

Plastic toy soldiers, a lost battle? – an analytical perspective

Soldadinhos de plástico, uma batalha perdida? – uma perspetiva analítica

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Abstract

The conservation and preservation of museum collections requires a detailed understanding of their constituent materials which are often natural, synthetic or semi-synthetic polymers. The use of a wide variety of instrumental techniques can give an extraordinary amount of quality information, by delivering complementary data regarding composition and structure.

This study was triggered by the Oporto Military Museum (Museu Militar do Porto) conservators who observed that a set of plastic toy soldiers dating back to the middle of the 20th century from the museum exhibition started to present severe and accelerated degradation process.

With this in mind, the authors envisaged a methodology for the characterisation of these soldier toys that comprised elemental, structural and morphologic analysis, to allow the identification of polymers, their additives, and the degradation products. The methodology comprised stereoscopic microscopy and VP-SEM-EDS to recognize the micromorphology, ATR-FTIR to identify the polymer, ¹H and ¹³C NMR to identify their additives, and micro-XRD to identify degradation products with a crystal structure.

With this complementary analytical approach the composition of the toy soldiers was identified as being made of cellulose acetate plastic with triphenyl phosphate and dimethyl phthalate as major additives, and crystalline efflorescence of triphenyl

phosphate were identified as a degradation product. This methodology shows to be very adequate for a detailed characterization of plastic artefacts in museum environments.

Keywords

Plastic objects; Multi-analytical method; Cellulose acetate; Triphenyl phosphate; Dimethyl phthalate

Resumo

A conservação e preservação de coleções em museus requer o conhecimento dos seus materiais constituintes, os quais podem ser, entre outros, polímeros naturais, sintéticos ou semi-sintéticos. O uso de variadas técnicas instrumentais podem fornecer uma quantidade extraordinária de informações de qualidade, ao proporcionar resultados complementares sobre a composição e estrutura.

Este estudo foi desencadeado pelos conservadores do Museu Militar do Porto, que observaram que um conjunto de soldadinhos de plástico em exposição no museu, que remontam a meados do século XX, começaram a apresentar um processo de degradação grave e acelerado.

Com o problema apresentado em mente, os presentes autores estabeleceram uma metodologia para a caracterização desses soldadinhos de plástico, que permitisse a identificação dos polímeros, dos seus aditivos, e dos produtos de degradação. A metodologia compreendeu a microscopia estereoscópica e microscopia eletrónica de varrimento de pressão variável (VP-SEM-EDS) para reconhecimento da micromorfologia, a espectroscopia de infravermelho com transformada de Fourier com reflexão total atenuada (ATR-FTIR) para a identificação do polímero, a ressonância magnética nuclear (^1H e ^{13}C RMN) para a identificação dos seus aditivos e a micro-difração de raios X (Micro-XRD) para identificar os produtos de degradação com uma estrutura cristalina.

Com esta metodologia de análises complementares, foi possível determinar a composição dos soldados de plástico como sendo constituída por acetato de celulose com fosfato de trifênio e ftalato de dimetilo como principais aditivos, e eflorescências cristalinas de fosfato de trifênio como produto de degradação. Esta metodologia mostra-se adequada para uma caracterização detalhada de artefactos de plástico em ambiente museológico.

Palavras-chave

Artefactos plásticos; Estudo multi-analítico; Acetato de celulose; Fosfato de trifênio; Ftalato de dimetilo

Introduction

Nowadays, plastics, a mixture of polymers and other substances added to improve their properties [1-2] are extensively present in numerous modern art museum collections worldwide. Unfortunately, many man-made mouldable polymeric materials are relatively short-living compared to other materials found in historical collections, such as wood, stone, parchment, paper and bone. Whereas the ageing and degradation of a plastic artefact in non-museum circumstances can be tackled through replacement, degradation in a heritage context takes with it the importance of originality and cultural significance.

In the specific case of plastic objects present in museum collections, the symptoms of initial degradation in this type of objects are not fully recognized until the first visible signs of advanced stage of degradation occur, such as changes in colour and gloss, shrinkage, deformation and the appearance of cracks [3]. Plastic degradation, once initiated, cannot be prevented, stopped or reversed, but sometimes it may be slowed down. The technological advances in several areas used to characterize this type of materials, do not yet allow to predict or determine their stability along the time in a museum environment [4].

