Organic Materials in Civil Engineering
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Chapter 6

Physico-Chemical Characterization of Organic Materials Used in Construction

Characteristics of materials which figure in technical specifications are mainly mechanical in nature, i.e. mainly considered from the macroscopic level. Consequently, the tests employed for characterizing them, whether for a preliminary study or for an acceptance procedure, are mechanical in nature and may entail considerable duration since we have to wait for the maturation of the test body. A microscopic approach, which is physico-chemical in nature, may often result in saving time and money by employing simpler and shorter tests and above all in gaining some data useful for the subsequent evolution of the material in the structure.

Thus a chemical analysis not only accomplishes an initial feasibility study, but is of prime importance in verifying that the material delivered is truly the same as the material planned in the project. A chemical analysis starts from the well known principle that if two samples have the same composition, these will in all probability demonstrate similar usage properties. However, this assumption should be taken with some reservations, as physical and constitutional properties may also come into play (for example, texture and isomerism).

These principles apply mainly to organic binder-based materials dealt with in Chapter 3, particularly in certification procedures. For manufactured products the demand is less frequent: it concerns practically only pathological cases. We will therefore consider that the methods described here are mainly for organic binder based materials. These could also be applied to manufactured products, but with the necessary refinements. We will see later that thermal methods are exceptions to this rule.

Besides, in certain cases, an analysis could yield elements for understanding or anticipating material behavior, by comparison with similar cases met with earlier. The diagnostic principle used in medicine finds a place in the field of pathology of structures, with all the necessary precautions required by an experimental science.

Generally speaking, the methods for material characterization should be considered as a whole, where each element must find its place: chemical methods as well as mechanical or rheological tests. It is not always necessary to fully analyze a product to characterize it in the context of its utilization. In some cases, bitumen for example, it is even preferable to abandon classic analysis in the strict sense of the term and resort to typical global methods – chemical, physical or rheological – as long as these are based on proven reasoning and designing.

6.1. Chemical analysis of formulated products

What is generally known as chemical "analysis" of a formulated product in the civil engineering field is nothing but, in most cases, the characterization of a material or product by chemical methods in order to answer one of the following questions:

– to which chemical family does the major constituent of this product belong?;

– how can a digital imprint of this product be established to check its delivery subsequently?;

– how can a sample be verified to show that it contains the necessary strength of the active ingredient for obtaining the expected performance?;

– how can it be verified whether a material is changing or not during the course of a given test?

The most commonly adopted methods to deal with these problems are infrared spectrometry for identifying the chemical family, supported by chromatographic methods if the products are very complex, and functional assays for quantitative determinations. To this list we may add thermogravimetric methods, which are particularly interesting for the characterization of polymers. However, bituminous materials are to be treated in an original manner: chemical analysis plays an important role, but for example is not the most appropriate answer to the second question above. It pales in comparison with physico-mechanical tests (essentially rheological testing) which treats the sample in a global manner and completes the information with data yielded from research. It is for this reason that this subject has been amply developed in Chapter 2 (section 2.2).

6.2. Infrared spectrometry

Organic molecules are essentially composed of carbon and hydrogen atoms, frequently with a low proportion of oxygen and nitrogen atoms. These can be distinguished mainly by the manner in which these atoms are organized. Therefore, for classifying these, it is imperative to use a method which is likely to take into account the molecular structure. Infrared spectrometry (or infrared spectroscopy, both terms are freely used) is generally well-suited for this purpose.

6.2.1. *Principle of the method*

All spectroscopic phenomena are associated to an interaction between electromagnetic radiation and the material being studied. The exchange of energy takes place following Planck's law:

$$\Delta E = h\nu$$

where ΔE represents a variation of the internal energy of the material and ν the frequency of the radiation emitted or absorbed.

Given that variations of ΔE are quantified, values of ν are not random. We also understand that for structural reasons, all exchanges of energy are also not so easy, or in other words, are not of the same intensity. We therefore refer to all these frequencies and their relative intensities as the electromagnetic spectrum.

This definition is very general and is valid irrespective of the sign of the phenomenon (absorption or emission) and irrespective of the amount of energies involved (Table 6.1).

The infrared spectroscopy (IR) corresponds to where:

– the exchange of energy is by absorption of light resulting in excitation of the material;

– the scale of energy coming into play is that caused by molecular vibrations.

Type	Wavelengths	Frequency
γ Rays	0.000 1 to 0.14 nm	3.10^{21} to 2.10^{18} Hz
X Rays	0.000 01 to 100 nm	3.10^{22} to 3.10^{15} Hz
Ultraviolet rays (UV)	10 to 400 nm/0.01 to 0.4 μm	3.10^{16} to 7.10^{14} Hz
Visible rays	0.4 to 0.8 μm	7.10^{14} to 4.10^{14} Hz
Infrared rays (IR) – used in analyses	0.8 to 400 μm 2.5 to 25 μm	4.10^{14} to 7.10^{11} Hz 10^{14} to 10^{13} Hz (4,000 to 400 cm^{-1})
Solar rays	0.2 to 5.3 μm	10^{15} to 6.10^{13} Hz
Hertzian waves	100 μm to 10,000 m	3.10^{12} Hz to 30,000 Hz
Electric waves	10 km to 1,000 km	30,000 to 300 Hz

Table 6.1. *Electromagnetic radiation*

The latter point is from where the use of radiation IR for the characterization of molecules and complex ions in general and particularly organic molecules originates.

The infrared spectroscopy can therefore be defined as a spectroscopy of molecular absorption.

We therefore, in practice, are faced with the following experience: the specimen is lit up by an infrared source and the light emitted is analyzed to determine which radiations are absorbed and to what intensities. The range of absorbed energies (or absorbance) depending on the frequency constitutes the infrared spectrum.

Two techniques can be used for absorption of the radiation by the sample: transmission and reflection.

The transmission technique is still the most often used today. This technique consists of placing the sample in a container, if it is a gas or liquid, or if a solid, in the form of a pellet obtained by pressurized plasticization of a dispersion of the finely ground sample with powdered KBr, or spread on a window with all supporting parts made in special optics, transparent to IR radiation (KBr, CsI, NaCl, KRS 5, ZnSe, CaF_2, etc.). The IR beam passes through the sample and the light transmitted is received by a detector, then analyzed by a Fourier transforming device which processes the signal and displays the spectrum on a computer screen, enabling all desired operations: spectrum printing, comparison with a data bank, detailed analysis of a particular area, etc. (Figure 6.1).

