ATR-FTIR SPECTROSCOPY FOR THE CHARACTERISATION OF MAGNETIC TAPE MATERIALS

Elena Gómez-Sánchez1,*, Stefan Simon1, Lars-Christian Koch2, Albrecht Wiedmann2, Tobias Weber2, Maurice Mengel2

The Music Archive of the Ethnological Museum (National Museums Berlin, Germany) houses a large number of recordings on phonograph cylinders and magnetic tapes. The project ILKAR (Integrated Solutions for Preservation, Archiving and Conservation of Endangered Magnetic Tapes and Cylinders) aims at prioritising the digitisation of the more than 10,000 magnetic tapes of the Archive. In this contribution, the usefulness of Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy for the characterisation of the constituent materials of magnetic tapes is discussed. The final aim of the research is the characterisation of the most endangered materials of the Archive's collection and the evaluation of their conservation state. A range of complementary techniques should aid in the characterisation of the main tape types housed in the archive and will help to achieve a better understanding of their decay processes.

1 Introduction

Since the first commercial magnetic tapes were developed in Germany in the 1930s for the recording of sound,1,2 millions of hours of recordings have been stored in archives all over the world. The 20th century has seen a rapid succession of formats being developed and then cast aside after a relatively short period of time (typically a few decades). Amongst the most common and most studied is the reel tape, an example of which is in Figure 1.

The recording mechanism of magnetic tapes relies on a magnetic layer capable of ‘storing’ the sound by retention of the magnetism impressed on them by the recording head. This layer is sustained over a base film, which provides structural support. Different materials have been used over time as base films, with acetate, polyvinylchloride and polyethylene terephthalate being the

Figure 1: A typical reel tape, with the so-called leader tape (red tape attached at the beginning, carrying no information) before the magnetic tape.
most widespread in their respective times. A polymeric binder keeps the magnetic layer particles attached to the base film while holding them together, and lubricants diminish the friction between tape and head in the magnetic layer on playback. Other components of magnetic tape formulations are typical additives of many other plastic materials, such as plasticisers, stabilising agents such as antioxidants, dispersants, antistatic agents and mineral fillers, which are often used to achieve the desired hardness, flexibility or adhesion on the final manufactured magnetic tape. On the other hand, all these components can potentially also have an impact on the final behaviour and long-term stability of the tapes.

In fact, some of these materials are not stable, and information is eventually lost unless it has been timely transferred to digital form. Two well-known decay mechanisms are the so-called 'vinegar syndrome' and 'sticky shed syndrome', affecting acetate based tapes and polyurethane binders, respectively.

Both processes are intimately related to the inherent stability of the materials and triggered by ambient humidity. In advanced stages both mechanisms render the tapes unplayable, posing a deeper problem than the loss of a single tape. In the case of acetate tapes, the acetic acid released on decay (and responsible for the name of the phenomenon) may potentially catalyse the degradation of other, not yet affected tapes stored nearby. It therefore becomes essential to identify and isolate these materials before the problem spreads, as well as to transfer the information they contain as soon as possible.

On the other hand, low molecular weight products arise as a result of the hydrolysis of certain polyurethane binders ('sticky shed syndrome') and migrate to the surface of the tape. These degradation products may inflict damage on the playback devices, which given their obsolescence are difficult to repair, putting in danger the digitisation of other, not yet affected tapes stored nearby. It therefore becomes essential to identify and isolate these materials before the problem spreads, as well as to transfer the information they contain as soon as possible.

As with many other modern materials, however, once these processes have started, in the best of cases they can only be slowed down in appropriate conditions, but not reversed. Moreover, these processes usually become noticeable once the damage is so widespread that digitisation of the information cannot be completed without consequences either on the quality of the copy, on the playback devices or on the tape itself.

Unfortunately, in many cases the information on damaged tapes can never be retrieved again and is thus lost forever. When dealing with originals, time management is essential. However well aware of this fact they may be, archivists and sound technicians in charge of these collections are usually left alone with the problem.

