

Lecture Notes in Chemistry 79

Evangelia A. Varella *Editor*

Conservation Science for the Cultural Heritage

Applications of Instrumental Analysis

 Springer

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O-H N-H C-H	C≡C C≡N X=C=Y (C, O, N, S)	Very few bands	C=O	C=N C=C	C-Cl C-O C-N C-C
4000	2500	2000	1800	1650	1550
Wavenumbers (cm ⁻¹)					
					650

Fig. 3.39 Location of important characteristic bands of organic structural groups

Contemporary procedures for spectra evaluation can be subdivided into two groups. Unsupervised procedures are employed for explorative data analysis or for empirical investigation of samples with no additional information available, e.g. cluster analysis (CA) and principal component analysis (PCA) (Fig. 3.40). Supervised procedures are used to assign new objects to already established classes (available additional knowledge), e.g. discriminant analysis (DA) and SIMCA. All these procedures nowadays are absolutely essential, in particular when large amounts of data like in spectroscopic imaging have to be dealt with.

3.4 Solid State NMR

D. Capitani, A. Spinella and E. Caponetti

3.4.1 Introduction

Nuclear magnetic resonance (NMR) is one of the most powerful and versatile techniques in many scientific fields. It can be applied to a wide variety of samples, both in liquid and in solid phase. Recently NMR technique has also been developed to investigate soft matter.

In this chapter the physical principles of NMR, a brief description of the instrument features and an evaluation of NMR technique in the field of cultural heritage, will be presented.

As conservation science requires nondestructive and minimally invasive investigation methods, only solid state NMR (ss-NMR) technique will be deepened. This because liquid state NMR, even if more established, is a destructive technique in which the sample must be dissolved in a solvent.

The NMR phenomenon consists in the absorption of energy in the range of radio frequencies by atomic nuclei subjected to a static magnetic field B_0 .

The analysis of an NMR spectrum can provide many types of information such as the number and type of chemical species in a molecule, rather as infrared

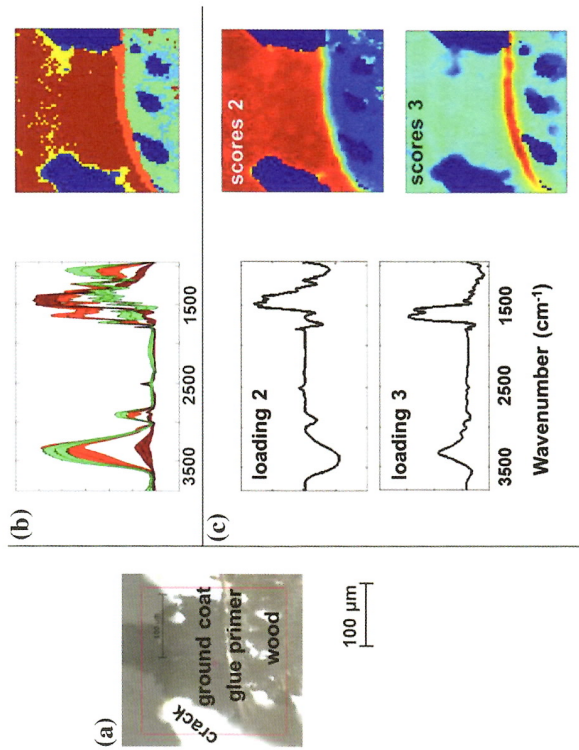


Fig. 3.40 Evaluation of spectroscopic images by chemometric procedures. **a** Cross-section of a painted art object (size $267 \times 267 \mu\text{m}^2$) A FT-IR image of 64×64 pixels was measured. Each pixel constitutes a complete FT-IR spectrum. **b** CA of the spectroscopic image. The spectra are clustered (indicated by color codes) according to their similarity. The color codes are then transferred to the position of the spectrum in the image. **c** PCA of the same data set. The loading plots indicate spectral positions of importance. The score plot reveals the importance of the respective loading at a particular location (*red*—high importance, *blue*—low importance) [17]

spectroscopy is used to identify functional groups. Furthermore, NMR can be used to elucidate molecular structure, to study mixtures of analytes, and to investigate molecular motions in liquid and solid samples.