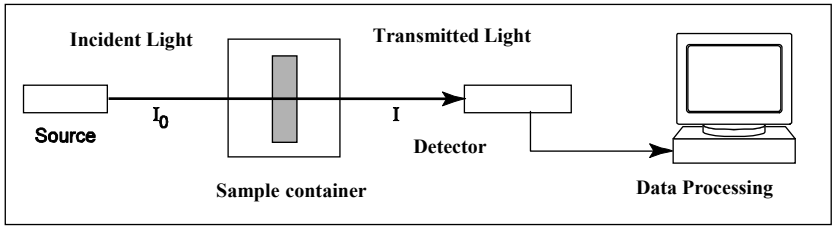

Figure 6.1. *Producing an IR spectrum by transmission*

The infrared spectrum strictly manifests itself as a diagram of transmittance T of the medium (reciprocal of its absorption A) according to the frequency ν of the radiation expressed in number of waves, the opposite of the wavelength λ as per the expression:

$$T = A^{-1} = \log \frac{I_T}{I_0}$$

where I_0 is the intensity of the incident radiation at the considered frequency and I_T is the intensity of transmitted radiation at the same frequency.

The frequency scale is generally graduated in cm^{-1} and is defined by the expression:

$$\lambda \text{ (micrometers)} \cdot \nu \text{ (cm}^{-1}) = 10^4$$

As an example, the spectrum of a paint film taken on a structure is represented in Figure 6.2. The allocation of characteristic bands of the components is marked directly on the diagram.

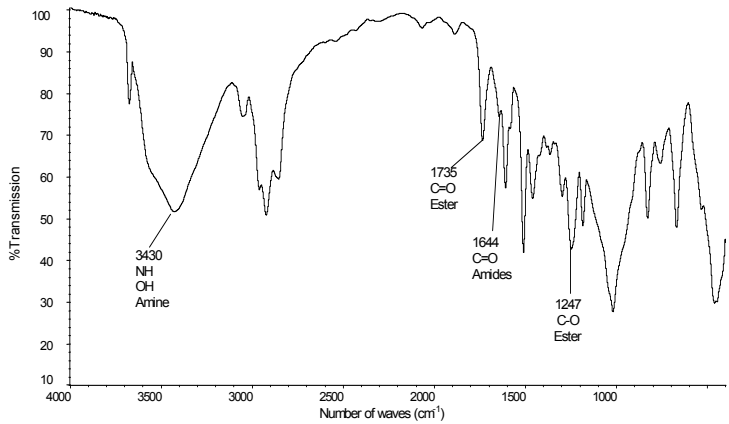

Figure 6.2. *Infrared spectrum of a paint film*

The reading of this spectrum is fairly straightforward. It was not always so: Fourier transform devices with the present clarity were available only in the last 10 years of the 20th century. It is for this reason that the IR spectrometry in vogue now is still often referred to by the term FTIR. In present day devices, the "detector" in Figure 6.1 is a Michelson Interferometer, wherein the global signal is processed mathematically. A Fourier transform therefore gives the "spectrum". This way, we can obtain instantaneous results and even follow the reaction kinetics in certain favorable cases.

Another technical improvement is the appearance on the market of the technique of *Attenuated Total Reflection* (ATR). It was rarely resorted to until recently because the reflected energy received was too small for available equipment to make use of the resultant spectrum. The technological progress in the design of equipment and devices enabling working by reflection (ATR, diffused or specular reflection) has made us re-examine this. As far as organic materials are concerned, it is predominantly the ATR which has proved to be interesting.

Therefore, we can now directly analyze a sample whose surface composition is to be investigated (for example, paint or protective coating), avoiding not only the loss of time, but also easier handling of sample preparation and its presentation in the equipment, an operation wherein there is some unavoidable loss of information for the sample itself. For small samples it is effectively a non-destructive method.

In practice, this technique consists of placing the sample in contact with a germanium crystal, which is lit by the infrared radiation having an incidence which allows total reflection but attenuated by the absorption of a spectrum of radiations corresponding to the vibrations of molecules constituting the sample (Figure 6.3).

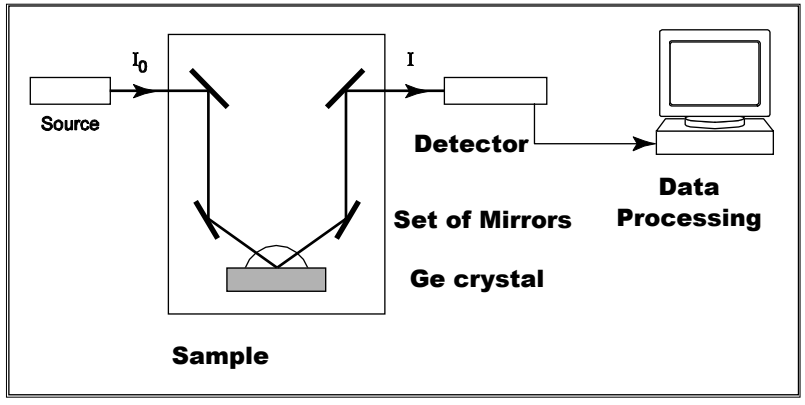

Figure 6.3. *Principle of Attenuated Total Reflection (ATR)*

The two spectra, by transmission and by reflection, are not strictly identical, but very similar. We can neglect these differences in a first approximation, always keeping in mind that when using IR spectroscopy, we always work by comparison and thus it is preferable to compare an ATR spectrum to another ATR spectrum. Let us however add that the problem posed by this difference can often be adjusted by the computer processing the data.

