INFRARED SPECTROSCOPIC INVESTIGATION OF CONCRETE ADDITIVES

K. ERŐSS–KISS, G. MESZLÉNYI,* D. VALTINYI** and T. MEISEL

Department of General and Analytical Chemistry,
Technical University, H-1521 Budapest

Summary

Rapid simple IR spectophotometric methods were developed for the identification and classification of concrete additives, suitable for the replacing of earlier time-consuming more expensive methods.

Location and contour of spectral bands, further the relative intensities of a few characteristic bands were used for identification.

Investigations discussed in this paper form a part of research work, undertaken with the aim to increase the use of concrete additives in Hungary, with special regard to economy of material and energy by their application.

Knowing the IR transmission properties of various additives containing known active substance, our object was to identify the active substances of unknown additives, and to predict on the basis of these properties, their expected concrete technological effect. The study of these effects (setting time, consistency, solidification and shrinkage modification) requires time-consuming and expensive measurements, which motivated the development of a simple, rapid method, giving reliable results.

From the location, contour and relative intensity of the IR absorption bands of the additives the type of the additive, and in most of the cases the additive itself could be identified in our work.

Antecedents

The chemical composition, structure recognition and mode of action of additives were studied already by several authors [1–27], but the IR spectra of the additives were not yet used for the above purposes.

---

* Joint Enterprise for the Development of Organic Chemical Industry, H-1085 Budapest, Stahly u. 13.

** Institute of Architecture, H-2000 Szentendre, Dózsa György út 26.

Experimental technique

One part of the additives was in the form of aqueous solution, these were evaporated in vacuum at 60 °C, potassium bromide pellets were made from the solid residue, and their spectra were taken with an IR spectrophotometer Model Zeiss UR-10.

From solid samples spectra were taken with pellet technique.

Samples investigated

Data of the 12 concrete additives studied are contained in Table 1.

Table 1

Properties of the concrete additives investigated

Marking of the sample	Trade name	Active substance	State and solids content %
P1	Plastol BF	lignin sulfonic acid-Na	brown liquid 34–36
P2	Barraplast 75L	lignin sulfonic acid-Na	brown liquid 32–35
P3	Barra Fluid	lignin sulfonic acid-Na with several aliphatic groups	brown liquid 37–40
P4	Barraplast C	lignin sulfonic acid-Na	brown liquid 25–28
F1	Melment L10	melamine-formaldehyde sulfonic acid-Na	colourless liquid 19–21
F2	Viskoment V	melamine-formaldehyde sulfonic acid-Na and lignin sulfonic acid-Na	brown liquid 24–25
F3	Barra Super	naphthalene sulfonic acid-Na and lignin sulfonic acid-Na	brown liquid 49–51
F4	Fliessmittel 78	the same as F2	yellowish liquid 20–21
F5	Daracem 190 HC	the same as F3	brown liquid 20–21
F6	Melment F 103	the same as F1 with several aliphatic groups	white powder 100
S1	Tricosal T4	formic-acid-Ca	white powder 100
S2	härter	formic-acid-Ca	white powder 100

P = plastifier; F = liquifier; S = solidification accelerator

Results

The IR spectra of the concrete additives, and structures of the principal active ingredients are shown in Figs 1–3. The assignment of the most important absorption bands is also given in the figures.

The spectra are in conformity with the assumed structure. In the case of two additives (P3, F6) the ratio of aliphatic hydrocarbons is considerably higher than in the others.

On the basis of the location and contour of the absorption bands, types *P*, *F* and *S* can be distinguished as summarized in Table 2.

The mode of distinguishing *P* samples from one another is summarized in Table 3.

The possible distinguishing of *F* samples is contained in Table 4.

The spectra of samples *S*1 and *S*2 are identical, and substantially differ from those of the other additives. On the basis of their bands they are presumably salts of formic acid.

