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spectra have been made by Lecomte and his coworkers (*6*, *7*), but unfortunately many of their data are somewhat out of date and are not always presented in the most useful form.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 gound 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

Table I. Index to Infrared Curves and Tables of Data

Type	Formula	No.
Boron		
Metaborate	$NaBO_2$	1
	$Mg(BO_2)_2.8H_2O$	2
	$Pb(BO_2)_2.H_2O$	3
Tetraborate	$Na_2B_4O_7.10H_2O$	4
	$K_2B_4O_7.5H_2O$	5
	$MnB_4O_7.8H_2O$	6
Perborate	$NaBO_3.4H_2O$	7
Misc.	H_3BO_3	8
	BN	9
Carbon		
Carbonate	Li_2CO_3	10
	Na_2CO_3	11
	K_2CO_3	12
	$3MgCO_3.Mg(OH)_2.3H_2O$	13
	$CaCO_3$	14
	$BaCO_3$	15
	$CoCO_3$	16
	$PbCO_3$	17
Bicarbonate	NH_4HCO_3	18
	$NaHCO_3$	19
	$KHCO_3$	20
Cyanide	NaCN	21
	KCN	22
Cyanate	KOCN	23
	AgOCN	24
Thiocyanate	NH_4SCN	25
	NaSCN	26
	KSCN	27
	$Ba(SCN)_2.2H_2O$	28
	$Hg(SCN)_2$	29
	$Pb(SCN)_2$	30
Silicon		
Metasilicate	$Na_2SiO_3.5H_2O$	31
	K_2SiO_3	32
Silicofluoride	Na_2SiF_6	33
Silica gel	$SiO_2.xH_2O$	34
Nitrogen		
Nitrite	$NaNO_2$	36
	KNO_2	36
	$AgNO_2$	37
	$Ba(NO_2)_2.H_2O$	38
Nitrate	NH_4NO_3	39
	$NaNO_3$	40
	KNO_3	41
	$AgNO_3$	42
	$Ca(NO_3)_2$	43
	$Sr(NO_3)_2$	44
	$Ba(NO_3)_2$	45
	$Cu(NO_3)_2.3H_2O$	46
	$Co(NO_3)_2.6H_2O$	47
	$Pb(NO_3)_2$	48
	$Fe(NO_3)_3.9H_2O$	49
Subnitrate	$BiONO_3.H_2O$	50
Phosphorus		
Phosphate, tribasic	$Na_3PO_4.12H_2O$	51
	K_3PO_4	52
	$Mg_3(PO_4)_2.4H_2O$	53
	$Ca_3(PO_4)_2$	54
	$Mn_3(PO_4)_2.7H_2O$	55
	$Ni_3(PO_4)_2.7H_2O$	56
	$Cu_3(PO_4)_2.3H_2O$	57
	$Pb_3(PO_4)_2$	58
	$CrPO_4 \cdot H_2O$	59
Phosphate, dibasic	$(NH_4)_2HPO_4$	60
	$Na_2HPO_4.12H_2O$	61
	K_2HPO_4	62
	$MgHPO_4.3H_2O$	63
	$CaHPO_4.2H_2O$	64
	$BaHPO_4$	65
Phosphate, monobasic	$NH_4H_2PO_4$	66
	$NaH_2PO_4.H_2O$	67
	KH_2PO_4	68
	$Mg(H_2PO_4)_2$	69
	$Ca(H_2PO_4)_2.H_2O$	70
Arsenic		
Metaarsenite	$NaAsO_2$	71
Orthoarsenate, tribasic	$Ca_3(AsO_4)_2$	72
Orthoarsenate, dibasic	$Na_2HAsO_4.7H_2O$	73
	Pb_2HAsO_4	74
Orthoarsenate, monobasic	KH_2AsO_4	75
Oxide	As_2O_3	76
Antimony		
Oxide	Sb_2O_3	77
	Sb_2O_5	78
Sulfur		
Sulfite	$(NH_4)_2SO_3.H_2O$	79
	Na_2SO_3	80
	$K_2SO_3.2H_2O$	81
	$CaSO_3.2H_2O$	82
	$BaSO_3$	83
	$ZnSO_3.2H_2O$	84
Sulfur (Contd.)		
Sulfate	$(NH_4)_2SO_4$	85
	$Li_2SO_4.H_2O$	86
	Na_2SO_4	87
	K_2SO_4	88
	$CaSO_4.2H_2O$	89
	$MnSO_4.2H_2O$	90
	$FeSO_4.7H_2O$	91
	$CuSO_4$	92
	$ZrSO_4.4H_2O$	93
	$Cr_2(SO_4)_3.K_2SO_4.24H_2O$	94
Bisulfate	NH_4HSO_4	95
	$NaHSO_4$	96
	$KHSO_4$	97
Thiosulfate	$(NH_4)_2S_2O_3$	98
	$Na_2S_2O_3.5H_2O$	99
	$K_2S_2O_3.H_2O$	100
	$MgS_2O_3.6H_2O$	101
	$BaS_2O_3.H_2O$	102
Metabisulfite	$Na_2S_2O_5$	103
	$K_2S_2O_5$	104
Persulfate	$(NH_4)_2S_2O_8$	105
	$K_2S_2O_8$	106
Selenium		
Selenite	Na_2SeO_3	107
	$CuSeO_3.2H_2O$	108
Selenate	$(NH_4)_2SeO_4$	109
	$Na_2SeO_4.10H_2O$	110
	K_2SeO_4	111
	$CuSeO_4.5H_2O$	112
Chlorate	$NaClO_3$	113
	$KClO_3$	114
	$Ba(ClO_3)_2.H_2O$	115
Perchlorate	NH_4ClO_4	116
	$NaClO_4.H_2O$	117
	$KClO_4$	118
	$Mg(ClO_4)_2$	119
Bromine		
Bromate	$NaBrO_3$	120
	$KBrO_3$	121
	$AgBrO_3$	122
Iodine		
Iodate	$NaIO_3$	123
	KIO_3	124
	$Ca(IO_3)_2.6H_2O$	125
Periodate	KIO_4	126
Vanadium		
Metavanadate	NH_4VO_3	127
	$NaVO_3.4H_2O$	128
Chromium		
Chromate	$(NH_4)_2CrO_4$	129
	Na_2CrO_4	130
	K_2CrO_4	131
	$MgCrO_4.7H_2O$	132
	$BaCrO_4$	133
	$ZnCrO_4.7H_2O$	134
	$PbCrO_4$	135
	$Al_2(CrO_4)_3$	136
Dichromate	$(NH_4)_2Cr_2O_7$	137
	$Na_2Cr_2O_7.2H_2O$	138
	$K_2Cr_2O_7$	139
	$CaCr_2O_7.3H_2O$	140
	$CuCr_2O_7.2H_2O$	141
Molybdenum		
Molybdate	$Na_2MoO_4.2H_2O$	142
	$K_2MoO_4.5H_2O$	143
Heptamolybdate	$(NH_4)_6Mo_7O_{24}.4H_2O$	144
Tungsten		
Tungstate	$Na_2WO_4.2H_2O$	145
	K_2WO_4	146
	$CaWO_4$	147
Manganese		
Permanganate	$NaMnO_4.3H_2O$	148
	$KMnO_4$	149
	$Ca(MnO_4)_2.4H_2O$	150
	$Ba(MnO_4)_2$	151
Complex ions		
Ferrocyanide	$Na_4Fe(CN)_6.10H_2O$	152
	$K_4Fe(CN)_6.3H_2O$	153
	$Ca_2Fe(CN)_6.12H_2O$	154
Ferricyanide	$K_3Fe(CN)_6$	155
Cobaltinitrite	$Na_3Co(NO_2)_6$	156
Hexanitratocerate	$(NH_4)_2Ce(NO_3)_6$	157
Chlorine		
Chloride	NH_4Cl	158
	$BaCl_2.2H_2O$	159
Mulling agents	Nujol, fluorolube	160