Physical, chemical and biological factors, alone or together, can contribute to the plastic accelerated degradation. Physical factors mainly involve the migration of the additives, besides the environment interactions that can cause brittleness or warping. Chemical factors, due to the interactions of plastic with oxygen, ozone, water, air pollutants and radiation, can cause severe changes to the polymer matrix or their additives, causing a great number of physical alterations in them and ultimately leading to their total degradation [5]. The biodeterioration promoted by microorganisms, especially fungi and bacteria that develop in the museum environments, causes severe surface alterations in the objects, causing stains or colour changes, leaving characteristic odour or even penetrating in the polymeric matrix, leading to their total decomposition [6-9].

The accelerated degradation of plastic artefacts in museums also raises concerns about public health and indoor pollution. The acidic by-products produced during cellulose acetate and cellulose nitrate degradation and the emission and migration of toxic additives, are examples to consider [10-16]. Besides their adverse health effect, the acidic by-products and the emitted additives are potentially hazardous to nearby artefacts, because they act as catalysts in the degradation processes [17-19].

The detailed characterization and identification of plastics in museum context, is therefore essential to evaluate the longevity of this kind of materials, which will allow to establish adequate storage conditions and to inform correct conservation practices [4, 20-21].

Several instrumental analytical techniques can be used to identify and characterize polymers and their additives, such as pyrolysis-gas chromatography-mass spectrometry

(Py-GC-MS), vibrational spectroscopy (FTIR or Raman) and nuclear magnetic resonance (NMR) [1, 22-24]. Preferably, the characterization methods should be non-destructive or minimum invasive for the objects to be analysed and whenever possible executed *in situ* since many objects cannot be transported out of the museum collection because of their size or for safety reasons. Techniques with quick response times and ease of use facilitate routine analysis of objects prior to conservation treatment [21, 25-26]. Nevertheless, the choice of complementary analytical techniques and number of analysis is frequently dependent on laboratory equipment facilities and research budgets.

This research was prompted by an urgent call from the Oporto Military Museum regarding a severe degradation process of a set of painted plastic toy soldier figurines (more than 10%) dating to the middle of the 20th century.

The manufacture of injection-moulded cellulose acetate toys was common, and previous studies have shown that this kind of material suffers several complex deterioration processes in the course of time [4, 20, 22, 27, 28].

The fast degradation of cellulose acetate is due to the possible release of acetic acid, diphenyl phosphate and phenol [29]. Diphenyl phosphate is a strong acid that can catalyse the deacetylation of cellulose acetate [30].

For the study of their material and degradation/alteration products an analytical procedure was set up, compromising always as possible minimum-invasive and non-destructive techniques. A combination of stereoscopic microscopy, VP-SEM-EDS, Micro-XRD, ¹H and ¹³C NMR and in-situ ATR-FTIR was used to identify and characterize the polymeric matrix and their additives, as well as crystalline efflorescence present on the surface of the toys.

Experimental

Toy soldier figurines

The Oporto Military Museum houses one of the biggest collections of toy figurines with over 12500 pieces made of lead, plastic and wood chip paste. Among these, some of the 1200 plastic figurines from S.E.G.O.M. (Société d'Édition Générale d'Objets Moulés), made in the 50's-60's of the past century started to present visible degradation symptoms with cracking and crystalline efflorescence. These figurines with 5 cm height are all from the same period and type and were produced by injection molding in a single operation, being after painted. The figurines showcases have no temperature and humidity control nor other type of environmental control (namely gas adsorbents/filters). For the present research 6 soldier figurines were selected for analysis (Figure 1), which presented different conservation condition, such as variable amount of crystalline efflorescence, loss of surface painting, deformation and appearance of cracks.



Figure 1. Example of the mid 20th century, S.E.G.O.M. toy soldier figurines studied presenting severe degradation (average height: 5 cm).

Characterization

To study these mid 20th century plastic objects we envisaged a methodology that comprised the combination of optical microscopy and VP-SEM-EDS to recognize the micromorphology, ATR-FTIR to identify the polymer and NMR to identify the additives, and Micro-XRD to identify the crystalline efflorescence.

