Infrared Spectra and Characteristic Frequencies of Inorganic Ions

Their Use in Qualitative Analysis

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Polyatomic ions exhibit characteristic infrared spectra. Although such spectra are potentially useful, there is very little reference to them in the recent literature. In particular, the literature contains no extensive collection of infrared spectra of pure inorganic salts obtained with a modern spectrometer. In order to investigate the possible utility of such data, the infrared spectra of 159 pure inorganic compounds (principally salts of polyatomic ions) have been obtained and are presented here in both graphical and tabular form. A table of characteristic frequencies for 33 polyatomic ions is given. These characteristic frequencies are shown to be useful in the qualitative analysis of inorganic unknowns. Still more fruitful is a combination of emission analysis, infrared examination, and x-ray diffraction, in that order. Several actual examples are given. It is evident that a number of problems involving inorganic salts containing polyatomic ions will benefit by infrared study. The chief limitation at present is the practical necessity of working with powders, which makes it difficult to put the spectra on a quantitative basis.

Although there has been a vast amount of work on the Raman spectra of inorganic salts (2, 4), the study of them in the infrared has been relatively neglected. Schaefer and Matossi (10) have reviewed work done up to 1930, most of which deals with reflection spectra. The most extensive surveys of infrared absorption spectra have been made by Lecomte and his coworkers (6, 7), but unfortunately many of their data are somewhat out of date and are not always presented in the most useful form. References to studies on a few ions are given in the books by Wu (12) and by Herzberg (3). There has recently been renewed interest in the detailed study of the infrared spectra of selected salts, as exemplified by the papers of Halford (8), Hornig (11), and their coworkers. The well-known Colthup chart (1) contains characteristic frequencies for nitrate, sulfate, carbonate, phosphate, and ammonium ions. An excellent recent paper by Hunt, Wisherd, and Bonham (5) contains the spectra of 64 naturally occurring minerals and related inorganic compounds.

Aside from sixteen spectra in this latter paper, there is in the literature no compilation of infrared spectra of inorganic salts obtained with a modern spectrometer. It therefore seemed worth while to make a fairly extensive survey to seek answers to the following questions: Is it generally possible to obtain good spectra? Do the ions possess frequencies which are sufficiently characteristic to be useful for analytical purposes? What is the effect on the vibrational frequencies of varying the positive ion? Is infrared spectroscopy useful in the analysis of salts?

This paper presents the spectra from 2 to 16 microns of 159 pure inorganic compounds, most of which are salts containing polyatomic ions. A chart of characteristic frequencies for 33 such ions is given. The use of these data for the qualitative analysis of inorganic mixtures is demonstrated. Finally, a number of interesting or puzzling features of the spectra are described.

A brief classification of the various types of vibrations in crystals may be appropriate. Ionic solids are considered first. In a crystal composed solely of monatomic ions, such as sodium chloride, potassium bromide, and calcium fluoride, the only vibrations are “lattice” vibrations, in which the individual ions undergo translatory oscillations. The resulting spectral bands are broad and are responsible for the long wave-length cutoff in transmission. In a crystal containing polyatomic ions, such as calcium carbonate or ammonium chloride, the lattice vibrations also include rotatory oscillations. Of greater interest in this case, however, is the existence of “internal” vibrations. These are essentially the distortions of molecules whose centers of mass and principal axes of rotation are at rest. The internal vibrations are characteristic of each particular kind of ion.

In molecular solids, such as benzene, phosphorus, and ice, the units are uncharged molecules held in the lattice by weak forces of the van der Waals type, and often also by hydrogen bonds. The same classification into internal and lattice modes can be made. A few examples of such solids are represented in this paper (boric acid, and possibly the oxides of arsenic and antimony).

Finally there are the covalent solids, such as diamond and quartz, in which the entire lattice is held together by covalent bonds. Here the distinction between lattice and internal vibrations disappears. One might at first expect an ill-defined and featureless spectrum, but such is not the case. Actually there are bands that are very characteristic. The situation is in some ways analogous to that in a polymer, which in spite of its size and complexity possesses a remarkably discrete spectrum. Silica gel is the only representative of this type included here.