Table II. Positions and Intensities of Infrared Absorption Bands

vw = very weak w = weak m = medium s = strong vs = very strong sh = shoulder b = broad vb = very broad sp = sharp imp. = impurity
* = KBr region (15–25μ) examined

1. Sodium metaborate $NaBO_2$

Cm.$^{-1}$	Microns	I
862	11.60	w
925	10.80	vs, b
1175	8.50	m
1310	7.64	vs
1655	6.05	m
3470	2.85	vs, vb

2. Magnesium metaborate $Mg(BO_2)_2.8H_2O$

Cm.$^{-1}$	Microns	I
808	12.4	s
838	11.95	m
892	11.2	vw
952	10.5	w
1005	9.95	m
1085	9.2	s
1130	8.8	s
1220	8.2	w
1370	7.3	s
1420	7.05	s
1640	6.1	w
3360	2.98	s
3500	2.86	s

3. Lead metaborate $Pb(BO_2)_2.H_2O$

Cm.$^{-1}$	Microns	I
960	10.3	s, vb
1340	7.45	m
1380	7.2	Nujol?
3280	3.05	m

4. Sodium tetraborate $Na_2B_4O_7.10H_2O$

Cm.$^{-1}$	Microns	I
712	14.05	w
775	12.9	w
828	12.1	s
943	10.6	s
1000	10.0	s
1075	9.3	w
1130	8.85	m
1260	7.95	m
1275	7.85	m
1360	7.35	vs
1420	7.05	vs
1460	6.85	Nujol?
1650	6.05	m
3330	3.0	vs

5. Potassium tetraborate $K_2B_4O_7.5H_2O$

Cm.$^{-1}$	Microns	I
705	14.2	vw
782	12.8	vw
833	12.0	s
918	10.9	s
1000	10.0	s
1060	9.45	vw
1085	9.2	s
1130	8.85	vw
1155	8.65	w
1240	8.05	m
1315	7.62	sh
1340	7.45	s
1440	6.95	s
1655	6.05	w
2480	4.03	vw
3330	3.03	s
3390	2.95	s
3560	2.81	s

6. Manganese tetraborate $MnB_4O_7.8H_2O$

Cm.$^{-1}$	Microns	I
990	10.1	
1065	9.4	s, vb
1150	8.7	
1370	7.3	s
1450	6.9	m
1640	6.1	w
3390	2.95	s

7. Sodium perborate $NaBO_3.4H_2O$

Cm.$^{-1}$	Microns	I
770	13.0	vw
833	12.0	w
852	11.75	w
877	11.4	vw
934	10.7	vs
1020	9.8	s
1075	9.3	m
1175	8.5	s
1240	8.05	s
1655	6.05	w
3330	3.0	vs

8. Boric acid H_3BO_3

Cm.$^{-1}$	Microns	I
807	12.4	m
885	11.3	vw
1195	8.37	s, sp
1450	6.9	vs
3270	3.15	s

9. Boron nitride BN

Cm.$^{-1}$	Microns	I
810	12.35	w
1390	7.2	s

10. Lithium carbonate Li_2CO_3

Cm.$^{-1}$	Microns	I
864	11.58	m
1445	6.92	s
1490	6.7	s

11. Sodium carbonate Na_2CO_3

Cm.$^{-1}$	Microns	I
700	14.3	m
705	14.2	m
855	11.7	vw
878	11.4	s
1440	6.95	vs
1755	5.7	m, sp
2500	4.0	m
2620	3.82	vw
~3000	~3.3	m, vb

12. Potassium carbonate K_2CO_3

Cm.$^{-1}$	Microns	I
865	11.55	m
900	11.1	vw
1450	6.9	vs
~3220	~3.1	m, vb

13. Magnesium carbonate, basic $3MgCO_3.Mg(OH)_2.3H_2O$

Cm.$^{-1}$	Microns	I
800	12.5	vw
855	11.7	vw
885	11.3	vw
1430	7.0	vs
1490	6.7	vs
3450	2.9	m, vb

14. Calcium carbonate $CaCO_3$

Cm.$^{-1}$	Microns	I
715	14.0	w
877	11.4	s, sp
1430	7.0	vs
1785	5.6	vw
2530	3.95	vw

15. Barium carbonate $BaCO_3$

Cm.$^{-1}$	Microns	I
697	14.35	w
858	11.65	s, sp
1440	6.95	vs

16. Cobaltous carbonate $CoCO_3$

Cm.$^{-1}$	Microns	I
747	13.4	vw
865	11.55	m
1450	6.9	vs
~3330	~3.0	w, vb

17. Lead carbonate $PbCO_3$

Cm.$^{-1}$	Microns	I
685	14.6	w
840	11.9	vw
1410	7.1	vs

18. Ammonium bicarbonate NH_4HCO_3

Cm.$^{-1}$	Microns	I
703	14.25	s
832	12.02	s, sp
993	10.08	s
1030	9.7	w, sp
1045	9.58	w, sp
1325	7.55	vs, b
1400	7.15	vs, sp
1620	6.17	s
1655	6.05	s
1890	5.3	w
2550	3.92	m
3060	3.27	vs, sp
3160	3.17	vs, sp

