

# **QUANTITATIVE ANALYSIS OF A SOLID SOLUTION USING FOURIER TRANSFORM INFRARED SPECTROMETRY: AN INSTRUMENTAL ANALYSIS EXPERIMENT**

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## **ABSTRACT**

When Fourier Transform Infrared (FTIR) instrumentation is used, along with careful selection of the analyte and the concentration range, quantitative infrared spectrometry is feasible (George et al. 1987, Skoog et al. 1998). For this experiment the feasibility of using FTIR for quantitative analysis of solid solutions (sample dispersed in potassium bromide and pressed into a pellet) was explored using a Thorn Smith Analyzed Unknown of potassium hydrogen phthalate (KHP). When sample pellets of similar transparency were used, the area of the peak at  $760\text{ cm}^{-1}$  varied linearly with concentration of KHP (obeyed the Beer-Lambert Law). The experimental procedure proved to be somewhat time intensive, but results were reproducible, accurate (3% error), and precise (10% RSD). The experiment gives students experience/practice with KBr sample preparation methods, FTIR operation, peak integration methods, and linear regression analysis of a calibration curve. The experiment is amenable to either the standard calibration curve method or the method of standard addition.

## **Keywords**

Quantitative FTIR, KBr pellet, Beer's Law, Instrumental Analysis

## **INTRODUCTION**

The Beer-Lambert Law,  $A=abc$ , predicts that when a compound absorbs monochromatic (single-wavelength) radiation, the absorbance (A) is directly proportional to its concentration (c) and to the path length of the measuring cell (b); "a" is the absorptivity, also called the extinction coefficient or optical density, for the compound at that wavelength (e.g., Harris 1999). Applications of this law are used routinely for quantitative analysis, especially with ultraviolet and visible radiation (UV-Vis).

Theoretically the Beer-Lambert Law should also apply for infrared radiation (IR), but several practical considerations limit its use. IR spectra are more complex and in many cases more intense than UV-Vis spectra, so selection of a wavelength and appropriate concentration range are more difficult. IR source intensities are significantly lower than UV-Vis sources and IR detectors are typ-

ically less sensitive as well. This requires wider slits which means that the monochromatic wavelength stipulation is compromised. In addition, IR absorption bands are relatively narrow, so a slight shift in the wavelength selector position can have a dramatic effect on the average absorptivity ( $a$ ) for the sample. Modern Fourier Transform IR (FTIR) instrumentation minimizes these problems and makes quantitative IR analysis more feasible (George et al. 1987, Skoog et al. 1998). In general, the sample used for quantitative IR analysis should have a fairly simple spectrum which contains at least one resolved peak (distinctly separated from any others) that is present in all dilutions of standards and samples in the concentration range where the Beer-Lambert Law is obeyed (George et al. 1987).

The purpose of the investigation reported here was to determine the feasibility of using FTIR spectroscopy for the quantitative analysis of a solid sample using potassium bromide as the "solvent" (KBr pellets). Solid samples present additional complications for quantitative analysis. The path length (pellet thickness) must be measured or carefully controlled to keep it constant. Light scattering from the solid and other anomalies within the solid matrix can also vary from pellet to pellet (George et al. 1987, Skoog et al. 1998). It was hoped, and subsequently proven, that standardization of the pellet making process would minimize these factors.

## METHODS

All spectra were collected with a Nicolet Avatar 360 FTIR (Nicolet Instrument Corp., Madison, WI) employing 32 scans with four  $\text{cm}^{-1}$  resolution (default parameters). The sample compartment was continuously flushed with nitrogen (A-OX Welding, Sioux Falls, SD) at a flow rate of 450 mL/min. The area of the peak at  $760 \text{ cm}^{-1}$  was determined using the manual integration feature of the Nicolet EZ-Omic software. Software defaults were used for the baseline points for integration of each peak unless a default point excluded a peak shoulder, in which case the point was manually adjusted.