In view of the fact that the concrete additives investigated contain identical or similar functional groups, their IR structural bands appear in the same intervals. However, the mutual ratio of the different functional groups shows already substantial differences, so that beside the modes described above we used for their identification also the intensity characteristics of the characteristic absorption bands of their principal groups in the following way:

Table 2

Separation of additives of types P, F and S on the basis of their IR spectral bands

Type	Mode of separation
P	Characteristic bands of lignin sulfonic acid-Na
F	Several bands of medium intensity in the 900 – 700 cm^{-1} range, which are absent in the case of P samples
S	A spectrum completely different from those above, there are no SO_3^- groups, bands characteristic of formic-acid-Ca

Table 3

Possible identification of P samples on the basis of their IR spectral bands

Additive	Mode of distinguishing
P1	At 1385 cm^{-1} a considerably more intensive band, than in the case of the other additives.
P2	Bands between 1500 and 1400 cm^{-1} are of the same intensity, as different from P1 and P3.
P3	In the absorption regions of the CH_2 group considerably more intensive bands than in the case of the others.
P4	Similar to P2, but with other contour of the band between 1300 and 1100 cm^{-1}

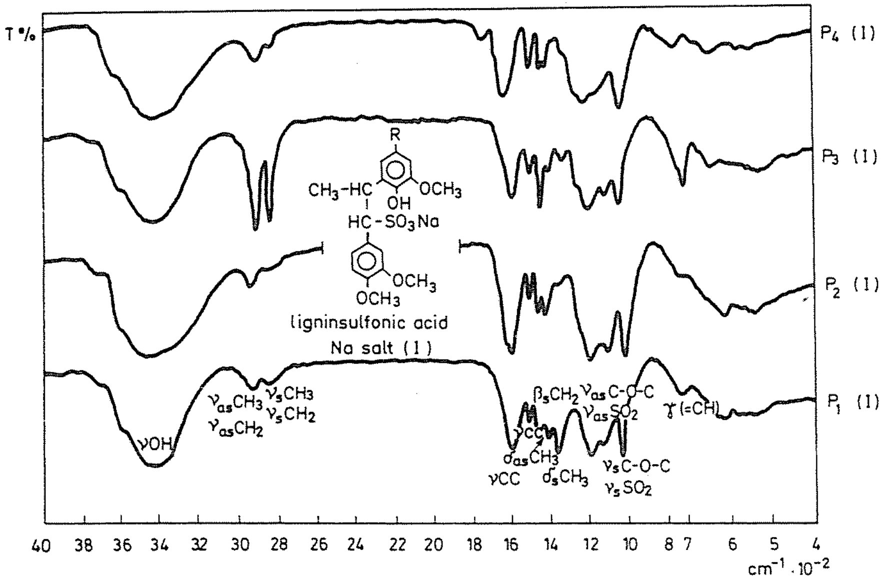
T %
P4 (I)
P3 (I)
P2 (I)
P1 (I)
R
CH3-HC
OH
OCH3
HC-SO3Na
OCH3
OCH3
ligninsulfonic acid
Na salt (I)
νOH
νasCH3
νasCH2
νsCH3
νsCH2
βsCH2
νasC-O-C
νasSO2
γ(=CH)
νCC
δasCH3
νCC
δsCH3
νsC-O-C
νsSO2
40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 7 6 5 4
cm-1 · 10-2

Fig. 1

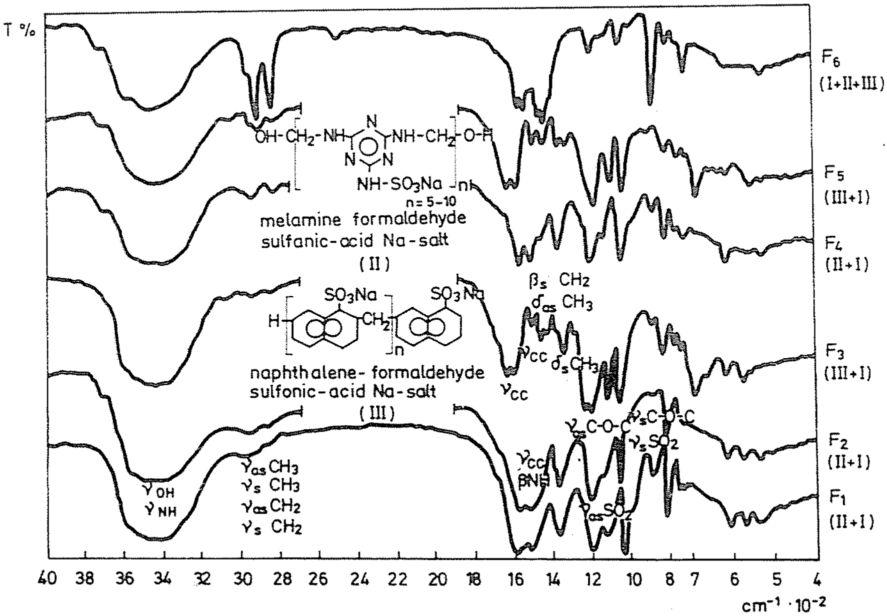
T %
F6 (I+II+III)
F5 (III+I)
F4 (II+I)
F3 (III+I)
F2 (II+I)
F1 (II+I)
OH-CH2-NH
N
NH-CH2-O-H
N N
NH-SO3Na
n
n= 5-10
melamine formaldehyde
sulfanic-acid Na-salt
(II)
SO3Na
SO3Na
H
CH2
n
naphthalene-formaldehyde
sulfonic-acid Na-salt
(III)
βs CH2
δas CH3
νcc
δs CH3
νcc
νas C-O-C
νs C-O-C
νs SO2
νcc
βNH
νas SO2
νOH
νNH
νas CH3
νs CH3
νas CH2
νs CH2
40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 7 6 5 4
cm-1 · 10-2