19. Sodium bicarbonate $NaHCO_3$

Cm.$^{-1}$	Microns	I
662	15.15	w (CO_2?)
698	14.35	s
838	11.95	s, sp
1000	10.0	s
1035	9.65	w, sp
1050	9.55	w, sp
1295	7.73	vs
1410	7.1	s, sp
1460	6.85	m, sp
1630	6.15	s
1660	6.02	
1900	5.27	m
2040	4.9	vw
2320	4.3	w (CO_2?)
2500	4.0	s, b
2940	3.4	w

20. Potassium bicarbonate $KHCO_3$

Cm.$^{-1}$	Microns	I
705	14.2	s
833	12.0	s, sp
990	10.1	s
1010	9.9	s
1370	7.3	m, sh
1410	7.1	vs
1630	6.15	vs
2380	4.2	w
2600	3.85	s, vb
2950	3.37	m

21. Sodium cyanide NaCN (Na_2CO_3 impurity)

Cm.$^{-1}$	Microns	I
865	11.55	m, imp.
1310	7.65	vw
1460	6.85	vs, imp.
1640	6.1	m
2080	4.8	s
2220	4.5	w, vb
3330	3.0	m, vb

22. Potassium cyanide KCN ($KHCO_3$, K_2CO_3 impurities)

Cm.$^{-1}$	Microns	I
833	12.0	m, imp.
882	11.35	vw, imp.
1440	6.95	s, imp.
1635	6.12	s
2070	4.83	s

23. Potassium cyanate KOCN ($KHCO_3$ impurity)

Cm.$^{-1}$	Microns	I
706	14.17	s, imp.
833	12.0	s, imp.
980	10.2	m, imp.
1010	9.9	m, imp.
1210	8.25	m, sp.
1310	7.65	w, sp.
1410	7.1	vs, imp.
1640	6.1	vs, imp.
2130	4.7	s, vb
2630	3.8	s, imp.

24. Silver cyanate AgOCN

Cm.$^{-1}$	Microns	I
1210	8.25	vw
1310	7.65	w
1345	7.43	vw
2170	4.6	vs
3450	2.9	vw

25. Ammonium thiocyanate NH_4SCN

Cm.$^{-1}$	Microns	I
1420	7.05	s
1650	6.05	m
2050	4.88	s
2860	3.5	m
3060	3.27	s
3149	3.18	s

26. Sodium thiocyanate NaSCN

Cm.$^{-1}$	Microns	I
758	13.2	w
950	10.5	vw, b
1620	6.18	m
2020	4.9	s
3330	3.0	m

27. Potassium thiocyanate KSCN

Cm.$^{-1}$	Microns	I
746	13.4	m
945	10.6	vw, vb
1630	6.13	m
2020	4.9	s
3400	2.95	m

28. Barium thiocyanate $Ba(SCN)_2.2H_2O$

Cm.$^{-1}$	Microns	I
1630	6.15	m
2060	4.85	vs, sp
3500	2.85	vs

29. Mercuric thiocyanate $Hg(SCN)_2$

Cm.$^{-1}$	Microns	I
835	12.0	vw
1105	9.05	vw
1150	8.7	vw
1370	7.3	s
1615	6.2	w
2090	4.78	s
3450	2.9	w

30. Lead thiocyanate $Pb(SCN)_2$

Cm.$^{-1}$	Microns	I
2030	4.93	s, sp
2080	4.8	w

31. Sodium metasilicate $Na_2SiO_3.5H_2O$

Cm.$^{-1}$	Microns	I
715	14.0	s
775	12.9	s
832	12.03	s
980	10.2	vs
1125	8.9	m
1165	8.58	m
1695	5.9	m
2330	4.3	m
3280	3.05	vs, vb

32. Potassium metasilicate K_2SiO_3

Cm.$^{-1}$	Microns	I
770	13.0	vw
990	10.1	vs, vb
1625	6.15	vw
3330	3.0	m

33. Sodium silicofluoride Na_2SiF_6

Cm.$^{-1}$	Microns	I
728	13.75	vs
790	12.7	m, sh
1105	9.05	vw

34. Silica gel $SiO_2.xH_2O$

Cm.$^{-1}$	Microns	I
800	12.5	w
948	10.55	w
1090	9.15	vs
1190	8.4	s, sh
1640	6.1	vw
3330	3.0	m

35. Sodium nitrite $NaNO_2$

Cm.$^{-1}$	Microns	I
831	12.05	m, sp
1250	8.0	vs
1335	7.5	m, sh

36. Potassium nitrite KNO_2

Cm.$^{-1}$	Microns	I
830	12.05	s, sp
1235	8.1	vs
1335	7.5	m, sp
1380	7.25	m
2560	3.9	vw
3450	2.9	vw

37. Silver nitrite $AgNO_2$

Cm.$^{-1}$	Microns	I
833	12.0	w
848	11.8	vw
1250	8.0	vs
1380	7.25	vs

38. Barium nitrite $Ba(NO_2)_2.H_2O$

Cm.$^{-1}$	Microns	I
820	12.2	w
1235	8.1	vs
1330	7.53	m
1640	6.1	m
3360	2.98	m, sp
3510	2.85	m, sp

39. Ammonium nitrate NH_4NO_3

Cm.$^{-1}$	Microns	I
830	12.05	w
1340	7.45	s
1390	7.2	
1630	6.13	w
1740	5.75	w
2440	4.1	w
3030	3.3	
3140	3.19	s
3410	2.93	

40. Sodium nitrate* $NaNO_3$

Cm.$^{-1}$	Microns	I
836	11.96	m, sp
1358	7.36	vs
1790	5.59	vw
2428	4.12	vw

41. Potassium nitrate KNO_3

Cm.$^{-1}$	Microns	I
824	12.14	m, sp
1380	7.25	vs
1767	5.66	vw

42. Silver nitrate $AgNO_3$

Cm.$^{-1}$	Microns	I
733	13.64	vw
803	12.45	w
835	11.98	vw
1348	7.42	vs

Table II. Positions and Intensities of Infrared Absorption Bands (*Continued*)

vw = very weak w = weak m = medium s = strong vs = very strong sh = shoulder b = broad vb = very broad sp = sharp imp. = impurity
* = KBr region (15–25μ) examined

43. Calcium nitrate $Ca(NO_3)_2$

Cm.$^{-1}$	Microns	I
820	12.20	w
1044	9.58	vw
1350	7.4	s
1430	7.0	s
1640	6.1	m
3450	2.9	s

44. Strontium nitrate $Sr(NO_3)_2$

Cm.$^{-1}$	Microns	I
737	13.57	s, sp
815	12.27	s, sp
1382	7.23	vs
1441	6.94	vs, sp
1795	5.57	vw, sp
2420	4.13	vw
3450	2.9	w, b

