Experiment 7. Raman Spectroscopy. Identification of unknown solution

Identification of Inorganic Anions in Solution.

Identification of individual anions in solution and qualitative analysis of a mixture containing several different anions is a traditional problem of classical analysis. IR spectroscopy is almost helpless in this case because of strong water absorption in aqueous solutions. Furthermore, most of common inorganic anions show no light absorption in visible range; only few of them show UV absorption suitable for direct spectrophotometric observation. Therefore, there is no simple direct spectroscopic technique for qualitative analysis of polyatomic inorganic anions.

Monoatomic anions show no Raman spectra in aqueous solution. Consequently, the consideration must be limited to polyatomic ions such as NO_2^-, NO_3^-, $H_2PO_4^-$, HPO_4^{2-}, HCO_3^-, CO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$, SCN^-, ClO_4^-, ClO_3^-. Because of the relatively small number of anions under investigation (no greater than 20), it is feasible to make your own library of Raman spectra .

Library:

Prepare a collection of 0.5-2 M stock solutions of appropriate sodium or potassium salts. Measure Raman spectra of these solutions in a quartz cuvette at standard conditions (30s single scan was sufficient in our experimental setup). Measure water scattering at exactly the same conditions, and subtract the water spectrum from each of the spectra measured. Save (and print) the resulting spectra.

1. Anion identification in an individual water soluble solid.

Procedure: Dissolve 0.1-0.2 g of the solid in 2-3 mL of deionized water (some gentle heating and ultrasonic treatment may be helpful to facilitate the dissolving). Place the resulting aqueous solution in a cuvette and measure the Raman spectrum at the same conditions as the standards (“library”) were measured. Subtract the scattering spectrum of the pure water. Compare the resulting spectrum with the library spectra and identify the anion.

Identification is possible even for ions with very close spectral parameters (like ClO_4^- and ClO_3^-, SO_4^{2-} and SO_3^{2-}, It is worth mentioning that contrary to traditional qualitative analysis, one can instantly distinguish ions with various degree of protonation: HCO_3^- and CO_3^{2-}, HSO_3^- and SO_3^{2-}, etc.

Another fascinating task is an identification of complex anions, for example, cyano- and nitro- complexes. Ammonium salts may cause a minor problem: a careful experimenter can notice the weak peaks of NH_4^+. They never interfere with the anion peaks.

2. Anion identification in the mixture of several (2-4) anions in solution

Procedure: For successful identification, concentrations of anions in the sample should be somewhere in the range of 0.1 – 2 M. Measure the Raman spectrum of the unknown solution, subtract the water scattering spectrum, and compare the resulting picture to the library spectra. With less obvious picture, the following procedure has been employed for spectra processing:

1) Identify the anion corresponding to the strongest peak.
2) Algebraically subtract with appropriate factor the library spectrum of this peak from your experimental spectrum. This is your first simplification.
3) Find the next prominent peak, and identify the appropriate anion, then proceed to step 2. If no strong peaks are visible, stop the analysis and report the list of anions found.

4) If library measurements and your assay were performed in identical conditions, and concentrations in library solutions are known (which is strongly recommended for the sake of reproducibility), one can estimate the approximate concentrations of each anion in the mixture from the factor used for algebraic subtraction in step 2.

In this case, some compositions (SO_3^{2-} and SO_4^{2-}, ClO_3^- and ClO_4^-, HPO_4^{2-} and SO_4^{2-}) may cause significant problem due to the insufficient resolution of the instrument. Changing the acidity of the sample by careful addition of HCl or NaOH may help in the presence of phosphates and carbonates. For example, gentle acidification of the sample to pH 6 results in almost complete conversion of SO_3^{2-} ion into HSO_3^-.