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Investigation of turquoise imitations and treatment with analytical pyrolysis and infrared spectroscopy

Bettina Schwarzinger, Clemens Schwarzinger*

Institute for Chemical Technology of Organic Materials, Johannes Kepler University, Linz, Austria

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ABSTRACT

Turquoise is an opaque mineral with a typical blue green color used in modern and traditional jewelry. As always when there is a higher demand for a material than supply, there is a vital interest for optimizing the product yield (reuse of waste), improving lower quality material or even producing imitations. Very often organic polymers are used in this context and their identification is a challenge not easily accomplished with traditional gemological techniques. The application of infrared spectroscopy and analytical pyrolysis can reveal the true composition of various "turquoise" samples. Whereas the first technique is especially capable of differentiating between natural and synthetic minerals and identifying surface treatments such as wax or polyurethane coatings, pyrolysis is exceptionally well suited to trace not only the surface coatings such as wax, polyurethane or (meth) acrylates, but also to identify binders used in pressing mineral powder (e.g. melamine formaldehyde resins) or epoxy resins which are also used to impregnate porous, otherwise instable materials.

1. Introduction

Turquoise is an opaque mineral with colors from sky blue or blue green to yellowish green often with brown, black or metallic matrix spider webbing through the material. It is found in only a few places on earth, in dry and barren regions where acidic, copper-rich groundwater reacts with minerals containing phosphorous and aluminum. This process results a hydrous phosphate of copper and aluminum ($CuAl_6(PO_4)_4(OH)_8$. $4H_2O$) [1]. It is long known as decorative stone (Pliny the Elder described it as "callaina" in his naturalis historia around 80 A.D.) [2], has already been used in jewelry in ancient Egypt around 3200 B.C. and can also be found in the famous mask of Tutankhamun [3]. In the south western part of the USA turquoise is found in several localities mainly in Nevada and Arizona and typically used in jewelry of many native Indian tribes, such as the Pueblo, Navajo, Hopi or Zuni [4]. Other famous locations where turquoise is found in larger quantities are Iran (formerly Persia), China, Mexico, or Australia [5].

Whenever there are valuable materials and a demand that is much higher than the natural supplies, people try to optimize the quality of lower grade natural materials or even use fake materials to imitate the genuine gemstone. In the case of turquoise several different steps of modification are known and classified by the CIBJO (the World Jewellery Confederation) into 5 groups: untreated natural material; impregnated with plastic; surface near-colorless waxing; Zachary treatment (colored and impregnated with a compound containing Potassium); and dyed [6]. To better understand those treatments one has to know that turquoise has a porous surface and can absorb moisture, sweat or other liquids that can alter its appearance or even destroy the stone. Thus, surface coating with wax is a widely accepted treatment, as it protects the stone against environmental influences, adds gloss and can easily be removed without damaging the stone (this treatment does not have to be disclosed). A polymer coating fulfills the same purpose, but is not easily removed (especially when done with thermosets) and thus has to be disclosed. Another way of adding value is to use the mineral powder that remains after cutting and grinding, and pressing it together with a thermosetting resin – these stones are generally labelled reconstructed or pressed turquoise. But there are also imitations of turquoise available, which means materials that are chemically different but look the same, such as dyed howlite, magnesite, gibbsite or fully synthetic products such as Viennese turquoise or Gilson turquoise [7–9]. The cheapest imitations available are just colored plastics.

In order to identify gemstones gemologists typically have only a very limited choice of instruments available, which in most cases are optimized for transparent gems. Refractive index, birefringence, dispersion, optical spectrum or inclusions − all of them are not of great help in the determination of non-transparent stones or their modifications. Density might help in some cases, but most interesting is the fact that people have been using pyrolysis unknowingly for quite some time

* Corresponding author.
E-mail address: clemens.schwarzinger@jku.at (C. Schwarzinger).

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Fig. 1. Turquoise samples analyzed in this study. The numbers refer to the descriptions listed in Table 1.

to determine several kinds of turquoise modifications: the tip of a hot steel needle is brought in contact with the gemstone in question and if it is made of plastic or impregnated with a polymer a characteristic smell can be observed. Pyrolysis-gas chromatography-mass spectrometry (Py-GC–MS) has already been successfully applied in other related fields, such as the investigation of amber [10], modern sculptures [11], oil paintings [12,13], traditional Asian lacquerware [14,15] or other cultural materials [16] so we believe in its potential for the characterization of polymeric materials used in combination with turquoise and likewise materials.

Thermally assisted hydrolysis and methylation-gas chromatography-mass spectrometry (THM-GC–MS) is a complementary pyrolysis technique, where tetramethylammonium hydroxide (TMAH) is added to the sample, which is subsequently pyrolyzed at a relatively low temperature [17]. It has been proven very valuable in the analysis of polar materials, including polar polymers, which might also be used as binder systems in turquoise composites.

In this study we have investigated various turquoise specimens, modified samples and imitations with analytical pyrolysis as well as infrared spectroscopy and compared the results in terms of scopes and