45. Barium nitrate $Ba(NO_3)_2$

Cm.$^{-1}$	Microns	I
729	13.72	s, sp
817	12.24	s, sp
1352	7.40	vs
1418	7.05	m, sp
1774	5.64	w, sp
2410	4.15	w, b

46. Cupric nitrate $Cu(NO_3)_2.3H_2O$

Cm.$^{-1}$	Microns	I
836	11.96	w
1378	7.26	vs
1587	6.30	s, sp
1790	5.58	vw
2431	4.11	vw
3170	3.15	w
3350	2.98	s, b

47. Cobaltous nitrate $Co(NO_3)_2.6H_2O$

Cm.$^{-1}$	Microns	I
807	12.4	vw, vb
836	11.96	w, sp
1372	7.29	vs
1640	6.1	m
3230	3.1	m, sh
3410	2.93	s

48. Lead nitrate $Pb(NO_3)_2$

Cm.$^{-1}$	Microns	I
726	13.77	w
807	12.39	vw
836	11.96	w, sp
1373	7.28	vs

49. Ferric nitrate $Fe(NO_3)_3.9H_2O$

Cm.$^{-1}$	Microns	I
835	11.98	w
1361	7.35	vs
1615	6.19	m
1785	5.6	vw
2440	4.1	vw
3230	3.1	s, vb

50. Bismuth subnitrate $BiONO_3.H_2O$

Cm.$^{-1}$	Microns	I
816	12.27	vw
1325	7.55	s
1380	7.25	vs
1640	6.1	vw
3390	2.95	m, b

51. Sodium phosphate, tribasic $Na_3PO_4.12H_2O$

Cm.$^{-1}$	Microns	I
694	14.4	real?
1000	10.0	vs
1450	6.9	vw
1660	6.03	m
3200	3.13	vs, b

52. Potassium phosphate, tribasic K_3PO_4

Cm.$^{-1}$	Microns	I
1000	10.0	vs, vb
1590	6.3	w, vb
3180	3.15	vs, b

53. Magnesium phosphate, tribasic $Mg_3(PO_4)_2.4H_2O$

Cm.$^{-1}$	Microns	I
768	13.05	w, b
887	11.3	vw, b
938	10.65	w
1010	9.9	s
1040	9.6	
1135	8.83	m
1155	8.65	w, sh
1230	8.13	w
1640	6.1	m
3260	3.07	s
3460	2.9	m, sh

54. Calcium phosphate, tribasic $Ca_3(PO_4)_2$

Cm.$^{-1}$	Microns	I
962	10.4	vw
1030	9.7	vs, vb
1085	9.2	
3230	3.1	m, b

55. Manganese phosphate, tribasic $Mn_3(PO_4)_2.7H_2O$

Cm.$^{-1}$	Microns	I
935	10.7	vw, sh
980	10.2	w
1020	9.8	s
1040	9.6	? sh
1070	9.35	s
1145	8.75	w
1250	8.00	w
1300	7.7	w
2470	4.05	vw
3170	3.15	
3330	3.0	m
3450	2.9	

56. Nickel(ous) phosphate, tribasic $Ni_3(PO_4)_2.7H_2O$

Cm.$^{-1}$	Microns	I
735	13.6	w, vb
877	11.4	w
943	10.6	w, sh
1005	9.95	s
1060	9.45	w, sh
~1440	~ 6.95	w (Nujol + ?)
1595	6.27	w
~3030	~ 3.3	s
3450	2.9	m, sp

57. Copper(ic) phosphate, tribasic $Cu_3(PO_4)_2.3H_2O$

Cm.$^{-1}$	Microns	I
645	15.5	m
855	11.7	m
925	10.8	s
960	10.4	s
1010	9.9	s
1070	9.35	s
1100	9.1	m, sh
1140	8.75	m
1290	7.75	m
3390	2.95	m

58. Lead phosphate, tribasic $Pb_3(PO_4)_2$

Cm.$^{-1}$	Microns	I
970 to 1040	10.3 to 9.6	vs, vb
3390	2.95	w, b

59. Chromic phosphate, tribasic $CrPO_4.H_2O$

Cm.$^{-1}$	Microns	I
1030	9.7	vs, vb
1625	6.15	w
3230	3.1	s, b

60. Ammonium phosphate, dibasic $(NH_4)_2HPO_4$

Cm.$^{-1}$	Microns	I
850	11.75	vw
900	11.1	m
953	10.5	s
1060	9.45	vs
1195	8.37	m
1220	8.22	
1415	7.05	m
1470	6.8	s
1530	6.55	vw
1710	5.85	w
1920	5.2	m
2200	4.55	w
2860	3.5	vs, vb

61. Sodium phosphate, dibasic $Na_2HPO_4.12H_2O$

Cm.$^{-1}$	Microns	I
865	11.55	s
958	10.45	w, sh
985	10.15	s
1070	9.35	vs
1125	8.9	w, sh
1145	8.75	vw, sh
1185	8.45	w
1265	7.9	w
1630	6.13	m
~2220	~ 4.5	w, vb
3280	3.05	vs, vb

62. Potassium phosphate, dibasic K_2HPO_4

Cm.$^{-1}$	Microns	I
837	11.95	s
934	10.7	s
990	10.1	vs, vb
1110	9.0	w, sh
1350	7.4	m, sp
1835	5.45	m
2380	4.2	m
2860	3.5	m

63. Magnesium phosphate, dibasic $MgHPO_4.3H_2O$

Cm.$^{-1}$	Microns	I
882	11.35	m
1020	9.8	s
1055	9.5	s
1160	8.6	s
1235	8.1	m
1645	6.07	m
1680	5.95	m, sh
2480	4.03	w
3300	3.03	s
3390	2.95	w, sh
3510	2.85	m

64. Calcium phosphate, dibasic $CaHPO_4.2H_2O$

Cm.$^{-1}$	Microns	I
880	11.35	m
990	10.1	
1050	9.5	s, vb
1125	8.9	
1350	7.4	?
1650	6.07	m
~2270	~ 4.4	m, vb
~3000	~ 3.3	m
3510	2.85	vw, sh

65. Barium phosphate, dibasic $BaHPO_4$

Cm.$^{-1}$	Microns	I
890	11.25	s
927	10.8	vw, sh
986	10.15	s
1060	9.45	vs
1120	8.95	m, sh
1250	8.0	s, sp
1710	5.85	m, b
2440	4.1	w
2700	3.7	w

