INVESTIGATION OF TURQUOISE IMITATIONS AND TREATMENTS WITH FTIR AND PYROLYSIS-GC-MS

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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 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 ($CuAl_6(PO_4)_4(OH)_8 \cdot 4H_2O$) [1].

Turquoise is rarely found in well-formed crystals, often it is an aggregate of microcrystals. If the crystals are packed closely together, the material has a finder texture and is less porous.

Imitation und Treatment

A number of turquoise imitations are found on the gemstone market. The first who produced an artificial imitation of turquoise were the Egyptians, later glass and enamel was used. Since 1890 Viennese turquoise is a misnomer for an imitation turquoise made by pressing precipitated aluminum phosphate which is then colored by copper oleate. In the 1970s the French company Pierre Gilson started producing “Gilson turquoise”. Dyed magnesite, calcite, howlite and dolomite were also observed as a turquoise substitute [2].

Because turquoise is a soft and brittle and also porous material it is often treated with epoxy resins, plastics or water glass. This treatment is more stable than waxing and oiling. Another method is to powder small turquoise pieces and mix it with a binding agent to get reconstructed turquoise.

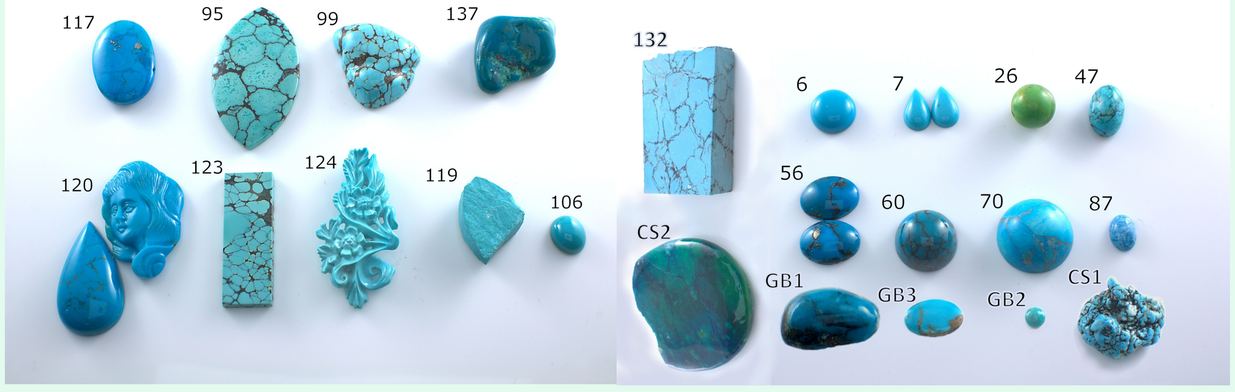

Fig. 1. Different turquoise samples analyzed in this study.