Although NMR spectroscopy has enormously contributed to chemical knowledge, there are two reasons why ss-NMR technique has developed only in the last three decades: the first one is that NMR for many years has almost exclusively been a technique used for structural determination of molecules in liquid state in the field of organic chemistry. The second reason is that ss-NMR requires spectrometer settings such as more powerful amplifiers, devices for the high speed spinning of the sample and multinuclear probes that are different from the ones used for liquid state NMR. These problems have been overcome with the improvement of the NMR technology and the availability of multinuclear probes that are able to investigate most of the nuclei of the periodic table. As a consequence ss-NMR has become a powerful technique used in a wide range of applications such as catalysis [18], soil investigation [19], polymers [20], material science [21], supramolecular chemistry [22]. A case study regarding ss-NMR application to the analysis of paper and parchment collected from a sixteenth century book will be presented in another chapter.

3.4.2 Principles and Concepts

The physical NMR phenomenon depends on the fact that many nuclei possess an angular momentum called nuclear spin. When a sample is placed in a magnet, nuclear spins generate a bulk macroscopic magnetisation. The simplest experiment consists in perturbing the system from the equilibrium applying a proper radio-frequency pulse and then monitoring the response of the system to the applied perturbation. The so-called NMR-active nuclei are those nuclei having a nuclear spin $I \neq 0$. The number N of energy levels generated by Zeeman effect for a certain nucleus in the presence of a static magnetic field B_0 depends on the nuclear spin I and can be calculated using the following equation:

$$N = 2I + 1 \quad (3.1)$$

Eq. 3.1. The number of nuclear energy levels calculated from the nuclear spin I

Because NMR signals are observed when transitions among energy levels occur, it is evident that nuclei with $I = 0$ do not give rise to any NMR signal. To simplify the discussion, in the following only nuclei with $I = 1/2$ will be considered. These nuclei generate only two energy levels, namely $m_I = +1/2$ and $m_I = -1/2$, where m_I is the spin quantum number. The energy difference ΔE between the two levels depends on the applied magnetic field B_0 and it is described by Eq. 3.2:

$$\Delta E = \gamma \hbar B_0 = \hbar \nu_L \quad (3.2)$$

Eq. 3.2. Energy difference between the two levels generated by Zeeman effect for a nucleus with $I = 1/2$. γ is the gyromagnetic ratio and it is a constant characteristic for each nucleus, \hbar is the Planck constant divided by 2π and ν_L is the Larmor frequency specific to each nuclear species.

The frequency ν_L known as Larmor frequency, is specific to each nuclear species. In the absence of magnetic field, all nuclear magnetic moments μ_i are randomly oriented. Since nuclei possess a magnetic moment, when a strong external magnetic field is applied along the z -axis, they align either against or with it, with a small excess of nuclei (population excess) aligned with the field.

As a result a bulk magnetisation $M = \sum_{i=1}^n \mu_i$ aligned with the applied field is generated. However, the only presence of B_0 is not sufficient to observe the NMR signal. This point may be easily explained calculating the ratio between the populations n_1 and n_2 of the two energy levels (E_1 and E_2) which is determined by the Boltzmann distribution. This ratio is obtained from Eq. 3.3:

$$\frac{n_1}{n_2} = e^{-\frac{\Delta E}{kT}} \cong 1 + \frac{\mu B_0}{kT} \quad (3.3)$$

Eq. 3.3. The Boltzmann distribution: n_1/n_2 is the ratio between the population of the two levels, $\Delta E = E_1 - E_2$ is the energy difference between the two levels, T is the absolute temperature, μ is the nuclear magnetic moment, k is the Boltzmann constant and B_0 is the static applied magnetic field.

Because the energy difference between the two levels $\Delta E = -\mu B_0$ at normal temperature is much lower than the thermal energy kT , it is evident that the ratio n_1/n_2 is just slightly higher than 1. Under these circumstances the population difference between the two energy levels is too low, thus preventing the observation of the NMR signal. In order to observe the signal the population difference must be increased applying a proper radio frequency pulse, in other words the system must be perturbed from the equilibrium.

In a semi-classical description, nuclear magnetic moments in a static magnetic field B_0 applied along the z -axis, precess at the Larmor frequency ν_L which is proportional to B_0 , see Eq. 3.4.

$$\nu_L = \gamma B_0 \quad (3.4)$$

Eq. 3.4: The Larmor frequency dependence from the magnetic field strength B_0 ; γ is the gyromagnetic ratio.

