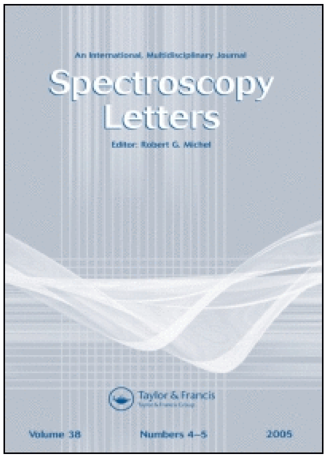

Spectroscopy Letters
An International Journal for Rapid Communication
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article: M. Scott Goodman and Kenneth F. Jonmaire , 'Contemporary Undergraduate Qualitative Analysis: Use of CCD-Based Raman, Atomic Emission, and Reflectance Spectrometers ', Spectroscopy Letters, 40:3, 453 - 463
To link to this article: DOI: 10.1080/00387010701295778
URL: http://dx.doi.org/10.1080/00387010701295778

Spectroscopy Letters, 40: 453–463, 2007

ISSN 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010701295778

Contemporary Undergraduate Qualitative Analysis: Use of CCD-Based Raman, Atomic Emission, and Reflectance Spectrometers

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Abstract: The classic undergraduate qualitative analysis is upgraded using a new generation of user-friendly, low-cost spectral instruments: (1) atomic emission spectrometer for identification of alkali and alkaline earth metals; (2) Raman spectrometer for identification of polyatomic ions; and (3) reflectance UV-Vis spectrometer for enhancement of color spot tests on metal ions. Qualitative analysis of various inorganic samples using both traditional and modern spectral methods is described.

Keywords: Atomic emission spectroscopy, CCD detector, chemical education, fiber optics, qualitative analysis, Raman spectroscopy, reflectance spectroscopy

INTRODUCTION

One-half century ago, inorganic qualitative analysis was an essential part of the college chemistry curriculum. Tens if not hundreds of textbooks were written on that subject; numerous laboratory experiments were developed. However, little of this can be found in a modern undergraduate laboratory. Most general chemistry courses limit qualitative analysis to

Received 29 August 2006, Accepted 19 October 2006

The authors were invited to contribute this paper to a special issue of the journal entitled "Undergraduate Research and Education in Spectroscopy." This special issue was organized by Associate Editor David J. Butcher, Professors of Chemistry at Western Carolina University, Cullowhee, North Carolina, USA.

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2–3 labs related to detection of 6–8 anions and 5–15 cations. These procedures are often considered boring and irrelevant to real-world problems—little surprise that many colleges skip inorganic qualitative analysis altogether. Analytical chemistry courses seldom even mention the identification problems, emphasizing the quantitative character of the subject instead. Some attention to the identification problem is given in the organic chemistry curriculum, but naturally it is limited to organic molecules only.

In spite of this gloomy picture, the science of identification is alive and well. The question "What is this white powder?" appears daily in forensic, environmental, and pharmaceutical practice. In the field of education, identification serves as an irreplaceable tool for developing logical reasoning in chemistry-related disciplines.

The usual qualitative analysis problem consists of identification of one or a few inorganic cations and anions in a solid sample or in an aqueous solution. The number of anions can be zero (pure metal or metal oxide); or if H^+ is the only cation present, the sample is an acid (or mixture of acids). To create a bridge between old-fashioned inorganic qualitative analysis and a modern university laboratory, we have attempted an introduction of several simple spectroscopic techniques. We consider these procedures so user-friendly that they can be employed by the students without much preliminary training. The following modifications to the traditional (purely chemical) approach are suggested:

1. Use of low-resolution Raman spectroscopy for identification of polyatomic anions.
2. Use of atomic emission spectroscopy for identification of Na, K, and Ca (Ba, Sr, Li, and Rb can be easily added to this list if desired).
3. Use of color spot tests for identification of 3d-transition metal ions (Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}) with spectrophotometric registration of the resulting color.

We have already described the use of a CCD-based emission spectrophotometer for alkali and alkali earth metal ion determination.[1] In this paper,we will concentrate on Raman determination of inorganic anions and will briefly describe the reflectance spectra of some spot test reactions.

