

Materials Characterization & Failure Analysis Laboratory

XPS Surface Analysis, WD-XRF, SEM/EDX, FTIR, Thermal Analysis (TGA, DSC, TMA), GC-MS, Optical Microscopy, Cross Section Analysis, Electrochemistry, Corrosion Analysis, Adhesive Bonding Failure Analysis, Mechanical Testing, Metallography, Fractography, RGA MS Contact Angle Measurement, UV-Vis, Reflectivity, Color Measurement, Density/Porosity

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SUBJ XPS and XRF Analyses and Optical Microscopy Examination of Tiles Said to Emit Odor When Wet

Summary

The principal results of the XPS and XRF analyses and the optical microscopy examination are:

- There is a surface glaze coating applied over a hard white layer about 0.5 mm thick on the baked clay substrate material of the tile.
- The surface was examined in many more areas than those whose images are shown in this report with similar results. All areas had numerous round holes in the glaze coating on the hard white layer.
- It is believed that the round holes are the result of the release of a gas with gas bubble formation as the coating material was cured or otherwise heated.
- The tile glaze is primarily an alumino-soda-calcia silicate.
- The hard, white layer material is primarily composed of SiO₂, Al₂O₃, ZrO₂, CaO, Na₂O, K₂O, and ZnO listed from most concentrated to least concentrated.
- Distilled water on the clean glazed surface beads up. When allowed to dry in laboratory air, water spots are formed, with heavy deposits at the perimeter of the water spot and thinner deposits in the interior of the water spots.
- The heavy perimeter deposit and the interior of the water spot have large

increases in carbon and sodium concentrations, with decreases of the surface silicon and aluminum concentrations relative to the outside of the water spot area analyzed.

- The 2.6 times increase in carbon in the heavy perimeter deposit compared to the outside the water spot clean glaze area is due to an increase in both the C – C bonds of organic material and of carbonates.
- The increase in the sodium in the perimeter deposit compared to the clean glaze area is due to some combination of hydrated sodium carbonate and sodium bicarbonate.
- The cause of the water spot deposits has to be that the glaze is not preventing the distilled water on the surface from dissolving organic materials and sodium carbonates from the underlying hard white layer material. This is because of the many round defects observed in the surface glaze. This formation of deposits on the glaze surface upon water exposure is certainly a serious fault with this floor tile. It is reasonable to believe that when a substantial surface area of the floor is wet, the dissolved materials from the underlying clay cause the wet clay smell that has been reported. The fact that water applied to the surface causes water spots as happens here is certainly a defect in appearance.

Samples and Background

A tile was received for examination and analysis to determine why the tile emitted a reported clay odor when wet. The floor tile is shown below.



Figure 1. The tile received at AME for examination is shown above. The tile was white with gray streaks through it as seen by the naked eye.

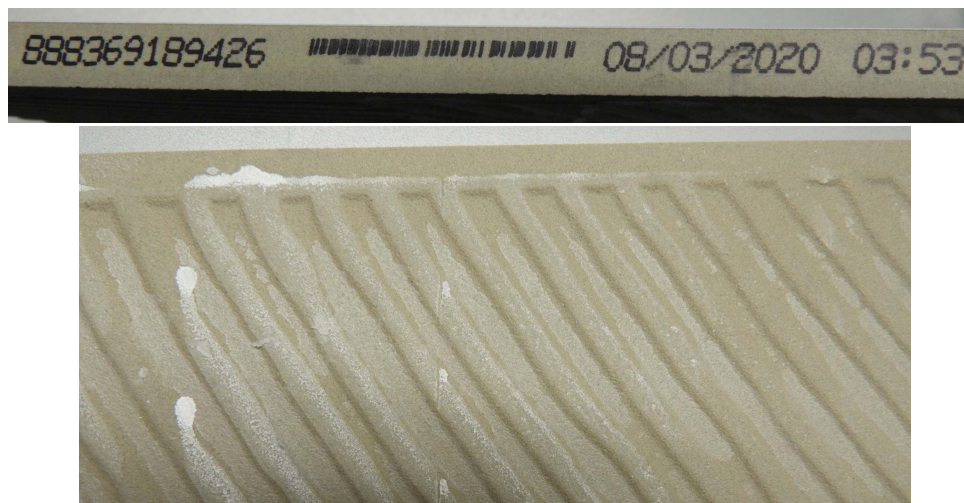


Figure 2. The edge of the tile is shown in the upper image and the back of the tile is shown in the lower image.

Tile Preparation

The tile was examined in a clean condition after wiping it with 91% isopropyl alcohol soaked towels and then again after allowing distilled water on its surface to dry in place. Distilled water on the surface of the tile beaded up and when these puddles of water dried, they left solid deposits on the surface of the tiles with the most dense deposits at the outer perimeter of the beaded water puddles.

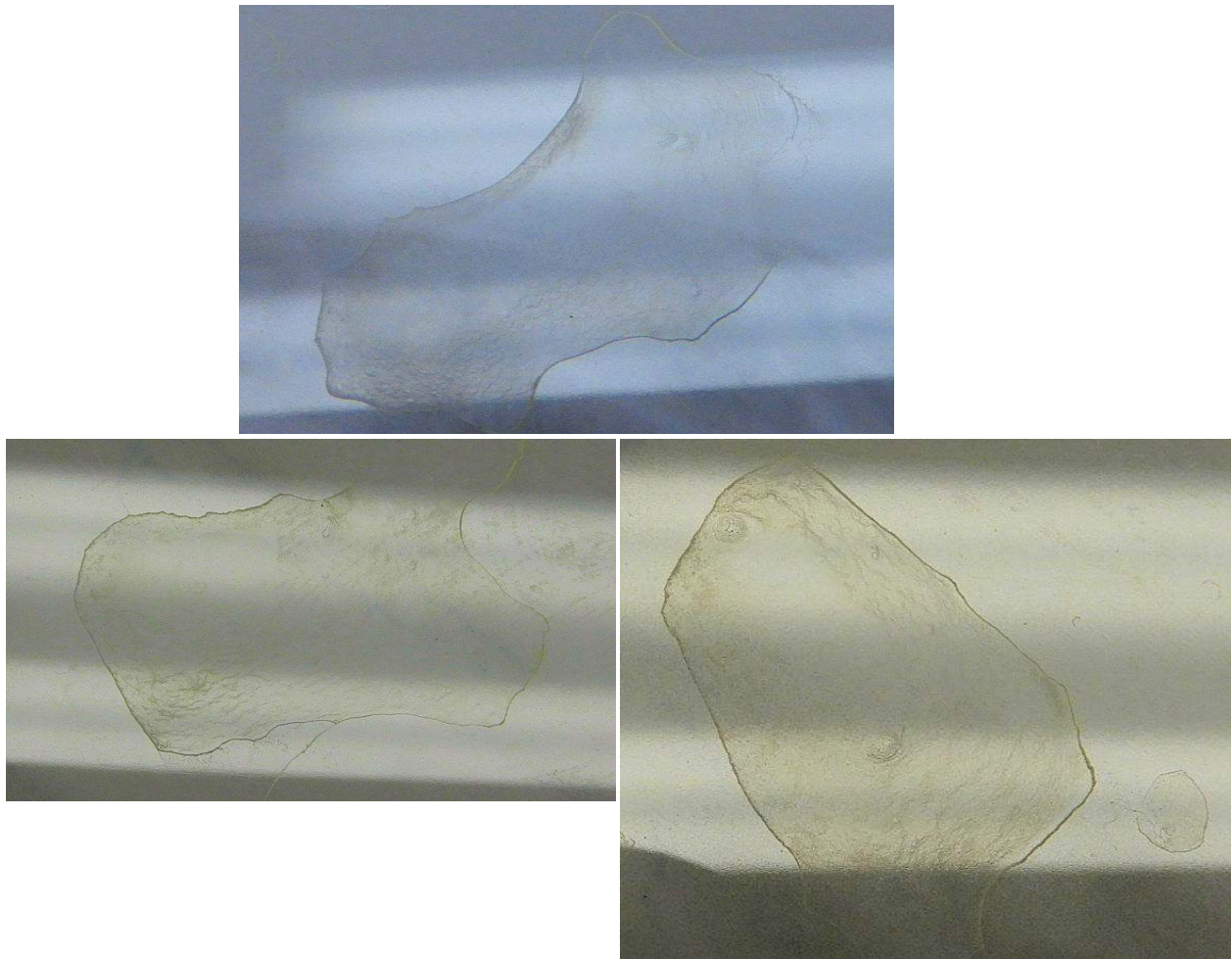


Figure 3. Some of the deposits on the surface of the tile after distilled water has dried on the tile surface are shown above. The water spots show up best in the reflected light from overhead lights, which limits the uniformity of the brightness in these images.