EXPERIMENTAL

Origin and Preparation of Samples. Practically all the samples were commercial products of C.P. or analytical reagent grade. The samples were ground to a fine powder to minimize the scattering of light, and were examined as Nujol mulls. When there were spectral features that were obscured by the Nujol bands, the samples were either run as a dry powder or mulled in fluorolube (a mixture of completely fluorinated hydrocarbons. Fluorolube is a product of the Hooker Electrochemical Co., perfluoro lube oil of E. I. du Pont de Nemours & Co.). Some compounds, such as ferric nitrate nonahydrate (No. 49) and calcium permanganate tetrahydrate (No. 150), seemed to mull up in their own water of hydration. When the fine powder was rubbed between salt plates, it acquired the appearance and feel of a typical mull, but no appreciable fogging of the salt plates resulted. For other compounds, such as potassium carbonate, breathing on the sample achieved the same result. This is not recommended, however, for it varies the water content unnecessarily, and with potassium carbonate some of the bands are shifted.

Although these techniques are satisfactory for qualitative examination, it may be of interest to list some other methods which have been mentioned in the literature for handling inorganic solids. Lecomte, who introduced most of them, has pointed out that a finely ground dry powder scatters very little radiation of wave length greater than 6 microns and consequently it may be used directly in that region (6, 7). He also suggests coating...
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<td>5. Potassium tetraborate</td>
<td>K₂B₄O₇·5H₂O</td>
<td>620</td>
<td>10.2 s, vb</td>
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<td>1320</td>
<td>7.2 s</td>
<td>1380</td>
<td>6.85 Nujol</td>
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<td>CaCO₃</td>
<td>715</td>
<td>14.05 w</td>
<td>775</td>
<td>12.7 w</td>
<td>828</td>
<td>12.1 s</td>
<td>940</td>
<td>10.6 s</td>
</tr>
<tr>
<td>15. Barium carbonate</td>
<td>BaCO₃</td>
<td>697</td>
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<td>11.05 s, sp</td>
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<td>855</td>
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<td>8. Boric acid</td>
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<td>350</td>
<td>8.8 s</td>
<td>4320</td>
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**Note:**
- **vw** = very weak
- **w** = weak
- **m** = medium
- **s** = strong
- **sh** = shoulder
- **b** = broad
- **vb** = very broad
- **sp** = sharp
- **imp** = impurity
- **=** KBr region (15-15 cm⁻¹) examined
Table II. Positions and Intensities of Infrared Absorption Bands (Continued)

| Cm.⁻¹ | Microns | I | Cm.⁻¹ | Microns | I | Cm.⁻¹ | Microns | I | Cm.⁻¹ | Microns | I |
|-------|---------|---|-------|---------|---|-------|---------|---|-------|---------|---|-------|---------|---|
| 43. Magnesium phosphate, tribasic | Mg(H₂PO₄)₂ | 53. Barium nitrate | Ba(NO₃)₂ | 54. Copper nitrate | Cu(NO₃)₂.3H₂O | 55. Chromium phosphate, tribasic | Cr₂(PO₄)₃ | 56. Cobalt nitrate | Co(NO₃)₂.6H₂O | 57. Cobaltous nitrate | Co(N₂H₄)₂.6H₂O | 58. Lead nitrate | Pb(NO₃)₂ | 59. Chrome nitrate | Cr₂O₃.2H₂O | 60. Bismuth nitrate | Bi₂O₃.2H₂O | 61. Sodium phosphate, tribasic | Na₃PO₄.12H₂O | 62. Zinc phosphate, tribasic | Zn₂(PO₄)₂.7H₂O | 63. Zinc phosphate, dibasic | ZnHPO₄.7H₂O | 64. Calcium phosphate, dibasic | CaHPO₄.2H₂O | 65. Calcium phosphate, monobasic | CaH₂PO₄.H₂O | 66. Ammonium phosphate | (NH₄)₃PO₄ | 67. Sodium phosphate, dibasic | Na₂HPO₄.12H₂O | 68. Potassium phosphate, dibasic | K₂HPO₄.12H₂O | 69. Potassium phosphate, monobasic | K₂H₂PO₄ | 70. Calcium phosphate, monobasic | Ca₃(PO₄)₂.12H₂O | 71. Sodium merserensite | Na₂SO₄ | 72. Potassium orthoarsenate, dibasic | K₂H₂AsO₄ | 73. Potassium orthoarsenate, monobasic | K₂HAsO₄ | 74. Sodium metaarsenite | Na₂H₂AsO₄ | 75. Sb₂O₃ | 76. Arsenic trioxide | As₂O₃ | 77. Antimony trioxide | Sb₂O₃ | 78. Antimony pentoxide | Sb₂O₅ | 79. Ammonium sulfite | (NH₄)₂S₂O₃ | 80. Sodium sulfite | Na₂S₂O₃ |
### Table II. Positions and Intensities of Infrared Absorption Bands (Continued)