For this study potassium hydrogen phthalate (KHP) was selected as the sample because a Thorn Smith Analyzed Unknown (Thorn Smith Laboratories, Beulah, MI) was available, and it proved to have a suitable IR spectrum. ACS reagent grade KHP (99.95%-100.05%, Aldrich Chemical Company, Inc., Milwaukee, WI) and Thorn Smith Analyzed KHP Unknown 277 were dried at  $100^\circ\text{C}$  for one hour prior to use. FTIR spectroscopic grade potassium bromide (KBr) (International Crystal Laboratories, Garfield, NJ) was dried at  $120^\circ\text{C}$  for 24 hours prior to use. All reagents and prepared samples were stored in a desiccator over Drierite (Hammond Drierite Company, Xenia, OH). Samples were massed on an Ohaus AP210 Analytical Plus electronic balance (Ohaus Corp., Florham Park, NJ).

*Pellet preparation:* Initially 0.0024 g of KHP was thoroughly mixed with 0.7784 g of KBr in a Wig-L-Bug (Crescent Dental Mfg. Co., Chicago, IL). This mixture was "diluted" to form the calibration standards by thoroughly mixing masses ranging from 0.01 g to 0.06 g with 0.21 g of KBr in the Wig-L-Bug (masses were recorded to four decimal places). Similarly, 0.0037 g of Un-

known 277 was thoroughly mixed with 0.6971 g KBr in the Wig-L-Bug. Aliquots of 0.01 to 0.06 g (recorded to four decimal places) of this mixture were each thoroughly mixed with 0.21 g of KBr in the Wig-L-Bug to form unknown pellets for analysis.

Then 0.17 g of each of these final mixtures was carefully transferred into the KBr pellet die and pressed into a pellet by applying 10,000 lb to the die for 10-15 seconds using a Carver Lab Press (Fred S. Carver, Inc., Summit, NJ). The mass of mixture used was kept constant (0.17 g) to keep the pellet thickness (path length) constant. Only pellets with a linear baseline absorbance and which were translucent and relatively homogeneous across their diameter were used in this study.

## RESULTS AND DISCUSSION

This study was conducted as a part of the lab for Augustana's Advanced Analytical Chemistry course which has two four-hour lab periods each week. Since the pellet making process was somewhat tedious, it was necessary to store some of the pellets so their spectra could be obtained in a later period. A primary concern then was the stability of the sample within the pellet. It was discovered that the O-H stretch peak at  $3500\text{ cm}^{-1}$  degraded significantly with time, even after one or two days, but the rest of the spectrum was quite stable and reproducible. Figure 1 shows this quite clearly; 1A shows the spec-

