

## SPECTROMETRIC METHODS FOR DETERMINING THE WATER CONTENT OF GLASS

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Major advances in spectrometric methods for determination of water in glass are reviewed. Techniques presently in use, infrared spectroscopy and nuclear magnetic resonance, together with their associated problems, are discussed. Suggestions for improvements are offered.

It is known that water can react with molten glass and combine with it chemically. The presence of water in the glass alters many physical properties, *e.g.*, it increases in the electrical conductivity and molten viscosity. It is, therefore, desirable to have an accurate and easy method for determining the water content of glass.

In 1934, Drummond (1) reported that fused silica he had prepared exhibited an infrared absorption band at 2.7 microns. He proposed that the band be attributed to an "impurity" in the glass but did not resolve the question of what the "impurity" was. This was answered in 1947 when Harrison (2) demonstrated that by bubbling dry gas through the molten silica the absorption band at 2.7 microns could be lowered. Harrison attributed the band to hydroxyl groups in the glass. However, no attempt was made to correlate the absorption difference with the actual water concentrations since these concentrations were not known.

In 1957 Russell (3) developed a technique for determining water concentrations in glass that involves bubbling dry gas through the molten glass for a time sufficient to ensure the removal of all the water. The weight loss of the glass or the weight gain of a desiccant through which the gas passes is then used to calculate the water concentration. This has become the standard method for calibrating other techniques.

Scholze (4) combined the method used by Russell (3) with infrared spectra for almost 150 binary, ternary, and quaternary silicate glasses. He found that the presence of water in glass leads to one or more absorption bands in the range of 2.7 to 4.0 microns, depending on the composition of the glass. Selecting the per cent transmis-

sion at the absorption band nearest 2.7 microns, he then applied Beer's Law.

$$E = \epsilon C = \frac{1}{d} \log(1/D)$$

$E$  = extinction

$\epsilon$  = extinction coefficient

$C$  = concentration of water

$d$  = sample thickness

$D$  = per cent transmission

The values for  $d$  and  $D$  are readily determined and  $C$  can be obtained by the Russell technique. The extinction coefficient,  $\epsilon$ , can then be calculated and used to calculate water concentrations for various values of  $d$  and  $D$ . However, the extinction coefficient is not constant but varies widely with composition, *e.g.*, from 6 to 107  $\text{cm}^2/\text{mole cm}$  for sodium silicate glasses. Therefore, the laborious calibration must be undertaken for each change in glass composition. In spite of this, other investigators (*e.g.*, 5, 6) have used the method of Scholze in determining the water contents of various glasses.

The method used by Scholze (4) was refined by Goetz and Vosahlova (7). They corrected the value selected for the per cent transmission by recognizing that less than 100% of the beam was transmitted even at wavelengths shorter than 2.7 microns. This increases the accuracy of the method but still leaves the problem of calibration.

A possible alternate method is nuclear magnetic resonance (NMR). The nucleus of the hydrogen atom possesses an intrinsic angular momentum or spin. When placed in a magnetic field, such nuclei can be made to resonate by absorption of radio frequency energy from an outside source. The resonant frequency is a function of the atom type. In principle, NMR should be able to

measure the water concentration in a glass by determining the amount of energy absorbed, which is a function of the number of hydrogen atoms present.

Three studies have used a variation of this technique. Meyer and Splathoff (8) applied this procedure to sodium silicate glasses without using any calibration samples. They compared their results to those determined by infrared spectroscopy and found that their results were substantially higher. Warmuth *et al* (9) used NMR on many different alkali silicate glasses and used materials such as  $\text{NH}_4\text{Cl}$  and  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$  as calibration samples. Their results were also high, by about 12%, when compared to the results of infrared spectroscopy. More recently, Jones *et al* (10) tried to calibrate their NMR method by melting the glass, allowing the water to diffuse out, and measuring the weight loss. However, they found that this method of determining water content was not sufficiently accurate to allow for calibration.

The authors believe that what is needed is a systematic study of the NMR technique on silicate glasses using the method of bubbling dry nitrogen through the molten glasses for an accurate calibration. The energy absorbed by a sample would be plotted *versus* the actual water concentration. Three different results are possible:

1. No correlation; the method does not work.
2. Data is a function of composition; new calibration is required for each composition. This is the case for infrared spectroscopy.
3. All data falls on one curve; only one calibration is required.

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