66. Ammonium phosphate monobasic $NH_4H_2PO_4$

Cm.$^{-1}$	Microns	I
900	11.1	w, vb
1080	9.25	m, b
1275	7.85	m
1420	7.05	w, sh
1440	6.95	m
~1610	~ 6.2	w, vb
~2270	~ 4.4	w, vb
2900	3.45	w, sh
3050	3.28	m

67. Sodium phosphate, monobasic $NaH_2PO_4.H_2O$

Cm.$^{-1}$	Microns	I
820	12.2	w, sh
873	11.45	m
925	10.8	s
983	10.15	s
1050	9.55	s
1125	8.9	m, sh
1170	8.55	m
1245	8.05	w, sh
1290	7.75	s
1640	6.1	m, vb
2350	4.25	s, b
2820	3.55	s, b

68. Potassium phosphate monobasic* KH_2PO_4

Cm.$^{-1}$	Microns	I
538	18.59	m
900	11.1	m, vb
1090	9.15	m, b
1300	7.7	m
1640	6.1	m, b
2320	4.3	m, b

69. Magnesium phosphate, monobasic $Mg(H_2PO_4)_2$

Cm.$^{-1}$	Microns	I
755	13.2	w, vb
943	10.6	
1040	9.6	m, vb
1150	8.7	
1235	8.1	w, sh
1640	6.1	m
3180	3.15	s, b
3360	2.98	

70. Calcium phosphate, monobasic, $Ca(H_2PO_4)_2.H_2O$

Cm.$^{-1}$	Microns	I
670	14.9	m, vb
855	11.7	w, vb
885	11.3	
915	10.9	vw, sh
950	10.5	s, b
1085	9.2	s, b
1160	8.6	w
1235	8.1	s, b
1640	6.1	m
2320	4.3	m, vb
~2980	~ 3.35	s, vb

71. Sodium metaarsenite $NaAsO_2$

Cm.$^{-1}$	Microns	I
697	14.35	vs, b
748	13.35	m
775	12.9	w, sh
833	12.0	s, sp
848	11.8	s, sp
1420	7.05	vw
1460	6.85	m, sp
3450	2.90	w, b

72. Calcium orthoarsenate, tribasic $Ca_3(AsO_4)_2$

Cm.$^{-1}$	Microns	I
840	11.9	vs, vb
885	11.3	
922	10.85	w, sh
1010	9.9	w, b
1560	6.4	m, vb
2320	4.3	m, vb
3175	3.15	m, b

73. Sodium orthoarsenate, dibasic $Na_2HAsO_4.7H_2O$

Cm.$^{-1}$	Microns	I
712	14.05	s, vb
836	11.95	vs, vb
1175	8.5	w
1280	7.8	w
1640	6.1	m
2175	4.6	w, b
2380	4.2	w (CO_2?)
~3130	~ 3.2	vs, b

74. Lead orthoarsenate, dibasic Pb_2HAsO_4

Cm.$^{-1}$	Microns	I
743	13.45	m, b
800	12.5	vs

75. Potassium orthoarsenate, monobasic KH_2AsO_4

Cm.$^{-1}$	Microns	I
750	13.3	m, b
850	11.75	m, b
1020	9.8	vw, b
1265	7.9	m, vb
1585	6.3	m, vb
~2275	~ 4.4	m, vb
~2740	~ 3.65	m

76. Arsenic trioxide As_2O_3

Cm.$^{-1}$	Microns	I
803	12.45	vs
840	11.9	w, sh
1040	9.6	vw, b

77. Antimony trioxide Sb_2O_3

Cm.$^{-1}$	Microns	I
690	14.5	w
740	13.5	vs
950	10.5	vw, b

78. Antimony pentoxide Sb_2O_5

Cm.$^{-1}$	Microns	I
685	14.6	vw, real?
740	13.5	s, vb
3225	3.1	w, b

79. Ammonium sulfite $(NH_4)_2SO_3.H_2O$

Cm.$^{-1}$	Microns	I
1105	9.05	vs, b
1410	7.08	vs, sp
3075	3.25	s

80. Sodium sulfite Na_2SO_3

Cm.$^{-1}$	Microns	I
960	10.4	vs, b
1135	11.35	w
1215	8.2	vw

Table II. Positions and Intensities of Infrared Absorption Bands (*Continued*)

vw = very weak w = weak m = medium s = strong vs = very strong sh = shoulder b = broad vb = very broad sp = sharp imp. = impurity
* = KBr region (15–25μ) examined

81. Potassium sulfite $K_2SO_3.2H_2O$

Cm.$^{-1}$	Microns	I
943	10.6	vs, vb
1100	9.1	vs, b
1175	8.5	s
1645	6.07	vw
1885	5.3	vw
3390	2.95	m

82. Calcium sulfite $CaSO_3.2H_2O$

Cm.$^{-1}$	Microns	I
653	15.3	m, b
945	10.6	vs, b
970	10.3	
1100	9.1	vw, vb
1210	8.3	vw
1625	6.15	m, sp
3400	2.94	s, sp

83. Barium sulfite $BaSO_3$

Cm.$^{-1}$	Microns	I
638	15.7	m
917	10.9	vs, b
990	10.1	w
1070	9.35	m, vb
1200	8.35	m
1410	7.1	vw

84. Zinc sulfite $ZnSO_3.2H_2O$

Cm.$^{-1}$	Microns	I
855	11.7	s, vb
945	10.57	w
1020	9.8	s
1100	9.1	m
1160	8.6	m
1630	6.13	m
3170	3.15	s
3390	2.95	

85. Ammonium sulfate $(NH_4)_2SO_4$

Cm.$^{-1}$	Microns	I
645	15.5	w
1105	9.05	vs, b
1410	7.1	vs, sp
1740	5.75	vw
3055	3.25	s, sp
3165	3.16	

86. Lithium sulfate* $Li_2SO_4.H_2O$

Cm.$^{-1}$	Microns	I
634	15.77	m
815	12.25	vw, real?
1020	9.8	vw
1110	9.0	vs
1170	8.55	m, sh
1380	7.25	Nujol + ?
1625	6.15	m, sp
3470	2.88	m

87. Sodium sulfate Na_2SO_4

Cm.$^{-1}$	Microns	I
645	15.5	w
1110	9.0	vs

88. Potassium sulfate* K_2SO_4

Cm.$^{-1}$	Microns	I
1110	9.0	vs

89. Calcium sulfate $CaSO_4.2H_2O$

Cm.$^{-1}$	Microns	I
667	14.95	s
1010	9.9	w, sh
1130	8.85	vs, vb
1630	6.13	s, sp
1670	5.95	w
2200	4.55	m, b
3410	2.93	s, b