Fig. 2

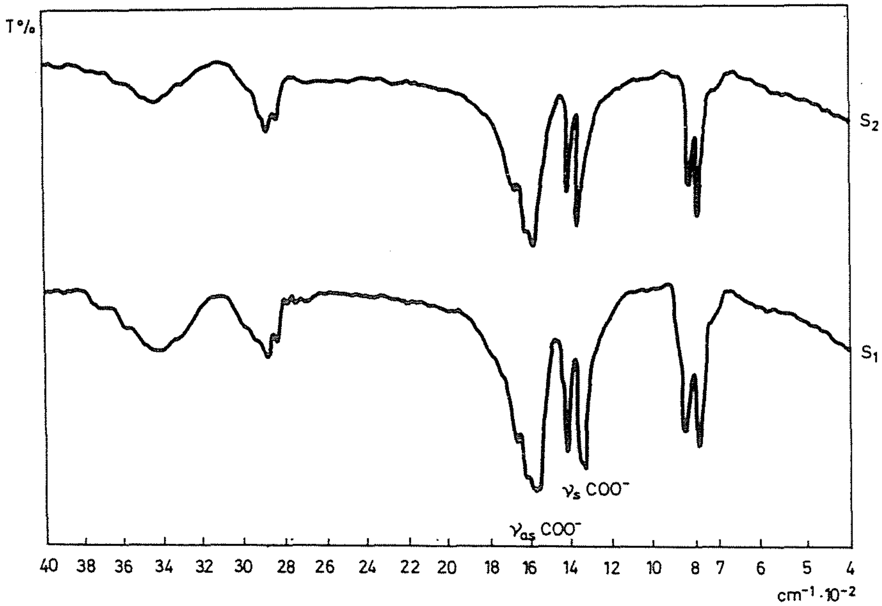

Fig. 3. The IR spectra of the concrete additives, the assignment of the most important absorption bands and the structures of principal active ingredients

At 3460, 2940, 1610, 1360, 1200 and 1050 cm^{-1} the absorbances of the —OH, —NH—, CH_3—, CH_2— stretching vibrations of the skeletal and NH— deformation vibrations, the CH_3— symmetric deformation vibration, and of the SO_3^- and C—O—C asymmetric and symmetric stretching vibration bands were calculated with the base line correction method. Then the percentage distribution of the intensities of the single additives at this six selected bands was calculated. Results are contained in Fig. 4.

From the figure the following can be established: on the basis of the intensities falling to band 3460 cm^{-1} types *P*, *F* and *S* can be well separated, and within the types even the single additives can be distinguished.

Table 4

Possibilities of the identification of F samples on the basis of their IR spectral bands

Additive	Mode of distinguishing
F1	Bands of melamine-formaldehyde Na + bands of the aliphatic groups.
F2	Near identical with F1.
F3	At 680 cm^{-1} an intensive band, at 1360 cm^{-1} a band.
F4	Near identical with F1 and F2
F5	Near identical with F3, at 1360 and 1380 cm^{-1} doublet.
F6	Different from the others, intensive bands in the absorption regions of aliphatic groups.

