition and chemical structure could be distinguished using the relative intensity values for the bands of the important groups in the sample.

Experimental and evaluation methods

IR spectra

IR spectra were taken of KBr pellets with a Zeiss Specord 75 spectrophotometer.

The origin of the samples and sample preparation techniques will be dealt with in the sections dealing with the specific problems.

The PRIMA supervised classification method

It is not intended to present here a detailed literature survey about supervised classification methods, among them the PRIMA method. We only refer to a few fundamental papers dealing with the principle and possible applications of the methods which contain a more or less complete list of references [3—6].

Assuming that the reader will study the fundamental papers mentioned, we only give a brief description of the PRIMA classification method used by us for spectrum evaluation.

Pattern recognition methods

The principle of pattern recognition

The aim of pattern recognition is to classify objects or phenomena into separate classes, categories or groups. Pattern recognition starts with the definition of the classes of objects, materials to be investigated. The property defining the class is generally a qualitative property which cannot be measured directly. In some cases it is a quantitative property which can be measured, but with difficulty or at great expense.

In addition to the class-defining property, the object has a number of other properties, known as features that can easily be observed or measured. If properties, features can be found that can be related to the class-defining property, then it is expedient to classify the objects indirectly on the basis of these features. The principle of pattern recognition is to achieve classification based on easily measurable features instead of the class-defining properties that are only qualitative or are difficult to quantify.

Depending on whether the classes are known or not, pattern recognition methods fall into two categories of markedly different functions: supervised classification and cluster analysis.

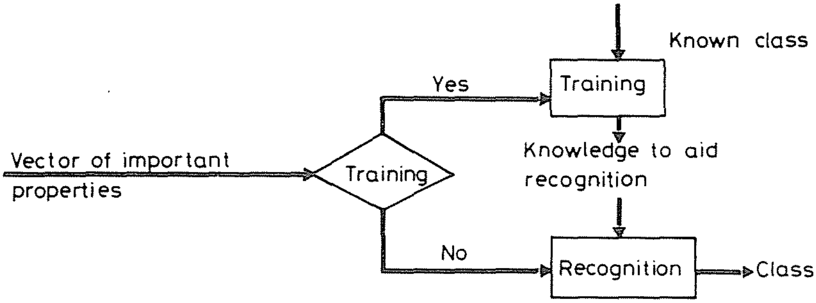

Fig. 1. Supervised classification

In the case of pattern recognition in the narrower sense, in the so-called supervised classification or training with a teacher program, the classes are known. In this case a prior knowledge, a set of objects of known classes is available. This is called the training set. Using this knowledge in the course of training or learning, the relationship between properties and classes is determined, in other words the knowledge needed for classification is defined. Then, based on this knowledge, in the recognition step the object of unknown class is classified. Accordingly supervised classification consists of two steps: training and recognition (Fig. 1).

The classes are characterized by two parameters: the centre of gravity and the inhomogeneity.

The average of a given property j in a class k can be calculated simply by the formula

$$\bar{X}_j^K = \frac{\sum_{i=1}^{I^K} X_{ij}^k}{I^K} \qquad j=1,\dots,J, \quad k=1,\dots,K$$

where $\bar{I}^k$ is the number of objects belonging to class k in the training set. The centre of gravity of the given class k is the vector formed from the property averages

$$\bar{X}^K = \begin{matrix} \bar{X}_1^K \\ \vdots \\ \bar{X}_j^K \end{matrix} \qquad k=1,\dots,K.$$

The spread of the class' in the pattern space can be characterized by the inhomogeneity or dispersion of the properties. The inhomogeneity of a property j in class k, s_j^k, is the dispersion of the property

$$S_j^k = \sqrt{\frac{\sum_{i=1}^{I^K} (X_{ij}^k - \bar{X}_j^k)^2}{I^{k-1}}} \qquad j=1,\dots,J, \quad k=1,\dots,K.$$

The inhomogeneity vector of a given class s^k is a vector formed from the property inhomogeneities, i.e.,

$$\mathbb{S}^K = \begin{pmatrix} S_1^K \\ \vdots \\ S_j^K \end{pmatrix} \qquad k = 1, \ldots, K.$$