There is a white layer on top of the baked clay, which was polished to remove a substantial fraction of its total thickness. That fraction was close to one-half. The polished fragment of tile is shown below:

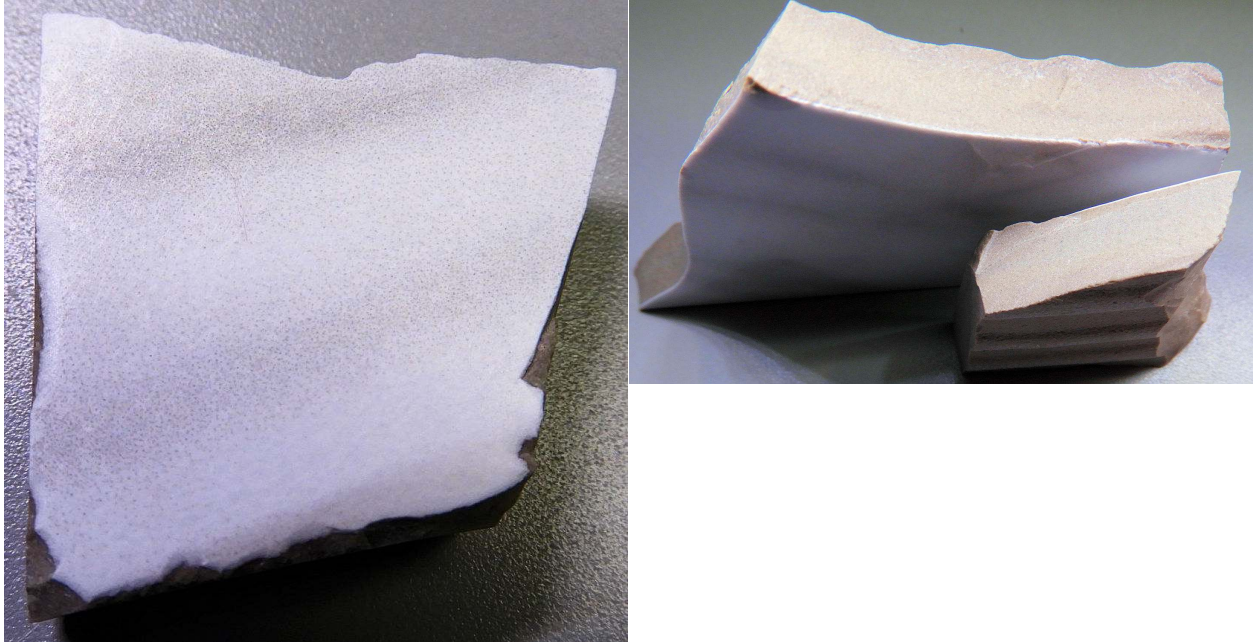


Figure 4. The tile fragment after polishing about half the hard, white surface overlayer away is shown above. The larger piece in the right image was not polished for comparison of the white layer before and after polish. It appears that at least half of the white layer was polished away. The surface became decidedly more dull after the thinner surface glaze was removed.

There are at least three layers of materials making up the floor tile. There is the baked clay base which makes up most of the tile thickness. On top of that, there is a thin white, very hard layer which is about 0.5 mm thick. Finally, there is a glossy glaze surface coating.

Optical Microscopy Examination

The tile surface was examined using an Olympus PMG-3 metallographic microscope equipped with an AmScope digital camera with a 5.1 MP Aptina Color CMOS detector (Figures 5-9, 12-15) or an AmScope inspection microscope using a 3.1 MP Aptina Color CMOS detector (Figures 10, 11). The images were acquired using the AmScope image acquisition program Version 3.7. The Olympus PMG-3 microscope has a polarized light capability and the Nomarski differential phase contrast capability.

Examination of the Clean Dry Tile

The tile surface was initially examined as-received. Then it was re-examined after wiping the surface with 3 towels soaked in 91% isopropyl alcohol (IPA). There were no substantial changes in the nature of the images acquired. The images shown here are those made after cleaning the surface with the IPA wiping.

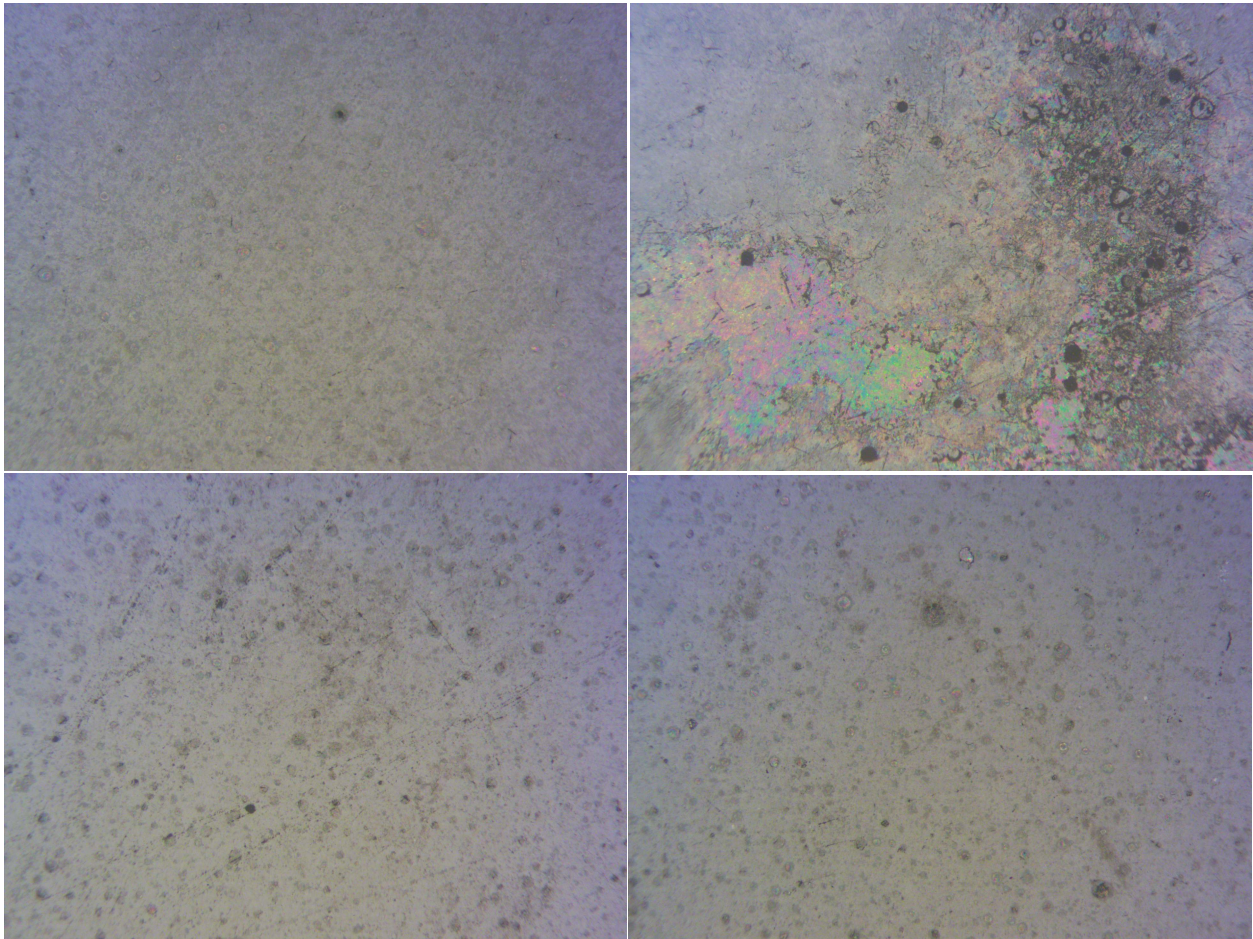


Figure 5. These images were made using reflected white light at an as-printed magnification of 35.82 times.