Stereoscopic microscopy

The soldier figurines were observed under a LEICA M205C stereozoom microscope to allow a deeper insight on some micromorphological features of the surface, such as the crystalline efflorescence and depth of cracking.

VP-SEM-EDS

Variable Pressure Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectrometry (SEM-EDS) was employed for micromorphology characterization and elemental composition of crystalline efflorescence. Toy soldier figurines were analysed without any preparation and sampling on a Hitachi S-3700N scanning electron microscope coupled with a Bruker XFlash 5010 SDD energy dispersive detector in variable pressure mode at 40 Pa and backscattering mode at operating conditions of 20 kV accelerating voltage and 10 mm working distance.

ATR-FTIR

In situ Fourier Transform Infrared Spectroscopy was performed on an Alpha-R spectrometer from Bruker Optics, with an Attenuated Total Reflection (ATR) module, on the bottom of one figurine base that did not present any painting or coating, hence allowing the direct analysis of the plastic substrate. Bruker OPUS 6.5 software was used for processing the spectra. The IR spectra were plotted in the region between 4000 and 600 cm^{-1} , with 128 scans and spectral resolution of 4 cm^{-1} .

Micro-XRD

Micro-X-ray Diffraction (μ -XRD) was used for the identification of crystalline phases directly on one toy soldier figurine that presented severe crystalline efflorescence, with no surface preparation, using a Bruker AXS D8 Discover micro-diffractometer with a one-dimensional Lynxeye detector, a Goebel mirror and a laser-video sample alignment system and motorized XYZ stage. Diffractograms were obtained in the range 5° to 75° 2θ , with step size of 0.05° , with a recording time of 2s per step. Diffraction data were registered using Cu K α radiation at 40 kV and 40 mA, with the incident beam collimated to 1mm diameter. For the identification of crystalline phase, the Bruker EVA software with International Centre for Diffraction Data Powder Diffraction Files (ICDD PDF) was used.

NMR spectroscopy

For the NMR analysis, two approaches were devised:

- a) collection of detached efflorescence crystals (4-6 mg) from the toy soldier figurines and solubilisation in 1 mL of 99.96 % deuterated methanol, CD_3OD (Euriso-top, France);
- b) preparation of solutions by the leaching technique. A small area of the object (typically 1 cm^2) on the bottom of the figurine base (same area analysed by ATR-FTIR) was washed (percolated) with approximately 1 mL of 99.96 % deuterated methanol, CD_3OD (Euriso-top, France). The percolate obtained was immediately placed in a NMR tube for further analysis.

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III HD 400 spectrometer at 400 MHz. ^1H shifts are reported relative to the ^1H signal of CH_3OH ($\delta=3.31$ ppm) reference. ^{13}C shifts are reported relative to the ^{13}C signal of CH_3OH ($\delta=49.00$ ppm) reference.

Results and Discussion

Stereoscopic microscopy (SM) and VP-SEM-EDS

SM shows that the efflorescences that are protruding from the figurines polymeric structure are colourless and needle-like shape crystals (Figure 2). SEM allowed further insight by allowing to observe that the morphology of the crystals varies from needle-like shape at lower magnifications to prismatic at higher magnifications (Figure 3). EDS analysis reveals that the crystals are essentially composed of carbon (C) and phosphorous (P). Furthermore, SEM-EDS did not reveal any presence of microbial contamination in the surface of the figurines.