90. Manganese sulfate $MnSO_4.2H_2O$

Cm.$^{-1}$	Microns	I
660	15.15	m
825	12.1	s
1025	9.78	m
1135	8.8	vs, vb
3225	3.1	s, b

91. Ferrous sulfate* $FeSO_4.7H_2O$

Cm.$^{-1}$	Microns	I
611	16.37	s, vb
990	10.1	vw
1090	9.2	vs, vb
1150	8.7	m, sh
1625	6.15	m
3330	3.0	s, b

92. Copper sulfate $CuSO_4$

Cm.$^{-1}$	Microns	I
680	14.7	m
805	12.45	m
860	11.6	m
1020	9.8	w, sp
1090	9.2	vs, vb
1200	8.35	s
1600	6.25	w, sh
~3300	~3.15	s, b

93. Zirconium sulfate* $ZrSO_4.4H_2O$

Cm.$^{-1}$	Microns	I
627	15.95	w
650	15.4	w
720	13.8	w
770	13.0	vw, sh
920	10.9	vw, sh
1030	9.7	w, sp
1080	9.25	vs, vb
1630	6.12	m
1650	6.05	m
3195	3.13	s

94. Chromium potassium sulfate $Cr_2(SO_4)_3.K_2SO_4.24H_2O$

Cm.$^{-1}$	Microns	I
1090	9.2	vs
1660	6.05	w, b
3370	2.97	m

95. Ammonium bisulfate NH_4HSO_4

Cm.$^{-1}$	Microns	I
855	11.7	m, b
1035	9.65	m, b
1180	8.5	m, b
1410	7.1	vw
3180	3.15	m

96. Sodium bisulfate $NaHSO_4$

Cm.$^{-1}$	Microns	I
~655	~15.3	m
773	12.95	vw
865	11.55	s
1045	9.55	s
1075	9.3	
1175	8.5	m
1235	8.1	s
1660	6.02	m
2600	3.85	vw
3470	2.88	m

97. Potassium bisulfate $KHSO_4$

Cm.$^{-1}$	Microns	I
820	12.2	w, sh
848	11.8	s
877	11.4	s
1005	9.95	s
1065	9.37	s, sp
1160	8.6	vs, b
1280	7.78	s
1325	7.55	w, sh
1640	6.1	w
2330	4.3	m, vb
2440	4.1	
2600	3.85	vw
2900	3.45	s, vb

98. Ammonium thiosulfate $(NH_4)_2S_2O_3$

Cm.$^{-1}$	Microns	I
953	10.5	s
1065	9.4	s
1390	7.18	s
1650	6.05	w
2960	3.4	s, vb

99. Sodium thiosulfate $Na_2S_2O_3.5H_2O$

Cm.$^{-1}$	Microns	I
677	14.8	s
757	13.2	vw, sh
1000	10.0	vs
1125	8.9	vs
1165	8.6	
1630	6.15	w
1660	6.03	m
2000	5.0	w, b
2080	4.8	
3390	2.95	vs

100. Potassium thiosulfate $K_2S_2O_3.H_2O$

Cm.$^{-1}$	Microns	I
658	15.2	m
676	14.8	
995	10.05	s
1120	8.95	vs
1625	6.15	vw
3300	3.03	w

101. Magnesium thiosulfate $MgS_2O_3.6H_2O$

Cm.$^{-1}$	Microns	I
~665	~15.0	s
1000	10.0	s
1115	8.95	vs
1645	6.08	m
2250	4.45	w, vb
3200	3.13	
3360	2.98	s
3450	2.9	

102. Barium thiosulfate $BaS_2O_3.H_2O$

Cm.$^{-1}$	Microns	I
680	14.7	s
690	14.5	
838	11.95	w, b
990	10.1	vs
1075	9.3	
1105	9.05	vs
1120	8.93	
1655	6.05	m
2060	4.85	vw
3280	3.05	s
3420	2.93	s, sp

103. Sodium metabisulfite* $Na_2S_2O_5$

Cm.$^{-1}$	Microns	I
456	21.93	m
512	19.53	m
531	18.83	m
660	15.17	m
667	15.0	
973	10.28	vs
1060	9.45	vs
1180	8.5	vs
1265	7.9	vw, sh

104. Potassium metabisulfite $K_2S_2O_5$

Cm.$^{-1}$	Microns	I
662	15.1	m
975	10.25	vs
1060	9.45	m
1080	9.25	m
1105	9.05	m
1175	8.5	vs
1250	8.0	vw, sh

105. Ammonium persulfate $(NH_4)_2S_2O_8$

Cm.$^{-1}$	Microns	I
637	15.7	vw
702	14.23	s
793	12.6	w
865	11.55	vw
1060	9.45	s, sp
1085	9.23	m, sp
~1190	~8.4	w, sh
1280	7.8	vs
1420	7.05	s
3260	3.07	s

106. Potassium persulfate $K_2S_2O_8$

Cm.$^{-1}$	Microns	I
710	14.1	s
1060	9.43	s, sp
1270	7.88	vs
1300	7.7	
3300	3.02	w

107. Sodium selenite Na_2SeO_3

Cm.$^{-1}$	Microns	I
730	13.7	vs
788	12.7	s
1125	8.9	w, b
1450	6.9	Nujol + ?
3330	3.0	w, b

108. Copper selenite $CuSeO_3.2H_2O$

Cm.$^{-1}$	Microns	I
714	14.0	vs
768	13.0	m, sh
807	12.4	vw, sh
918	10.9	m
1570	6.35	w
1650	6.05	w
2270	4.4	vw, vb
~3120	~3.2	?
3450	2.9	?

109. Ammonium selenate $(NH_4)_2SeO_4$

Cm.$^{-1}$	Microns	I
770	13.0	
800	12.5	vs, vb
837	11.95	
860	11.65	
1235	8.1	w
1420	7.05	s
1640	6.1	m
2320	4.3	m
~3140	~3.18	vs

110. Sodium selenate $Na_2SeO_4.10H_2O$

Cm.$^{-1}$	Microns	I
735	13.6	vw, sh
793	12.6	vs
838	11.95	vs
873	11.45	vs
1105	9.05	m
1125	8.9	m, sp
1165	8.6	w
1240	8.07	m
1390	7.2	s
1640	6.1	m
2350	4.25	s
3220	3.1	m
3500	2.85	s, sp

111. Potassium selenate K_2SeO_4

Cm.$^{-1}$	Microns	I
810	12.35	vw, sh
824	12.13	s, sp
857	11.67	vw
875	11.42	vw
897	11.15	m
1085	9.22	vw
1110	9.0	vw
1140	8.75	vw
1375	7.28	vs
1745	5.73	w, sp
2390	4.18	w, sp