The music archive of the Ethnological Museum of Berlin houses among other collections a large number of recordings on magnetic tapes, focusing on historical and contemporary music from all over the world. The total length of all original audiovisual recordings is now estimated at more than 12,700 h, excluding commercial recordings (April 2009). A number which perhaps makes it small when compared to massive archives in institutions like the Deutsches Musikarchiv or the BBC, which may afford automated solutions for the digitisation of their holdings, but still big enough that its digitisation will take a non-negligible amount of time. The key question is: where to start with the digitisation? In other words, which tapes must be transferred now on the basis of the stability of their materials, and which will remain in an acceptable condition until the information in the most endangered ones has already been transferred?

This is the starting point for the ILKAR project1 with the main focus on determination of risk factors which allow for the assessment of the state of degradation of recorded material dating from as early as 1952. ILKAR aims at applying a range of non-invasive techniques in order to find markers for degradation and develop criteria and workflows which will enable a more efficient use of the available timeframe. The identification of more sensitive materials following this approach will allow for the development of a timely, rationally designed digitisation strategy in order to target more endangered materials first.

In this work Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy (ATR-FTIR) is proposed for the non-invasive characterisation of the main components in the formulation of both binders and base materials of reel tapes. Thus far, transmission mode FTIR had been used destructively in THF extracts of magnetic tapes2 for the same purpose. In the frame of the EC-project PrestoSpace, the use of Solid Phase Microextraction (SPME) coupled with GCMS was implemented for the analysis of VOCs coming from magnetic tapes, attempting to identify specific markers for degradation processes. On the

---

1. ILKAR is the German acronym for Integrated Solutions for Preservation, Archiving and Conservation of Endangered Magnetic Tapes and Cylinders, www.ilkar.de
A systematic and representative sampling procedure was designed in the frame of ILKAR in order to acquire a good impression of the most common and the most endangered and damaged materials. Survey criteria were derived from similar condition surveys, with modifications to accommodate to the characteristics of the archive involved.5 The developed survey document will be available on the ILKAR project website.

The first phase of the survey was finished in February 2010. Until then, 577 tapes were surveyed. Among the most common materials that could be identified were tape types Agfa PEM 468 Professional, BASF LGS 52 and Agfa Gevaert PEM 468. A significant number of tapes were not branded. From the surveyed tapes, over 150 were chosen for analysis with ATR-FTIR, both on the basis of representativeness with respect to the results of the survey, and trying to account for the different degradation states present. Of each main type, several tapes were analysed. As a first result of the survey it could be noticed, however, that the archive was in a better condition than expected.

In this work, only the results for the most common types are presented. A more complete account of the different FTIR types found thanks to the survey will be published elsewhere, as will be the study of the tapes showing degradation.

Analyses were performed on both sides of the tapes, so that information on the binder in the magnetic layer and of the base material could both be obtained. The analysis of the front side, the ‘information layer’, allowed the polymeric binder in the magnetic layer to be studied, while analysis of the backside allowed the analysis of the base material in those samples without back-coating.2 The low penetration depth of ATR ensures that both sides can be analysed independently, given the thickness of the layers. Figure 2 presents the typical layer constitution of a magnetic tape in a typical reel tape. The cross-section shows the magnetic or information layer (15-20 μm) on which the magnetic particles are embedded in a polymeric binder along with other components such as lubricants, while the similarly polymeric base film (~35 μm) can be seen below the former. The metallic particles, as studied by ESEM, and non-invasively with X-ray fluorescence, in most cases contained iron oxides which did not interfere with the study of the infrared bands of the organic components.

2 Experimental

2.1 Preparation of cross section

The embedding material was the two component epoxy resin EpoFix (Struers). After hardening of the embedding material, the sample was polished on abrasive papers with different gradations. A digital microscope (Keyence VHX-500FD; lenses VH-Z20 from 20x to 200x and 100x VH-Z100 by up to 1000x) was used to photograph the cross section.

2.2 Environmental Scanning Electron Microscopy (ESEM)

Scanning electron microscope model Quanta 200 from Fei, with a tungsten cathode, under low-vac or environmental-mode imaging without need of applying a conductive coating.