MATERIALS AND METHODS

Recommended instrumentation for inorganic qualitative analysis laboratory:

(a) CCD-based spectrophotometer adjacent to a gas burner for atomic emission tests.

(b) Same or similar instrument set for reflectance measurements. A specialized reflectance probe is helpful but not necessary because of the nonquantitative nature of the measurements.

(c) A low-resolution Raman instrument with a cuvet compartment suitable for a standard 1-cm cuvet.

The PC2000 plug-in Spectrometers from OceanOptics Inc. (Dunedin, FL, USA) were used for both emission and absorbance measurements. We have used an R-2001 spectrometer (Raman Systems Inc., Austin, TX, USA), which includes a 500-mW, 785-nm diode laser along with an S2000 fiber optics spectrophotometer and has a working range of $\sim 200-2700\ \mathrm{cm}^{-1}$. A simple cuvet compartment that fits to a standard 1-cm quartz (or glass) cuvet was employed. A 1-mL sample was necessary for the measurement. After collection, the spectra were processed using the SpectraProcessor software package (ACD Labs Inc., Toronto, ON, Canada).

RESULTS AND DISCUSSION

Raman Identification of Inorganic Anions

Numerous educational Raman experiments have been proposed for inorganic and physical chemistry classes.[2–6] Several new books[7–11] describe Raman spectroscopy and its analytical applications in detail. Nevertheless, Raman spectroscopy receives far less attention than IR or UV-visible methods. It was suggested[4] that two of the major reasons for this are (a) the cost of the commercial instruments and (b) inaccessibility to a large database of standard Raman spectra for routine use. Recent developments in instrumentation have made these obstacles obsolete. The introduction of commercially available CCD detectors and diode array lasers significantly reduced the price of dispersive Raman spectrophotometers.[12] For low-resolution instruments, this cost is now below the level of a FTIR (Fourier Transform InfraRed) spectrometer. At the same time, many commercial databases have appeared in several recent years making automatic search a feasible option. However, the question of applicability of the instrument, which is affordable and simple but of low resolution, to traditional analytical problems remains open. What effect does low resolution have upon the performance of a Raman spectrometer? Several publications had addressed this question.[3,12]

Identification of individual anions in solution and qualitative analysis of a mixture containing several different anions is a traditional educational problem of classical analysis. IR spectroscopy is almost helpless in this case because of the strong water absorption in aqueous solutions. Furthermore, most common inorganic anions show no light absorption in the visible range; only a 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. High-resolution Raman data for various polyatomic anions in solid state and in aqueous solution have been collected;[10,11] results of low resolutions[6] were used for calculations of molecular properties.

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^-, and ClO_3^-. Solid salts of these anions show Raman spectra that vary with the cation nature and the crystal structure of particular chemical compound.[10,11] In contrast, all soluble salts of the same anion show the same Raman spectrum when measured in an aqueous solution. This feature significantly simplifies the identification. Most recently published undergraduate laboratory procedures in qualitative analysis will limit the list of polyatomic anions to SO_4^{2-}, CO_3^{2-}, PO_4^{3-}, and NO_3^-;[13] some others will add the acetate ion. Older textbooks provided a lengthier list. Of course, such selections depend on the level of chemical erudition of the class; the instructor can easily adjust the complexity of the problem even within one group of students.

Because of the relatively small number of anions under investigation (no greater than 20), it is more convenient to use your own library of low-resolution spectra rather than try to use a commercial high-resolution database. To make the library, prepare a collection of 0.5–2 M stock solutions of appropriate sodium or potassium salts. Measure the Raman spectra of these solutions in a quartz cuvet under standard conditions (30 second single scan was sufficient in our experimental setup). Measure water scattering under exactly the same conditions, and subtract the water spectrum from each of the spectra measured. Save (and print) the resulting spectra.