Before defining the class distance, the basic concept of the PRIMA method, the concept of a property component of the class distance must be introduced. The jth property component of the class distance with respect to the kth class is

$$d_j^k(X_{ij}, \bar{X}_j^K) = \frac{1}{S_j^k}(X_{ij} - \bar{X}_j^k) \qquad i = 1, \ldots, I, \quad j = 1, \ldots, J, \quad k = 1, \ldots, K.$$

On the basis of property components, the basic idea of this method, the class distance can be defined as

$$d^K(\mathbb{X}_i, \bar{\mathbb{X}}^K) = \sqrt{\frac{1}{J} \sum_{j=1}^{J} [d_j^k(X_{ij}, \bar{X}_j^k)]^2} \qquad i = 1, \ldots, I, \quad k = 1, \ldots, K.$$

which means that the square of the class distance is the average of the squares of the property components. If the property component definition is applied, the class distance can take the form

$$d^K(\mathbb{X}_i, \bar{\mathbb{X}}^k) = \sqrt{\frac{1}{J} \sum_{j=1}^{J} \frac{1}{(S_j^k)^2}(X_{ij} - \bar{X}_j^k)^2} \qquad i = 1, \ldots, I, \quad k = 1, \ldots, K.$$

The class distance of the given point is the average distance for a single property of the point measured from the centre of gravity of the class weighted by the class weight vector.

Training with the PRIMA method means the determination of class centres of gravity $X^1, \ldots, X^k$ and class inhomogeneity vectors $\mathbb{S}^1, \ldots, \mathbb{S}^k$.

Recognition with the PRIMA method consists of two steps. First, the class distances of the object $\mathbb{X}^*$ to be recognized, i.e.,

$$d^1(\mathbb{X}^*, \bar{\mathbb{X}}^1), \ldots, d^K(\mathbb{X}^*, \bar{\mathbb{X}}^k)$$

are evaluated. In the second step, the class or classes to which the unknown object — represented in the property space by the point $\mathbb{X}^*$ — belongs must be decided.

There are several possible ways of evaluating the class membership. Classification can be done by assigning the object to the kth class for which the class distance is minimal, i.e.

$$\min_k \{d^1, \ldots, d^K\}.$$

A more practical solution is achieved if the class membership is determined by the condition

$$d^K(\mathbf{X}^*, \bar{\mathbf{X}}^k) \leq d$$

which means that the object $\mathbf{X}^*$ belongs to the kth class if the above condition is satisfied, where d is a suitably selected limit value, the so-called class distance threshold. In this case an object can belong naturally to more than one class or even be an outer. The threshold value d depends on the problem and is best evaluated iteratively.

The scheme of the joint application of IR spectroscopy and the PRIMA supervised pattern recognition method is shown in Fig. 2.

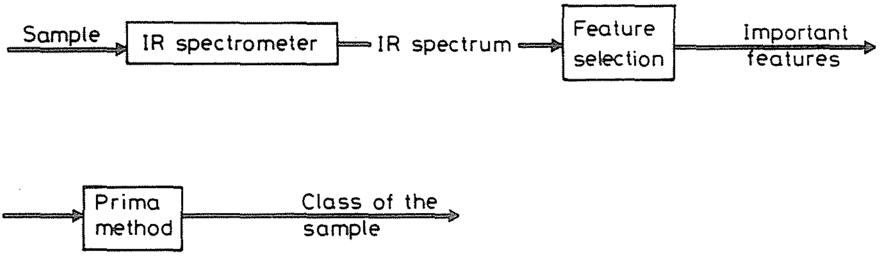

Fig. 2. Classification based on IR spectra using the PRIMA method

Results and discussion

Identification of concrete additives

A method based on the evaluation of IR spectral data with the PRIMA method was developed for the identification of 8 different plasticizes, 9 set-retarders, 3 set-accelerators, 5 air-pore formers and 2 different sealers. The details of the method have been described in refs [7—12].

Studies on the cross-linking of dextran-based gel filters

Gel filters are used as column packings of the modern separation technique, gel filtration. Different types of polymers are produced by various manufacturers for this purpose. The Hungarian firm Reanal produces polyacrylamide and dextran based gels.