2.3 Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy (ATR-FTIR)

The spectra were recorded with an IR spectrometer model ‘Spectrum One’ (Perkin Elmer) with the Universal ATR Sampling Accessory in transmission mode, in the range of 4000 - 550 cm⁻¹. The resolution was 4 cm⁻¹.

The obtained IR - spectra of the samples were compared with reference spectra from commercial (Sadler) or customer databases, or with the IRUG Database.

3 Discussion

3.1 Survey

The tapes chosen for analysis in the present work had been previously identified as the most common brands in the archive an ongoing survey of its holdings. Before the beginning of the project the music archive at the Ethnological Museum had very little information on the most prevalent damage types, damaged materials, or the actual conservation state of the tape collections. This situation is characteristic for many other audio archives.

Other hand, some authors have recently cast doubts on the possibility of a simple diagnostic tool due to the plethora of tape formulations, which leads to different behaviours. Given this variability of behaviours from tape to tape, however, and if tapes are to be assessed for the urgency of their digitisation as based on their conservation state, non-invasive techniques are essential for the identification of the main tape materials and damage types.

The present work deals with the identification of the main materials of magnetic tape formulations as a first approach for the development of a prioritised digitisation protocol. Future work will concentrate on the study of the degradation of these materials both with FTIR and other supporting techniques.
derivatives are commonly used as base materials. Additives forming part of the formulation are fillers, dispersion stabilisers, lubricants, and antistatic agents.\(^8\) The perspective of identifying all the components forming part of the formulation of a specific tape is overwhelming, but main materials are, in practice, identifiable to a certain extent, provided a comprehensive infrared database of polymeric materials is available.

Below some examples are given of the identification of the main components of the most common tapes in the music archive of the Ethnological Museum.

The spectrum corresponding to the back side of a BASF LGS 52 tape is shown in Figure 4. In this case it is easy to identify PVC as the base material, there being only a few traces (1736 cm\(^{-1}\)) of what is possibly a carbonyl containing lubricant or plasticiser.\(^9\) The characteristic bands of PVC\(^10\) can be found at 2964, 2915, 2853 cm\(^{-1}\) (CH and CH\(_2\) stretching, st), 1426, 1329 and 1253 cm\(^{-1}\) (CH\(_2\) and CH deformation), 1095 (C-C st), 964 cm\(^{-1}\) (CH\(_2\) def), and 686, 634 and 607 cm\(^{-1}\) (C-Cl st). PVC is a relatively stable material when compared to cellulose acetate, which suffers from the well known 'vinegar syndrome'. In the archive, some examples of this material could be found forming part of the collection (Figure 5). This spectrum shows\(^11\) the typical frequencies corresponding to cellulose acetate [1738 cm\(^{-1}\) (C=O st), 1367 cm\(^{-1}\) (CH\(_3\) sym def), 1215 cm\(^{-1}\) (C-O st), 1031 cm\(^{-1}\) (C-O-C st)].

The analysis of the front side of tape BASF LGS 52 was also carried out. The comparison with commercial databases allowed for the tentative assignment of the structure of the binder as a poly(vinyl chloride-co-maleate ester) copolymer (Figure 6). Features which

3.2 Identification of base and binder materials

In the patent literature a wide range of polymers are mentioned as being used for the manufacturing of magnetic tapes. The use of poly(etherurethanes), poly(esterurethanes), copolymers of vinylchloride, vinylacetate and vinylalcohol, copolymers of vinylchloride and acrylonitrile, etc, as well as mixtures of them have been reported as binding media,\(^6,7\) while PVC, polyethylene terephthalate (PET) and cellulose

![Figure 2. Cross-section of a magnetic tape (tape type Agfa PEM 468 Professional).](image2)

![Figure 3: Acquisition of the FTIR spectrum of a magnetic tape (information side below).](image3)

![Figure 4: Back side spectrum of a BASF LGS 52 tape (Nowak collection).](image4)
Belgian company Gevaert, adopting the name Agfa Gevaert. In the same year, the eastern Agfa changed its name to ORWO (which stands for Original Wolfen, in reference to the company's original headquarters).