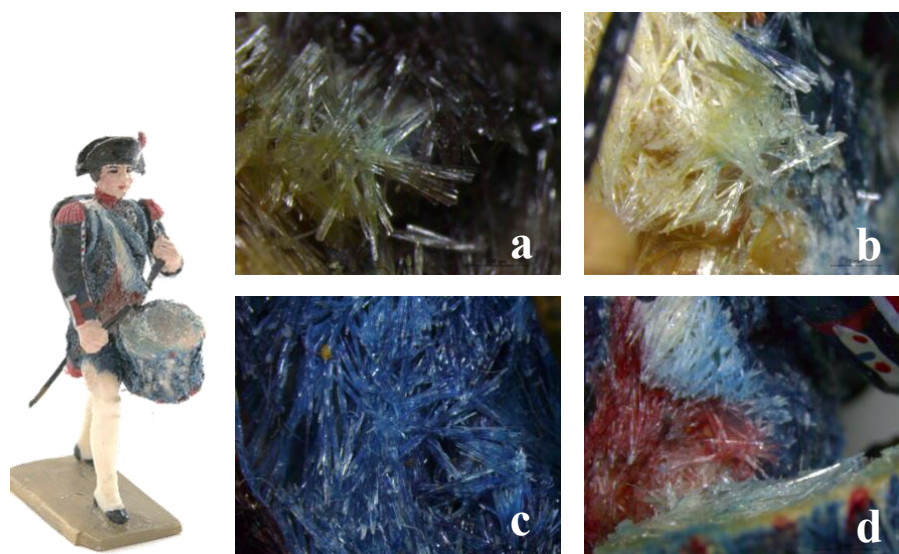


Figure 2. Detail of crystal structures morphology observed by stereozoom microscope directly on the toy soldier figurines, drum (*a, b*) and jacket (*c, d*).

ATR-FTIR

ATR-FTIR is a useful, non-destructive tool capable to identify and classify polymers from a wide range of sources and also some additives.

The ATR-FTIR spectra (Figure 4) show three strong patterns of bands found in saturated molecules, consistent with cellulose acetate, and typically referred to as “rule of three”. The first band at 1749 cm^{-1} is due to carbonyl stretch of the ester group, while the second band at 1235 cm^{-1} is due to asymmetric stretching of C-C-O of the ester group. The last large band appearing at 1051 cm^{-1} is the result of asymmetric O-C-C bond stretching attached to the carbonyl carbon. In addition, smaller bands located at 1370 cm^{-1} are caused by methyl groups found in acetate esters [22]. Other smaller bands present at 1589 , 1488 , 1287 , 1187 , 1124 and 966 cm^{-1} suggest the presence of the additives triphenyl phosphate and dimethyl phthalate [31-32]. These additives are common plasticizers for cellulose ester plastics, and the triphenyl phosphate is also used as a flame retardant [2].