The applicability of these gels depends on their characteristic parameters such as grain size, particle size distribution, water retention ability and swelling time. However, the determination of these parameters is a complicated and time-consuming task. These properties depend mainly on the degree of cross-linking. We have developed a method for estimating the degree of cross-linking based on the evaluation of IR spectra by the PRIMA method.

Literature survey

Of the literature dealing with dextran-based gels we only mention the fundamental paper by T. Kemmer and L. Boross [13].

Samples

IR spectral data of Sephadex (imported) and Molselect (Reanal) gels of known water retention were used in the training phase. Water retention is given as the amount (g) of water bound by 1 g of gel, like G-10, . . ., G-200 etc. The symbol G refers to the dextran skeleton. The gel may be made mode apolar by introducing hydroxypropyl groups which block the polar hydroxy groups. These gels are designated by LH.

The training set was as follows:

Sephadex: G10, G25, G50, G100, LH20.
Molselect:G10, G25, G50, G75, LH20.

Several samples of each kind were used.

Sample preparation

2 mg of the solid, crystalline sample was weighed and was homogenized with 300 mg potassium bromide, added in three equal portions, in an agate mortar for 3 minutes. Homogenization was then continued in a vibration mill for 2 minutes. Pellets were made in vacuum.

Results and discussion

Sephadex gels are produced by cross linking with epichlorohydrin the linear polysaccharide, dextran built of glucose units in 1,6-α-glucoside bonds. Epichlorohidrin produces 1,3 glyceride ether bonds between dextran chains. The structure of cross-linked dextran gels is demonstrated in Fig. 3. The chromatographic properties of dextran gels are determined by the number of cross linkages as they reduce the number of polar bydroxy groups thereby reducing the water retention of the gel. The structure of the cross-linked polymer also determines the pore size of the gel and the range of molecular masses for which separation can be achieved. The greater the number of cross

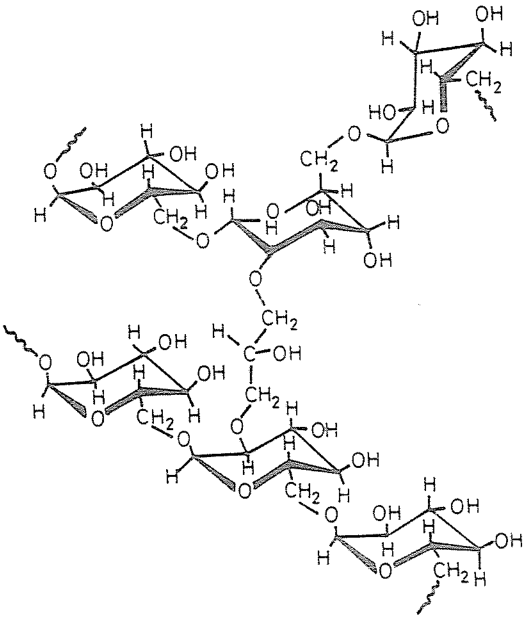

Fig. 3. Structure of cross-linked dextran gels

linkages (the smaller the G and LH number), the smaller is the pore size of the gel and the higher is the limit of molecular weight up to which molecules can enter the gel (limit of size exclusion). The way of preparation, chemical structure and chromatographic properties of Molselect gels produced by Reanal are similar to those of Sephadex gels, but much less experience is available on their behaviour.

The aim of our studies was to find during the training a correlation between the chromatographic properties and IR spectrum data using the PRIMA method based on the IR spectra of Sephadex and Molselect gels of known water retention and chromatographic behaviour and with this knowledge in the course of recognition to predict the chromatographic behaviour of newly prepared gels with unknown structure based on their IR spectra. The IR spectra of various Sephadex and Molselect gels seem very similar, therefore the spectrum of only one of the numerous spectra taken is shown here in Fig. 4 along with the assignations, using the symbols suggested by Holly, Sohár and Varsányi for designating the different vibration modes of the groups building up the large molecule.