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<tr>
<th>Cm.</th>
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<th>Intensities</th>
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### 82. Calcium sulfate CaSO₄. 2H₂O

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<td>Na₂VO₄·4H₂O</td>
<td>Na₂Cr₂O₇</td>
<td>K₂WO₄</td>
</tr>
<tr>
<td>600</td>
<td>14.05</td>
<td>730</td>
</tr>
<tr>
<td>129. Ammonium chromate</td>
<td>139. Potassium dichromate</td>
<td>147. Calcium tungstate</td>
</tr>
<tr>
<td>(NH₄)₂CrO₄·3H₂O</td>
<td>K₂Cr₂O₇</td>
<td>CaWO₄</td>
</tr>
<tr>
<td>745</td>
<td>15.4</td>
<td>790</td>
</tr>
<tr>
<td>130. Sodium chromate</td>
<td>140. Potassium permanganate</td>
<td>148. Sodium permanganate</td>
</tr>
<tr>
<td>Na₂CrO₄</td>
<td>K₂MnO₄</td>
<td>Na₂MnO₄·2H₂O</td>
</tr>
<tr>
<td>640</td>
<td>20.1</td>
<td>640</td>
</tr>
</tbody>
</table>

* = strong, sh = shoulder, impurity, region (10-25 μm) examined
one of the salt plates with a very thin layer of solid paraffin to hold the particles in place (6, 7). The fine powder may be prepared by grinding, by evaporation of a suitable solvent (6, 7), or by sedimentation (5). Vacuum evaporation which has been used for preparing films of ammonium halides (11), may be useful for other relatively volatile inorganic materials.

Spectroscopic Procedures. All samples were examined from 2 to 16 microns with a Baird Model A infrared spectrophotometer. Wave lengths are accurate to about ±0.03 micron, although for broad bands the error of judging the center may exceed this. It was sometimes found that duplicate spectra for the same compound differed by more than this amount. Some possible reasons are mentioned below.

Representative examples of several ions were examined in the potassium bromide region with this same spectrometer. Likewise, a series of ten nitrates was examined in the rock salt region with the same instrument in order to fix the wave lengths of absorption more accurately.

No attempt was made to put the spectra on a quantitative basis.

RESULTS

The spectra are presented at the end of this paper. Table I lists the compounds examined and gives the numbers of the corresponding spectral curves. Table II summarizes the positions of the bands in wave numbers and in microns, and gives estimated peak intensities. If more precise wave numbers have been determined with the Perkin Elmer spectrometer, they are used. Asterisks indicate those compounds examined in the potassium bromide region.

The spectra themselves are shown in graphical form. Nujol bands are marked with asterisks; portions of curves run in fluoro-lube are indicated by an F. The spectra of Nujol and Fluorolube are included for comparison (No. 160). In a few cases the powder was used without a mulling agent; these are indicated by P.

The purities of the samples are indicated in the legends for the curves. Some idiosyncrasies of the curves warrant mention. Many of them show weak remnants of the carbon dioxide bands near 4.3 and 14.8 microns. The latter always appears as a sharp upward pip. Many of the curves exhibit a drop in transmission near 15 microns and then a small increase beginning at 15.5 microns. The initial decrease is due to the absorption by the sodium chloride plates, which was not compensated in the reference beam. The reason for the later increase is not known, but it is not real. It has the effect of suggesting an incorrect position for bands near 16 microns. For example, in ferrous sulfate heptahydrate (No. 91) the curve indicates a band at 650 cm.⁻¹ (15.5 microns), but actually it is at 611 cm.⁻¹ (16.5 microns).

DISCUSSION OF RESULTS

The spectra range in quality from surprisingly good ones, with sharp, intense bands (see curves for barium thioceyanate dihydrate, No. 28; strontium nitrate, No. 44; and ammonium hexanitratocerate, No. 157,) to very poorly defined ones such as those for potassium silicate, No. 69; and monobasic potassium orthoarsenate, No. 157. The spectra of ten nitrates are shown in Figure 1 in the form of a line graph. It is seen that two characteristic frequencies occur, one at 610 to 680 cm.⁻¹ (m) and the other at 1080 to 1130 cm.⁻¹ (s). There is enough variation between the individual sulfates so that it is often possible to distinguish between them from the exact positions of the bands. Table III presents similar data for ten nitrates. Again there are characteristic frequencies, at 815 to 840 cm.⁻¹ (m) and 1350 to 1380 (vs). The authors have been unable to find any orderly relation between the positions of these nitrate bands and a property of the positive ion, such as its charge or mass. This is not surprising, for there are at least three reasons why a frequency may shift slightly as the kind of positive ion is changed.