Anion Identification in a Solid Sample

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

Identification is possible even for ions with very close spectral features (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-}, HSO_4^- and SO_4^{2-}, and so forth (Fig. 1). The addition or removal of a hydrogen atom from the oxoanion results in an easily seen alteration in the Raman spectrum due to the difference in symmetry and properties of

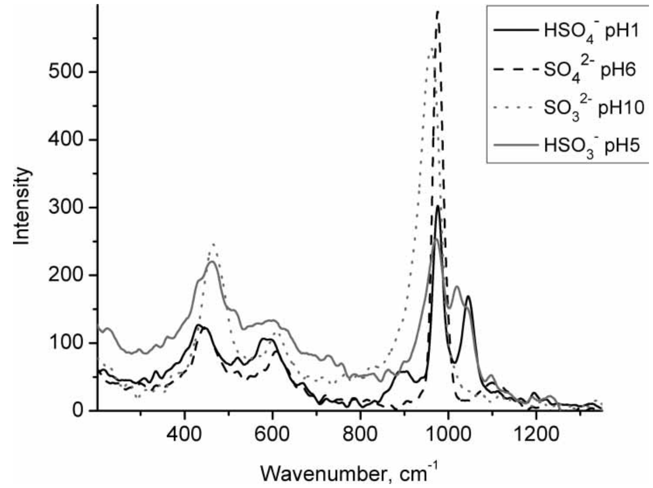

Figure 1. Difficult pairs of anions: sulfite and sulfate at various pH.

the vibrating moiety. Such a change is significant enough to be detected with a low-resolution instrument.

Another fascinating task is the identification of complex anions, for example, cyano- and nitrocomplexes. Ammonium salts may cause a minor problem: a careful experimenter can notice the weak peaks of NH_4^+ at 1680 and 1420 cm^{-1}. They never interfere with the anion peaks (Figure 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 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. For example, nitrite, nitrate, sulfate, and thiocyanate can be easily identified in a mixture by simply comparing the most prominent peaks with the library (Fig. 3). With less obvious results, the following procedure has been employed for spectra processing:

1. Identify the anion corresponding to the strongest peak.
2. Algebraically subtract (with the appropriate factor) the library spectrum of this peak from your experimental spectrum. This is the first simplification.

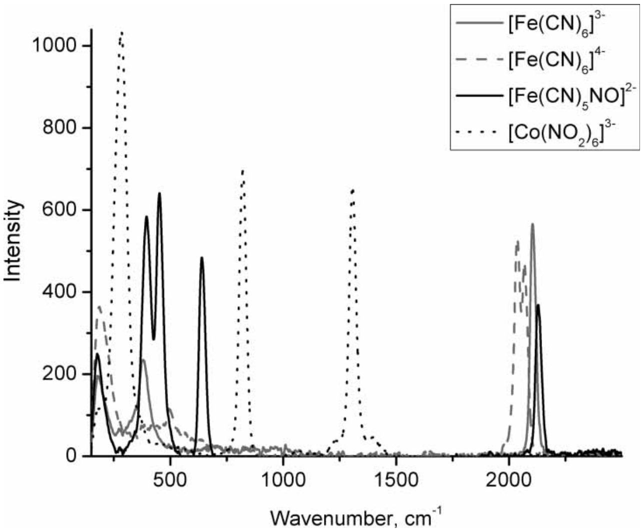

Figure 2. Low-resolution Raman spectra of several 3d metal complexes.

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 under identical conditions, and the concentrations of the 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.

Two examples of four component mixtures are shown in Fig. 3. Certain compositions (SO_3^{2-} and SO_4^{2-}, ClO_3^- and ClO_4^-, HPO_4^{2-} and SO_4^{2-}) may cause significant problems 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 case 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^- (see Fig. 1). Visual verification of results is simple and convenient for a low-resolution instrument. Although high-resolution spectra will contain much more detail and thus simplify the identification, it is hardly necessary for these uncomplicated examples.

Most of the general and analytical chemistry textbooks dedicate significant attention to acid–base equilibria in solutions of sulfuric, nitric, perchloric, carbonic, phosphoric, and acetic acids. It is obvious that no changes are visible in the solution in all mentioned circumstances (with a limited exception of CO_2 release from carbonate solutions of relatively high