112. Copper selenate $CuSeO_4.5H_2O$

Cm.$^{-1}$	Microns	I
770	13.0	m, b
858	11.65	s
922	10.85	m
1600	6.25	m, sp
3220	3.1	s
3390	2.95	

113. Sodium chlorate $NaClO_3$

Cm.$^{-1}$	Microns	I
935	10.7	s, sp
965	10.35	vs
990	10.1	

114. Potassium chlorate $KClO_3$

Cm.$^{-1}$	Microns	I
938	10.65	w
962	10.4	vs

115. Barium chlorate $Ba(ClO_3)_2.H_2O$

Cm.$^{-1}$	Microns	I
913	10.95	vs, vb
953	10.5	
1610	6.2	m, sp
3540	2.83	s, sp
3570	2.80	s, sp

116. Ammonium perchlorate NH_4ClO_4

Cm.$^{-1}$	Microns	I
1060	9.45	vs
1135	8.8	s, sh
1420	7.05	s
3330	3.0	s, sp

117. Sodium perchlorate $NaClO_4.H_2O$

Cm.$^{-1}$	Microns	I
1100	9.1	vs, b
1630	6.14	s, sp
2030	4.93	vw
3570	2.80	s, sp

118. Potassium perchlorate $KClO_4$

Cm.$^{-1}$	Microns	I
637	15.7	w
940	10.65	vw
1075	9.3	s
1140	8.75	s, sh
1990	5.02	vw

119. Magnesium perchlorate $MgClO_4$

Cm.$^{-1}$	Microns	I
652	15.35	m
945	10.58	w
962	10.4	w
1060	9.45	vs
1130	8.85	vs
1625	6.15	s, sp
2100	4.8	w, vb
3540	2.83	s

Table II. Positions and Intensities of Infrared Absorption Bands (*Concluded*)

vw = very weak w = weak m = medium s = strong vs = very strong sh = shoulder b = broad vb = very broad sp = sharp imp. = impurity
* = KBr region (15–25μ) examined

120. Sodium bromate $NaBrO_3$

Cm.$^{-1}$	Microns	I
807	12.4	vs

121. Potassium bromate $KBrO_3$

Cm.$^{-1}$	Microns	I
790	12.65	vs

122. Silver bromate $AgBrO_3$

Cm.$^{-1}$	Microns	I
765	13.08	s
797	12.55	vs
1280	7.25	Nujol + ?

123. Sodium iodate $NaIO_3$

Cm.$^{-1}$	Microns	I
767	13.05	vs
775	12.9	
800	12.5	m

124. Potassium iodate KIO_3

Cm.$^{-1}$	Microns	I
738	13.55	vs
755	13.25	s
800	12.5	w

125. Calcium iodate $Ca(IO_3)_2.6H_2O$

Cm.$^{-1}$	Microns	I
748	13.35	m
760	13.15	m
775	12.9	s
817	12.25	s
827	12.1	vw, sh
838	11.93	vw, sh
1610	6.20	w, sp
3350	2.98	m
3450	2.9	

126. Potassium periodate KIO_4

Cm.$^{-1}$	Microns	I
848	11.8	vs

127. Ammonium metavanadate NH_4VO_3

Cm.$^{-1}$	Microns	I
690	14.5	s, vb
843	11.85	s
888	11.25	s
935	10.7	s
1415	7.08	s, sp
3200	3.12	s, sp

128. Sodium metavanadate $NaVO_3.4H_2O$

Cm.$^{-1}$	Microns	I
693	14.4	s, b
828	12.08	s
910	11.0	vw
935	10.7	s
957	10.45	
3450	2.9	w, b

129. Ammonium chromate $(NH_4)_2CrO_4$

Cm.$^{-1}$	Microns	I
745	13.4	m
843	11.85	m, sh
865	11.55	vs, b
935	10.7	m, sh
1410	7.1	s
1650	6.05	m
2860	3.5	m, sh
2990	3.35	s
3120	3.2	m, sh

130. Sodium chromate Na_2CrO_4

Cm.$^{-1}$	Microns	I
680	14.7	m
820	12.2	vs, b
855	11.7	
890	11.2	
915	10.90	m, sh
1665	6.0	s, sp
2125	4.7	m, b
3170	3.15	vs, b

131. Potassium chromate K_2CrO_4

Cm.$^{-1}$	Microns	I
858	11.65	w, sh
	11.45	vs
935	10.7	s

132. Magnesium chromate $MgCrO_4.7H_2O$

Cm.$^{-1}$	Microns	I
695	14.4	w, vb
765	13.1	w, b
855	11.7	m, sh
877	11.4	vs
1620	6.17	s
1650	6.08	
2270	4.4	m, b
3260	3.07	vs, b

133. Barium chromate $BaCrO_4$

Cm.$^{-1}$	Microns	I
850	11.75	vs b
885	11.3	
930	10.75	s, sh
3450	2.9	w

134. Zinc chromate $ZnCrO_4.7H_2O$

Cm.$^{-1}$	Microns	I
720	13.9	m
795	12.55	s
875	11.4	s
940	10.65	
1050	9.5	s, b
1090	9.15	
1185	8.45	m
1620	6.15	vw
1820	5.5	vw, b
2700	3.7	w, b
3450	2.9	s, b

135. Lead chromate $PbCrO_4$

Cm.$^{-1}$	Microns	I
825	12.1	vw, vb
855	11.7	
885	11.3	

136. Aluminum chromate $Al_2(CrO_4)_3$

Cm.$^{-1}$	Microns	I
745	13.4	s, vb
950	10.5	s, b
1010	9.9	s
1300	7.7	vw
1625	6.15	m
3460	2.89	s
3520	2.82	

137. Ammonium dichromate $(NH_4)_2Cr_2O_7$

Cm.$^{-1}$	Microns	I
730	13.7	vs
877	11.4	m
900	11.1	m
925	10.8	s, sh
950	10.55	s
1410	7.1	s, sp
2850	3.5	m, sh
3060	3.27	s
3170	3.15	

138. Sodium dichromate $Na_2Cr_2O_7.2H_2O$

Cm.$^{-1}$	Microns	I
737	13.55	vs
780	12.8	m
890	11.25	s, sp
910	11.0	m, sp
935	9.07	vs
1385	7.2	Nujol + ?
1630	6.13	s, sp
1650	6.06	
3500	2.85	s

139. Potassium dichromate* $K_2Cr_2O_7$

Cm.$^{-1}$	Microns	I
568	17.61	w
760	13.15	vs
795	12.55	m
885	11.3	m, sp
905	11.05	m, sp
920	10.85	w, sh
940	10.65	vs, b
1305	7.65	vw