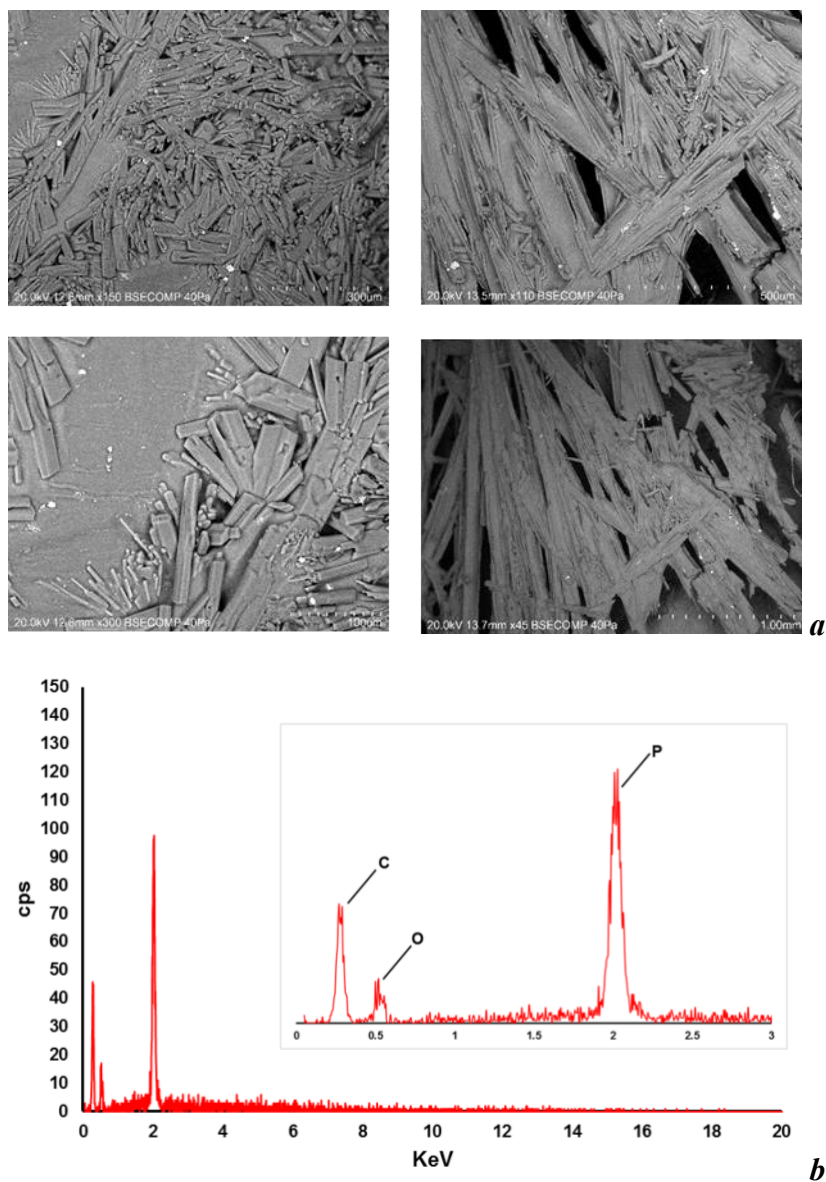


Figure 3. Detail of the crystal structures morphology observed by VP-SEM (in Backscattering mode) (a) and EDS spectrum of the crystals obtained directly on a toy soldier figurine (b).

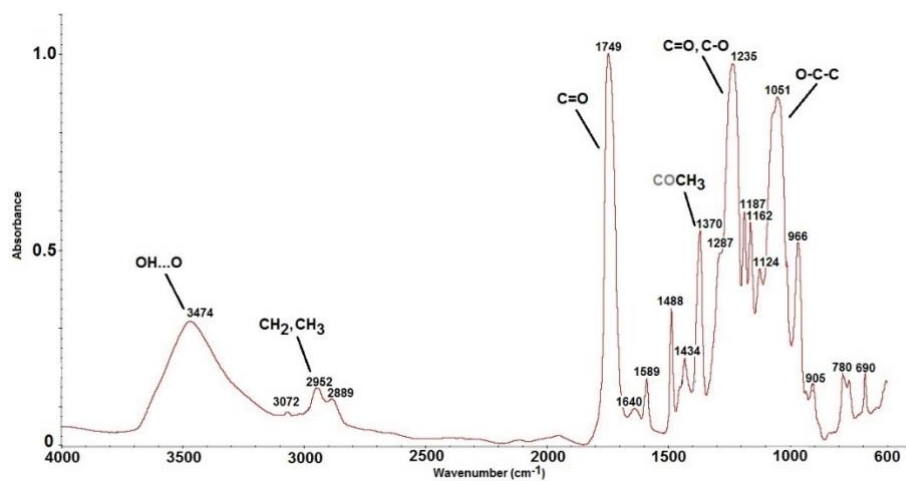


Figure 4. *In situ* ATR-FTIR spectrum of a toy soldier figurine.

Micro-XRD

X-ray diffraction performed directly on the crystal efflorescence's exhibits the typical XRD pattern of triphenyl phosphate (indexed reference PDF 26-1882) (Figure 5). These results are in line with the observations by SEM-EDS on the crystals that showed elemental compositions of C and P and those by ATR-FTIR, performed on the plastic matrix, which indicated the presence of two distinct additives, namely, triphenyl phosphate and dimethyl phthalate.

Similar crystal structures of triphenyl phosphate have previously been identified in heritage objects as part of the degradation of cellulose acetate [28, 33].