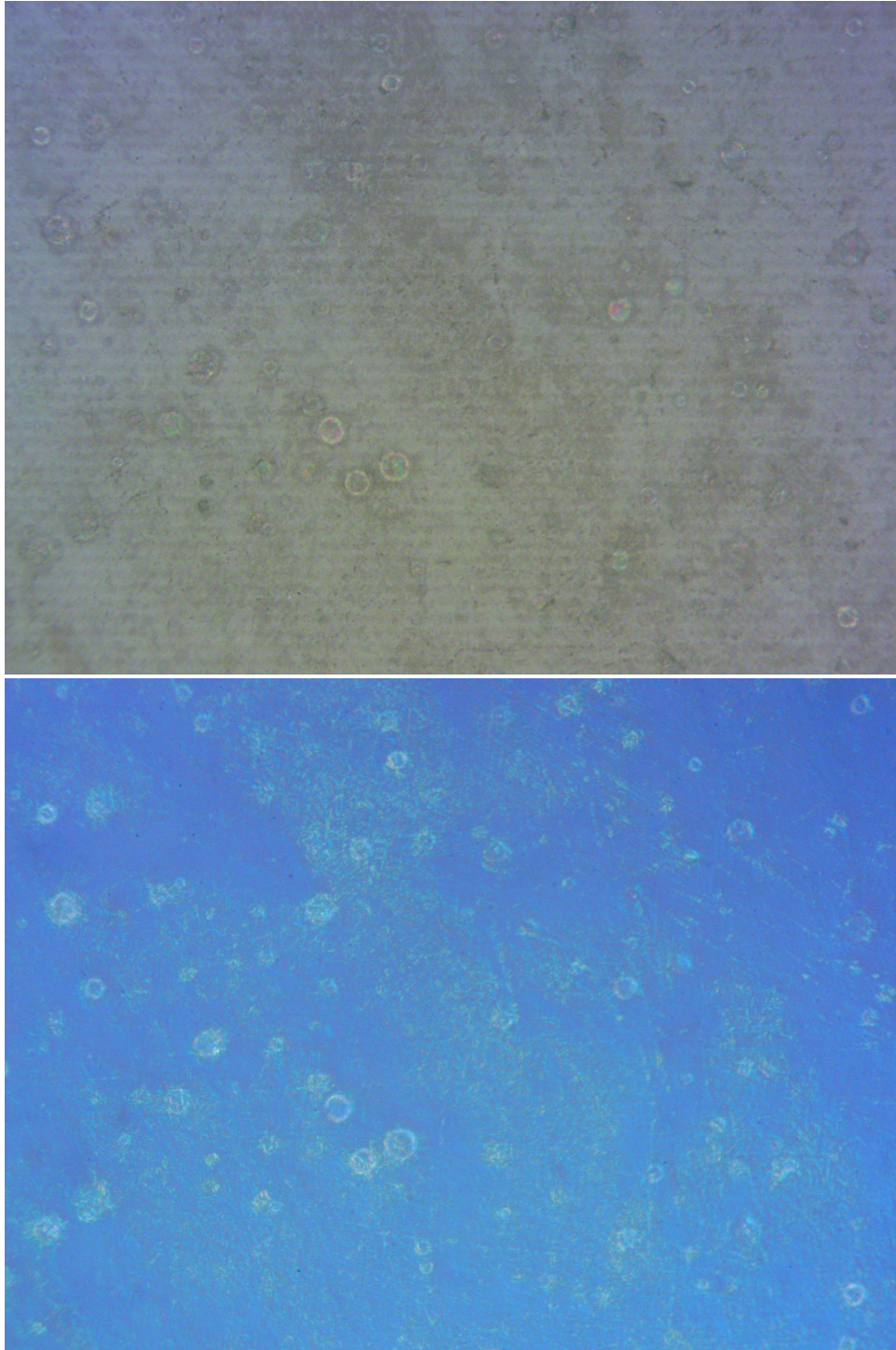


Figure 6. The tile surface is shown with white reflected light in the upper image and with polarized light in the lower image. The as-printed magnification is 110.85 times. Note the many very round features, which show up in better contrast in the polarized light image. The white, hard overlayer has a glossy coating on it which when cured appears to have emitted gas bubbles which formed very round holes in the coating.

