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PY-GC-MS APPLIED TO THE IDENTIFICATION OF SYNTHETIC RESINS IN BRAZILIAN PAINTING

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ABSTRACT

Works of art are appreciated for their material and immaterial value. Restoring objects of art is a delicate procedure, mostly due to the irreversibility of the interventions. Hence, it is recommended to study the chemical composition of the object to avoid errors. The premise for restoring or conserving these objects is their physical preservation, i.e., it is advisable to avoid sampling and, when necessary, samples must be minute. The analytical techniques that fulfill these requirements are limited. Mass spectrometry (MS) is a versatile technique due to its hyphenation possibilities. Recently, it has being employed in the identification of natural and synthetic resins in works of art. Electron ionization (EI) is a powerful method of molecular fragmentation employed in the detection of volatile organic compounds by mass spectrometry. In this work, two micrograms (µg) of sample from a Brazilian contemporary painting were analyzed by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) technique. A microfurnace-type pyrolyzer was coupled to a gas chromatograph, using a non-polar capillary column. The electron ionization was achieved applying 70 eV electron energy. This technique is suitable for the analysis of material from objects of art, being specific, accurate and requiring minimal sampling. The synthetic resin diallyl phthalate (DAP) was identified by the Py-GC/MS technique.

1. INTRODUCTION

Artists of past times, such as renaissance painters, had access to a limited number of resources and materials to create their works of art. Some of these materials are waxes, gums, vegetal and animal oils, vegetal resins and organic and inorganic pigments. In the 20th century, an offer of newly developed synthetic materials erupted in the art shops, especially in Europe. Some brave modern and contemporary artists slowly incorporated in the production of objects of art these new materials, such as polymers, exotic metal alloys, adhesives and synthetic paints [1].

Chemical analyses of works of art produce valuable information to conservators and restorers. Since most interventions are irreversible, it is important to predict material compatibility before acting. The challenge is to find analytical techniques that are sensitive, multielemental and preserve the object, i.e. noninvasive and non-destructive techniques.

Recently, some analytical techniques aid in the identification of materials of art, such as x-ray fluorescence spectrometry [2] and Raman spectroscopy [3].

Mass spectrometry (MS) differs from spectroscopic techniques, such as nuclear magnetic resonance and Raman, for not utilizing light to identify compounds. Typically, MS is employed as a detection technique coupled to a separation technique, such as gas chromatography (GC).

The pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) technique requires only few micrograms (µg) of sample and present high sensitivity and specificity [4], characterizing a vast list of organic products used by artists, such as synthetic polymeric resins, natural varnishes and binders, proteins and dyes [5].

In this work, Py-GC/MS was used in the identification of the synthetic resin present in "Mandala da felicidade" (**Figure 1**), painted by Brazilian contemporary artist Sara Goldman-Belz. This painting is part of the collection of *Pinacoteca do Estado de São Paulo* and presents a drying problem, the media drips from the canvas, rendering impossible its public exhibition. One goal of this work is to provide restorers the chemical information needed to solve this problem successfully.

Figure 1: Mandala da felicidade, Sara Goldman-Belz

2. EXPERIMENTAL

2.1 Electron ionization

The MS technique is based on the detection of charged particles. The conversion of electrically neutral molecules to molecular ions (M^+) can be achieved utilizing a high-energy electron beam (50 – 70 eV), named electron ionization (EI). The fragmentation of the M^+ subsequent to ionization is characteristic to each compound present in the sample. To guarantee a majority of intramolecular fragmentation, the mass spectrometer is kept under vacuum (10^{-3} - 10^{-6} torr). Since most organic compounds ionization energies range from 5 to 15 eV, the excess energy from the electron source creates a multitude of ionization reactions.

2.1. Sample

Material from the painting was collected on a polyurethane board over several months (**Figure 2**). A few micrograms (2 -3 µg) were then transferred to the pyrolysis crucible adding a drop of methanol. The methylation process solubilizes the sample and promotes the formation of a homogeneous film and a uniform combustion.