The system is perturbed from equilibrium applying along x - or y -axis, a radio-frequency field B_1 , which oscillates at the proper radio-frequency ν_1 . When ν_1 is equal to the Larmor frequency, the resonance condition occurs. This is the reason why the NMR spectrum gives information for a single nuclear species at once. At the resonance the field B_1 interacts with the magnetisation M to produce a torque which moves the magnetisation towards the xy plane. Since the precession frequency about the static magnetic field B_0 is equal to the rotating B_1 frequency, the magnetisation will remain perpendicular to the B_1 field component. To summarise, the magnetisation will precess about B_1 and, at the same time, it will precess about B_0 . The B_1 field is applied as a pulse duration t_p which usually lasts for a few microseconds. The angle θ (flip or tip angle) through which the magnetisation is tipped from the z -axis, is easily calculated: $\theta = \gamma B_1 t_p$. Each duration t_p of the radio-frequency pulse produces a particular tip angle. The intensity of the detected signal depends on the chosen tip angle. As an example, the signal will be maximum for a tip angle of $\pi/2$, or it will be null at π .

As the radiofrequency pulse is switched off, nuclei relax back to equilibrium generating a signal called free induction decay (FID). The frequency domain spectrum is obtained by applying a Fourier transformation to the FID, see Fig. 3.41.

It is worth noticing that, after perturbing a system with a radio-frequency pulse sequence, the system will return back to equilibrium through a process called “relaxation” characterised by a time constant known as “relaxation time”. Relaxation times are parameters tightly related to the properties of the investigated material.

The main source of chemical information in high-resolution NMR spectroscopy is the chemical shift which is a very sensitive probe of the chemical environment of each resonating nucleus. This property is due to the fact that, in presence of B_0 , the electrons surrounding a nucleus, generate a small magnetic field opposite to B_0

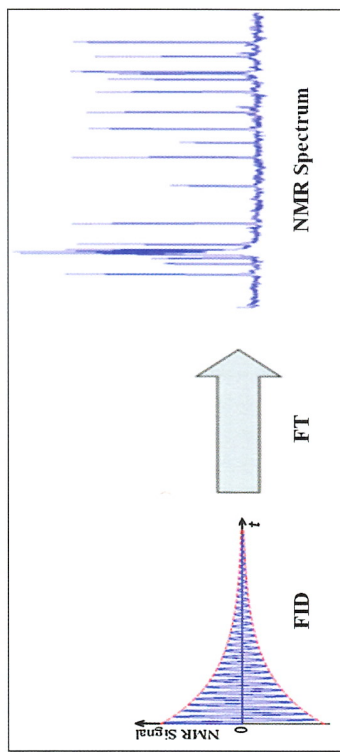


Fig. 3.41 By applying a Fourier transformation to the signal in the time domain (FID), the NMR spectrum in the frequency domain is obtained

which shields the nucleus, the higher the electron density surrounding the nucleus, the higher the shielding effect. Thus, B_0 is not the effective magnetic field at which nuclei are subjected but it is slightly changed by the additional magnetic field generated by the electron currents. As a consequence, nuclei of the same species in different chemical environments resonate at slightly different frequencies. This allows one to obtain structural information from the position of the signals in the spectrum. As an example, the ^{13}C NMR spectrum of ethylbenzene is reported in Fig. 3.42. Note that different carbon nuclei in the molecule give signals at different positions, i.e. different chemical shifts.

Other important structural information can be obtained by investigating the coupling constants accounting for the coupling between nuclei through 1, 2 and 3 bonds. In addition to one-dimensional NMR spectroscopy, two dimensional approaches have been developed for the determination of the structure of complex molecules like proteins. A detailed discussion of these techniques that goes beyond the scope of this chapter can be found in specialised books [23, 24].

In liquid state, the Brownian motion of molecules averages to zero the dipolar interactions among nuclei, besides the position of lines in the spectrum does not depend on the orientation of the molecules on respect to the applied magnetic field. Therefore, spectra of liquid samples show sharp and well-resolved signals.