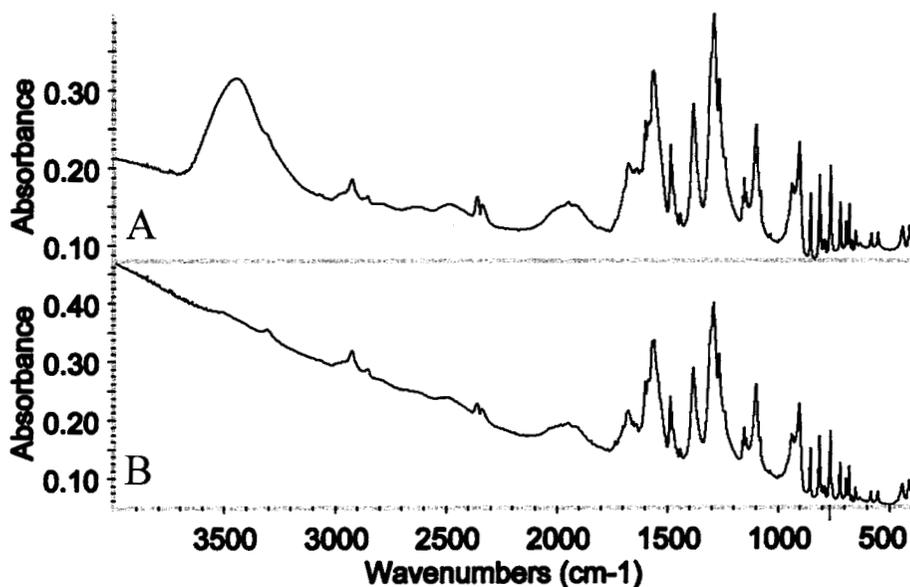


Figure 1. Sample FTIR spectrum of a KHP standard pellet (0.0554 mg KHP/g pellet). A) Spectrum obtained on the day the pellet was made. B) Spectrum obtained six months later, pellet stored in a desiccator. Marker on the x-axis indicates the location of the peak ( $760\text{ cm}^{-1}$ ) used for quantitative analysis.

trum of a freshly prepared pellet of KHP standard, and 1B shows the spectrum of the same pellet after six months. It was speculated that the disappearance of the  $3500\text{ cm}^{-1}$  peak was due to exchange of the acidic hydrogen of KHP and potassium from the KBr with subsequent outgassing of the HBr. The phenomenon was not investigated further. It should be noted that the peak (doublet) centered near  $2350\text{ cm}^{-1}$  was due to  $\text{CO}_2$  in the sample chamber. More extensive flushing with nitrogen eliminated this peak. However, it was found that the presence of  $\text{CO}_2$  had no adverse effect on the quantitative analysis of KHP, so no further attempt was made to completely remove  $\text{CO}_2$  from the sample chamber.

Figure 2 shows an expanded view of the  $600\text{ cm}^{-1}$  to  $900\text{ cm}^{-1}$  region of the spectra from Figure 1. This region is quite stable and reproducible over time (2A is with the fresh pellet and 2B is the same pellet six months later). After analyzing a large number of pellets, it was discovered that few of the pellets produced spectra with a flat baseline. Further analysis showed that spectra with a tilted, but linear, baseline (as in Figure 1B) were usually suitable for quantitative analysis, but spectra with a curved or zigzagged baseline were not. In addition it was noted that spectra with a nonlinear baseline (curved or zigzag) were obtained from pellets that appeared opaque or had a non-uniform appearance across their diameter. It was reasoned that the higher baseline absorbance was caused by increased light scattering for that pellet, one of