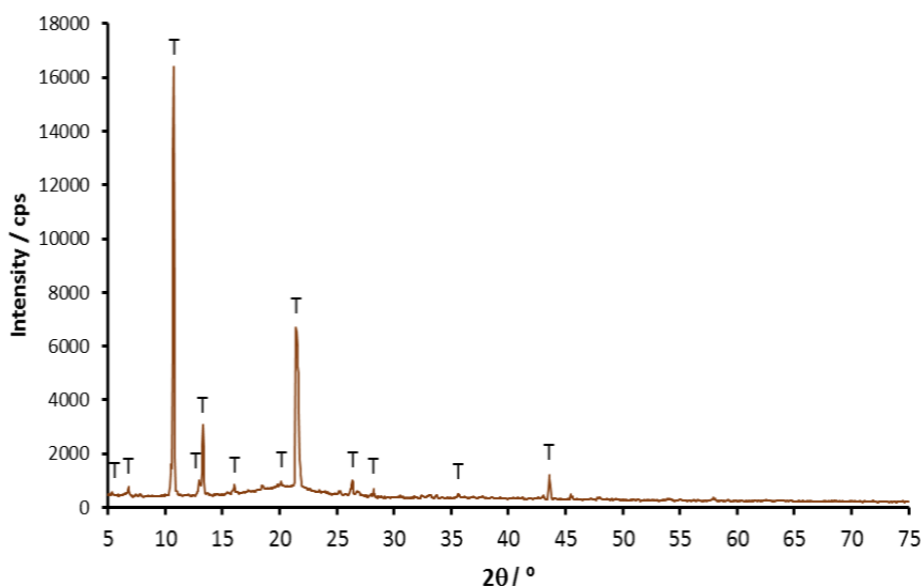


Figure 5. X-ray diffractogram of the crystals: T indicates triphenyl phosphate.

NMR

NMR is a powerful tool that identifies organic molecules, capable of identifying mixtures of polymer additives.

The ^1H NMR spectrum of object leachate (Figure 6) clearly presents a mixture of two major organic compounds, namely, triphenyl phosphate and dimethyl phthalate.

Triphenyl phosphate presents three magnetically equivalent groups, with five aromatic protons each, in a system $\text{AA}'\text{BB}'\text{C}$. The two *ortho* protons, resonate as a multiplet at $\delta=7.23\text{-}7.25$ ppm, the *meta* protons as a multiplet at $\delta=7.40\text{-}7.43$ ppm and the *para* proton as also a multiplet at $\delta=7.27\text{-}7.29$ ppm.

Dimethyl phthalate presents two doublets of doublets at $\delta=7.62$ ppm and $\delta=7.73$ ppm, in a system $\text{AA}'\text{BB}'$, assignable to four aromatic protons of the phthalate, and a singlet at $\delta=3.88$ ppm generated by a methyl group.

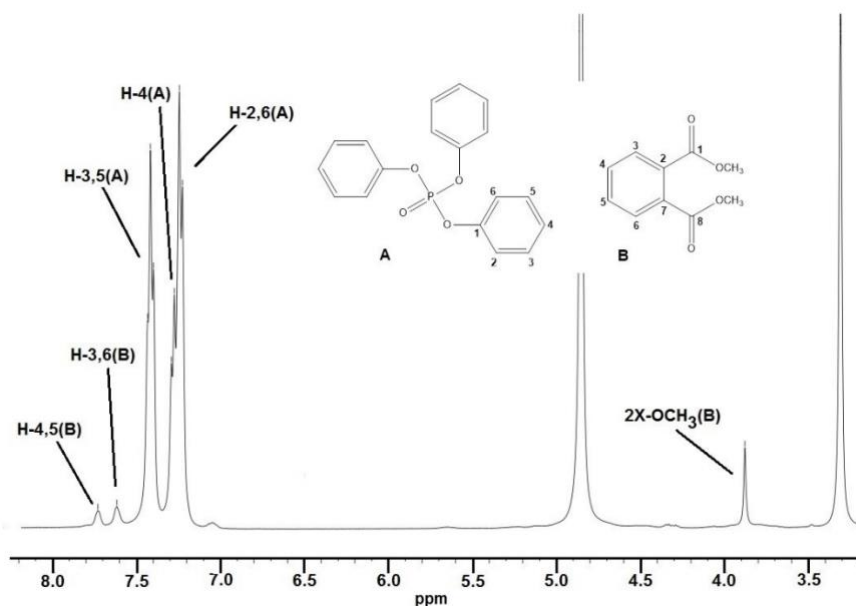


Figure 6. ^1H NMR spectrum of object leachate in CD_3OD .

All proton assignments are presented in Table 1.