As the cross linking process of dextran gels goes forth, the number of hydroxypropylene groups increases, with the formation of one cross linkage two C—O—C and two CH_2 groups are formed and while two OH groups disappear, one new OH group is formed.

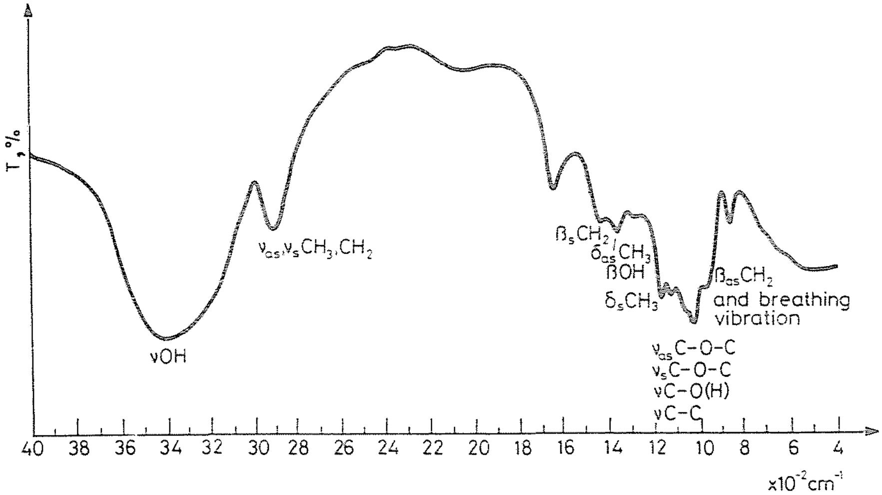

Fig. 4. IR spectrum with band assignation of a gel filter

It follows from this that the per cent relative absorbance values mentioned in the introduction calculated for the characteristic bands of the above groups (15 bands), will depend on the degree of cross linking, so the samples with different degrees of cross linking can be distinguished. Sephadex and Molselect samples with different water retention (G10, G25, G50, G100 and H20) received as standards were classified into five groups. Using the PRIMA method, in the training step the position of the classes in the pattern space was characterized by the centre of gravity and inhomogeneity (dispersion) of the classes. The dispersions of the properties varied between 0.1 and 0.2% for the classes. The recognition ability of the program was 100% with respect to the training set. Unknown Sephadex and Molselect gels were identified by the pattern recognition method by selecting the standard with which a specific sample was identical or which was closest to it. This method enabled the chromatografic properties of a gel to be predicted based on IR data without making time consuming test.

Investigation of humic acids extracted from coals and bore-hole samples

Humic acids are organic polymer molecules and constitute a biologically important group of humic materials. In the present short report only some fundamental works are cited from the wide literature on the formation, IR spectroscopic investigation and structure of humic acids [14—24]. The scheme of formation is presented in Fig. 5. Different authors suggested different