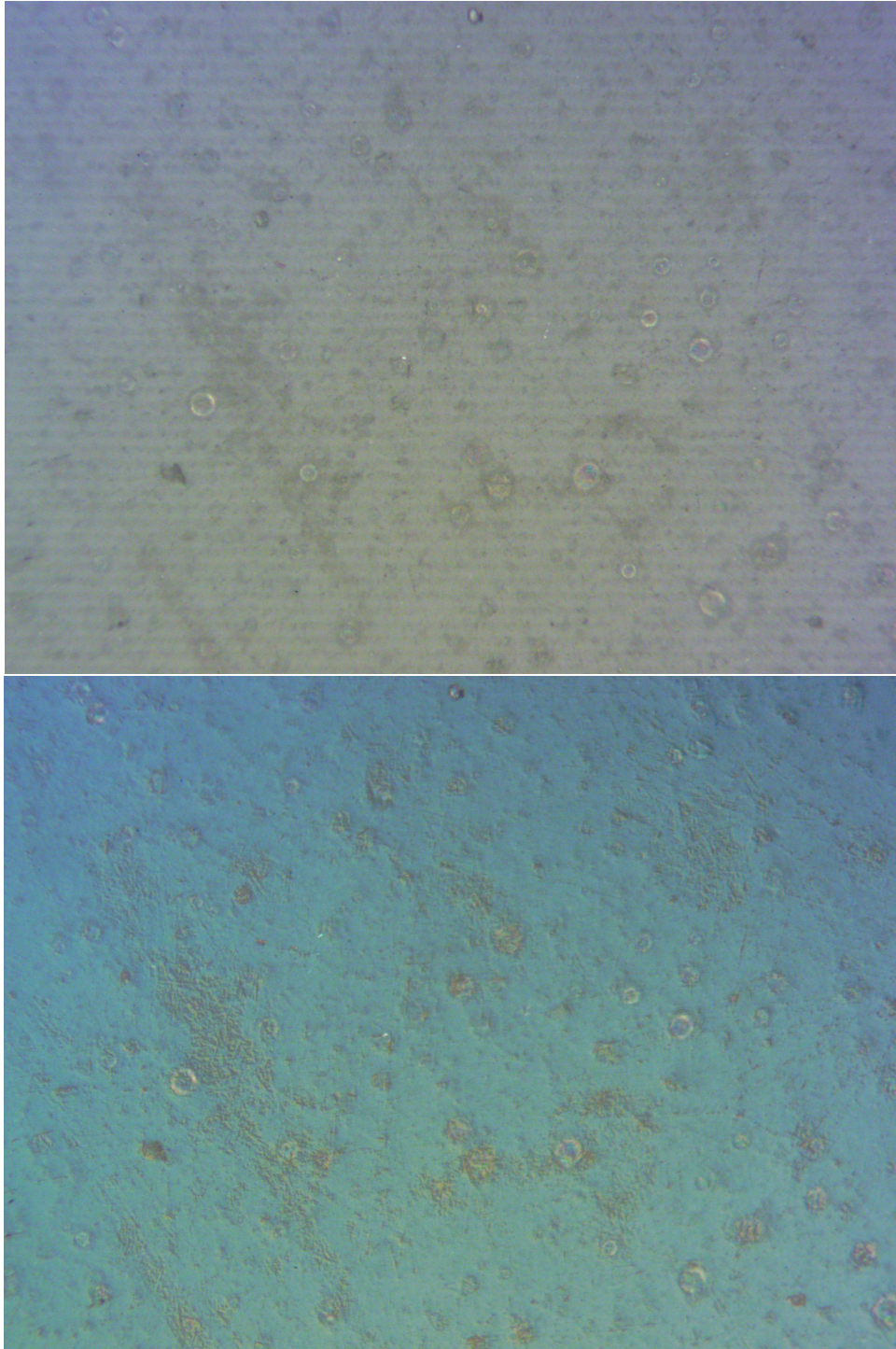


Figure 7. Another example of the round features in the glossy surface coating on the tile is shown here with the white light image above and a polarized light image below. There is also a blue polarized light image of this area that makes the holes in the coating look like those in Figure 6. The as-printed magnification is again 110.85 times.

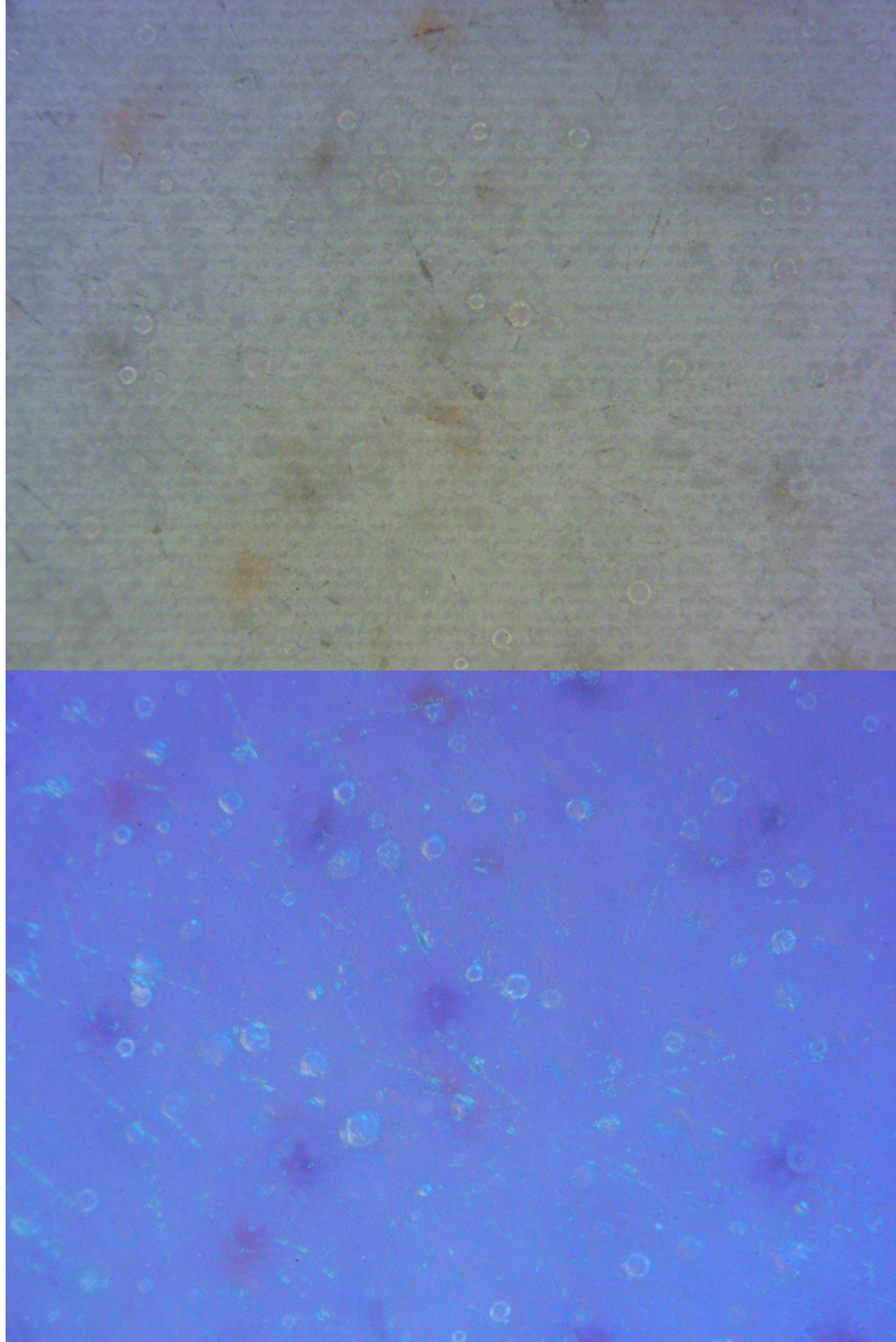


Figure 8. Still another area of the tile with numerous round features due to holes in the glossy top coating on the tile. The upper image is the reflected white light image and the lower one is a polarized light image. The as-printed magnification is 110.85 times.