According to this, the tape type named Agfa PEM 468 Professional should have been produced before 1964, while the tapes branded Agfa Gevaert PEM 468 were very likely manufactured after that date. The information layer of tapes marketed under the latter name and which could be found in the archive provided two kinds of spectra, one of them coinciding with the one shown by the former Agfa PEM 468 Professional. A possible explanation for this is that Agfa Gevaert kept fabricating tapes with the binder formulation of at least one of its mother companies.\(^2\)

It should be noted at this point that none of the tapes analysed in this work showed signs of external damage, seemingly being in a good state of conservation, and playable.

Below, the spectrum of the information layer of one of the kinds of tape type Agfa Gevaert PEM 468 (collection tape no. 141.020) is shown. The graph shows the comparison with a poly(etherurethane) with aromatic groups in its hard segment (Figure 7). Bands used for the identification of this polymer are at 3292 cm\(^{-1}\) (H-bonded NH st), 3122 cm\(^{-1}\) (aromatic CH st), 2919, 2851 and 2797 cm\(^{-1}\) (CH\(_2\) st), 1725 and 1705 cm\(^{-1}\) (free and hydrogen bonded C=O st, respectively), 1598 cm\(^{-1}\) (according to different authors, NH def\(^{12}\) or Ar C-C st\(^{13}\)), 1531 cm\(^{-1}\) (C-N st, N-H def), 1413 cm\(^{-1}\) (C-C st, aromatic ring), 1368 cm\(^{-1}\) (CH\(_2\) def), 1311 cm\(^{-1}\) [C-N (C(=O)-NH)], 1222 cm\(^{-1}\) (C-N st), 1103 cm\(^{-1}\) (C-O-C asym st, polyether), 1072 cm\(^{-1}\) (C-O-C asym st, urethane), 1017 cm\(^{-1}\) (aromatic ring), 817, 769 cm\(^{-1}\) (CH def, aromatic ring).

Among non-marked tapes which were also analysed, the presence of poly(esterurethane) could be identified, as can be seen in Figure 8. Typical bands\(^{14,15}\) shared with the reference polyurethane are 3317 cm\(^{-1}\) (N-H st), 2921 cm\(^{-1}\) and 2864 cm\(^{-1}\) (C-H st), 1726 cm\(^{-1}\) and 1698 cm\(^{-1}\) (C=O st, free and H-bonded, respectively), 1595 cm\(^{-1}\) (NH def\(^{12}\) or Ar C-C st\(^{13}\)), 1528 cm\(^{-1}\) (C=N st, N-H def), 1413 cm\(^{-1}\) (C-C st, aromatic ring), 1308 cm\(^{-1}\) (C=N st, NH), 1219 cm\(^{-1}\) (C=N st, NH), 1167 and 1075 cm\(^{-1}\) (C-O-C st). Discrepancies below 800 cm\(^{-1}\) could be due to different substituents on the polymeric chain (especially in the aromatic moiety) of both materials, and particularly in the case of tape 281.010 to the presence of an unknown component, not unique to this tape type (cf. Figure 6).

\(^{11}\) According to former employees of Agfa recently contacted in the course of the project (13.05.11), the appearance of two formulations under the same name Agfa Gevaert PEM 468 could be more likely explained by forgery.
In the case of tape type Agfa PEM 468 Professional (tape AW1), the spectrum obtained from the analysis of the information layer showed to be more complex than in the previous cases (Figure 9).

Since some historical material with no recorded information was available in the archive, some pieces of the tape were submitted to solvent extraction at RT for 2 h. Different solvents were considered, partial separation of some components being finally achieved with acetone.

The spectrum of the soluble fraction after treatment with acetone and evaporation of the solvent is shown in Figure 10. The presence of PVC or a related copolymer seems to be well justified under the light of the assignment of the bands found in the spectrum of the binder in tape type BASF LGS 52. Similarly, a possible minor content of polyurethane seems to be present. Further unidentified component(s), as evidenced by the bands at 1095 cm\(^{-1}\) and two different, very intense bands in the C=O stretching region (1728 and 1712 cm\(^{-1}\)) are also noticeable in the spectrum.