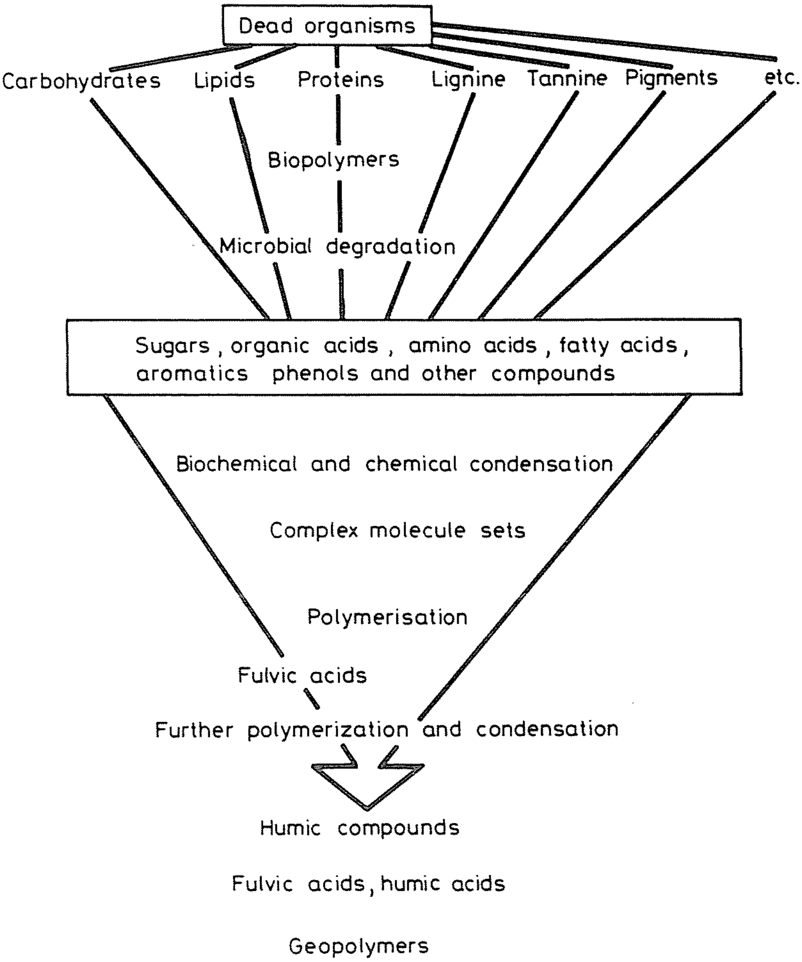

Fig. 5. Scheme of the humification process

structures for these compounds, of which the one proposed by Fuchs is shown in Fig. 6. We have studied bore-hole samples taken from different depths and coal samples from different geological ages. Humic acids were extracted and the IR transmission properties studied in order to find correlation between the chemical structure of humic acids and the depth of the origin of bore-hole samples and the geological age of the coals.

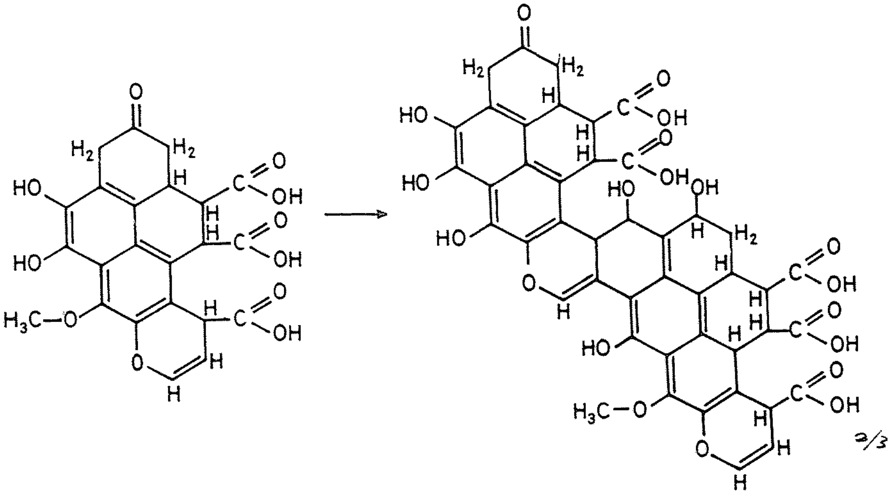

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Fig. 6. Monomer and molecule of humic acid as proposed by Fuchs [14]

Samples

35 humic acid samples extracted from coal samples taken from different depths were studied. The characteristic IR spectrum data of the samples are summarized in Table 1.

The IR spectral data of humic acids obtained from different layers of a brown coal field and from lignite and brown coal from Várpalota, Dudar and Ajka are presented in Table 2.

Sample preparation

Humic acids were extracted from the samples by extraction with 0.5 mol/l Sodium hydroxide at 80 °C for 24 h. Then the extract was transferred to a tube, centrifuged, then the solution was acidified with 6 mol/l HCl. The humic acid thus precipitated was allowed to stand for 6 h, then centrifuged and dried at 60°.

Results and discussion

The band positions in the spectra of humic acids of different origin were identical, differences appeared only in the relative band intensities. This is due to the fact that the humic acids studied are composed of identical groups, but their ratios are different, depending on the depth and geological age.