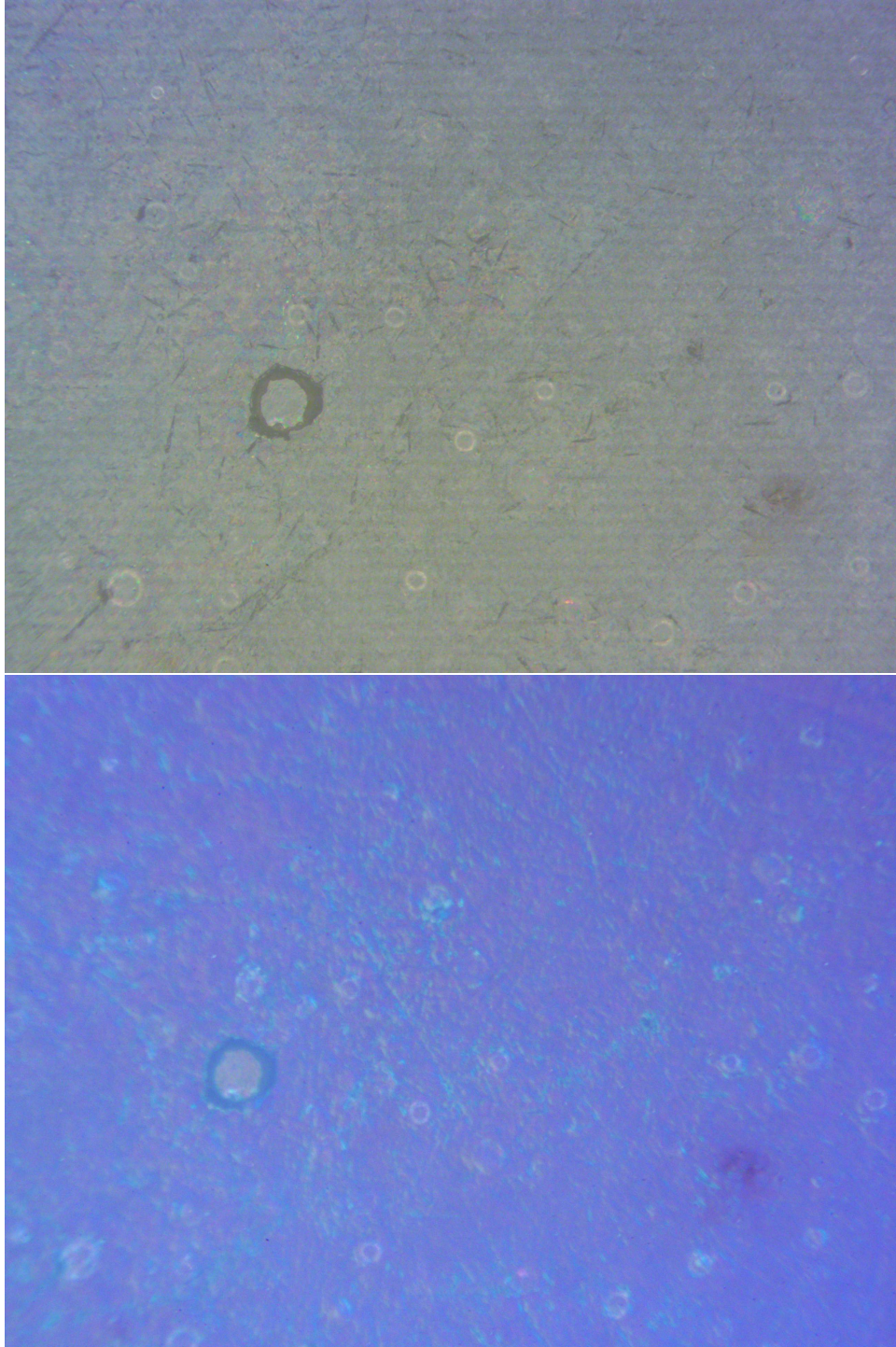


Figure 9. Another area of the tile surface with many round holes through the glossy top surface coating on the thin white layer. The hole on the left was anomalously large in this area, but all of the areas examined had numerous round holes in the coating such as those shown in the images above. The top image is again reflected white light and the bottom image is a polarized light image. The as-printed magnification is again 110.85 times.

Examination of the Wet Tile After Drying

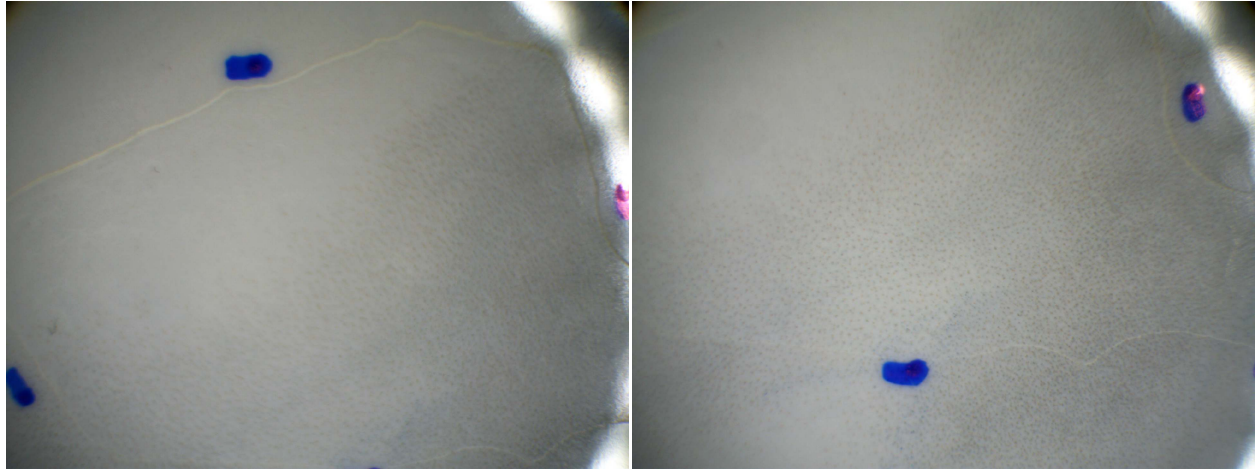


Figure 10. A water spot left after the distilled water dried is shown above. Only the outer perimeter of precipitated materials can be seen as a thin line here. Blue tick marks were made just outside the perimeter to make it easier to find under the microscope, especially once the sample was inside the XPS chamber. The as-printed magnification is 2.67 times.

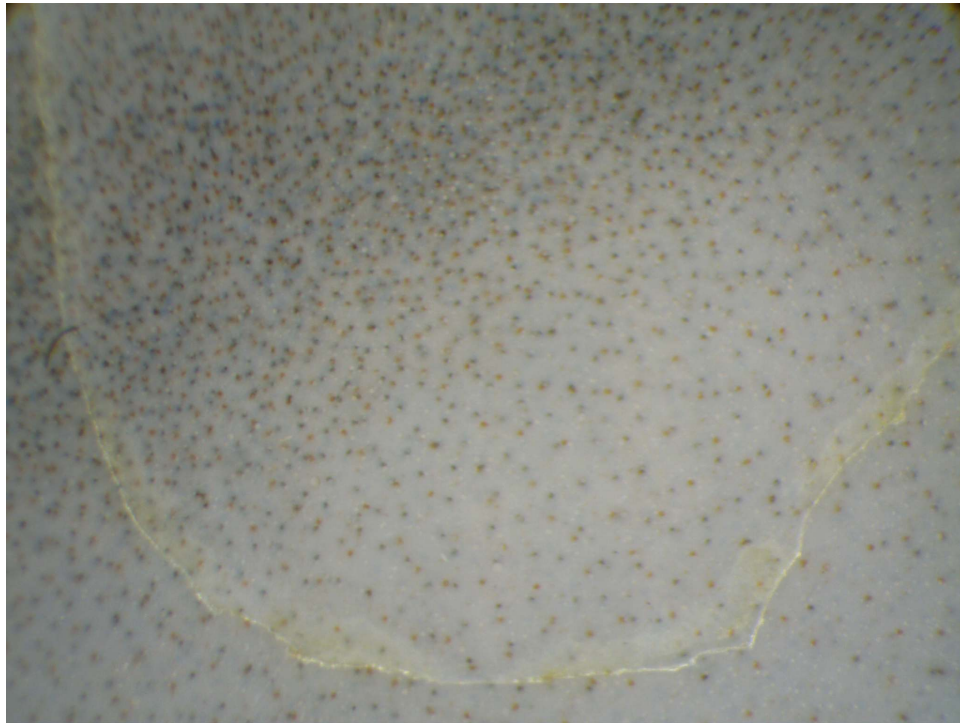


Figure 11. This is the water spot on which XPS analysis of the materials deposited on the surface upon drying the water was performed. The analysis areas were inside the deposit above the lower perimeter heavy deposit where there was less deposited material, in the lower perimeter heavy deposit area, and outside the perimeter where no water bead had sat. The as-printed magnification is 12.71 times.