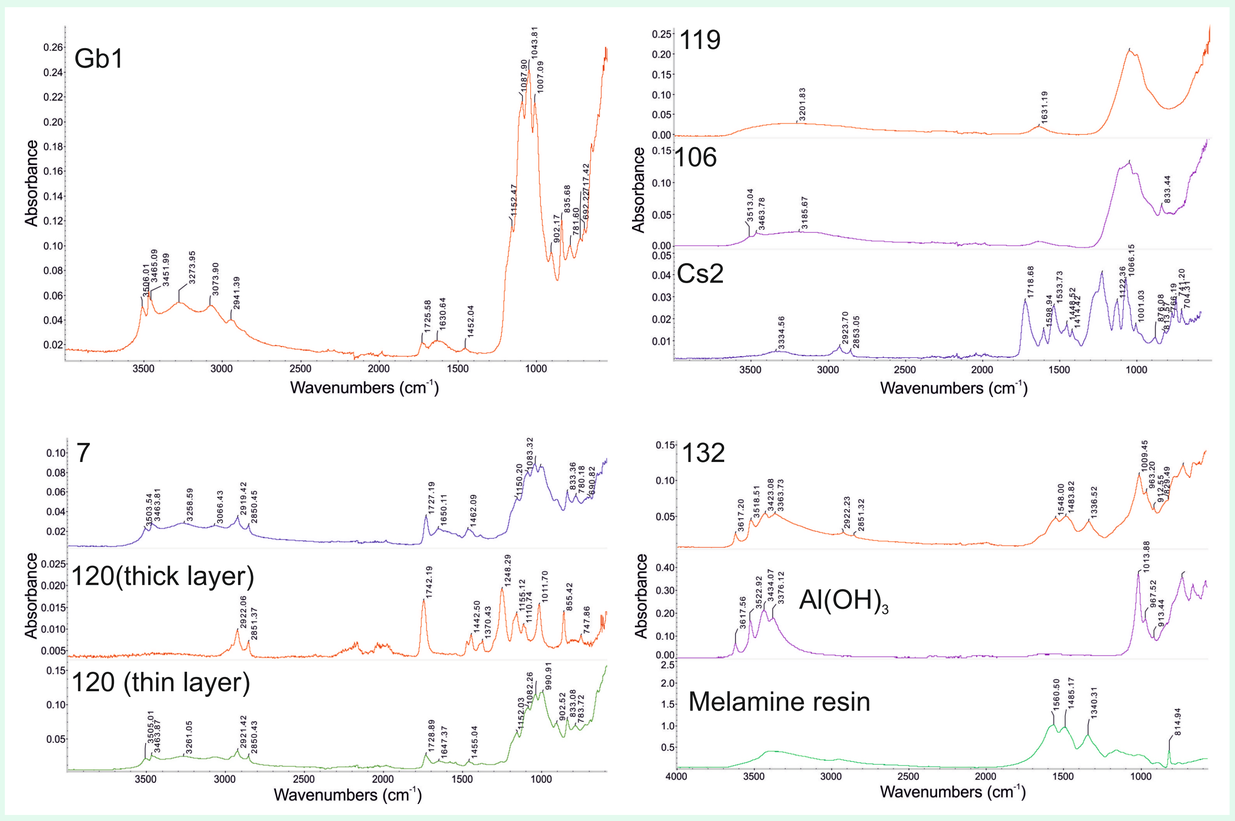

Fig. 2. FTIR spectra of natural, untreated turquoise (Gb1); imitations: Viennese turquoise (119), Gilson turquoise (106), and dyed magnesite (Cs2); modifications: wax coated (7), acrylate coated (120); reconstructions: gibbsite ($Al(OH)_3$) with melamine formaldehyde resin (132).