Effect of Varying Positive Ion. One of the purposes of this study was to ascertain whether the various ions have useful characteristic frequencies. It was therefore of interest to know the effect of altering the positive ion. The spectra of ten sulfates are shown in Figure 1 in the form of a line graph. It is seen that two characteristic frequencies occur, one at 610 to 680 cm.⁻¹ (m) and the other at 1080 to 1130 cm.⁻¹ (s). There is enough variation between the individual sulfates so that it is often possible to distinguish between them from the exact positions of the bands. Table III presents similar data for ten nitrates. Again there are characteristic frequencies, at 815 to 840 cm.⁻¹ (m) and 1350 to 1380 (vs). The authors have been unable to find any orderly relation between the positions of these nitrate bands and a property of the positive ion, such as its charge or mass. This is not surprising, for there are at least three reasons why a frequency may shift slightly as the kind of positive ion is changed.

The different changes and radii of the various positive ions produce different electrical fields in the various salts. These doubtless affect the vibrational frequencies of the negative ions.

(Continued on page 1302)
Sodium metaborate,
NaBO₂
C.P.

Magnesium metaborate,
Mg(BO₂)₂·8H₂O
C.P.

Lead metaborate,
Pb(BO₂)₂·5H₂O
C.P.

Sodium tetaborate,
Na₂BO₃·10H₂O
C.P.

Potassium tetaborate,
K₂B₄O₇·5H₂O
C.P.
Manganese tetrahydroxide, 
MnBO₄·8H₂O
C.P.

Sodium perborate, 
NaBO₄·4H₂O
C.P.

Boric acid, H₃BO₃
C.P.

Boron nitride, BN
Pure

Lithium carbonate, 
Li₂CO₃
AR
Sodium carbonate, $\text{Na}_2\text{CO}_3$

Potassium carbonate, $\text{K}_2\text{CO}_3$

Magnesium carbonate, basic, $3\text{MgCO}_3\cdot\text{Mg(OH)}_2\cdot3\text{H}_2\text{O}$

$\text{Unk.}$

Calcium carbonate, $\text{CaCO}_3$

Barium carbonate, $\text{BaCO}_3$
Cobaltous carbonate, CoCO₃
Unk.

Lead carbonate, PbCO₃
Unk.

Ammonium bicarbonate, NH₄HCO₃
C.P.

Sodium bicarbonate, NaHCO₃
C.P.

Potassium bicarbonate, KHCO₃
C.P.
Sodium cyanide, NaCN

N\textsubscript{a}CO\textsubscript{3} impurity

Potassium cyanide, KCN

KHC\textsubscript{O} and K\textsubscript{2}CO\textsubscript{3} impurities

Potassium cyanate, KOCN

Considerable K\textsubscript{H}CO impurity

Silver cyanate, AgOCN

"Highest purity"

Ammonium thiocyanate, NH\textsubscript{4}SCN

AR
Sodium thiocyanate, NaSCN

Potassium thiocyanate, KSCN

Barium thiocyanate, Ba(SCN)₂·2H₂O

Mercuric thiocyanate, Hg(SCN)₂

Lead thiocyanate, Pb(SCN)₂
Sodium metasilicate, $\text{Na}_2\text{SiO}_3\cdot\text{H}_2\text{O}$

Potassium metasilicate, $\text{K}_2\text{SiO}_3$

Sodium silicofluoride, $\text{Na}_2\text{SiF}_4$

Silica gel, $\text{SiO}_2\cdot\text{H}_2\text{O}$

Sodium nitrite, $\text{NaNO}_2$
Potassium nitrite, $\text{KNO}_3$

Silver nitrite, $\text{AgNO}_3$

Barium nitrite, $\text{Ba(NO}_3)_2\cdot\text{H}_2\text{O}$

Ammonium nitrate, $\text{NH}_4\text{NO}_3$

Sodium nitrate, $\text{NaNO}_3$
Potassium nitrate, KNO₃

Silver nitrate, AgNO₃

Calcium nitrate, Ca(NO₃)₂

Strontium nitrate, Sr(NO₃)₂

Barium nitrate, Ba(NO₃)₂
Cupric nitrate, Cu(NO₃)₂.3H₂O
C.P.