In the solid state, the dipolar interactions among nuclei are not averaged to zero, causing a marked enlargement of signals. Furthermore, in the solid state the position of signals depends on the orientation of molecules on respect to B_0 . As a consequence, each single crystal gives rise to a distribution of lines (powder spectrum) which are very close to each other, causing a further enlargement of the line width (chemical shift anisotropy). In the case of nuclei with spin higher than $1/2$, the interaction between the nuclear quadrupolar electric momentum and the electric field gradient generated by electrons, is another source of line broadening, however, the case of quadrupolar nuclei will not be discussed. Another problem is that experiments on solid samples may be very time-consuming as nuclear relaxation times may be very long. To overcome these difficulties, three techniques

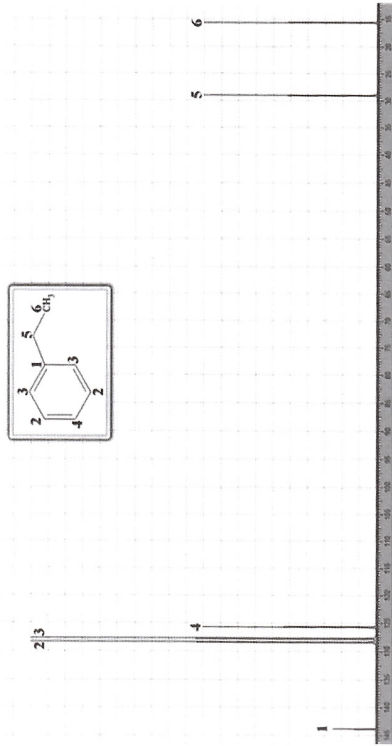


Fig. 3.42 ^{13}C NMR spectrum of ethylbenzene

of acquisition have been developed, namely magic angle spinning, dipolar decoupling and cross polarisation. The first two techniques average the dipolar interactions among nuclei and the chemical shift anisotropy effect, while the third one allows the obtainment of spectra of low abundant (dilute) nuclei in a reasonable time.

Many terms of Hamiltonian which cause line broadening in solid samples, involve the geometric factor ($3\cos^2\theta - 1$) which accounts for the orientation of the shielding/dipolar tensor on respect to the applied magnetic field B_0 . It is easy to demonstrate that by spinning the sample at the magic angle, i.e. 54.74° , the geometric factor ($3\cos^2\theta - 1$) is averaged to zero on the NMR timescale. Therefore, this technique is routinely used to remove the effects of chemical shift anisotropy and to assist in the removal of dipolar coupling.

The *magic angle spinning* technique involves the high speed spinning of the powdered solid sample packed in a rotor at the *magic angle* with respect to the direction of the static magnetic field, see Fig. 3.43.

The *dipolar decoupling* technique involves the irradiation of abundant nuclei (such as protons) having dipolar interaction with dilute nuclei (such as carbons) that must be observed. The high power decoupling thus allows the removal of the dipolar broadening to obtain a spectrum with much more sharp lines.

The *cross polarisation* technique is applied to dilute nuclei such as ^{13}C or ^{29}Si characterised by a low natural abundance (1.1 % for ^{13}C and 4.7 % for ^{29}Si) and low gyromagnetic ratio, and thus having a very weak observable net magnetisation. The NMR experiments on dilute nuclei are very time-consuming since they require a high number of scans. The CP technique consists in transferring the polarisation from abundant to dilute nuclei. The overall effect of the CP technique is to enhance the signal to noise ratio (S/N).

The polarisation transfer between nuclei with different Larmor frequencies is obtained by varying the radio-frequency pulses (B_1) of the two nuclear species allowing the matching of their energy levels. This matching is called Hartman-

Fig. 3.43 The magic angle spinning of a solid sample

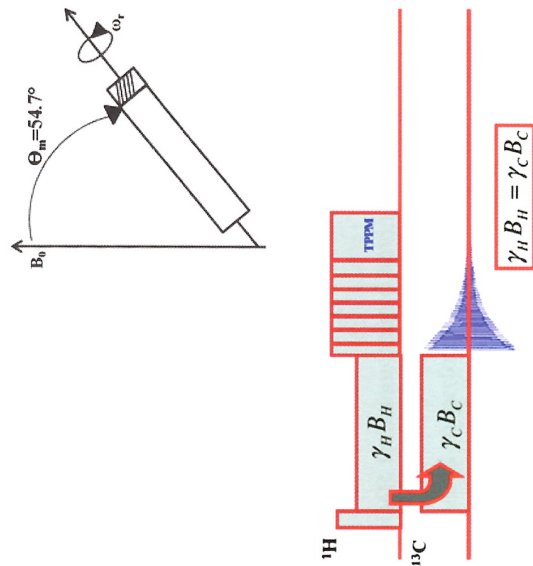
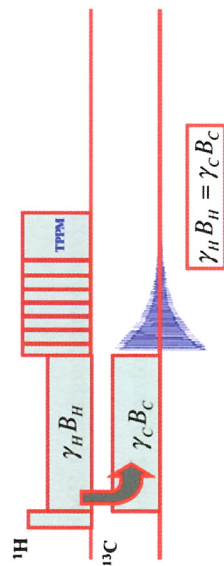


