

Identification of Glass Samples by Their Magnesium Content

References

- Harris, Daniel C. Atomic Spectroscopy. *Quantitative Chemical Analysis*, 4th edition; W. H. Freeman: New York, 1995; Chapter 21.
- Hill, Steve J. Atomic Absorption Spectrometry -- Techniques -- Flame atomic absorption spectrometry. In *Encyclopedia of Analytical Science*; Townshend, Alan, Ed.; Academic Press: New York, 1995; Vol. 1, pp 221-228.
- Koizumi, Hideaki. Atomic Absorption Spectrometry -- Theory and Instrumentation. In *Encyclopedia of Analytical Science*; Townshend, Alan, Ed.; Academic Press: New York, 1995; Vol. 1, pp195-221.
- Koons, R.D.; Fiedler, C.; Rawalt, R.C. Classification and Discrimination of Sheet and Container Glasses by Inductively Coupled Plasma-Atomic Emission Spectrometry and Pattern Recognition. *J. Forensic Sci.* 1988, 33, pp 49-67.

Goal

To compare known and questioned pieces of glass and to determine if they could have a common origin.

Suggested Method of Analysis

Dissolution of the glass with hydrofluoric acid, followed by atomic absorption analysis of the resulting solution to determine the concentration of magnesium.

Materials

Glass samples stored in sealable plastic bags

Collect separately pieces of windshield glass, headlamp glass, bottle glass, etc. You should be able to collect free samples from a junk yard or collision repair facility.

Concentrated (48%) HF

WARNING: Hydrofluoric acid is highly corrosive and toxic. Wear gloves and work in a fume hood.

Concentrated (12 M) HCl

Concentrated HNO₃

La(NO₃)₃ • 6H₂O, ultrapure

Magnesium turnings

10-mL plastic centrifuge tubes

Ultrasonic bath

Preparing the Evidence

From the suspects: Windshield or headlamp glass from different automobiles should be assigned to each of the suspects. Put two small pieces of each glass into separate marked, sealable, plastic bags.

From the crime scene: Place a few small pieces of headlamp glass from one of the suspects and some bottle glass on a roadside. Sweep up the glass and accompanying debris, and store it in a marked, sealable, plastic bag.

Processing the Glass Samples

Separate glass from the scene from any other debris present and rinse it with deionized water. Examine by eye the glass from the crime scene and attempt to differentiate the pieces by their source(s). It may not be possible to tell how many kinds of glass are present by simple visual inspection.

Break off some small pieces of glass (one or two fragments approximately 1/4" square will do) from the larger pieces found at the scene. Do not mix glass from different pieces as you do not know if they come from the same source or not. Rinse the fragments again with deionized water and place them in a beaker of concentrated nitric acid for thirty minutes. Rinse three times with deionized water and then with ethanol. Next place the beaker containing the glass in an 80° C oven for approximately ten or fifteen minutes to dry the sample.

Place a piece of clean glass in a plastic weighing boat on a plastic tray or cutting board. Nest another clean weighing boat on top of the first one containing the sample. Use a hammer to smash the sample into smaller pieces. The glass will cut through the plastic if care is not taken. The best way to crush the glass is to strike directly on top of the sample, firmly, and then reposition the sample in the weighing boat so that no holes are created. It is possible to get three good blows in one weighing boat, which should be enough to produce some very fine dust. This dust is used for the refractive index measurements and for the magnesium analysis.

Prepare the suspect glass samples in the same way. However, as all the glass in each sample is known to come from the same source, the chips from different glass fragments within a sample may be mixed.

Solution Preparation

The diluent for the standard and sample solutions should be 1% (v/v) HCl and 0.1% (w/v) lanthanum nitrate hexahydrate in water. For a 500-mL batch, dilute 5 mL concentrated HCl and 0.5 g $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ to 500 mL with deionized water. Store the diluent in a plastic bottle.

To prepare the magnesium stock solution dissolve 0.500 g of magnesium turnings in a minimum volume (~8 mL; added slowly) of 6M HCl. All of the metal is dissolved in about an hour. Dilute the solution to 500 mL with 1% (v/v) HCl in water, and store it in a plastic bottle.

Two wavelengths of light can be used with the atomic absorption spectrophotometer to measure the absorbance of magnesium atoms depending on the concentration of magnesium in the prepared sample solution. More sensitive measurements can be made at 285.2 nm with recommended standard concentrations between 0.01 and 0.20 mg/L. Headlamp glass samples likely will require this wavelength and lower range of standard concentrations. Bottle and windshield glasses usually require the use of a lower wavelength (202.6 nm) and higher standard Mg concentrations, 0.1 mg/L to 10 mg/L. Prepare 4 or 5 standards in each concentration range by appropriate dilution of the magnesium stock solution with the diluent solution. Prepare these working standard solutions daily and use immediately.

Dissolving the Glass Samples

Weigh 5 mg (to the nearest 0.01 mg) of clean, dry glass dust into a small, plastic centrifuge tube. Don some rubber gloves and work in a fume hood. Use disposable plastic pipettes to measure 0.50 mL of concentrated (48%) hydrofluoric acid and 0.25 mL of concentrated (12 M) hydrochloric acid into the centrifuge tube. Cap the tube and sonicate the sample for one hour. After sonication, the glass should be completely dissolved. Uncap the sample tube and heat it to 80° for several hours to evaporate the solution to dryness. This removes volatile HF and HCl.

Next, to the dried sample add two drops each of concentrated hydrochloric acid and deionized water. Mix well to dissolve the residue. It may not all dissolve. Reheat the tube (uncapped) to again evaporate the solvent. After drying is complete, add four drops each of concentrated hydrochloric acid and deionized water. Add the acid first and mix well to attempt to dissolve the residue most quickly. Leave the sample overnight in the tube (capped); all of the solid should be dissolved by the next day.

Dilute the sample with diluent solution to exactly 10 mL in a volumetric flask, and store the sample solution in the same centrifuge tube.

Standards and the Calibration Curve

Follow the directions for operation of the atomic absorption spectrophotometer with flame atomization and make absorbance readings in triplicate for each standard and sample solution. Perform linear regression of the absorbance versus magnesium concentration (mg/L) to find the concentration of magnesium in the unknowns. Calculate the milligrams of magnesium per gram of glass for each sample.