Cobaltous nitrate, Co(NO₃)₂.6H₂O
AR

Lead nitrate, Pb(NO₃)₂
AR

Ferric nitrate, Fe(NO₃)₃.9H₂O
AR

Bismuth subnitrate, Bi(NO₃)₃.6H₂O
Unk.
Sodium phosphate, tribasic, Na₃PO₄·12H₂O

AR

Potassium phosphate, tribasic, K₃PO₄

C.P.

Magnesium phosphate, tribasic, Mg₃(PO₄)₂·4H₂O

C.P.

Calcium phosphate, tribasic, Ca₃(PO₄)₂

C.P.

Manganese phosphate, tribasic, Mn₃(PO₄)₂·7H₂O

C.P.
Nickel(II) phosphate, tribasic,
\( \text{Ni}(\text{PO}_4)_{2} \cdot 7\text{H}_2\text{O} \)

C.P.

Copper(II) phosphate, tribasic,
\( \text{Cu}(\text{PO}_4)_{2} \cdot 3\text{H}_2\text{O} \)

C.P.

Lead phosphate, tribasic,
\( \text{Pb}_3(\text{PO}_4)_2 \)

C.P.

Chromium phosphate, tribasic,
\( \text{CrPO}_4 \cdot \text{H}_2\text{O} \)

C.P.

Ammonium phosphate, dibasic,
\( \text{(NH}_4\text{O})_2\text{HPO}_4 \)

C.P.
Sodium phosphate, dibasic, Na₂HPO₄·12H₂O
C.P.

Potassium phosphate, dibasic, K₂HPO₄
C.P.

Magnesium phosphate, dibasic, MgHPO₄·3H₂O
C.P.

Calcium phosphate, dibasic, CaHPO₄·2H₂O
C.P.

Barium phosphate, dibasic, BaHPO₄
C.P.
Ammonium phosphate, monobasic, $\text{NH}_4\text{H}_2\text{PO}_4$.

Sodium phosphate, monobasic, $\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}$.

Potassium phosphate, monobasic, $\text{KH}_2\text{PO}_4$.

Magnesium phosphate, monobasic, $\text{Mg(H}_2\text{PO}_4)$.

Calcium phosphate, monobasic, $\text{Ca(H}_2\text{PO}_4)\cdot\text{H}_2\text{O}$.
Sodium metaarsenite, \( \text{NaAsO}_2 \)

Calcium orthoarsenate, tribasic \( \text{Ca(AsO}_3)_2 \)

Sodium orthoarsenate, dibasic \( \text{NaHAsO}_3 \cdot \text{H}_2\text{O} \)

Lead orthoarsenate, dibasic \( \text{PbHAsO}_3 \)

Potassium orthoarsenite, monobasic \( \text{KHAsO}_4 \)
Arsenic trioxide, $\text{As}_2\text{O}_3$

Unk.

Antimony trioxide, $\text{Sb}_2\text{O}_3$

Unk.

Antimony pentoxide, $\text{Sb}_2\text{O}_5$

c.p.

Ammonium sulfite, $(\text{NH}_4)_2\text{SO}_3\cdot\text{H}_2\text{O}$

Unk.

Sodium sulfite, $\text{Na}_2\text{SO}_3$

AR.
Potassium sulfite,
K₂SO₄.2H₂O
C.P.

Calcium sulfite,
CaSO₄.2H₂O
C.P.

Barium sulfite,
BaSO₄
C.P.

Zinc sulfite,
ZnSO₄.2H₂O
C.P.

Ammonium sulfite,
(NH₄)₂SO₄
Unit.
Lithium sulfate, Li$_2$SO$_4$·H$_2$O

Sodium sulfate, Na$_2$SO$_4$

Potassium sulfate, K$_2$SO$_4$

Calcium sulfate, CaSO$_4$·2H$_2$O

Manganese sulfate, MnSO$_4$·2H$_2$O
Ferrous sulfate, FeSO₄·7H₂O

Unk.

Copper sulfate, CuSO₄

AR

Zirconium sulfate, ZrSO₄·4H₂O

c.p.

Chromium potassium sulfate, Cr₂(SO₄)₁₂·K₂SO₄·24H₂O

Unk.

Ammonium bisulfate, NH₄HSO₄

c.p.
Sodium bisulfate, NaHSO₄
AR

Potassium bisulfate, KHSO₄
AR

Ammonium thiosulfate, (NH₄)₂S₂O₃
C.P.

Sodium thiosulfate, Na₈S₂O₅·5H₂O
AR

Potassium thiosulfate, K₈S₂O₅·H₂O
C.P.
Magnesium thiosulfate, MgS2O3·6H2O
C.P.

Barium thiosulfate, BaS2O3·H2O
C.P.