Fig. 3.44 Cross polarisation pulse sequence. The equation describing the Hartman-Hahn condition is reported in the insert



Hahn condition [25]. As an example, in the case of proton and carbon systems, the Hartman-Hahn condition is: $\gamma_C B_{1C} = \gamma_H B_{1H}$, where γ_C and γ_H are the carbon and proton gyromagnetic ratios, respectively. Since γ_H is four times γ_C the match occurs when the strength of the applied radio-frequency field B_{1C} is four times the strength of the applied proton field B_{1H} . As a consequence, there is an enhancement of the dilute spin signal intensity by as much as the ratio of gyromagnetic ratios of the abundant and dilute spin. In the case of proton and carbon nuclei, because $\gamma_H/\gamma_C = 4$, the enhancement factor is 4. It is important to note that the Hartman-Hahn condition (i.e. the contact between the two nuclear species) must be maintained for a time (*contact time* τ_C) that allows the maximisation of the NMR signal. On the other hand, τ_C cannot exceed a certain value, depending on the analysed sample, above which relaxation processes occur thus causing a loss of the signal intensity. A representation of the CP pulse sequence is reported in Fig. 3.44.

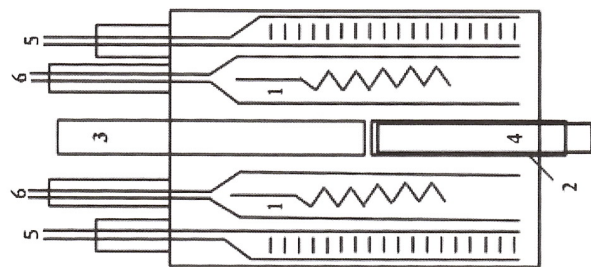
In the presence of cross-polarisation, because polarisation is being transferred from protons to carbons, the shorter T_1 relaxation time of protons dictates the recycle delay for signal averaging. As a result, the time of acquisition of carbon spectra is markedly shortened on respect to carbon spectra acquired without cross-polarising.

3.4.3 The NMR Spectrometer

In modern high field NMR spectrometers the static magnetic field B_0 is generated by a superconducting magnet (Fig. 3.45).

The magnet is constituted by an outer stainless steel or aluminium dewar which contains liquid nitrogen and an inner dewar containing the superconducting coil (1) immersed in liquid helium in order to reach the very low temperature needed to make

Fig. 3.45 Internal section of an NMR superconducting magnet: 1 Magnet coils and liquid He dewar; 2 Shim coils system; 3 Spinner assembly; 4 Probehead; 5 Liquid N₂ ports; 6 Liquid He ports



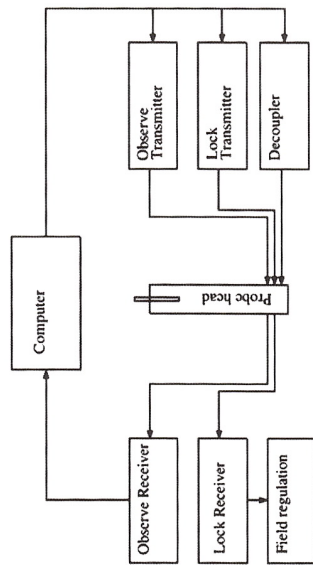
the material constituting the coils superconducting. A set of shim coils providing a room-temperature homogeneity adjustment is inside a room-temperature bore (2), a spinner assembly is equipped with the system for spinning the NMR sample holder (3). The probe-head (4) is introduced into the magnet from the bottom and is connected to at least three cables providing the ²H lock, ¹H and ^YX frequencies. In the case of solid state dedicated probeheads the lock channel is not necessary. The probehead transmits the radio-frequency energy to the sample and also detects the signal from the sample which is positioned within the rf coil of the probehead itself. The rf coil needs to be tuned for the specific sample to be analysed. Another important part of the spectrometer is the cabinet which is shown in Fig. 3.46.