Table 1

Some characteristic data of humic acids obtained from bore-hole samples

No. of sample	Symbol of sample	Depth of origin [m]	Classification by the PRIMA method
1	365	289.2	I.
2	367	294.6	
3	372	323.3	
4	374	324.3	
5	379	395.0	II.
6	383	361.0	
7	388	363.3	
8	395	391.0	
9	396	391.5	
10	397	392.0	
11	398	392.5	
12	399	393.0	
13	401	394.0	
14	403	395.0	
15	405	396.0	
16	406	396.5	
17	419	429.3	III.
18	430	459.3	
19	438	488.7	
20	451	684.9	IV.
21	458	714.4	
22	460	715.4	
23	469	865.8	V.
24	475	919.0	
25	485	1212.2	VI.
26	490	1219.3	
27	506	1328.2	VII.
28	508	1330.8	
29	521	1411.3	
30	529	1466.4	VIII.
31	538	1533.9	IX.
32	542	1542.8	X.
33	543	1543.3	
34	549	1575.3	XI.
35	553	1586.0	XII.

Table 2

Some characteristic data of humic acid samples extracted from lignite and brown coal

No of sample Property	1	2	3	4	5	6
Symbol of coal	V 53	V 50	D	AA	AJ	Ap
Place of origin	Várpalota	Várpalota	Dudar	Ajka	Ajka	Ajka
Geological age	Miocene	Miocene	Eocene	Cretaceous	Cretaceous	Cretaceous
Degree of carbonisation	Sbc	Sbc	Hbc	Bbc	Bbc	Bbc
Heat value	12970	12648	14840	12958	12742	13311
Ash %	8.65	9.34	5.82	7.83	8.48	9.11
Symbol of humic acid samples extracted from coal	HV 53	HV 50	HD	HAA	HAJ	HAP
Classification by the PRIMA method	I.		II.	III.		

Abbreviations:
Sbc = soft brown coal
Hbc = hard brown coal
Bbc = bright brown coal

In Fig. 7 are shown the spectra of two samples, the one from a bore-hole (down to 325 m) and the other from a Miocene brown coal, with the bands due to the different vibration modes of the groups designated.

We have studied the relative intensities of the bands noted as a function of the depth in the case of bore-hole samples and of the age in the case of coals. We have stated that the relative amount of CH-groups decreases to a smaller, whereas that of carbonyl groups to a greater extent with the depth. The proportion of aromatic hydrocarbon units also increases with the depth. Similar tendencies were observed in the case of coal samples as the age increased.

The samples were classified arbitrarily based on their origin. For bore-hole samples 12 classes were made according to the depth, while for coal samples 3 classes, based on the geological age. (See Tables 1 and 2). Then the relative absorbances were determined for 14 bands, and in addition to this the values were calculated at 1710, 1690 and 1030 cm^{-1} referred to the absorbance value determined at 1600 cm^{-1}. Thus, training was done with 17 data for each sample, using the PRIMA method. The recognition ability of the program was 100% for humic acids extracted from coals, and 80% for those obtained from bore-hol samples. The lower recognition ability in the latter case is quite understandable since a number of factors may influence the structure of humic acids in addition to the depth, such as the origin from land- or aquatic environment, conditions of sedimentation etc.