Sodium metabisulfite, Na2S2O5
Unk.

Potassium metabisulfite, K2S2O5
AR

Ammonium persulfate, (NH4)2S2O8
AR
Potassium persulfate, $\text{K}_2\text{SO}_4$

Sodium selenate, $\text{Na}_2\text{SeO}_4$.

Copper selenate, $\text{CuSeO}_3\cdot2\text{H}_2\text{O}$

Ammonium selenate, $\text{(NH}_4\text{)}_2\text{SeO}_4$

Sodium selenate, $\text{Na}_2\text{SeO}_3\cdot10\text{H}_2\text{O}$
Potassium selenate, K$_2$SeO$_4$

C.P.

Copper selenate, CuSeO$_3$.5H$_2$O

C.P.

Sodium chlorate, NaClO$_3$

AR

Potassium chlorate, KClO$_3$

AR

Barium chlorate, Ba(ClO$_3$)$_2$.H$_2$O

C.P.
Ammonium perchlorate
\( \text{NH}_4\text{ClO}_4 \)
C.P.

Sodium perchlorate.
\( \text{NaClO}_4\text{H}_2\text{O} \)
C.P.

Potassium perchlorate.
\( \text{KClO}_4 \)
AR

Magnesium perchlorate.
\( \text{Mg(ClO}_4)\text{H}_2\text{O} \)
Unk.

Sodium bromate.
\( \text{NaBrO}_3 \)
C.P.
Potassium bromate, KBrO₃

Silver bromate, AgBrO₃

C.P.

Sodium iodate, NaIO₃

C.P.

Potassium iodate, KIO₃

Unk.

Calcium iodate, CaIO₃·3H₂O

C.P.
Potassium periodate, KIO₄
C.P.

Ammonium metavanadate, NH₄VO₃
C.P.

Sodium metavanadate, NaVO₃·H₂O

Ammonium chromate, (NH₄)₂CrO₄
Unk.

Sodium chromate, Na₂CrO₄
Unk.
Potassium chromate,
\( \text{K}_2\text{Cr}_2\text{O}_7 \)

MgCrO₄·7H₂O

Barium chromate, BaCrO₄

ZnCrO₄·7H₂O

PbCrO₄
Aluminum chromate, 
$\text{Al}_2\text{Cr}_2\text{O}_7$

C.P.

Ammonium dichromate, 
$\text{NH}_4\text{Cr}_2\text{O}_7$

C.P.

Sodium dichromate, 
$\text{Na}_2\text{Cr}_2\text{O}_7\cdot 2\text{H}_2\text{O}$

C.P.

Potassium dichromate, 
$\text{K}_2\text{Cr}_2\text{O}_7$

Unk.

Calcium dichromate, 
$\text{CaCr}_2\text{O}_7\cdot 2\text{H}_2\text{O}$

C.P.
141. Copper dichromate, CuCr₂O₄·2H₂O
C.P.

142. Sodium molybdate, Na₂MoO₄·2H₂O
AR

143. Potassium molybdate, K₂MoO₄·2H₂O
C.P.

144. Ammonium heptamolybdate (NH₄)₂Mo₇O₂₄·4H₂O
AR

145. Sodium tungstate, Na₂WO₄·2H₂O
C.P.
Potassium tungstate, $\text{K}_2\text{WO}_4$

Calcium tungstate, $\text{CaWO}_4$

Sodium permanganate, $\text{NaMnO}_4\cdot3\text{H}_2\text{O}$

Potassium permanganate, $\text{KMnO}_4$

Calcium permanganate, $\text{CaMnO}_4\cdot4\text{H}_2\text{O}$
Barium permanganate, B₄MnO₇
C.P.

Sodium ferrocyanide, Na₂Fe(CN)₆.10H₂O
C.P.

Potassium ferrocyanide, K₂Fe(CN)₆.12H₂O
AR

Calcium ferrocyanide, Ca₂Fe(CN)₆.12H₂O
Pure

Potassium ferricyanide, K₃Fe(CN)₆
AR
Sodium cobaltinitrite, Na₂Co(NO₃)₄

AR

Ammonium benzonitritocerate, (NH₄)₃Co(NO₃)₄

AR

Ammonium chloride, NH₄Cl

AR

Barium chloride, BaCl₂·2H₂O

AR

Nujol (N); Fluorolube (F)
Table IV. Use of Infrared Spectra in Qualitative Analysis