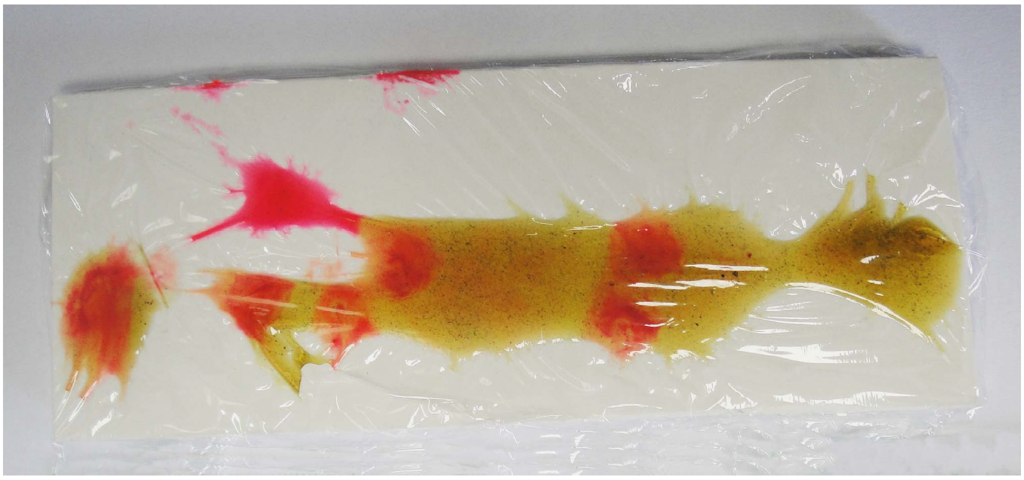

Figure 2: Sample from the painting "Mandala da Felicidade"

2.2 Instrumentation

The instrument used was a Frontier Lab microfurnace pyrolyzer mounted over a Shimadzu Co. GCMS-QP5000. The temperatures of the furnace and the interface were, respectively, 610 °C and 300 °C, with a pyrolysis time of 0.20 min. The GC furnace initial temperature was 40 °C (2 min) with a 10 °C min^{-1} rate and a final temperature of 350 °C (2 min). The column employed was nonpolar, 0.25 mm internal diameter, 0.25 µm thickness and 30 m length. The MS split was 1:150 and the m/z was scanned from 35 to 500 u.

RESULTS AND DISCUSSION

The chromatogram of the sample from the painting "Mandala da felicidade" is presented in Figure 3. The painting sample is heated during pyrolysis and its decomposition products are then separated in the GC column. The time in which they are eluted are represented in the abscissa. Each peak represents a different compound and the peak of interest is zoomed for better visualization. The analysis was performed in triplicate. Retention time and mass spectra for the pyrolysis products were the same.

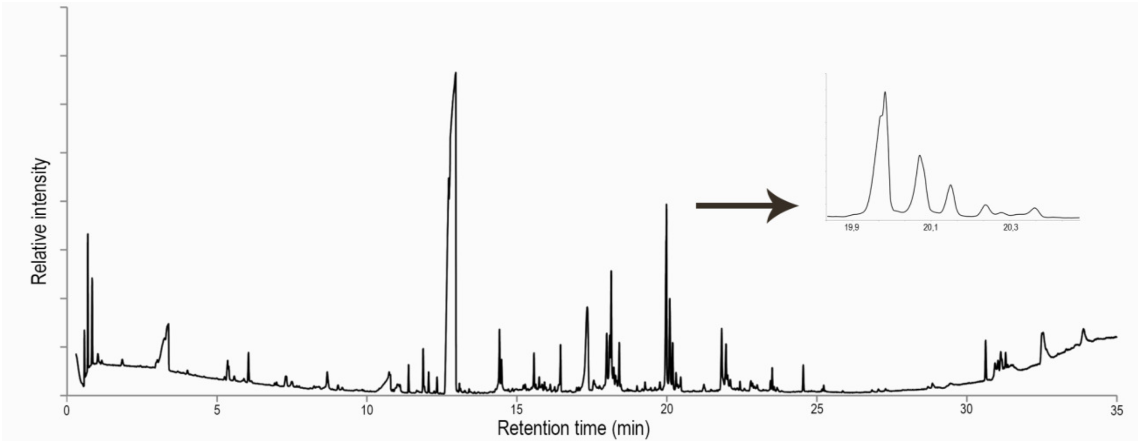

Figure 3: Chromatogram resulting from the pyrolysis of the painting sample

Subsequent to the chromatographic separation, the compounds are finally analyzed in the mass spectrometer and each generates a MS spectrum. The identification of compounds is based on a similarity search performed on a commercial library, available on the software coupled to the equipment. The compounds identified in the sample are listed on **Table 1,** IUPAC nomenclature is in parenthesis.

Table 1: Identification of compounds and retention time for the sample at 610 °C

Compound	Retention time (min.)
Azomethane (Dimethyldiazene)	1:07
Allyl formate	1:20
Malic acid (2-hydroxybutanedioic acid)	5:30
Benzoic acid	10:62
2-Bromo-1-phenyl-1-propanone	11:35
Phthalic anhydride (2-Benzofuran-1,3-dione)	16:40
2-Heptene	18:14
Diallyl phthalate (Bis(prop-2-enyl) benzene-1,2-dicarboxylate)	20:05
Adipic acid (Hexanedioic acid)	24:30
Cyanoacetic acid (2-Cyanoacetic acid)	30:50
Dipropyl phthalate (Benzene-1,2-dicarboxylic acid)	33:78

An azo pigment was identified, confirming the predilection of contemporary artists for the synthetic organic pigments, namely azo and phthalo. The presence of acetone (1-propanone, C_3H_7O) indicates a solvent or an ageing/degradation product. The substance of interest though is the synthetic resin diallyl phthalate (DAP) ($C_{14}H_{14}O_4$) (**Figure 4**), a thermosetting polymer used since the 1950's as molding agent. Allylic resins present great post-mold stability and adherence to metals. Mass spectrum (**Figure 5**) fragments confirms the identification of DAP molecule, as reported by Tsuge [5].