6.2.2. *Case of ATR: theoretical considerations*

From a macroscopic point of view, when an electromagnetic wave propagating in vacuum encounters a dielectric under a suitable angle of incidence, it splits into two waves, one refracted in the dielectric and the other reflected. The energies coming into play and the beam directions are covered by the Descartes-Snellius and Fresnel's laws. As a first approximation, we can consider that the material is non-absorbent:

$$n = \frac{c}{v}$$

The angle of refraction is defined by the Descartes' Law, which introduces the refraction index n, defined as the ratio of the speed of the light in vacuum and the speed of the phase of the light wave in the dielectric, the square of which is equal to the dielectric constant of the medium:

$$\varepsilon = n^2$$

When the light wave propagates from a dense optical medium towards a less refracting medium, the diopter crossover can take place only if the angle of incidence is lower than a limit i_L defined by:

$$\sin i_L = n$$

where n represents the refractive index of the less refracting medium with respect to the more refracting one.

When $i > i_L$, we observe a total reflection translating itself as a phasing out of the electric fields, which are incidental and reflected, from where it emerges that for every instance we cannot write E' = - E. This assumes the existence of a refracted wave.

This wave, known as evanescent when the medium is non-absorbent, is special in nature: it does not transport any energy, it propagates in parallel to the diopter and its amplitude decreases as a function of its distance to the diopter, faster with shorter wavelengths (Figure 6.4).

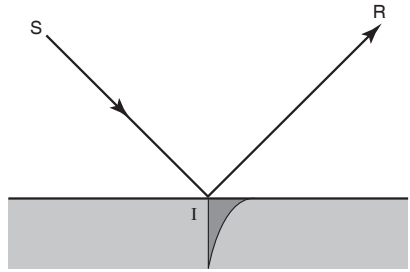

Figure 6.4. *Evanescent waves*

This phenomenon becomes more important as soon as the studied medium can no longer be considered as perfectly transparent. In the spectral regions where it becomes absorbent, the preceding theory must be taken up not by using the electric field E but the electric displacement D:

$$D = \varepsilon E + p$$

where ε is the dielectric constant of the medium and p is the polarization field of the dielectric. As p and E are generally in quadrature phase, the solution of Maxwell equations is obtained by using the complex index, n*:

$$n^* = n - j\kappa$$

whose modulus can be bound to the dielectric constant with the equation:

$$\varepsilon = n^{*2} - \kappa^2$$

The considerations, studied earlier, remains correct when they are considered through the complex referential, i.e. when the parameter κ which causes the reduction of the wave in the medium throughout its propagation is taken into account. It is referred as the coefficient of extinction. This coefficient κ varies according to the length of the light wave under consideration and theses variations $\kappa(\lambda)$ constitute the *spectrum of absorption*.

6.2.3. *Utilization and limits of infrared spectroscopy*

Analyzing a pure product by IR spectroscopy proves to be relatively easy: spectral libraries available on electronic media make their identification simple and quick. If it refers to a new molecule, a detailed study of its infrared spectrum gives indications about its structure and particularly about chemical functions contained therein (but this should always be confirmed by other methods in case a complete identification is desired, which however remains exceptional).

The analysis of a formulated product, i.e. a mixture, is complicated because the spectra of its different constituents are superimposed (as well as those of their interactions) and could give the whole the impression of a chain of mountains being worked upon by erosion. However, a good spectroscopist is generally able to "view" something significant behind the spectrum of the product as is. He will have to follow it up with some chemistry for confirming his intuition or to start off with other hypotheses. We are obviously not dealing with the realm of occult science, but experimental science since the problem itself gives direction to research.

To illustrate this proposition we may go back to the questions listed earlier:

To which chemical family does the major component of the product analyzed belong?

A similar question may arise during a study or an examination. The researcher formulates it in this manner based on his own experience and his knowledge of relations between the structure and property of materials. IR spectroscopy generally answers to this question well as a method for functional analysis. However the complexity of the sample may make the answer difficult and require a preliminary chemical treatment which we will see later while on the subject of fractionation methods.

How can a "digital imprint" of the product be established in order to subsequently check its delivery?

Here again the IR spectroscopy generally meets the requirement in principle, but we must ensure beforehand that the spectrum obtained has a minimum readability, otherwise it will be of no use. We encounter here, as in the first case, the problem of complex mixtures, which may require specific treatments before spectral analysis. Furthermore, we should not forget that the IR spectrum is not sensitive to the molecular weight of the molecules or the ions studied. Therefore, we should not

consider this as sufficient for answering the concerned question, particularly when oligomers are involved.

How can it be verified that a sample contains the necessary strength of the active ingredient for obtaining the expected performance?

This question comes under quantitative analysis and more precisely functional assays where IR spectroscopy is used but rarely. We can simply recall that the method is based on the Beer-Lambert law:

$$A = \log \frac{I_0}{I_T} = \varepsilon . l . c$$

where A represents the absorbence of the material at the frequency of the light considered and defined, as we have seen earlier from the ratio of intensities of incident and transmitted light of the same frequency. It is therefore sufficient to find a characteristic absorption band and trace a calibration straigth line to get the assay.

How can it be verified whether a material is undergoing a change during the course of a given test?

We now come back to the case raised in the second question: the comparison of a sample having undergone a physico-chemical change with respect to its original state is a field in which infrared spectroscopy excels, as long as the original spectrum is sufficiently "readable" and the structural transformations clearly appear on the spectrum of the changed sample. This technique is now commonly used in synthesis for verifying whether the desired compound has been obtained and its purity. It is also interesting to follow the change time brings about in a material, particularly with respect to artificial aging tests.

This list is not exhaustive, but already gives indications on the range and general areas for using infrared spectrometry in the field of characterization of organic materials used in civil engineering.

We can therefore see a difficulty arising, when the material is composed of a complex mixture. Two cases are then to be considered:

– the product is composed of a major constituent and we have to define a method for preparing the sample so as to recognize the corresponding family in the "digital imprint" created by the spectrum;

– the assigned objective is a fine analysis of the sample in the framework of a specific study.

In the first instance, we can often answer this question through a simple single step separation. The "chemical survey" of the sample gives sufficient data for the spectroscopist to provide the information required by the interested person. This evidently supposes the availability of an experienced chemist, with good knowledge of the method, but today a very specialized person is not required as spectroscopy forms an integral part of the initial training of all chemists. On the other hand, experience is never acquired in one day.

In the second case it is necessary to start with a fractionation, as we will see now. We will also see that the IR spectroscopy makes a strong contribution to this operation.