The interpretation of ^{13}C NMR spectrum (Figure 7) allow the unequivocally assignment of all carbon signals (Table 1), confirming the presence of the additives detected in ^1H NMR. The ^{13}C NMR technique proved to also be a complementary tool for the polymer additives characterization.

Furthermore, the ^1H and ^{13}C NMR spectrum of object efflorescences, Figure 8 and Figure 9 respectively, identify clearly the needle shape crystals as triphenyl phosphate, in a state of high purity.

Table 1. ^1H and ^{13}C assignments of the additives, triphenylphosphate (A) and dimethyl phthalate (B), in CD_3OD .

Additive	Position	^1H δ (ppm)	^{13}C δ (ppm)
A	1	---	151.7
	2	7.23-7.25	121.1, 121.2
	3	7.40-7.43	131.2
	4	7.25-7.29	127.2
	5	7.40-7.43	131.2
	6	7.23-7.25	121.1, 121.2
B	1, 8	---	169.7
	2, 7	---	133.3
	3, 6	7.62	129.9
	4, 5	7.73	132.5
	2 x OCH_3	3.88	53.2

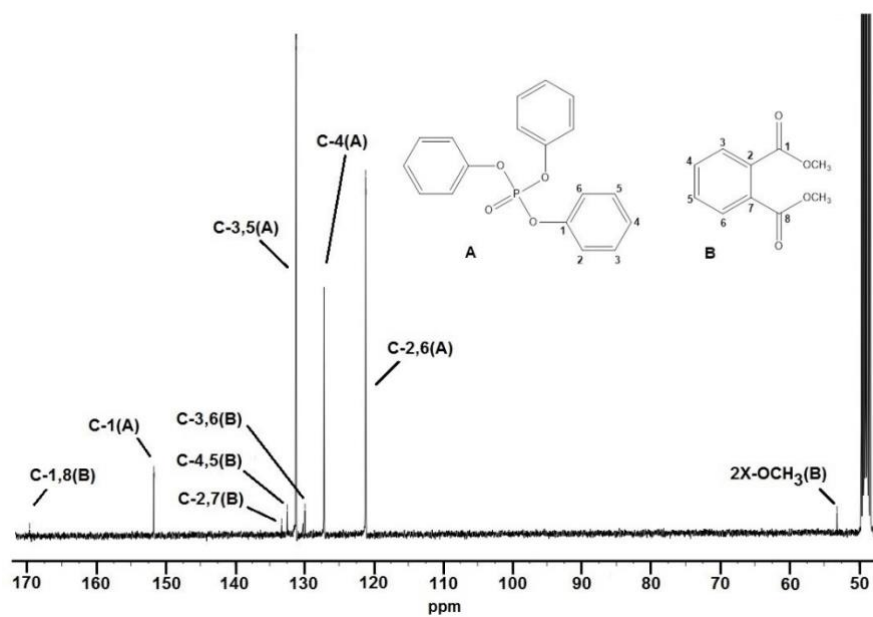


Figure 7. Tasks performed during fieldwork: *a*) cleaning of structures; *b*) laser scanning.