The computer controls the radio-frequency and pulses generation. Typically three radiofrequency channels, namely the observed, the lock and the decoupling channel, are present inside the cabinet. The frequencies, after the amplification are transmitted to the probehead. As the output from the sample is small the output stage consists of a radio receiver able to amplify the signal. Then the signal is digitised and fed into the computer memory.

3.4.4 Evaluation of ss-NMR as Used in Conservation Science

A chemical characterisation of materials associated with archaeological, historical and artistic objects, completes the information obtained through the study of historical documents, supplying information on their nature and the modifications that might have occurred due to manufacturing processes and/or natural ageing.

Fig. 3.46 Diagram of a NMR cabinet



Recently, in this field the ss-NMR technique started having an important role even if some drawbacks must be taken into consideration. The main drawback is that 50–80 mg of material is required to perform the analysis when using the standard 4 mm rotor to contain the sample. Nevertheless, the method is non-destructive and the sample can be recovered after the NMR experiment and investigated with different techniques. This is possible because the sample does not require any treatment before the acquisition. Furthermore, the quantity of information obtained from the same sample by means of an NMR experiment is often a sufficient reason for planning this kind of analyses. Besides, the use of 4 mm rotors with an internal insert to reduce the volume, or the use of 2.5 mm rotors, permits to lower the quantity of sample needed for the analysis (10–12) mg.

Solid state NMR is a powerful technique in the field of conservation science. First of all the NMR observables are specific for the chemical element under investigation and are sensitive to distances in short and medium ranges. Besides, even in the solid state, the study of the cross-polarisation dynamics process in many cases allows the obtention of quantitative results.

A very interesting aspect is that ss-NMR can be used in the investigation of amorphous materials such as glasses and amorphous polymers used as conservation materials. As an example, the network structure in fluoride-containing aluminosilicate glasses has been studied through a quantitative determination of the coordination aluminum sites using ²⁷Al MAS NMR and the triple-quantum magic angle spinning (3QMAS) technique [26].

Some examples of ss-NMR application in the field of cultural heritage are reported in the following in order to highlight its potentiality.

The characterisation of stone material coming from the Cheops pyramid was performed by ²⁹Si and the ²⁷Al ss-NMR spectroscopy [27]. In particular, the hypothesis that a clay binder was added to stone material in order to obtain some sort of concrete was studied.

ss-NMR technique was applied in the UNESCO World Heritage site of Guanajuato City Main Church (Central Mexico) in which building stones from seventeenth century were analysed by ²⁹Si and ²⁷Al MAS NMR in order to determine the degradation degree and to plan preservation and restoration interventions [28].

An interesting ss-NMR application is represented by a rubber analysis. This natural polymeric material is slightly soluble and slightly volatile, so that techniques such as gas chromatography (GC-MS) or liquid chromatography (LC-MS) cannot be utilised. It was possible to demonstrate that the old Mesoamerican populations used a process similar to the modern vulcanisation by comparing ^{13}C ss-NMR spectra of samples from an ancient manufacturing with the spectrum of a modern rubber [29]. Recently ^{23}Na and ^1H solid state NMR has been used to study the salt quantity in the Statue of a Soldier eroded by salt weathering in La Rochelle (France). By quantitative (NMR) measurements of the amount of both Na and H ions in the solution inside a material, the salt concentration was determined. Furthermore, information on the pore size distribution in the manufacture was obtained by ^1H and ^{23}Na NMR experiment [30].

The study of the interactions between archaeological wooden samples and polyethylene glycol (PEG) was reported. Through ^{13}C ss-NMR it was possible to visualise the degradation extent in archaeological wood even after the conservation process. In addition, the investigation of the cross-polarisation dynamic allowed one to demonstrate that almost 30 % of PEG was in close molecular interaction with lignin [31].

As the ss-NMR spectra can be used as a fingerprint of samples constituted by a complex mixture of analytes, analytical procedures can be applied through the use of standards and reference materials. This is the case of the geographic origin assessment of several amber samples through the use of ^{13}C ss-NMR spectroscopy [32].

The ss-NMR can nowadays be applied to characterise artistic, archaeological and historical objects. The interpretation of the obtained data, together with the study of historical documents, is used to obtain information about the geographical origin and the use of the objects under investigation. Therefore, the integration of different research areas will allow to disseminate and to present in exhibitions not only the object itself, but also the technique used to create it and the description of its constituent materials. This new approach can be useful to reveal how the techniques of production have evolved over time.

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