6.3. Methods of fractionation

Behind this generic term we can classify two concepts: the actual fractionation of a complex mixture where the different components will then have to be analyzed and methods of fine fractionation, which themselves yield the information required to identify the fractions obtained. The first is similar to the immediate analysis and the second concerns essentially the chromatographic methods.

The developments which follow mainly concern organic binder based material, products for repairing and protecting, paints, concrete admixtures and curing compounds, scrap or pollution collected during an examination as well as bituminous products. Finished products, geosynthetics or prefabricated elements are rarely subjected to a refined analysis in the present context.

6.3.1. *Fractionation of complex mixtures*

The techniques used for separating, one from the other, the different constituents of a formulated organic product can be classified in three categories: separation by phases, distillation and extraction by solvents. We will try to give in the following lines a schematic overview of these techniques, the first of which forms part of the current practice, the second is used more rarely and the third rarer still.

6.3.1.1. *Separation of phases*

When a product is in the form of a suspension of solid particles in fluid medium (like the case of paints or all "filled" products), we always start the analysis by a separation of the product in two phases: the solid part on the one hand and the fluid part on the other. For this purpose, we resort to a vigorous centrifuging, either on the product as it is, or if the medium is too viscous, after dilution with an appropriate solvent, which can be eliminated later by distillation. The two phases thus obtained are then analyzed separately: firstly we record their infrared spectra, then the organic phase is studied using methods which will be described later and the mineral phase is identified by elementary centisemal analysis, if the IR spectrum cannot be used directly.

The operation can be carried out in a quantitative manner. We can thereby determine the mineral content of the primary product. If, in another test sample, we evaluate the dry extract after evaporation of the solvent, we can obtain by difference the binder and the solvent content.

6.3.1.2. *Distillation*

Strictly speaking, fractional distillation of binary mixtures assumes the utilization of a column, whose height increases with closer boiling points of the two constituents, and an exchange at all levels between the ascending gaseous phase and the descending liquid phase.

In practice, where we no longer deal with binary exchanges, we generally mean by distillation (or more precisely, fractional distillation) the operation consisting of heating the mixture and separating by condensation in a cooler, the gaseous phase formed during heating, into different fractions. We identify these fractions by their *distillation interval* (temperature interval in which the distillate is collected in the recipient).

This procedure yields in a number of cases, samples which are sufficiently pure for later identification by infrared spectroscopy, but should not be considered quantitatively except with great caution, because its reproducibility is not good except in simple instances. Moreover, to avoid degrading the initial mixture by prolonged heating at high temperature, we work more often under reduced pressure ("vacuum distillation"). We then notice that vacuum pumps generally do not provide a perfectly stable pressure, with rates of heating not always perfectly adjustable, there may be several disturbances, with the result that fractions obtained can no longer be validly identified by their distillation intervals. On the other hand, the

technique remains interesting for isolating from a complex mixture a constituent with a relatively low molecular weight compared to others (hence with distant boiling point so that the separation is effective).

These difficulties further explain the existence of "standard distillations", which is only distillation for namesake, because there is practically no exchange between descending liquid phase and ascending gaseous phase, but which will help to characterize in certain "standard" conditions a mixture like coal tar. This technique can be used for the analysis of complex materials, such as certain coal tar epoxy based products (paints, waterproofing materials).

6.3.1.3. *Solvent extraction*

This technique is a generalization of the separation phase, which was studied earlier: we add to the mixture to be identified a second phase, the solvent, the role of which is to dissolve a part of the mixture in order to obtain two fractions, with simpler chemical compositions: the solution and the insoluble fraction.

We can carry out extractions by "selective solvents", i.e. by liquids which dissolve only one constituent of the mixture at a time (or one part of the mixture). The phase separation already discussed earlier can be related to this type of extraction. Solvents most commonly used are: water, alcohols, ethyl ether, petroleum ether, acetone, benzene and chloroform. The separation generally takes place in the cold, using the technique called "stripping", i.e. by washing the sample with the solvent till nothing more is dissolved, but we can also remove them at high temperature. In that case, we use an extractor of the Soxhlet or Kumagawa type.

A second method consists of a "liquid-liquid extraction" where we make use of the difference in solubility between different constituents of the mixture with respect to two solvents, immiscible between themselves, for example an organic solvent (ether, benzene, chloroform) and water or a 50/50 mixture of water/alcohol. Making use of the pH of the aqua phase, we can separate basic and acidic constituents of a mixture.

The extraction generally takes place in a separating funnel, but we can also make use of a more sophisticated crosscurrent apparatus.

6.3.2. *Chromatographic methods*

The term chromatography and the principle behind this process appeared due to the Russian botanist Tswett who used this around 1906 in his work for separating colored pigments (particularly chlorophyll). Forgotten since, chromatography was brought back into use by Khun and Lederer in 1931 and later by Martin and Synge in 1941. From then on, its use became widespread under this term which encompasses certain number of methods no longer related to its etymological meaning but which can be commonly defined. We will first deal with column chromatography, which is most commonly used, but its principle can be easily extended to other media: thin layer, silica sticks, paper, etc.

6.3.2.1. *Column chromatography*

All separations in chromatographic column are based on the flow of a mobile phase initially containing the mixture to be analyzed across a fixed or stationary phase contained in the column, and on the partition of the different constituents of the mixture between the two phases. The elementary operation of partition takes place many times by the relative movement of the two phases; the greater the affinity of the constituents towards the stationary phase, the greater the retarding effect of the stationary phase on the mixture constituents, while the mobile phase tends to be reverse, drawing along its movement. The different constituents of the mixture migrate at very different rates and the separation occurs gradually.

These techniques are used in the chemical or pharmaceutical industries as methods of fractionating mixtures, but only exceptionally in the field of civil engineering. These call for apparatuses specially adapted for obtaining significant quantities of separated fractions. On the contrary, when we need to detect only the presence of different constituents or even in certain cases to titrate them, its utilization is incomparably more pronounced, especially for the study of organic materials used in civil engineering.

It is only this type of chromatography that we will henceforth deal with.

At the column exit, the mobile phase is continuously analyzed by detectors: katharometer, flame ionization detector or electron capture detector for gaseous phase, differential diffractometer, fixed wavelength UV detector, viscometric detector for liquid phase. The signal obtained is recorded and converted graphically as a diagram giving its intensity as a function of time intervals called chromatogram (Figure 6.5).