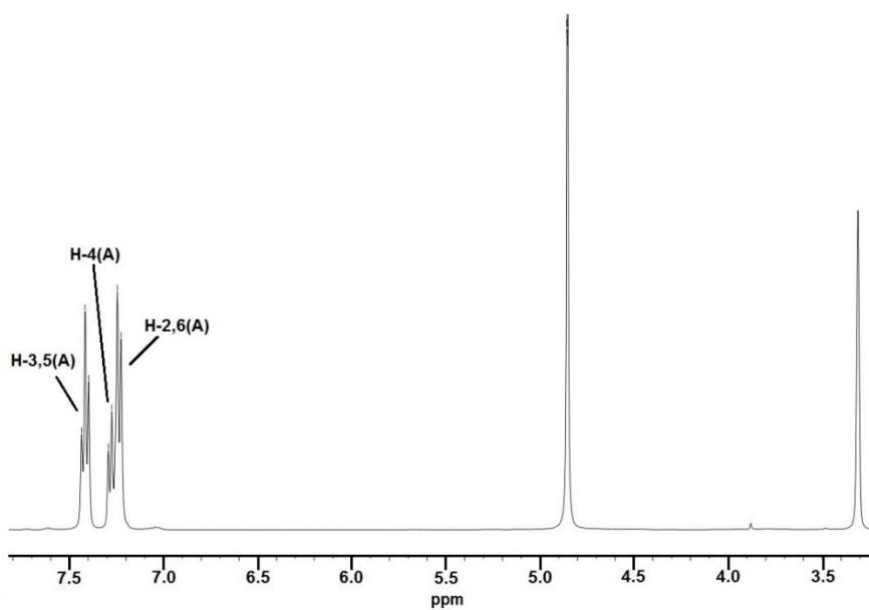


Figure 8. ^1H NMR of object efflorescences in CD_3OD .

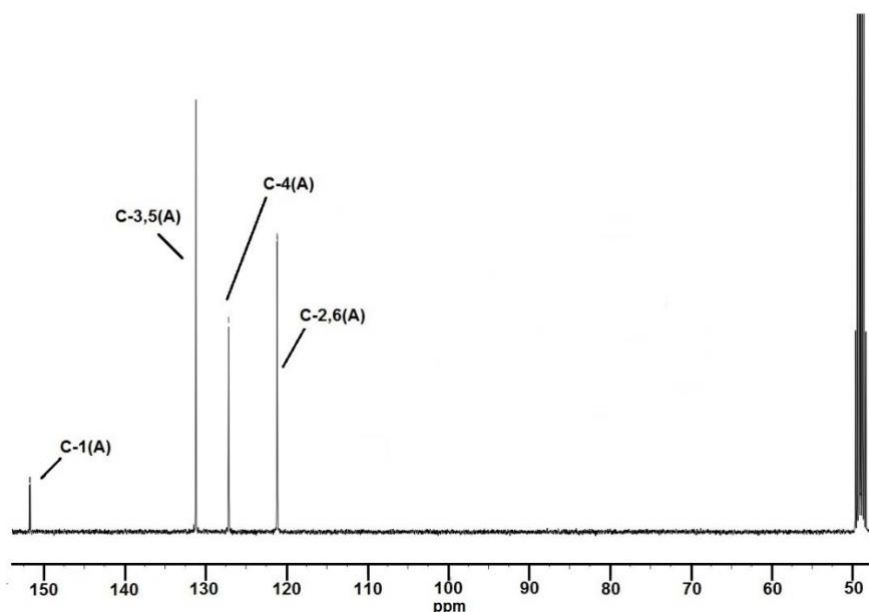


Figure 9. ^{13}C NMR of object efflorescences in CD_3OD .

Conclusion

The present multi-analytical study allowed the identification of the polymer used for the manufacture of the plastic toys, cellulose acetate, two additives, dimethyl phthalate and triphenyl phosphate, and the identification of a very pure crystalline efflorescence composed by one of the additives, triphenyl phosphate. The in situ attenuated total reflection-fourier transform infrared spectroscopy (ATR-FTIR) analysis allowed the identification of the polymer nature and the indication of the two additives. The ^1H and ^{13}C nuclear magnetic resonance (NMR) analysis allowed an unequivocally identification of the additives and showed the very pure nature of the crystalline efflorescence. The micro-XRD analysis allowed the characterisation of the crystallographic structure of the efflorescence, as triphenyl phosphate. The SM and SEM-EDS analysis allowed the morphological observation of the surfaces. Preventive conservation measures are being undertaken to prevent the fast degradation of this collection, including removal from the museum showcase of the toy soldier figurines that present this pathology and study of the optimal microclimatic conditions of the showcase including ventilation and acid vapours adsorbents.

Acknowledgments

The authors would like to thank the Oporto Military Museum (Museu Militar do Porto) and project THE SCREAM (POCI-01-0145-FEDER-031577) for the financial support through program POCI-FEDER-Alentejo2020 and to the research unit HERCULES Laboratory (grant no. UID/Multi/04449/2013). The authors fully acknowledge the anonymous reviewers and the editors of the journal by their valuable remarks, comments and corrections to the submitted version of the manuscript, which significantly contributed to the quality of the paper.

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RECEIVED: 2020.01.10

REVISED: 2020.11.02

ACCEPTED: 2020.12.09

ONLINE: 2020.12.15



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