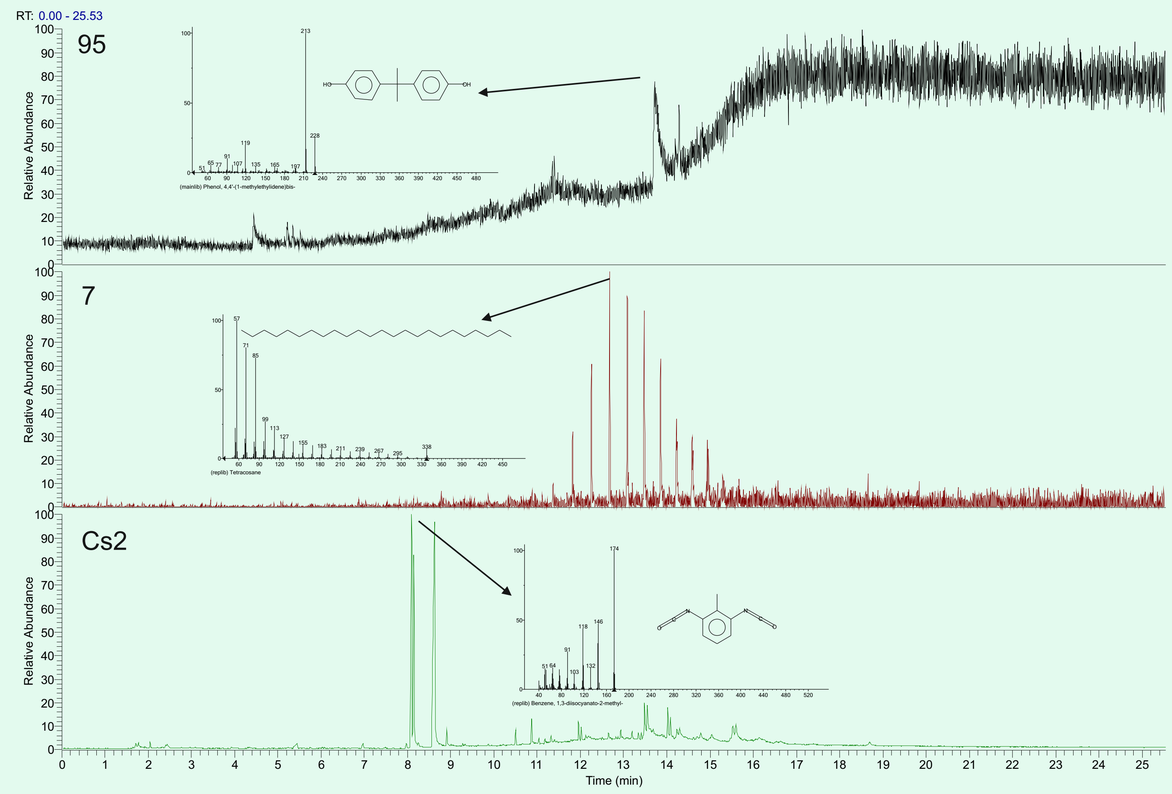

Fig. 3. Py-GC-MS of the black vein of a matrix turquoise (95), a wax impregnated specimen (7), and a polyurethane imitation (CS2) together with indicative pyrolysis products.

Results and Discussion:

Identification of natural turquoise can be done with FTIR (Fig. 2) mainly by verifying the presence of the γ OH streching vibration of water (3073 and 3274 cm^{-1}). A lot of treatments like oiling, waxing or polymer impregnation can also be indicated with this simple technique, but when it comes to the exhaustive identification of treatments, a lot of information can be gathered by pyrolysis-GC-MS. In this approach a tiny amount of sample (~ 50 µg) is heated to 700 °C and the volatile products are separated and identified with gas chromatography - mass spectrometry.

Figure 3 shows the pyrograms of the samples 95, 7, and Cs2. In the first sample bisphenol A, which is indicative of epoxy resins, has been found in the black veins. The second sample is a high quality turquoise which has been rubbed in paraffin wax to protect it against moisture and sweat and to improve its gloss. Sample Cs2 is a cheap pebble that was coated with a polyurethane varnish, revealed by the presence of toluene diisocyanates.

Figure 4 shows the analysis of sample 132, in this case tetramethylammonium hydroxide was added prior to pyrolysis, a technique known to be extremely sensitive for polar materials. Here an inorganic material (gibbsite, $Al(OH)_3$) has been mixed with a melamine formaldehyde resin to form a „reconstructed” turquoise.

Conclusion:

We could show that FTIR and pyrolysis-GC-MS are very powerful methods when it comes to the identification of turquoises which have been stabilized with organic materials or which are complete scams. This kind of information is hardly accesible with conventional gemological tools.

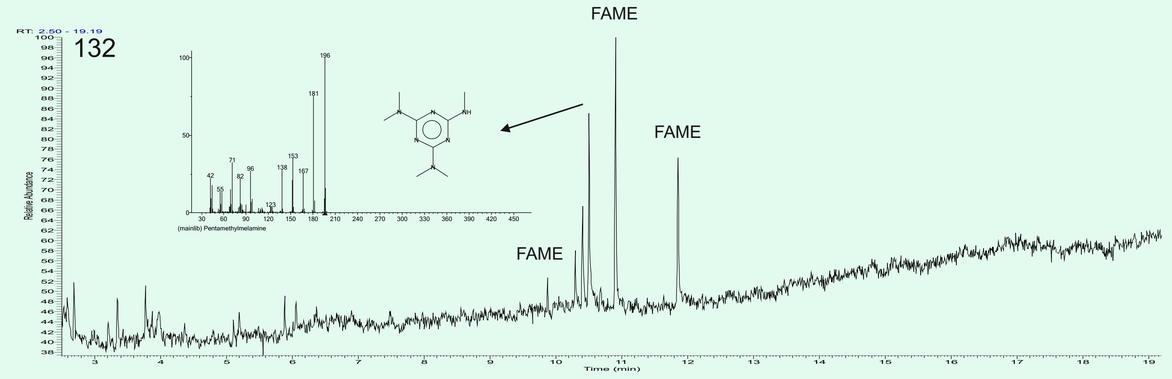

Fig. 4. THM-GC-MS analysis of a sample made of gibbsite and a melamine formaldehyde resin (132) showing tetra-, penta-, and hexamethylmelamine as well as fatty acid methyl esters (FAMEs).

References:

[1] W Eppler; Natural and Synthetic Turquoise; Gems&Gemology (1974) 226-229

[2] T Lind, K Schmetzer, H Bank; The Identification of Turquoise by Infrared Spectroscopy and X-ray Powder diffraction; Gems&Gemology (1983) 225-232

[3] J Celka, J Sejkora, I Macek, R Mailkova, L Wang, R Scholz, Y Xi; Raman and Infrared spectroscopic study of Turquoise Minerals; Spectrochimica Acta PartA: Molcular and Biomolecular Spectroscopy (2015) 173-182

Acknowledgment:

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