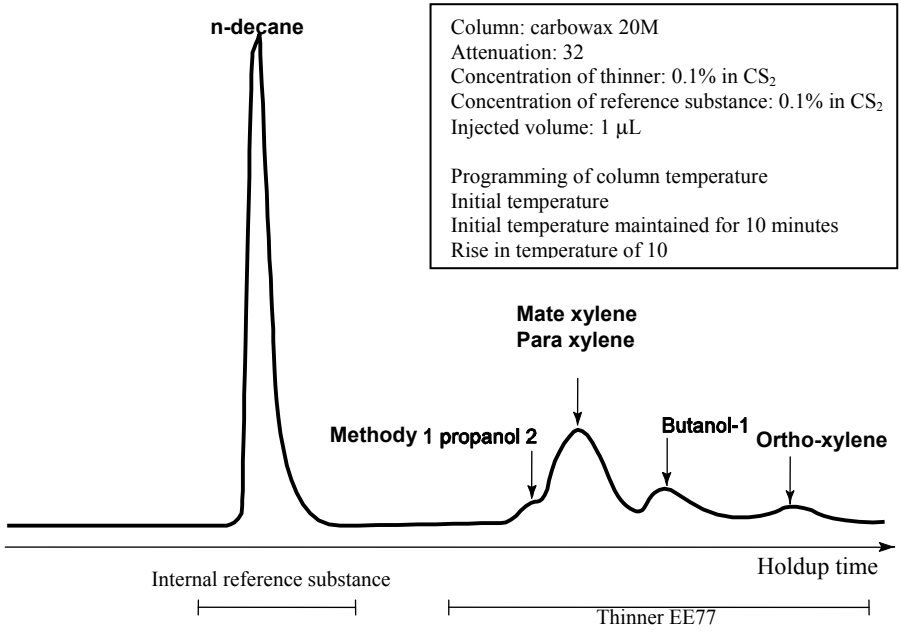

Figure 6.5. *Chromatogram in gaseous phase of a commercial solvent*

There are different types of column chromatographies, which we can classify in two different ways, according to the physical nature of the phases or according to the phenomenon of differential preponderance used for the separation (Table 6.2).

All these methods are not applied to the same degree for chemical analyses of organic materials and products:

– the chromatography in gaseous phase is essentially used for analyzing paint solvents or the detection of organic pollutants with relatively low molecular weights (hydrocarbons or derivatives). An original use is the simulated distillation of bitumen (see section 2.3);

– chromatography in liquid phase, SEC or HPLC is mainly used for study of bituminous binders as we have seen in Chapter 2.

Mobile phase	Stationary phase	Differential phenomenon	Specific name	Common name
Gas	Mineral powder	Adsorption	Gas-solid chromatography	Gas Chromatophy (GC)
	Glass shell		Capillary chromatography	
	Liquid	Partition	Gas-liquid chromatography	
Liquid	Mineral powder	Adsorption	Adsorption chromatography	Liquid Chromatography
	Permeable gel	Steric exclusion	Steric exclusion chromatography or gel permeation chromatography (SEC or GPC)	
	Ion exchanger resin	Ion exchange	Chromatography on ion exchanger resin	
High pressure liquid, solvent mixture	Specific gel	Affinity with the gel according to solvent polarity (+ possibility to work with an elution gradient)	High performance liquid chromatography (HPLC)	

Table 6.2. *Classification of column chromatography*

Generally speaking, these methods belong to indirect analysis. Chromatography, which to begin with, was a fractionation method has thus become a method for identification. In fact, when we know to fabricate and calibrate columns precisely to internal dimensions and packing (chemical composition of medium, granularity, eventual water content, etc.) and thereby their effectiveness with respect to a given separation, if we have an apparatus guaranteeing a constant rate of the fluid vector and a definite temperature, we can obtain recurring and reproducible results. In these conditions, each substance can be identified in given experimental conditions by its

coefficient of retention, or ratio of the movement of the substance considered with respect to the fluid vector at a given time, so much so that by injecting successively into the column the mixture to be examined and the reference substance (chosen from those which we are looking to reveal in the mixture), we can make identifications. We must add that with an appropriate detector, we can even work on the assays.

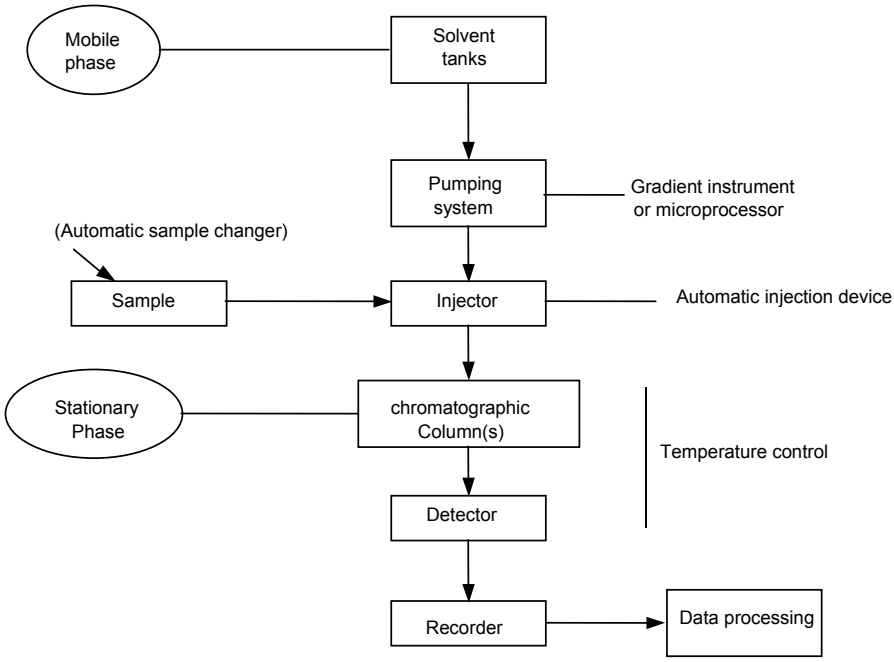

Figure 6.6. *Block diagram. Chromatography in liquid phase*

The simple and compact equipment set-up used for the gaseous phase chromatography gets more complex when we pass on to the liquid phase. However, it is of the modular type and gets assembled like a game of building blocks (Figure 6.6).