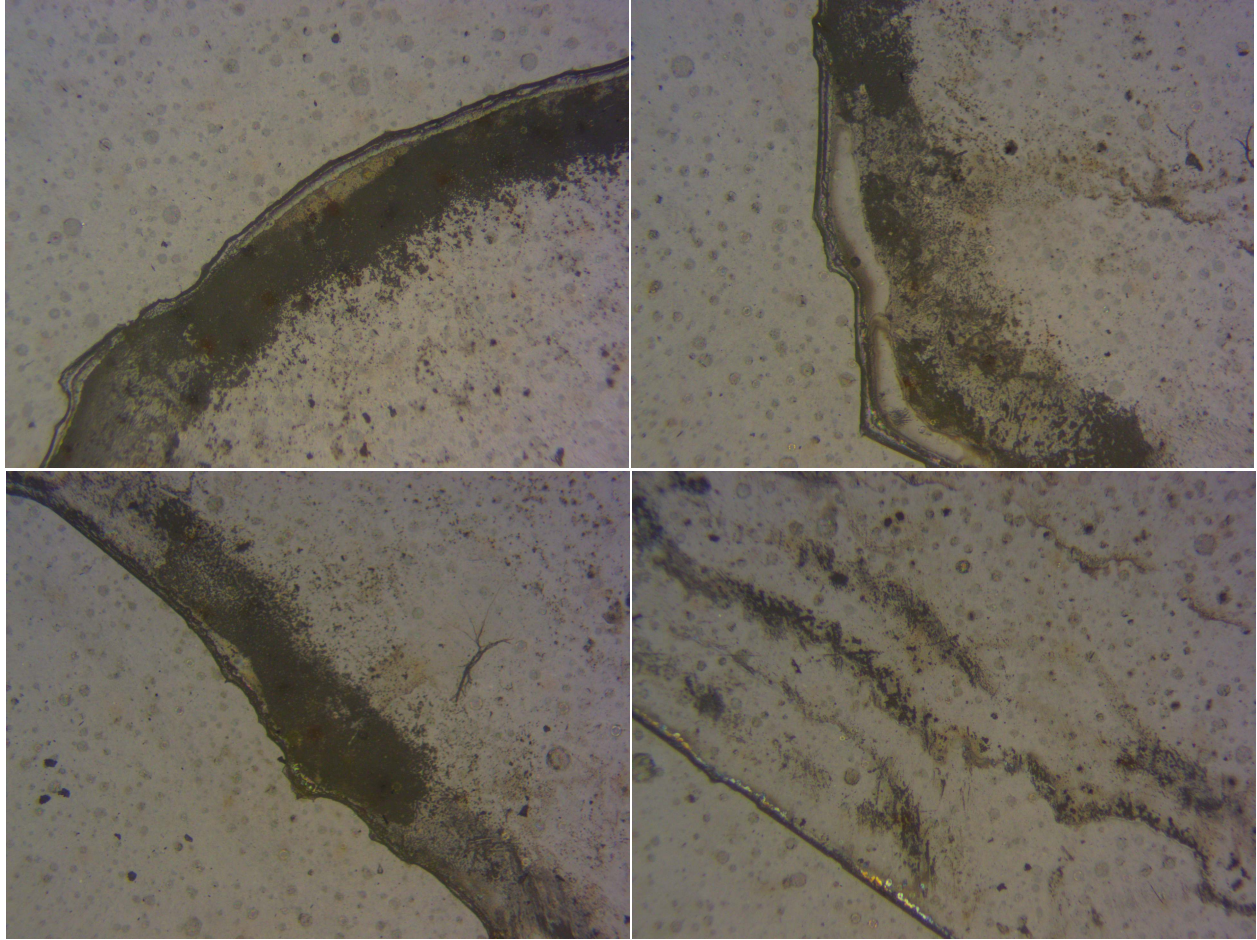


Figure 12. Photomicrographs of the perimeter deposits of the water spot shown in Figures 10 and 11. The area analyzed by XPS on the perimeter was that of the upper right image in this set. The as-printed magnification here is 35.82 times.

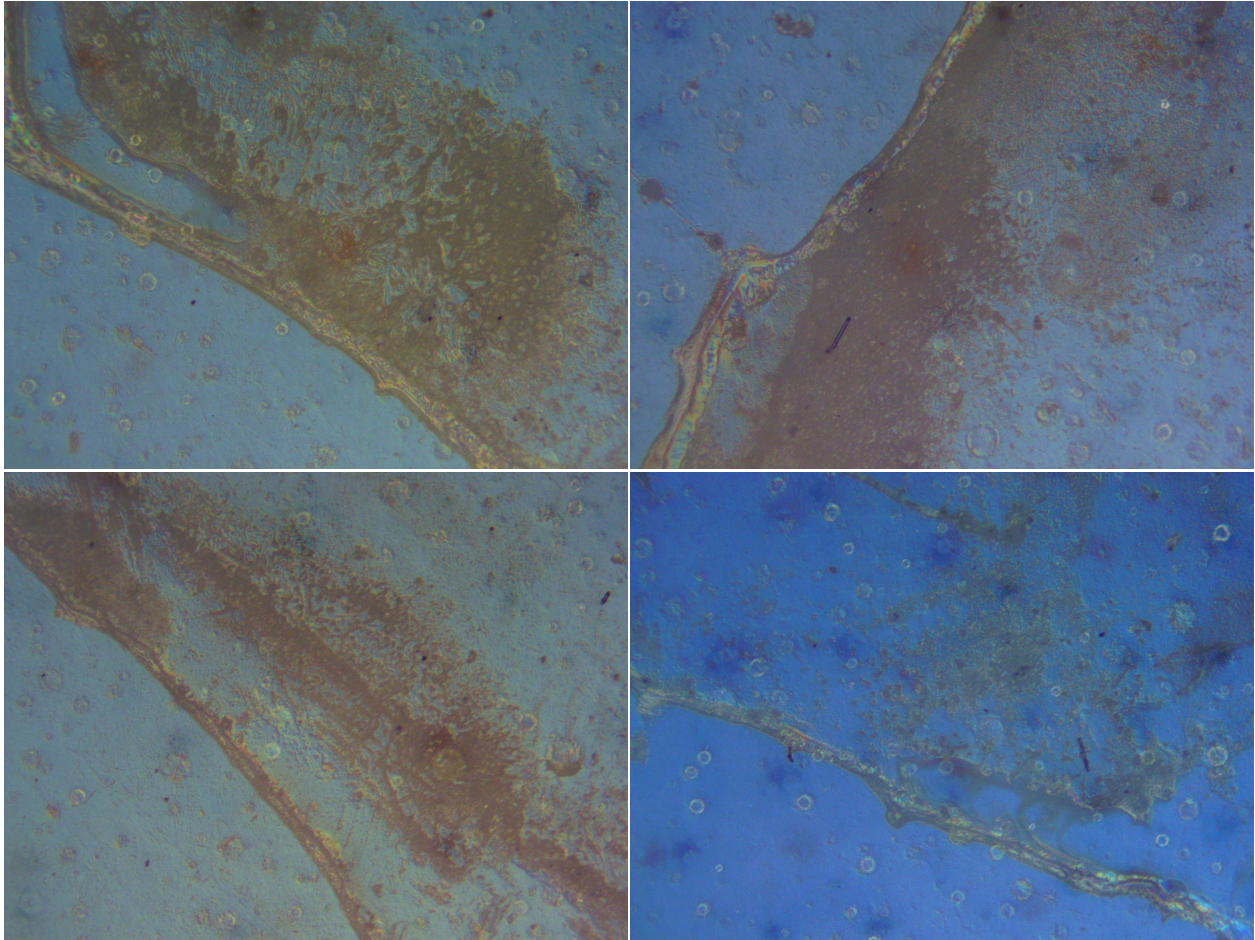


Figure 13. The photomicrographs above are made in the Nomarski differential phase interference contrast mode. This mode makes the surface glaze defects more apparent, as well as making the definition of the surface deposits a bit more detailed. The as-printed magnification is 71.65 times.

The surface deposits from the dried water spots must be due to the water dissolving minerals from the hard, white layer under the surface glaze by means of access through the many small round holes in the glaze.

Polished White Overlayer

The white overlayer after polishing half or a bit more of it away is shown in the following images.