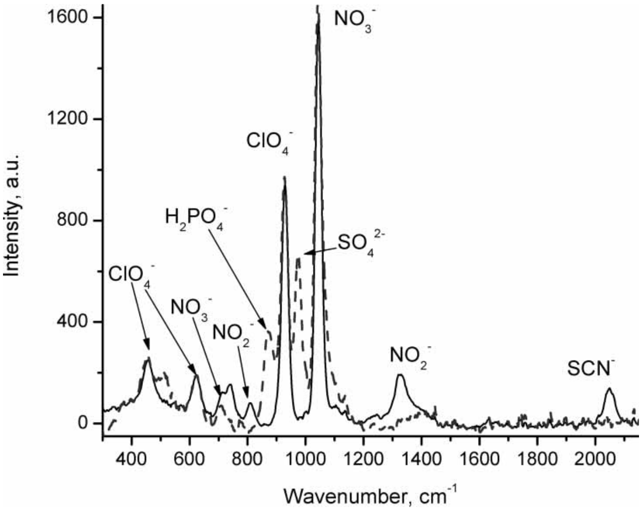

Figure 3. Low-resolution Raman spectra of four-component mixtures suitable for a direct identification. Dashed curve: sulfate, phosphate, perchlorate, nitrate. Solid curve: nitrate, nitrite, perchlorate, thiocyanate.

concentration). Students are expected to "believe" the instructor that the protonation or deprotonation occurs at some particular pH value; to have any visible effect, one should add an indicator. Raman spectra provide the necessary visualization of protonation phenomena. An example of Raman spectra of nitric acid solutions is shown in the most recent edition of *Quantitative Chemical Analysis* by Harris.[14] Such demonstration is very simple: you prepare solutions of an acid and a conjugate base (i.e., the corresponding anion), measure Raman spectra, and compare them. The difference between protonated and deprotonated form is significant enough to be viewed with the low-resolution spectrometer (Fig. 4). Perchloric acid is an important exception; it shows the same Raman spectrum in 60% $HClO_4$ solution as in $NaClO_4$ solution demonstrating that there is no protonation of perchlorate ion even at such high acidity (see Fig. 4).

Identification of Monoatomic Anions

We do not see an easy direct way to identify monoatomic Cl^-, Br^-, or I^- ions using Raman spectroscopy. Therefore, we currently use the old-fashioned way: to check the presence of halide ions with $AgNO_3$ solution in diluted nitric acid. If this test is positive, we detect Br^- and I^- using extraction of Br_2 and I_2 in an appropriate organic solvent after oxidation with aqueous Cl_2. Reflectance or absorbance spectra of Br_2 and I_2 solutions can be easily recorded to aid in the identification.

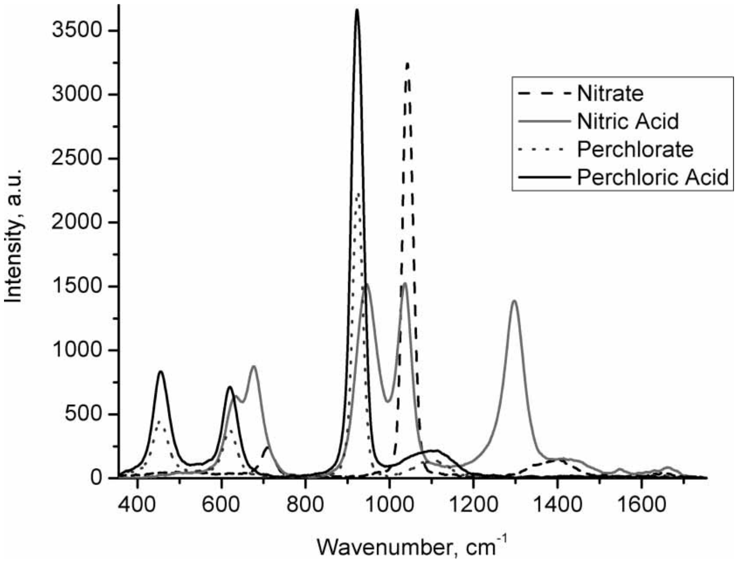

Figure 4. Low-resolution Raman spectra of 60% perchloric (black) and nitric (gray) acids. Spectra of nitrate and perchlorate ions are shown (dashed lines) for comparison.