The *steric exclusion chromatography* (SEC) or *gel permeation chromatography* (GPC) corresponds to a case where the stationary phase is a gel, the mobile phase is a liquid, and where the fundamental criterion for separation is the size of the

molecule. It therefore enables separation of two chemical families which are more or less identical in their structure, but with clearly different molecular weights (which is not possible with other chromatographies in liquid phase).

Moreover, even if this fractionation is not strictly quantitative, the SEC chromatogram could be considered like a spectrum for distribution of molecular sizes of the sample, an element helpful to usefully complete more traditional means of analysis and inspection of products (particularly infrared spectrometry).

Many interpretations are given to the phenomenon observed in this type of chromatography in liquid phase. It is now generally agreed that the elution of the molecules of the solute is slowed down by their penetration into the pores of the gel filled with solvents. The bigger molecules expelled from the pores are eluted before the smaller ones with the result that we can see a partition based on molecular sizes. However, for certain types of solutes, solvents and gels, other interactions also intervene which get superimposed on the principal phenomenon and it is difficult to give a simple, theoretical interpretation to the phenomena coming into play.

The equipment assembly consists of a solvent tank, a constant rate pump, an injection system, a set of columns, a detector (differential refractometer, a UV spectrometer adjusted to an appropriate wavelength, or both the meters in series) and a recorder.

The solvent used is very often tetrahydrofurane but we can also use, in certain cases, other products like benzene, chloroform, etc.

If the GPC sorts the macromolecules according to their size (or strictly, according to hydrodynamic volume), we can use another method of sorting according to their polarity by making use of their differential affinities according to the solvent. *High performance liquid chromatography (*LCHP) uses the same type of equipment as the SEC but in different operating conditions:

– the solvent is injected under pressure of a few MPa (it is possible to work up to 15 but in practice we use the range from 3 to 7) so as to accelerate the processes;

– we can vary the composition of the elution solvent in a continuous manner as per a pre-selected program starting from two pure solvents (a technique known as elution gradient).

The complementary nature of these two techniques has enabled research to make great progress, notably in the study of road binders like what we saw earlier.

6.3.2.2. *Other types of chromatography*

Chromatography can also be practiced on other types of media: paper, solid divided into thin layers, silica rods as mentioned earlier.

If chromatography on paper and thin layer is rarely used at present for study of materials in civil engineering, *chromatography on silicon rods* constitutes an interesting technique, particularly for the characterization of bitumen by the SARA method (see section 2.2.3).

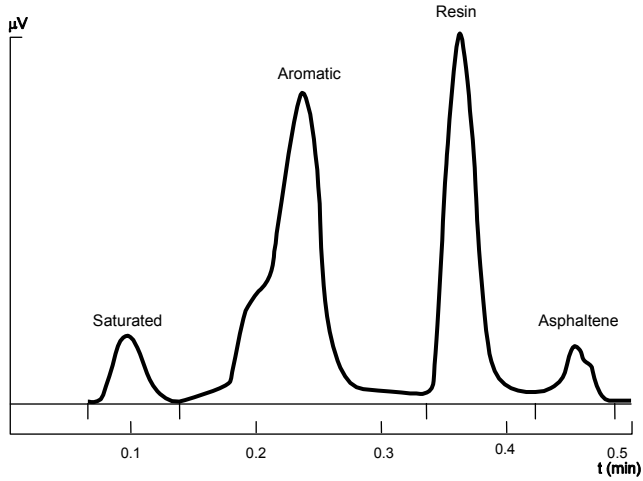

Figure 6.7. *Chromatogram on silica rods of a common bitumen*

The medium is in the form of fine silica rods or sticks which are placed in a rigid frame capable of receiving about 10 of these laid in parallel. A drop (1µL) of the mixture to be analyzed is placed on the rod, close to its tip, and the frame is then placed vertically in a recipient containing the first eluent. Then, after a first drying, we repeat the operation with a second eluent and so on. Finally the frame is installed in an apparatus containing a flame ionization detector before which the rod moves at constant speed. The detection signal gives a curve comparable to a classic chromatogram (Figure 6.7).

6.4. Thermal methods

Another information is obtainable from energy variations which occur at the time of phase changes or chemical reactions of the sample (dehydration, oxidation, etc.). Thermogravimetric methods are therefore very precious and find applications in the domain of organic materials for the analysis of paints, polyethylene sheaths used as protection of suspension cables, geomembranes and geosynthetics in general.

Thermogravimetric analysis (TGA) is the technique which enables the measurement of variations of mass of a sample as according to the time and temperature following a predetermined program for raising the temperature.

Thermal Differential Analysis (TDA) enables the recording of the difference of temperature between a sample and an inert reference subjected together to a given program of temperatures. Thereby a weight loss may correspond to an evaporation of a constituent (water of crystallization for a mineral constituent for example) or to the decomposition of a constituent of the mixture and helps to trace this constituent for identification. The transfer of oxygen into the measuring compartment at the end of the heating (800-1,000°C) is used to enable the proportioning of carbon in the sample.

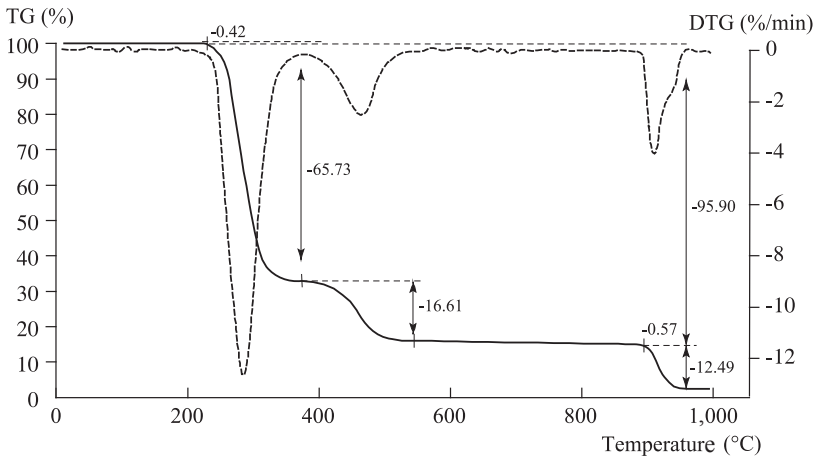

Figure 6.8. *Thermogram used for the proportioning of carbon black in a sample of geomembrane of the type filled PVC (the two initial of weighs losses correspond to the mixture constituting the formulated PVC and the last to the carbon black). The curve obtained helps to fix points of inflection*

A *Differential Scanning Calorimetry* (DSC) is used to determine phase transition temperatures of materials and their thermodynamic nature.