Next the spectrum of the magnetic film after treatment with several solvents was analysed (Figure 11). Although the identification of the components remained uncertain.

(Images and references to Figures 7, 8, 9, and 10 are included in the text.)

III. Acetone, THF and water. For the sake of clarity only the most relevant spectra are included here.
ning on the information layer after extraction with solvents could not be identified with certainty, from Figure 11 there seems to be some common features between this spectrum and propylene glycol derivatives (in Figure 11, tripropylene glycol), namely the intense band at 1095 cm\(^{-1}\), as well as characteristic CH\(_3\) frequencies (2965 cm\(^{-1}\), stretching, and 1373 cm\(^{-1}\), symmetric deformation). A poly(etherurethane) bearing a propylenoxidepolyether moiety as component may also not be ruled out.\(^{16}\) The use of two different polymeric systems for the manufacture of magnetic tape binders has been described in the literature on the manufacture of magnetic tape binders.\(^{9,10}\)

In Figure 11 the IR spectrum of silica and that of an iron oxide are also given for comparison; while the presence of an iron species is present as confirmed by ESEM analysis, it seems less likely that silica is, given the absence of characteristic Si-O stretching bands at 799 and 780 cm\(^{-1}\).

4 Conclusions

ATR-FTIR has been used non-destructively for the analysis of information-containing magnetic tape materials without compromising the sound quality. It is a key technique in distinguishing typically unstable (i.e. endangered) materials from relatively stable ones in collections, allowing a timed digitisation of the unique information the holdings contain.

In this study, the base materials of certain common tapes (BASF LGS 52) of the music archive of the Ethnological Museum of Berlin could be identified as PVC. PVC is a relatively stable material with respect to tapes presenting cellulose acetate as the base material, for example, and which has also been found in the archive and identified with ATR-FTIR. The identification of both materials in the same archive allows making an informed decision as to which tapes need to be digitised first, attention focusing first in cellulose acetate tapes.

On the other hand, infrared analysis of the information layer of the most common tapes allowed us to identify poly(etherurethanes), PVC or its copolymers, and mixtures of them as the prevalent polymeric binders. Poly(esterurethanes) forming part of the formulation of magnetic tapes are known to be susceptible to undergo certain degradation mechanisms, while poly(etherurethanes) have not to date been documented to be so. Although poly(esterurethanes) were also identified in the archive by ATR-FTIR, main tape types present poly(etherurethanes) in their formulation instead of the former.

To the best of our knowledge, this is the first non-invasive IR spectroscopic study on audio magnetic tapes for the systematic characterisation of binders and base materials. The information obtained through this study will allow the development of a prioritised digitisation strategy, as well as help in dealing with tapes with no brand specification. A representative number of spectra of the most characteristic tape materials will be made available for reference purposes in the ILKAR website and/or in the IRUG database.

Future work within ILKAR will include degradation studies in different tape materials by comparison of the FTIR spectra of tapes in different conservation states. The survey of the collection should provide with the needed specimens for these studies. Also, analysis of the VOCs emitted by these tapes should shed some light on the degradation processes they undergo.

5 Acknowledgements

The authors would like to thank the "Kulturstiftung des Bundes" (Federal Cultural Foundation) and the "Kulturstiftung der Länder" (Cultural Foundation of the German States) for the financial support of this study.

Perkin Elmer, especially Mr Hoffmann, are gratefully acknowledged for the generous temporal cession of an ATR-FTIR Spectrometer for the Open Labs at Altes Museum (Berlin) during the exhibitions kulturGUTerhalten and Anders zur Welt kommen. Das Humboldt-Forum im Schloss. We would also like

IV. In fact, this spectrum bears resemblance to that of a previously published for a polyurethane, albeit in a very different context.\(^{16}\)
to thank Sabine Schwerdtfeger for the ESEM analysis of the cross section, and especially Prof. Dr. Karl Molt for his help editing the IR figures in this article.

6 References