<table>
<thead>
<tr>
<th>No.</th>
<th>Emission</th>
<th>Infrared</th>
<th>X-ray</th>
<th>Final Combined Analysis</th>
<th>Actual Composition</th>
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<tbody>
<tr>
<td>1</td>
<td>Na</td>
<td>NaHCO₃</td>
<td>NaHCO₃</td>
<td>NaHCO₃</td>
<td>NaHCO₃</td>
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</tr>
<tr>
<td>2</td>
<td>Si</td>
<td>NH₄⁺</td>
<td>NH₄NO₃</td>
<td>NH₄NO₃</td>
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<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Na</td>
<td>K₂CO₃</td>
<td>Nothing</td>
<td>Na₂CO₃</td>
<td>K₂CO₃</td>
</tr>
<tr>
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<td></td>
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</tr>
<tr>
<td>4</td>
<td>Cd</td>
<td>NaBrO₃</td>
<td>NaBrO₃</td>
<td>NaBrO₃: 10H₂O</td>
<td>NaBrO₃: 10H₂O</td>
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<tr>
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<td></td>
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<td></td>
</tr>
<tr>
<td>5</td>
<td>As</td>
<td>NaAsO₃</td>
<td>NaAsO₃</td>
<td>NaAsO₃</td>
<td>NaAsO₃</td>
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<tr>
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</tr>
<tr>
<td>6</td>
<td>Mo</td>
<td>K₂SO₄</td>
<td>K₂SO₄</td>
<td>K₂SO₄</td>
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</tr>
<tr>
<td>7</td>
<td>Pb</td>
<td>Ca₃(PO₄)₂</td>
<td>Ca₃(PO₄)₂</td>
<td>Ca₃(PO₄)₂</td>
<td>Ca₃(PO₄)₂</td>
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</tr>
<tr>
<td>8</td>
<td>Ba</td>
<td>A nitrate</td>
<td>Ba(NO₃)₂</td>
<td>Ba(NO₃)₂</td>
<td>Ba(NO₃)₂</td>
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</tr>
</tbody>
</table>

Changing the positive ion may produce a different crystalline arrangement, resulting in a different symmetry or intensity of the electrical field around a negative ion.

A difference in the type or extent of hydration probably alters some of the frequencies.

On the other hand, Hunt, Wisherd, and Bonham (3) found that for anhydrous carbonates there is an approximately linear relationship between the wave length of the 11- to 12-micron band and the logarithm of the mass of the positive ion(s). Hunt has kindly pointed out that the authors' data fit his curve, with the exception of lithium carbonate.

Characteristic Frequencies of Inorganic Ions. Just as with sulfates and nitrates, most other polyatomic ions exhibit characteristic frequencies. These are summarized in Figure 2. It is evident that they are distinctive and that they do not have a great spread in wave numbers.

Qualitative Analysis. The usefulness of these characteristic frequencies in qualitative analysis is obvious. It appeared that the infrared spectrum might give, rapidly and easily, some information about the polyatomic ions that are present in an unknown inorganic mixture. If only one or two compounds are involved, it might even be possible to narrow the possibilities to a few specific salts. It also seemed that a combination of infrared, emission, and x-ray analysis might be very effective. Presumably emission analysis would determine the metals, infrared would say something about the polyatomic ions, and x-ray analysis might give their combination into specific salts.

To explore this possibility, a series of eight synthetic mixtures was prepared and analyzed independently by the three techniques. (A photographic x-ray procedure was used.) This information was then pooled, the data were re-examined, and a combined analysis was obtained. The test was not completely fair because it was known that infrared spectra have been obtained for nearly all the inorganic salts in the laboratory, and that these same salts would be used in making up the mixtures. In addition, the components were mixed in roughly equal amounts by bulk.

The results are shown in Table IV. The analysis of mixture 3 is discussed in greater detail below. It is apparent that no one of the techniques by itself is powerful enough to give a complete analysis of even these idealized unknowns. This is partly because there was no prior information about the content of the samples, and therefore every possibility had to be considered. As with any other analysis, much more detailed and reliable
results can be obtained if there is some advance information about the nature of the unknowns. However, Table IV also shows that the three techniques are nicely complementary, and that together they are capable of providing a considerable amount of information even when such prior knowledge is lacking. Although there are two or three surprising errors in the combined analyses, the over-all results are very encouraging. It is especially noteworthy that the actual chemical compounds are given in many cases.

The proper sequence in using these techniques is the order infrared, emission, and then x-ray. The first two present certain possibilities for the x-ray analysis which greatly simplify its interpretation.