This method consists of recording, according to time and temperature, the difference of thermal flow between the sample and the shell of the container, as well as the flow between the reference material and the shell, resulting from a predetermined rise in temperature. The chemical reactions and phase changes which involve absorptions or release of heat are reflected as endothermic or exothermic peaks on the curve recorded. Glass transitions is reflected as points of inflexion in the curve (Figure 6.9).

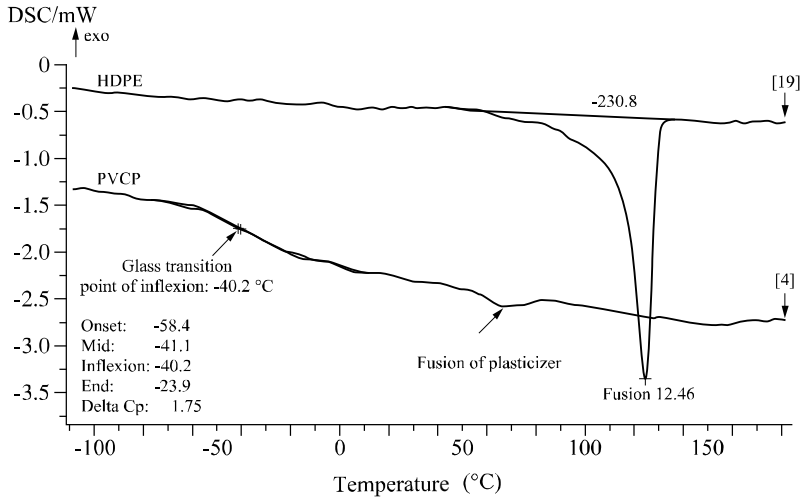

Figure 6.9. *DSC curves of two samples of geomembranes (plastified PVC and HDPE)*

The interpretation of this set of curves generally bring in other determinations and calls for a good knowledge of the phase change phenomenon.

The DSC is mainly used, as far as organic materials are concerned, for the determination of glass transition temperatures, a fundamental characteristic in the field of amorphous polymers constituting materials under study. It is also used for the characterization of road asphalts: assays of crystallizable materials, detection and proportioning of certain added polymers.

6.5. Quantitative analysis and functional assays

An analysis based on only qualitative elements would be incomplete. The methods of identification and fractionation, which have been described earlier, are essentially to convey to the analyst a knowledge which is as complete as possible of the chemical nature of the constituents of the product studied, but generally do not give proportions of these constituents within the mixture. Moreover, and particularly when it refers to a reactive product, these methods are not always capable of specifying the reactivity of certain complex molecules. For this we have to resort to assays referred to as functional, when these are based on the reaction of a chemical function of the constituent to be proportioned with an appropriate reagent, which is the most common case.

These assays are generally volumetric, i.e. the quantity of the added reagent is measured by its volume (with a burette). The titration is done more often in a *non-aqueous medium* because the organic molecules are only rarely soluble in water. The end of assay is identified by *potentiometry*: the products analyzed are generally colored, hence the use of color changing reagents is difficult and above all this technique enables automating the process and recording the assay curve.

Lastly, we must add that these assays, whose first objective concerns quantitative determination of the constituents of a mixture, would also in many cases confirm the presence of a body previously identified by infrared spectrography or help in the interpretation of a particularly complex spectrum.

We do not propose to develop the theory of volumetric assays in non-aqueous media and their monitoring by potentiometry, which forms an integral part of the basic formation of chemists. On the contrary, it would be interesting to draw up in the form of a table the full range of functional assays of organic materials as practiced by the Chemical Analysis Laboratory attached to LCPC, an organization for research and expertise in the field of civil engineering (Table 6.3). We will also note in passing the existence of a “non-thiophenic sulfur” assay specifically for bituminous materials [LAM 67].

Function	Reaction	Titration reagent	Solvent	Electrodes	Concerned Products
Acidity - carboxylic	- direct: ①	CH_3ONa/ methanol-benz.	Pyridine	Pt/calomel	Bitumen Mineral Oils Products for repair and protection of concrete
- hydroxylic	- by difference between carboxylic acidity and total acidity (①) The second inflexion corresponds to the hydoxylic acidity. We titrate directly the carboxylic acidity and the total acidity				
Alkalinity - total	- direct: ②	$HClO_4$/acetic acid	Acetic acid	Glass/calomel	EP: "Hardener" part Dopes for adhesiveness and emulsions for bitumen
	- direct: ③	$HClO_4$/ dioxanne	Acetonitrile	Glass/calomel	
- amines II+III	Imination of amines I by reaction with formaldehyde then dosing as per ③				
- amines III	Acetylation of amines I and II by reaction with acetic anhydride then dosing as per ②				
Alcohol (index for hydroxyle)	- in return: * Esterification by acetic anhydride in excess then dosing by soda * Reaction with phenylisocyanate in excess, destruction of excess by dibutylamine in excess then dosing as per ②.				PUR, EP and EPPUR: "base" part
Ester (index of saponifi-cation)	- in return: ④ Saponification by KOH alcohol in excess	HCl/ethanol	Ethanol	Glass/calomel	Glycero-phtaliques and derivatives EP: "base" part
Epoxide (index of epoxide)	- direct: ⑤	HI/water (KI + HCl added)	Propanol (reflux)	Indicat.colored: blue of bromophenol	EP: "base" part
	- in return: ⑥ Hydrolysis by HCl in excess	$AgNO_3$/water	Dioxanne-acetone	Ag/Hg_2SO_4 (or combination Ag / AgCl)	
Isocyanate (index of isocyanate)	- in return: Reaction with dibutylamine in excess then dosage in excess as per ②				PUR and EPPUR: "hardener" part
Organic Chlorine	Mineralization as per Schöniger (combustion in O_2) then direct dosage as per ⑦ below:				Binders chlorinated rubber, chlorinated paraf. PVAC
	Direct dosage (⑦)	$AgNO_3$/water	Water	Ag/ Hg_2SO_4	
Sulfur (sulfur non-thiophenic)	- in two stages: * Total alkalinity as per ② in return, that is ⑧ below * Complexation by mercuric acetate and dosage as per ⑧, or ⑨ ➔ Result (S non-thiophenic) = Result (⑨) – Result (⑧)				Bitumen EP: "hardener" part
	Dosage ⑧ (in return after neutralization with $HClO_4$ in excess)	CH_3COONa/ acetic acid	Acetic acid	Glass/ calomel	