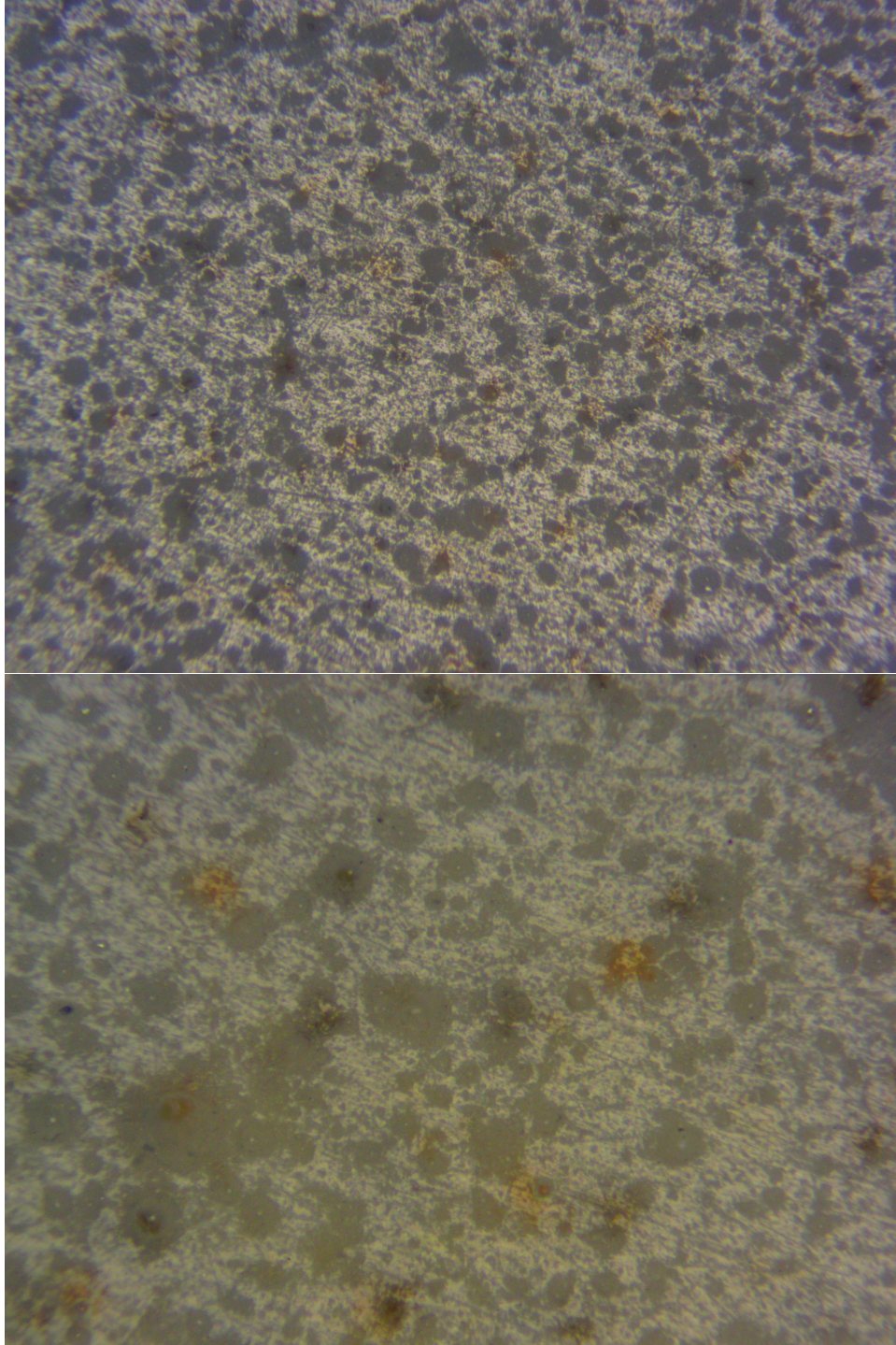


Figure 14. Images of the polished white overlayer are shown. The upper image is at an as-printed magnification of 55.42 times, while the lower image magnification is 110.85 times.

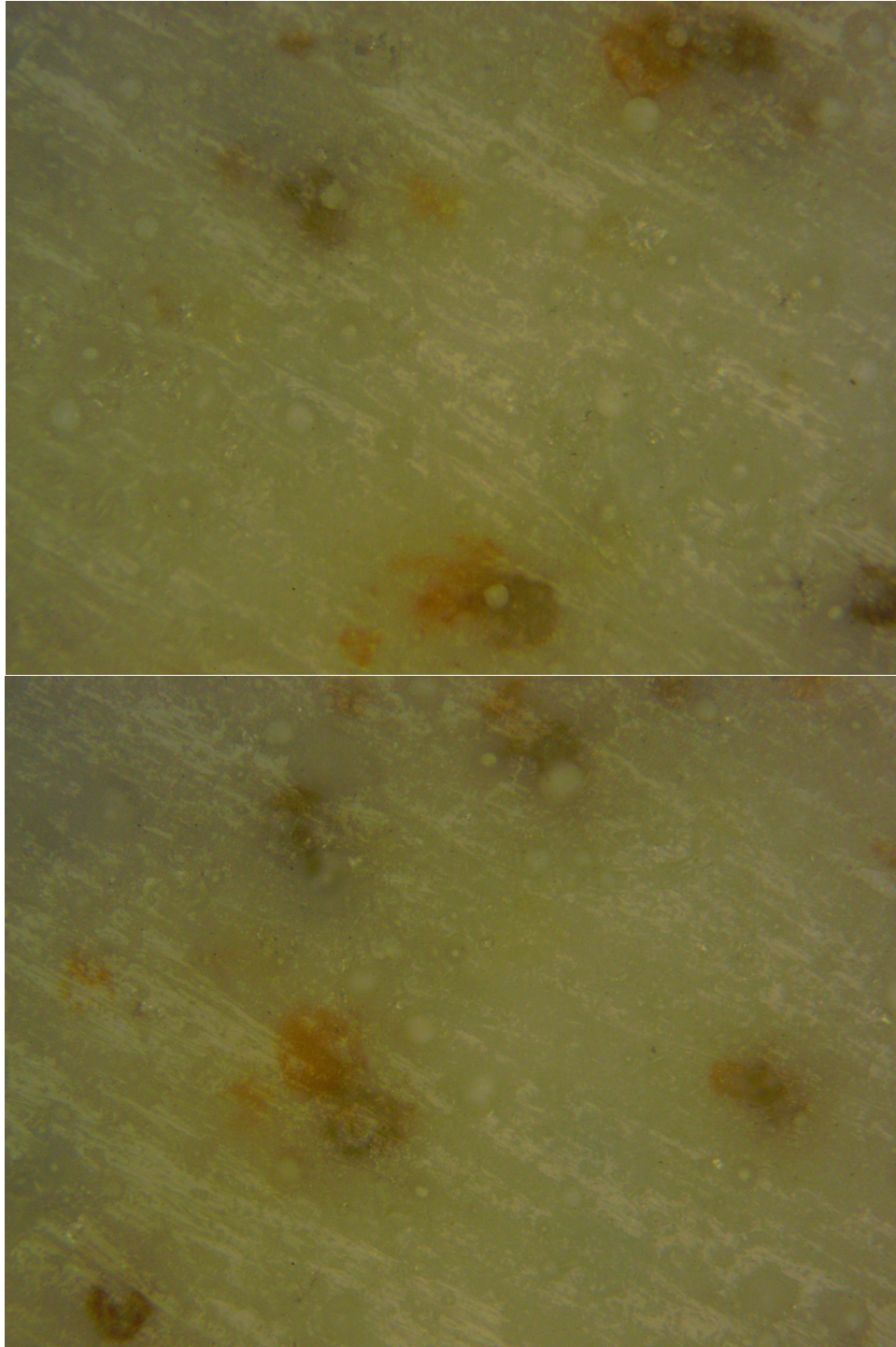


Figure 15. The polished surface of the white layer is shown in these images as an as-printed magnification of 221.7 times.

XRF Analysis

The XRF analysis was performed using a Thermo Scientific ARL PERFORM'X 1500 wavelength-dispersive spectrometer with quantitative elemental concentration analysis for all elements from carbon to uranium using sequential analysis with three detection crystals. It has the capability to analyze areas of 0.5 mm, 1.5 mm, 10 mm, or 29 mm in diameter. It can analyze samples either under vacuum or under helium. The depth of analysis is a couple of micrometers.

The floor tile surface was analyzed over an area of 29 mm diameter. The shiny, as-received (though isopropyl alcohol cleaned) surface was analyzed. It was then also analyzed after a bit more than half of the white surface layer over the baked clay was polished away. The results in weight percent of the oxide composition are given in Table 1.