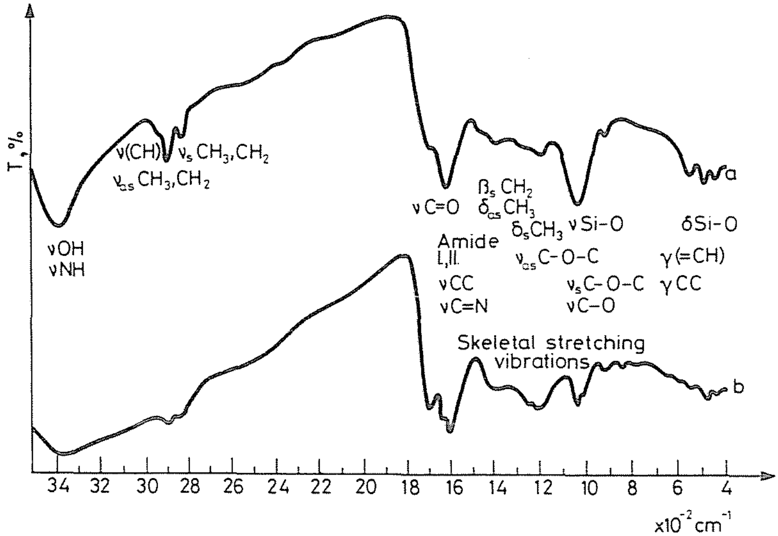

Fig. 7. IR spectrum with band assignation of humic acid extracted from a bore-hole sample (down to 325 m)
(a) and of that obtained from a Miocene brown coul (b)

In conclusion it has been stated that the geological age of coal samples or the depth of the origin of bore-hol samples can be estimated by studying IR spectrum data by the PRIMA method, and samples containing very complicated high molecular constituents may be grouped according to their origin.

Investigation of the changes in the chemical composition of tobacco plant parts

IR reflection properties of tobacco plant parts have been studied by several researchers, but it appears that their IR transmission properties have not been investigated. The purpose of the present investigations was to thowlight on the chemical processes taking place during the ripening of tobacco plant on the basis of changes in the IR transmission properties, and also to study the effect of the mode of cultivation and of the nature of the plant part (leaf, tendril, flower, stem) on the chemical composition.

Literature

Of the vast literature available on the chemical constituents of tobacco plants and their determination only some important papers are cited here [25—39]. A detailed literature survey will be given in a separate paper devoted to this specific subject.

Samples investigated

The samples studied are listed in Table 3.

Table 3

Some characteristic data of the tobacco samples studied

Type of tobacco	Mode of cultivation	date	part of the plant	number of the leaf	number of samples
"kapa"	silo I.	July 2.	complete		1
"kapa"	silo I.	July 2.	leaf		1
"kapa"	silo I.	July 2.	tendril-flower		1
"kapa"	silo I.	July 2.	stem		1
"kapa"	silo I.	July 2.	plant with stem		1
"kapa"	silo II.	July 9.	complete		1
"kapa"	silo II.	July 9.	leaf		3
"kapa"	silo II.	July 9.	tendril-flower		3
"kapa"	silo II.	July 9.	stem		1
"kapa"	silo III.	July 16.	complete		1
"kapa"	silo III.	July 16.	leaf		5
"kapa"	silo III.	July 16.	tendril-flower		4
"kapa"	silo III.	July 16.	stem		1
"kapa"	bed-type I.	July 2.	complete		1
"kapa"	bed-type I.	July 2.	leaf		1
"kapa"	bed-type I.	July 2.	tendril-flower		1
"kapa"	bed-type I.	July 2.	plant with stem		1
"kapa"	bed-type II.	July 9.	complete		1
"kapa"	bed-type II.	July 9.	leaf		4
"kapa"	bed-type II.	July 9.	tendril-flower		4
"kapa"	bed-type II.	July 9.	stem		1
"kapa"	bed-type III.	July 16.	complete		1
"kapa"	bed-type III.	July 16.	leaf		4
"kapa"	bed-type III.	July 16.	tendril-flower		4
"hevesi"	—	—	leaf	1	1
"hevesi"	—	—	leaf	2	1
"hevesi"	—	—	leaf	3	1
"hevesi"	—	—	leaf	5	1
"hevesi"	—	—	leaf	7	1

Sample preparation

Tobacco plant parts were dried at 105 °C to constant wight, then powdered in an agate mortar. The fine powder thus obtained was used to prepare KBr pellets.

Results and discussion

The constituents present in tobacco plant can be classified as follows:

- — carbohydrates (including monosaccharides as well as polysaccharides like cellulose),
- — nitrogen-containing compounds (proteins, amino acids, alcaloids, volatile bases),
- — organic acids,
- — other organic compounds present small amounts (phenols, resinous materials, volatile oils, aroma substances),
- — inorganic consituents (sand, salts of calcium, potassium, magnesium and sodium with sulphate, nitrate and chloride).

The chemical composition of tobacco leafs is the result of complicated metabolic processes, and is also influenced by the growth, conditions of cultivation and other factors.