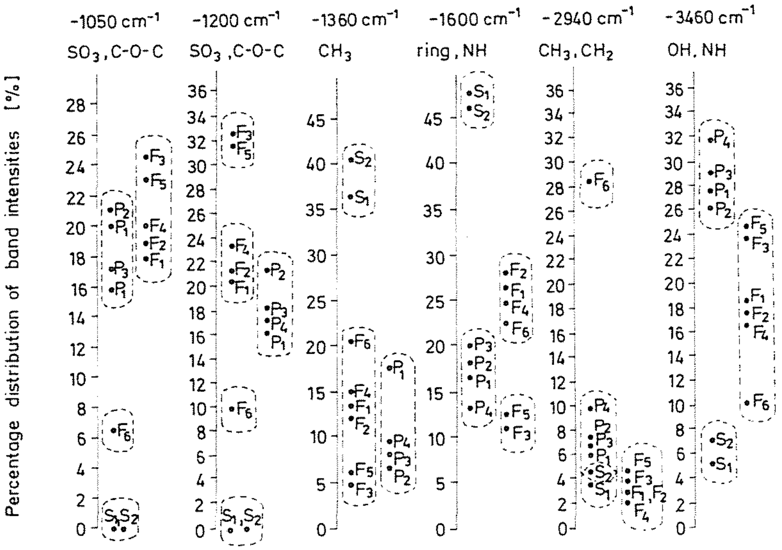

Fig. 4. The percentage distribution of the intensities of single additives at six selected bands

S samples are well separated at all the bands from the others.

Moreover, *P* and *F* samples can be well separated on the basis of their intensities at the bands appearing at 1600 and 2940 cm^{-1}.

We wish to continue our work with the reproduction of results achieved so far, with the spectrophotometry of further additives, and with the elaboration of a method, suitable for the detection and identification of 0.5 to 2% additive in hydrated cement.

References

1. BALÁZS, GY.–TAMÁS, F.–ZIMONYI, GY.: Solidification of concrete with chemicals. BME–MTI, Budapest 1965.
2. ALTNER, W.–REICHER, W.: Acceleration of concrete solidification. Verlag für Bauwesen. Berlin 1972.
3. RATINOV, V. B.–ROZENBERG, T. I.: Handbook for the concrete-technological application of chemical additives. Stroyizad. Moscow 1975.
4. ERDÉLYI, A.–VALTINYI, D.: Development of cellular concrete and additives forming air-pores. ÉTK. Budapest 1976.
5. RIXOM, M. R.: Application of concrete additives. The Construction Press. London 1977.
6. ERDÉLYI, A.–VALTINYI, D.: Mode of action and concrete-technological use of chloride-free accelerators. BME Közl., Budapest 1978.
7. HOROVITZ, J.: Investigation of the possible aplication of additives in concrete technology. ÉTI, Budapest 1979.
8. BUDAI, T.–HOROVITZ, J.: Additives in concrete and mortar technology. ÉTK, Budapest 1980.
9. VENAUT, M.: Revue des Materiaux, *3*, 394–446 (1967).

10. Rahimbajev, S. M.–Bas, Sz. M.: Zhurnal Prikladnoy Khim., *12*, 2618–2624 (1968).
11. Aignesberger, A.–Fah, L.–Rhey, T.: ACI Journal, *69*, 608–616 (1971).
12. Khalil, S. M.–Ward, M. A.: Cement and Concrete Research, *3*, 677–688 (1973).
13. Krähner, A.: Silikattechnik, *12*, 409–411 (1973).
14. Flatan, A. S.: Concrete, *2*, 45–47 (1974).
15. Ivanov, F. M.–Batrakov, V. G.: Beton, Zhelyezobeton, *6*, 2–4 (1974).
16. Müller, L.: Zement-Kalk-Gips, *2*, 69–74 (1974).
17. Hohn, R.: Deutsche Bauzeitung, *8*, 945–948 (1975).
18. Riedel, W.–Liebzeit, J.: Baustoffindustrie, *3*, 11–15 (1976).
19. Hewlett, P.–Rixom, R.: Concrete, *9*, 39–42 (1976).
20. Bonzel, J.: Beton, *10*, 394–399 (1977).
21. Manns, W.–Zeus, K.: Beton, *2*, 63–66 (1979).
22. Komar, A. A.–Babajev, S. T.: Beton, Zhelyezobeton *9*, 16–17 (1981).
23. Lütkehaus, M.: Baugewerbe, *20*, 35–43 (1981).
24. Wischers, G.: Beton, *9*, 337–340 (1981).
25. Hime, W. G.–Mivelaz, W. F.–Connolly, J. D.: Analytical Techniques for Hydraulic Cements and Concrete, ASTM STP 395, Am. Soc. Testing Mats. (1965), 18.
26. Wischers, G.: Beton, *10* 385–389 (1981).
27. Saiki, Y.: J. Res. Onoda Cement Co., *17*, 130–136 (1965).

Dr. Klára Erőss-Kiss
Gábor Meszlényi
Dániel Valtinyi
Tibor Meisel
H-1521 Budapest