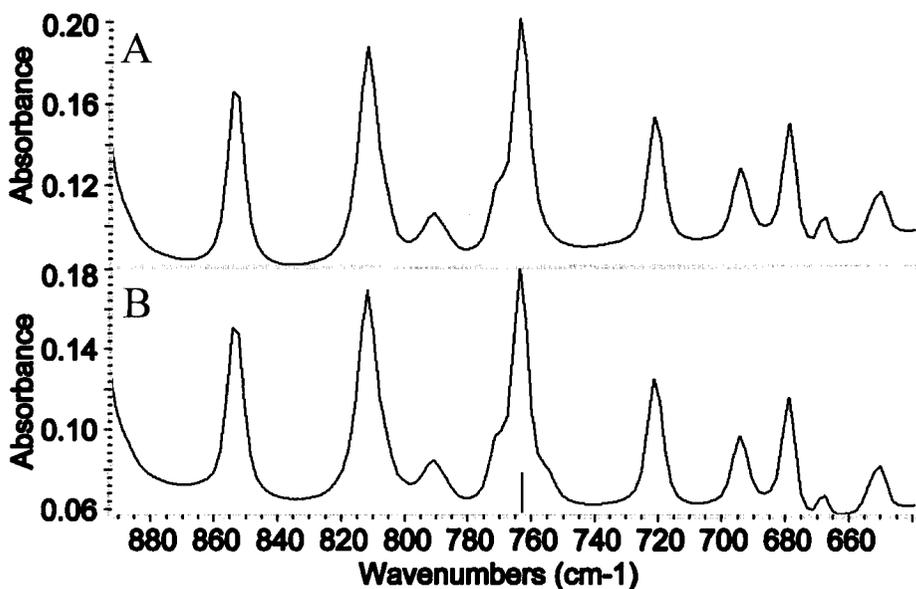


Figure 2. Spectrum of Figure 1 (KHP standard pellet) expanded around the region of interest. A) Spectrum obtained on the day the pellet was made. B) Spectrum obtained six months later, pellet stored in a desiccator. Marker on the x-axis indicates the location of the peak ( $760\text{ cm}^{-1}$ ) used for quantitative analysis.

the problems associated with quantitative analysis with solid samples (George et al. 1987, Skoog et al. 1998). Only pellets which were homogeneously translucent across the majority of their diameter and which produced spectra with a linear baseline absorbance were used for the quantitative analysis. A few pellets rejected by these criteria were actually suitable for quantitative analysis (false negatives), but all of the pellets selected by these criteria proved suitable (no false positives). The visual criterium provided a simple means of preselecting pellets that were likely "to work" early in the process. The Nicolet Omnic software (full version only, not EZ) provided a baseline correction feature that may have been able to "salvage" some of the rejected pellets, however, due to the time constraints in the lab, the students did not attempt to learn how to use this feature.

Four standard KHP pellets and three pellets with Unknown 227 proved to be suitable (translucent with low baseline absorbance) for this study. The spectra of the KHP standards (Figure 2) exhibited several well-resolved peaks in the  $600\text{ cm}^{-1}$  to  $900\text{ cm}^{-1}$  region that should be suitable for quantitative analysis. The spectra from Unknown 227 (Figure 3) were essentially identical to that of the standard KHP (Figure 1). The  $600\text{ cm}^{-1}$  to  $900\text{ cm}^{-1}$  region was also similar, but some of the peaks were not as well formed in the Unknown 227 pellets (Figure 4). The peak at  $760\text{ cm}^{-1}$  was reasonably well formed in the spectra from all seven pellets, so it was selected as the basis for the quantitative analysis. Spectra were found to be surprisingly reproducible over time. Spectra taken six months after the pellet was formed produced essentially the same peak area measurement as that from spectra of the freshly prepared pellet.

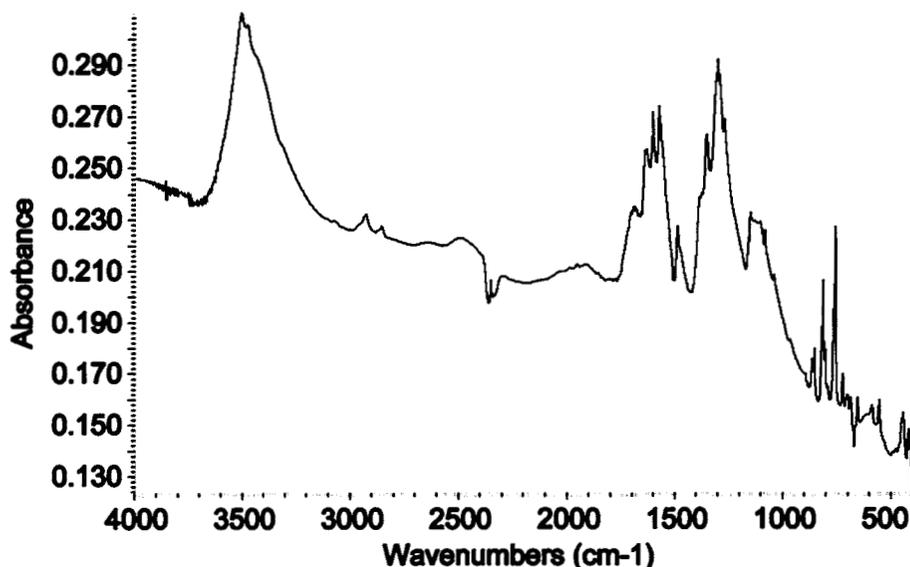


Figure 3. Sample FTIR spectrum of KHP Unknown 227 pellet obtained on the day the pellet was made.