Table 1. The weight percent concentrations of the oxides in the tile from the walking surface and after polishing away a bit more than half of the white overlayer as measured by XRF.		
Oxide	As-Received Surface	Polished White Overlayer
SiO ₂	55.94	52.48
Al ₂ O ₃	17.85	19.57
CaO	8.22	7.55
ZrO ₂	5.88	7.92
Na ₂ O	5.28	6.04
K ₂ O	2.82	3.15
ZnO	2.75	1.94
MgO	0.49	0.42
BaO	0.25	0.24
P ₂ O ₅	0.13	0.17
Fe ₂ O ₃	0.11	0.13
HfO ₂	0.07	0.16
TiO ₂	0.06	0.08
SrO	0.05	0.04
SO ₃	0.04	0.03
Y ₂ O ₃	0.02	0.02

The immediate surface glaze with the round holes in it observed by the optical microscopy examination, has a composition similar to that of the underlying thick white layer. However, it has more silica, CaO, and ZnO in it. The subsurface white overlayer has more alumina, zirconia, Na₂O, and K₂O in it. It is the Na₂O that is primarily leached from the white layer when the tile is wet.

XPS Analysis

The XPS analysis was performed over an elliptical area irradiated by the low-energy (1487 eV) monochromatic aluminum K α x-ray with a major axis of 1.28 mm and a minor axis of 0.64 mm. This is an area of approximately 0.64 mm². The x-ray angle of incidence and the take-off angle relative to the horizontal plane is 35°. A wide-angle ($\pm 13^\circ$ solid angle) input lens, hemispherical analyzer, and a multi-channel detector make the spectrometer very efficient with respect to the input x-ray flux. The depth of the analyzed volume is determined by the small mean-free path of the emitted photoelectrons, such that about half the signal comes from the outer 6 nm of the surface, about 70% from the outer 10.5 nm, and about 90% from the outer 20 nm of the surface. The elemental survey spectra cover the binding energy range from 0 to 1100 eV, with a step size of 0.5 eV. This step size, with the monochromator, the moderate analyzed area size, and a high signal-to-noise ratio, provides high quantitative accuracy and sensitivity.

The XPS system consists of a turbomolecular pumped introduction chamber, an ion pumped sample preparation chamber, and an analysis chamber which is also ion pumped. When samples are inserted into the Analysis Chamber, they pass through the Preparation Chamber, which decreases the exposure of the Analysis Chamber to water vapor and hydrocarbons from the Introduction Chamber. Briefly on introduction into the Analysis Chamber, the pressure is typically in the low 10⁻⁸ Torr range, but within a minute of closing the gate valve to the Introduction Chamber, it is in the 10⁻⁹ Torr range and usually in the low 10⁻⁹ Torr range long before data acquisition has been completed. We also make a practice of segregating the samples of different customers to minimize cross contamination.

The quantitative elemental concentration results of the XPS analysis for the water spot and its environs are given in Table 2. Outside the water spot, the carbon concentration is very low at 19.94 atomic percent (at.%), compared to the much higher concentration in the interior of the water spot of 45.50 at.%, and the even higher perimeter ring concentration of 52.63 at.%. This makes it clear that the distilled water sitting on the glaze surface is dissolving organic material out of the underlying clay through the circular defects in the glaze. The other remarkable increase in concentration is that of sodium, which outside the water spot is 2.29 at.%, inside in the interior of the water spot is higher at 3.80 at.%, and at the perimeter deposits is a very high 10.62 at.%.

Outside of the water spot, the silicon and aluminum concentrations are much higher than in the interior of the water spot and still higher than in the heavy deposits at the perimeter of the water spot.

The high energy resolution results for the purpose of identifying the chemical species for the surface of the glaze outside the water spot are given in Table 3. The glaze surface is that of a silicate of silicon, aluminum, sodium, and calcium. The nitrogen binding energy matches with that of urethane. There is very little to no carbonate on the surface.

The chemical species from the high energy resolution results for the heavy deposit at the perimeter of the water spot are given in Table 4. The big increase in carbon on the surface was shown to be due to a near tripling of the C - C bond concentration and a big increase in carbonates. The C - O bonds clearly seen in the outside the water spot area analyzed were reduced by a factor of 10. The huge increase in sodium in the deposit compared to the outside the water spot area is due to some combination of Na_2CO_3 and NaHCO_3 . The Ca 2p3 binding energy also decreased, indicating it may be hydrated calcium carbonate or it may be a calcium silicate. The reduced concentrations of silicon and aluminum are in the form of silicates, though the ratio of aluminum to silicon has increased.

TABLE 2. XPS surface analysis results in atomic percent concentrations of elements in the surface of the glaze on the floor tile after distilled water dried and left water spots on the tile surface.

Element	Outside the Spot	Inside the Spot with Barely Visible Deposit	On the Spot Perimeter with a Thick Deposit
Carbon	19.94	45.50	52.63
Oxygen	48.54	34.77	28.66
Nitrogen	0.99	1.06	0.78
Silicon	23.72	11.12	5.43
Aluminum	3.14	1.70	1.04
Magnesium			
Calcium	0.92	1.03	0.64
Sodium	2.29	3.80	10.62
Potassium	0.34		
Phosphorus		0.71	
Sulfur			0.20
Chlorine		0.33	
Zinc	0.11		

Table 3. High energy resolution XPS results for the surface of the glaze outside the water spot.						
Element	Element at. %	Component Binding Energy (eV) Measured	Component Binding Energy (eV) Corrected	Component %	Component at. %	Component Identity
C 1s	19.94	283.86	285.00	76.06	15.17	C – C
		285.36	286.50	12.48	2.49	C – O, C – C(=O) – O – C Ester
		287.70	288.84	11.46	2.28	C – C(=O) – O – C Ester, C – O – C(=O) – NH – C Urethane
O 1s	48.54	531.05	532.19	61.03	29.62	
		531.93	533.07	38.97	18.92	
N 1s	0.99	399.27	400.41	100.00	0.99	C – O – C(=O) – NH – C Urethane
Si 2p	23.72	101.94	103.07	100.00	23.72	23.72 Si Al _{0.132} Na _{0.097} Ca _{0.039} O _{2.285}
Al 2p	3.14	73.71	74.85	100.00	3.14	Si Al _{0.132} Na _{0.097} Ca _{0.039} O _{2.285}
Na 1s	2.29	1071.67	1072.81	100.00	2.29	Si Al _{0.132} Na _{0.097} Ca _{0.039} O _{2.285}
Ca 2p3	0.92	347.03	348.17	100.00	0.92	Si Al _{0.132} Na _{0.097} Ca _{0.039} O _{2.285}

Table 4. High energy resolution XPS results for the surface of the perimeter deposit of the water spot.						
Element	Element at. %	Component Binding Energy (eV) Measured	Component Binding Energy (eV) Corrected	Component %	Component at. %	Component Identity
C 1s	52.63	283.64	285.00	80.57	42.40	C – C
		285.14	286.50	0.48	0.25	C – O
		287.18	288.54	18.95	9.97	Na ₂ CO ₃ • n H ₂ O, NaHCO ₃ • n H ₂ O, CaCO ₃ • n H ₂ O, C – C(=O) – NH – C
O 1s	28.66	530.10	531.46	40.85	11.71	
		531.19	532.45	48.85	14.00	
		534.82	536.18	10.30	2.95	Adsorbed water in sodium carbonates
N 1s	0.78	398.41	399.77	100.00	0.78	C – C(=O) – NH – C
Si 2p	5.43	101.81	103.17	100.00	5.43	Aluminosilicates
Al 2p	1.04	73.24	74.60	100.00	1.04	Aluminosilicates
Na 1s	10.62	1070.19	1071.55	100.00	10.62	Na ₂ CO ₃ • n H ₂ O, NaHCO ₃ • n H ₂ O
Ca 2p3	0.64	346.43	347.79	100.00	0.64	CaCO ₃ • n H ₂ O and/or calcium silicate