Table 6.3. *Principal functional assays and applications*

6.6. General diagram for in-depth analysis of complex mixtures

As a conclusion to this chapter on the analysis and identification of organic materials used in construction, we can show in a diagram (Figure 6.10) the general sequence of operations carried out by a chemist in charge of this work in the case of an unknown mixture. We may say that this is the very basis of his methodology, of his reflexes as an analyst.

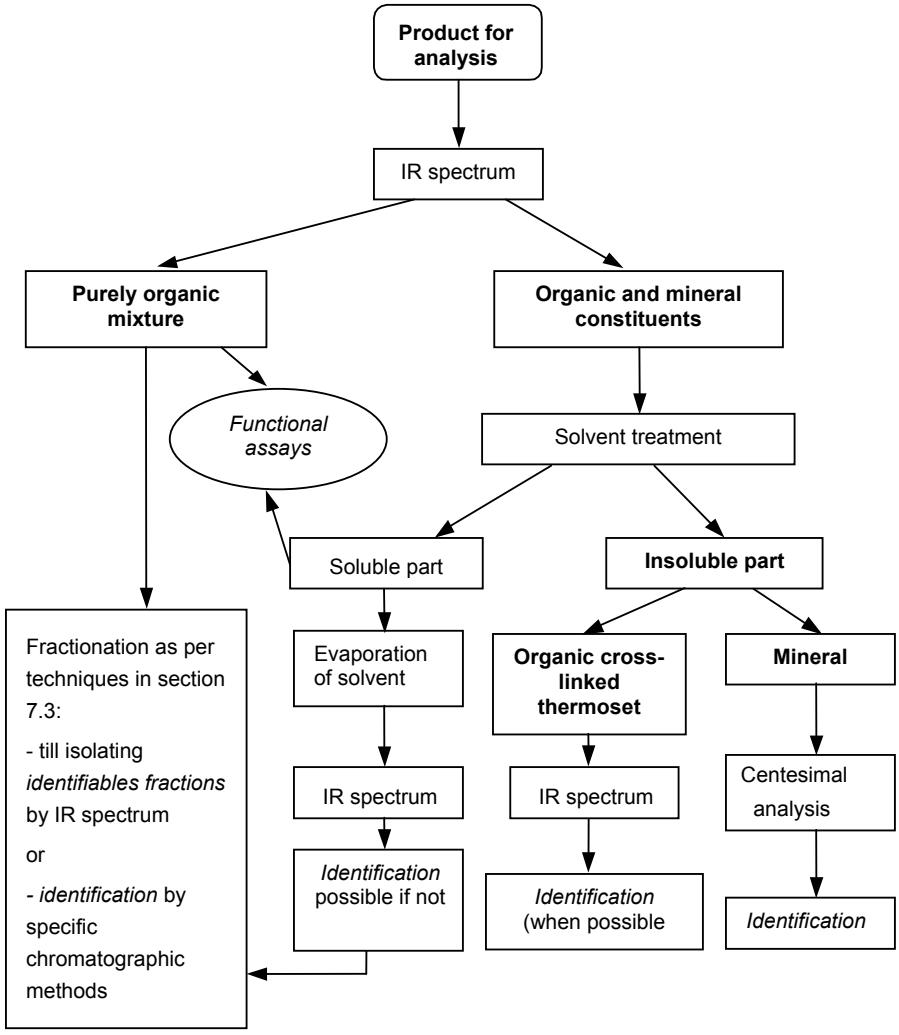

Figure 6.10. *Identification of complex mixtures. Theoretical diagram for fractionation*

In the majority of cases, however, the work of an analyst only concerns a part of this diagram: a particular methodology would apply to each family of products. The most striking example concerns bituminous material.

Similarly, we may classify the use of *thermal methods*. These do not appear on this diagram but can be used at times for the identification of a given material.

Finally, we need not stress the important fact that analysis is essentially a tool meant for unraveling the structure of a material at a given time, that it is indispensable in pathological diagnostics when we have taken the precaution to have made earlier an identification card of the "fresh" material, that it is a marvelous check tool for ensuring that the material conforms to the reference sample, but it cannot conclude directly *ex abrupto*, whether an unknown product is apt or not to render a service as defined by mechanical parameters.

6.7. Conclusions

From this rapid survey of the physico-chemical methods of analysis of organic materials used in civil engineering, a few recommendations may stay in our minds:

– the case of bituminous materials should be treated separately (see Chapter 2);

– before "doing an analysis" we should always ask ourselves what we are exactly looking for and for what purpose the results will be used. This makes possible at the same time the justification of the analysis (or to abandon the requirement, if need be) and the determination of the level of accuracy;

– the major questions that can easily be answered by analysis are the following:

- to which chemical family does the major constituent of the product belong?;

- how can a "digital imprint" of the product be established to inspect the delivery later?;

- how can it be verified whether a sample contains the strength of the active material necessary for obtaining the performances expected?;

- how can it be verified whether a material has changed or not during the course of a given test?

We should finally emphasize that chemical analysis is never complete in the sense that it is always possible to push the investigation further with respect to accuracy. A conscientious analyst knows this and should take all necessary reservations in this regard. But reciprocally, we should not consider, for example, the infrared spectrum as exhaustive information and the spectroscopist as the most clear-headed visionary …