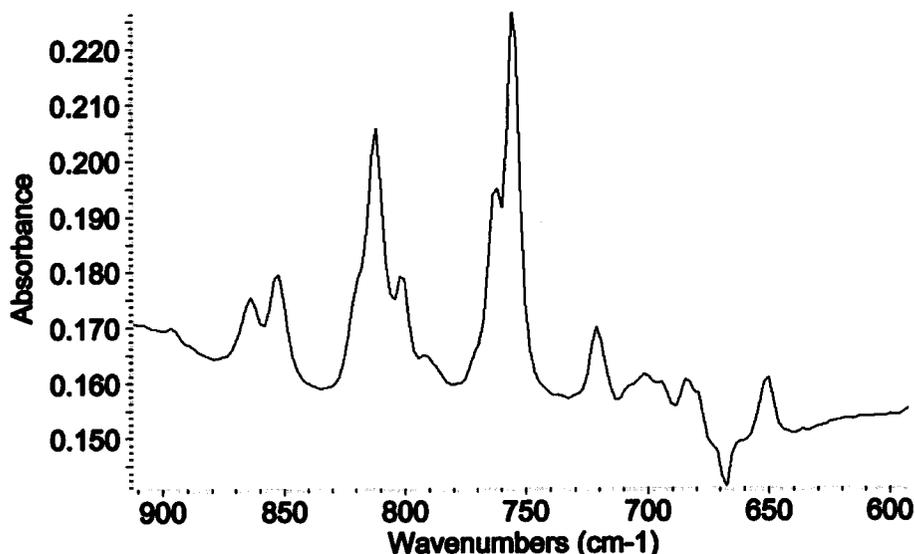


Figure 4. Spectrum of Figure 3 (KHP Unknown 227 pellet) expanded around the region of interest.

The data for the KHP standard pellets are listed in Table I. To ensure that instrumental operating conditions were constant (standard spectroscopic practice), only spectra of these pellets obtained in the same class period were used for the quantitative analysis. One of the samples was run twice to check for spectrum reproducibility. As can be seen from Figure 5, the calibration curve (peak area vs. KHP concentration) for this data was quite linear, with a slope of 1.96 g pellet/mg KHP (SD 0.4) and a y-intercept of -0.2 (SD 0.2) (essentially 0).

Table I: Data for the KHP Calibration Standards

<b>KHP Concentration</b> <b>(mg KHP/g pellet)</b>	<b>Peak Area</b> <b>(counts)</b>
0.0172	0.093
0.0314	0.313
0.0554	0.740
0.0653	1.029
0.0653	1.046