The advantages of this physical analysis include small sample requirement, reasonable time, and the ability to determine the actual compounds in many cases. It is evident, too, that any or all of these three techniques are valuable preliminaries to a chemical analysis on an unknown material, especially a quantitative one.

**Variability of Spectra.** It is not uncommon to find that the spectra of two samples of the same compound are somewhat different. There are several possible reasons for this.

**Impurities.** In the spectra of sodium cyanide, potassium cyanide, and potassium cyanate (Nos. 21, 22, 23) bands have been marked that are plainly due to the corresponding carbonates and bicarbonates.

**Crystal Orientation.** It is well known that the spectra of anisotropic crystals depend on the orientation of the sample. Consequently it is desirable to have completely random orientation of the crystallites to avoid such effects. This is an additional reason for grinding the sample very finely.

**Polyomorphism.** Different crystalline forms of the same compound are often capable of exhibiting slightly different infrared spectra (11).

**Varying Degrees of Hydration.**

Several examples of variable spectra have been observed, for which the cause is not definitely known. Two different samples of potassium metabisulfite, K2S2O6, were examined, and proved to have different patterns of band intensities in one region (see curve 104). In potassium carbonate there is a band at 880 cm.⁻¹ or at 865 cm.⁻¹, and in one spectrogram out of a total of ten both bands appear. There is no clear correlation between position and water content.

Figure 3 shows that the mode of preparation is important. It compares the spectra of two lead nitrate samples, one prepared normally with Nujol and one with very little Nujol. Differences near 1300 cm.⁻¹ and 850 to 700 cm.⁻¹ are striking. This may be an orientation effect.

A more baffling case of unexpected variation was observed with unknown No. 3. In analyzing this by infrared, calcium sulfate dihydrate was missed completely and magnesium perchlorate was reported in its place. The reason is brought out in Figure 4. Pure calcium sulfate dihydrate has a single broad band centered near 1140 cm.⁻¹ (8.8 microns), whereas in mixture 3 a strong doublet was observed at 1080 and 1140 cm.⁻¹. The origin of the doublet was puzzling because no other component of 3 but calcium sulfate has a band near here. Calcium sulfate dihydrate had been run as a Nujol mull and mixture 3 as a dry powder. Reversing each did not change their spectra. Then calcium sulfate dihydrate was mixed with each of the other components in turn in the dry state, and the mixtures were examined as Nujol mulls. It was found that the mixture with potassium thiocyanate gave a doublet. With sodium thiocyanate there was also a doublet, but it was much less pronounced.

It seems unlikely that a chemical reaction between calcium sulfate dihydrate and potassium thiocyanate could account for these peculiar results, because the materials are in the solid state. Two other possible causes are changes in crystal structure, presumably caused by changing the hydrate, and an orientation effect. The following observations seem to rule out variable water content as a cause, and suggest the orientation effect.

A calcium sulfate dihydrate–potassium thiocyanate mixture heated at 170° C. for 3 days gave the two bands near 1100 cm.⁻¹. Only one band was found after the salt plates were separated and the mull exposed to air for an hour.
Another portion of the same heated mixture was exposed to air under more humid conditions for an hour and then milled in Nujol: two bands again resulted. This mull was opened to the air for an additional half hour, and only one band was found.

When calcium sulfate dihydrate alone was heated overnight at 170° C., three bands were found. The sulfate vibration absorbing near 1100 cm.

Another portion of the same heated mixture was exposed to air overnight and then milled in Nujol: two bands again resulted. This mull was opened to the air for an additional half hour, and only one band was found.

Miscellaneous Observations. Anomalous Dispersion and Christiansen filter Effects. These have been adequately described in the literature (5, 9). Examples will be seen in the sharp bands near 3 and 6 microns in sodium and magnesium perchlorate (Nos. 26 and 115), and of potassium ferricyanide near 5 microns (No. 26, and 115).

WATER AND HYDROXYL BANDS. The sharpness of the water bands near 3 and 6 microns in sodium and magnesium perchlorate (Nos. 117, 119), and the high value of their O—H stretching frequency (>3500 cm.

In bicarbonate there is a band at 2500 to 2600 cm.

is evidence that these are O—H stretching frequencies of the hydroxyl groups attached to the central atom.

BARIUM CHLORIDE. Several chlorides of the purely ionic type were examined to observe how the bands due to water of hydration varied. Among these was barium chloride dihydrate (No. 159). Surprisingly it has a strong band at 700 cm.

Compounds with No Absorption. Nickel hydroxide, ferric oxide, cadmium sulfide, and mercuric sulfide have no absorption in the rock salt region aside from water and hydroxyl bands.

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