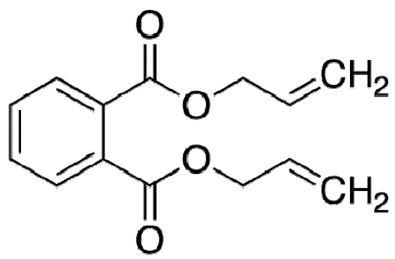

Figure 4: Chemical structure of diallyl phthalate

It is noteworthy that no markers for natural products were identified, such as proteins, oleic acids, shellac, dammar or terpenes [6]. Neither were identified synthetic resins normally used in the art manufacture, such as Paraloid B72, Laropal K80 and Regalrez [7, 8].

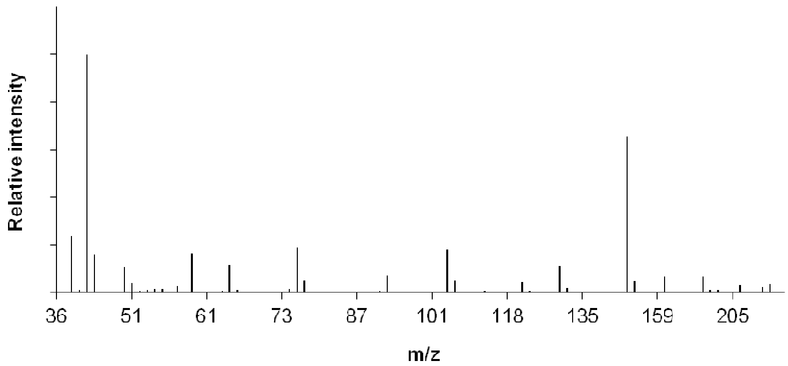

Figure 5: Mass spectrum of diallyl phthalate

CONCLUSION

The Py-GC/MS is suited for the analysis of objects of art presenting great sensitivity, specificity and requiring no sample preparation.

The difficulty in drying, mentioned in the beginning of this work, could be related to the formation of polar groups (organic acids) in a non polar media, which causes exudation [9]. This might be caused by the use of non conventional art materials, whose degradation mechanisms are not yet established.

More studies will be conducted, employing vibrational molecular spectroscopy, for the confirmation of molecular structures, and scanning electron microscopy, for the visualization of paint material distribution.

This work presents the first stage of a 4-year graduate project, aiming to achieve a general observation of sample composition. Therefore, methodology validation and complementary analyses are yet to be performed.

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REFERENCES

1. M. Schilling, S. Lake, E. Steele, S. Q. Lomax, “Modern science and contemporary paintings”, *The Getty Conservation Institute Newsletter*, **17 (3)**, pp. 4-10 (2002).
2. M. Mantler, M. Schreiner, “X-ray fluorescence spectrometry in Art and Archeology”, *X-ray spectrom.*, **29**, pp. 3-17 (2000).
3. R. J. H. Clark, “Raman microscopy as a structural and analytical tool in the fields of art and archeology”, *J. Mol. Struc.*, **834**, pp. 74-80 (2007).
4. A. Shedrinsky, N. S. Baer, “The application of Analytical Pyrolysis to the Study of Cultural Materials”, in: T. P. Wampler (ed.), *Applied Pyrolysis Handbook*; CRC Press, Florida, USA (2007).
5. S. Tsuge, H. Ohtani, C. Watanabe, “Pyrolysis-GC/MS data book of synthetic polymers”, Elsevier, Amsterdam, AN (2011)
6. D. Scalarone, O. Chiantore, “Py-GC/MS of Natural and Synthetic Resins”, in: M. P. Colombini, F. Modugno (eds.), *Organic Mass Spectrometry in Art and Archeology*, John Wiley & Sons, Chichester, UK (2009).
7. T. Learner, “The Analysis of Synthetic Paints by Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC/MS)”, *Studies in Cons.*, **46 (4)**, pp. 225-241 (2001).
8. C. A. Menke, R. Rivenc, T. Learner, “The use of direct temperature-resolved mass spectrometry (DTMS) in the detection of organic pigments found in acrylic paints used by Sam Francis”, *Int. J. Mass Spectrom.*, **284**, pp. 2-11 (2009).
9. I. A. T. Bronken, J. J. Boon, “Hard dry paint, softening tacky paint, and exuding drips on *Composition* (1952) by Jean-Paul Riopelle”, in: K. J. van den Berg, *Issues in contemporary oil paint*, Springer, Cham, Switzerland (2014).