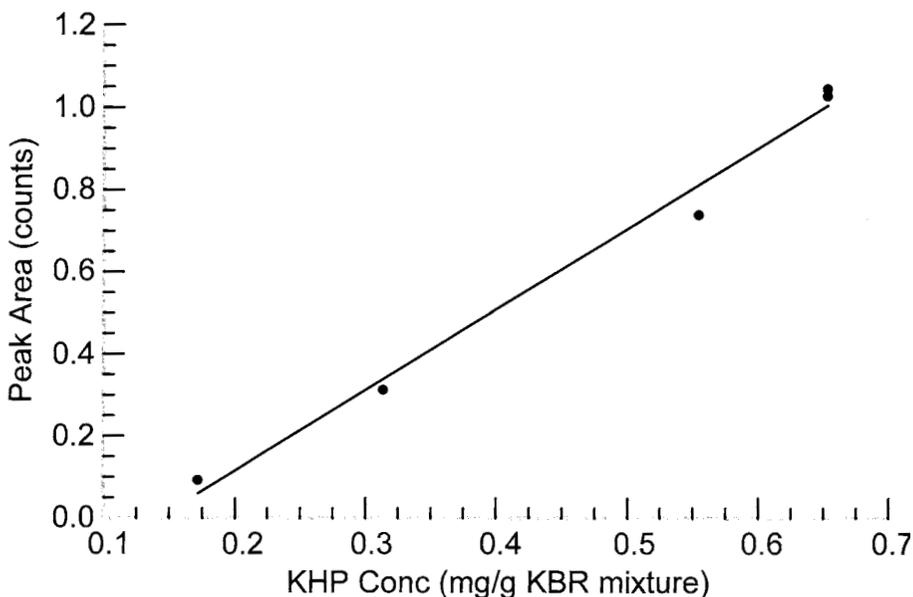


Figure 5. Calibration curve using data from Table I, slope = 1.96 g pellet/mg KHP, y-intercept = -0.2.

The data for the Unknown 227 tablets is presented in Table II. The average percentage of KHP in Unknown 227 was determined to be 55.4 % (RSD 10%). Measurements of sample masses were limited to two significant figures because of the low concentrations required to achieve adherence to the Beer-Lambert Law, so the relative standard deviation of 10% achieved here is primarily derived from uncertainty in mass measurements. The calculated percentage of KHP compares well with the accepted value of 53.62% for Unknown 227, a 3.4 % error.

The average pellet thickness (path length) measured with a caliper for the seven pellets used here was 0.52 (SD 0.01) mm, verifying that use of a consis-

Table II. KHP Unknown Data

<b>Unk Conc</b> <b>(mg Unk/g pellet)</b>	<b>Peak Area</b> <b>(counts)</b>	<b>Calc KHP Conc</b> <b>(mg KHP/g pellet)</b>	<b>Percent KHP</b> <b>in Unknown 227</b>
1.066	0.8754	0.5866	55.04%
0.9404	0.712	0.5034	54.28%
0.9288	0.776	0.5360	57.71%

tent mass of KHP/KBr mixture produces a constant pellet thickness. The variation in the thickness is about the same as the variations expected for the mass and peak area measurements (two significant figures), so, in this case, path length variability should have a minimal effect on accuracy and precision of the results. This was verified by including pellet thickness in the calculations of the percentage of KHP (peak area vs. thickness\*KHP concentration). When pellet thickness was included, the percent of KHP increased slightly to 57.0 % and the RSD decreased to about 4.7 % (based on two unknown pellets, one pellet did not survive long enough to obtain a thickness); virtually identical results for the two significant figures expected here.

### CONCLUSION

Using FTIR for quantitative analysis of solid solutions of KHP works reasonably well. With proper attention to details and careful selection of pellets, the method is accurate, precise, and reproducible. The relative accuracy (3% error) and precision (10%RSD) are in the range expected for spectrometric methods and can probably be reduced a bit further with practice.

When used as an experiment in an Instrumental Analysis course, the experiment will give students experience/practice with KBr sample preparation methods, FTIR operation, peak integration methods, and linear regression analysis using a calibration curve. Baseline correction methodology can be easily incorporated. The experiment is amenable to either the standard calibration curve method or the method of standard addition.

This lab can be quite time intensive; the students spent about twenty hours (five four-hour lab periods) collecting the necessary data for this lab; data analysis was done outside of lab time. Their experience suggests several possibilities for streamlining this experiment. One way is to predetermine an appropriate compound and the concentration range needed. Another possibility is to store and reuse the calibration standards, reducing sample preparation to the unknown samples only.

Next time this experiment is run, the use of an evacuated KBr pellet die will be investigated to see if that will increase the success rate for pellet production. The use of the baseline correction feature of the Nicolet Omnic software will also be investigated to see if that can "salvage" spectra with nonlinear baselines.

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