In 1975 about 1500 compounds were known to be present in tobacco leafs, in addition to complicated brown colouring materials and resinous compounds. The quality of tobacco depends on the ratio of the constituents, some of which improve while others worsen the quality. The ratio of constituents depends of the tobacco species, on the nature of the plant part, age of the plant and other factors.

A number of classical and instrumental methods are available for determining the components, which are in general time consuming and expensive.

The IR spectroscopic technique developed by us is as follows.

Many of the constituents of tobacco plant parts absorb at the same frequency, the bands overlap sometimes. However, each band is predominantly caused by one compound.

The relative absorbances calculated as described above are characteristic of the ratio of the components. The training program of the PRIMA method was made using relative absorbances calculated from the IR spectra of different parts of tobacco plants of known species, cultivated under known, controlled conditions and for a known time. The classes were defined based on these factors (see below). With this program unknown samples of tobacco can be identified by finding their nearest neighbours.

Only a short outline of the method will be given here, the details will be published elsewhere.

The IR spectrum of one of the samples is presented in Fig. 8, where the characteristic vibration modes of the groups are also given. It is also shown which of the bands are predominantly due to the carbohydrate or the protein content and which are due to all the constituents.

The most characteristic feature of the complex processes taking place during the ripening is that the amount of carbohydrates is greatest at the bloom period, and it is higher before the bloom than after it. Polysaccharides change in a different way, depending on their nature, their amounts usually increase during the ripening to the withering.

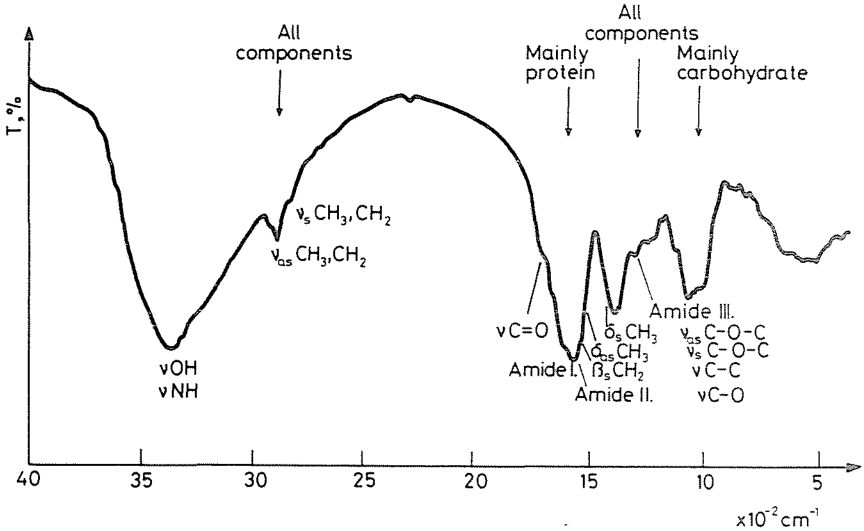

Fig. 8. IR spectrum with band assignation of a tobacco plant sample

In the seedling period protein formation is small then it increases significantly, then decreases after the bloom. However the amount of protein is less characteristic of the age of the plant than that of the carbohydrates. The protein content depends also on the position of the leaf, upper leaves contain more protein than lower ones. It follows from this that the relative absorbances calculated for 14 selected bands and three additional ratios (which are characteristic of the carbohydrate-protein ratio) follow sensitively the chemical changes proceeding during the development of the plant and are characteristic of the plant part (leaf tendril-, flower etc.) The results provided by the PRIMA method are as follows:

— when samples were classified into five groups according to the origin (leaf, tendril-flower, stem, plant with stem and whole plant) the recognition ability was 97—100%.

— for the above 5 groups 3 classes were formed according to the three subsequent days of sampling. The recognition ability was 100%, except one case.

— a further classification was based on the way of cultivation-silo or bed-type. The recognition ability was 100%.

— 5 tobacco samples from county Heves were studied separately.

The samples were leaves of a single plant taken from different heights, from the uppermost to the lowermost.

For the 5 classes the recognition ability was always 100%.

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