Reflectance Spectra of Color Spot Tests

Color spot reactions of 3d metal ions are described in detail in numerous books on spot test analysis based mostly on works of Feigl and Tananaev and their numerous students and followers.[15,16] In this work, we did not employ any new reactions; the well-known tests were adopted in order to obtain the brightest colors. These tests seldom pose any significant problems to an experienced chemist; at the same time, students are often confused with the colors they observe. For example, the characteristic color of nickel dioximate is often mistaken with the orange color of interfering Fe(II) dioximate or even with "rusty" iron (III) hydroxide that appear when the appropriate precautions against interference are not taken. It is also easy to confuse colors of Co^{2+} and MnO_4^-; $Ni(NH_3)_6^{2+}$ and $Cu(NH_3)_4^{2+}$, and so forth. A very simple spectrophotometric measurement can remove much of the ambiguity from the identification (Fig. 5).

Recommended Procedure for 3d Metal Identification

Run color tests listed in the laboratory instruction (e.g., http://staff.buffalostate.edu/nazareay/che112/ex9.htm). If no effect is observed, record the negative. If the test is positive or questionable, measure the spectrum of the resulting color spot. Compare the maxima and the shape of the absorption

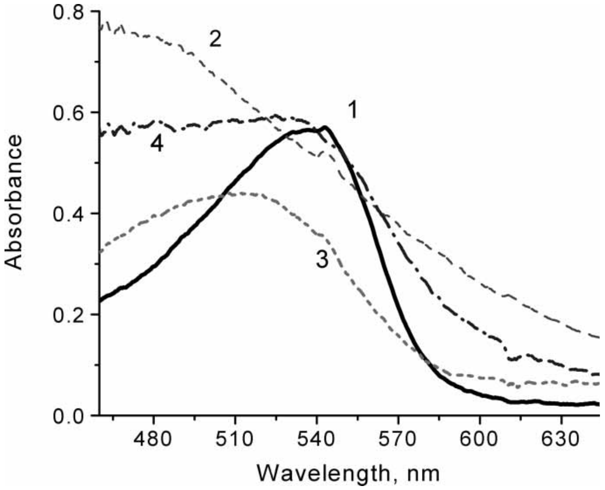

Figure 5. Reflectance spectra of nickel dimethylglyoximate (1) and possible interfering colored species: iron (III) hydroxide (2), cobalt (II) ion (3), iron (II) dimethylglyoximate (4).

bands with those from the library. Only spectra that are similar (same maxima) to the standard are considered as positive.

Procedure for Identification of Unknown Sample

The sample can be either a solid (powder) or a concentrated (10–20%) aqueous solution. For sake of simplicity, solids that are insoluble in water or diluted nitric acid should be avoided. Students receive the list of possible anions and cations.

Before tests, the solid samples need to be dissolved in a small volume of water (100–200 mg in 1–2 mL). The following tests are performed:

1. Raman spectrum of the aqueous sample is measured and interpreted as described in the Raman section, thus giving the information about polyatomic ions.
2. Tests for Cl^-, Br^-, and I^- are performed.
3. A small amount of solution is introduced into a flame and is tested for alkali and alkaline earth metals.
4. Color tests are performed for 3d metal ions as described in "Reflectance Spectra of Color Spot tests." Even without much experience, 40–60 min are usually enough to identify the composition of a simple sample (e.g., an inorganic salt). Students are then expected to write a formula of the compound. Contrary to the traditional approach, compounds like $NaHCO_3$ and Na_2CO_3 can be easily differentiated; binary salts like $KFe(SO_4)_2$ also cause little problem. For advanced students, even some complex compounds like $K_4Fe(CN)_6$ can also be included.

CONCLUSIONS

Low-resolution Raman instrument and a CCD-based spectrophotometer are necessary and affordable tools for an undergraduate chemistry laboratory. Use of simple and user-friendly spectral instruments enhances quality of chemical education and makes traditional approaches appear contemporary and attractive.

ACKNOWLEDGMENTS

This laboratory setup was tested with chemistry and forensic chemistry students at SUNY College at Buffalo in 2004–2006; without their patience and helpful comments, this project could not have been accomplished. The financial support from OceanOptics Inc. (educational grant B132) and SUNY SCAP 2004 and 2005 grants is gratefully acknowledged. The authors thank Dr. Monde Qhobosheane (OceanOptics Inc.) for reading and commenting on the article.

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