140. Calcium dichromate $CaCr_2O_7.3H_2O$

Cm.$^{-1}$	Microns	I
725	13.8	vw
830	12.05	m
900	11.1	m
940	10.65	s
1625	6.15	m
3450	2.9	s

141. Copper dichromate $CuCr_2O_7.2H_2O$

Cm.$^{-1}$	Microns	I
750	13.3	s, vb
940	10.65	s
1625	6.15	m
3450	2.9	s

142. Sodium molybdate $Na_2MoO_4.2H_2O$

Cm.$^{-1}$	Microns	I
820	12.2	vs
855	11.7	m
900	11.1	m, sp
1680	5.95	w
3280	3.05	s

143. Potassium molybdate $K_2MoO_4.5H_2O$

Cm.$^{-1}$	Microns	I
825	12.1	vs
900	11.1	m
3310	3.02	m

144. Ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}.4H_2O$

Cm.$^{-1}$	Microns	I
663	15.1	vs
836	11.95	m
877	11.4	vs
913	10.95	w, sh
1420	7.05	s
1640	6.1	w
3080	3.25	s, b

145. Sodium tungstate $Na_2WO_4.2H_2O$

Cm.$^{-1}$	Microns	I
810	12.35	w, sh
822	12.15	vs, b
850	11.75	
925	10.8	w
1670	6.0	w
3310	3.02	s

146. Potassium tungstate K_2WO_4

Cm.$^{-1}$	Microns	I
750	13.3	vw
823	12.15	vs, b
925	10.8	w
1680	5.95	w
3170	3.15	m
3320	3.01	w, sh

147. Calcium tungstate $CaWO_4$

Cm.$^{-1}$	Microns	I
794	12.6	vs, vb
1640	6.1	w
3390	2.95	m

148. Sodium permanganate $NaMnO_4.3H_2O$

Cm.$^{-1}$	Microns	I
840	11.9	vw, sh
896	11.15	vs
1625	6.15	s, sp
2000	5.0	w, b
2060	4.85	
3510	2.85	s

149. Potassium permanganate $KMnO_4$

Cm.$^{-1}$	Microns	I
845	11.85	w
900	11.1	vs
1725	5.8	w

150. Calcium permanganate $Ca(MnO_4)_2.4H_2O$

Cm.$^{-1}$	Microns	I
840	11.9	m
905	11.05	vs, b
1625	6.15	s, sp
3470	2.88	vs

151. Barium permanganate $Ba(MnO_4)_2$

Cm.$^{-1}$	Microns	I
840	11.9	m, sp
877	11.4	s
913	10.95	s
935	10.7	m

152. Sodium ferrocyanide $Na_4Fe(CN)_6.10H_2O$

Cm.$^{-1}$	Microns	I
1625	6.15	s, sp
2000	5.0	vs
2020	4.95	m, sh
3390	2.95	vs
3510	2.85	

153. Potassium ferrocyanide $K_4Fe(CN)_6.3H_2O$

Cm.$^{-1}$	Microns	I
930	10.75	vw
995	10.05	vw
1630	6.13	s, sp
1650	6.07	m
2015	4.96	vs
3410	2.93	s
3510	2.85	

154. Calcium ferrocyanide $Ca_2Fe(CN)_6.12H_2O$

Cm.$^{-1}$	Microns	I
1615	6.18	m
2015	4.96	vs, sp
3390	2.95	vs, b

155. Potassium ferricyanide $K_3Fe(CN)_6$

Cm.$^{-1}$	Microns	I
2100	4.77	s

156. Sodium cobaltinitrite $Na_3Co(NO_2)_6$

Cm.$^{-1}$	Microns	I
847	11.8	s, sp
1333	7.5	vs
1430	7.0	vs
1575	6.35	m
1645	6.07	w
2665	3.75	vw, sp
2780	3.6	vw, sp
3450	2.9	m

157. Ammonium hexanitratocerate $(NH_4)_2Ce(NO_3)_6$

Cm.$^{-1}$	Microns	I
745	13.42	s, sp
803	12.45	m, sh
807	12.4	s, sp
815	12.25	vw
1030	9.7	s, sp
1050	9.5	vw
1260	7.95	vs
1325	7.55	w
1420	7.05	s
1530	6.6	vs, b
3210	3.11	s, b

158. Ammonium chloride* NH_4Cl

Cm.$^{-1}$	Microns	I
1410	7.1	s, sp
1780	5.75	w, b
2000	5.0	vw
2860	3.5	m
3070	3.26	s
3150	3.17	

159. Barium chloride $BaCl_2.2H_2O$

Cm.$^{-1}$	Microns	I
700	14.3	vs, vb
1615	6.18	s, sp
1645	6.07	s, sp
3370	2.97	vs

160. Nujol

Cm.$^{-1}$	Microns	I
2918	3.427	s
2861	3.495	s
1458	6.859	m
1378	7.257	m
720	13.89	w

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 a Perkin-Elmer 12B spectrometer. Likewise, a series of ten nitrates was examined in the rock salt region with this 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 fluorolube 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).

Table III. Infrared Bands of Various Nitrates (Cm.$^{-1}$)

Intensity	m, sp[a]	w	m, sp	w	vs	s	s	vs	vw
$NaNO_3$	..	..	836	..	1358	..	..	1790	2428
KNO_3	..	..	824	..	1380	..	..	1767	..
$AgNO_3$	733	803	835	..	1348	..	..	..	..
$Ca(NO_3)_2.xH_2O$	..	..	820	1044	(1350)	(1430)	(1640)	..	..
$Sr(NO_3)_2$	737	..	815	..	1387	1441	..	1795	2420
$Ba(NO_3)_2$	729	..	817	..	1352	1418	..	1774	(2410)
$Fe(NO_3)_3.9H_2O$	..	..	835	..	1361	....	1615	(1785)	..
$Co(NO_3)_2.6H_2O$	..	(807)	836	..	1372	..	(1640)	..	..
$Cu(NO_3)_2.3H_2O$	..	..	836	..	1378	....	1587	1790	2431
$Pb(NO_3)_2$	726	807	836	..	1373	..	..	..	..

Bands >3000 cm.$^{-1}$ are omitted.
( ) Baird values, less accurate.

[a] w, m, s = weak, medium, strong. sp = sharp. v = very.

DISCUSSION OF RESULTS

The spectra range in quality from surprisingly good ones, with sharp, intense bands (see curves for barium thiocyanate dihydrate, No. 28; strontium nitrate, No. 44; and ammonium hexanitratocerate, No. 157,) to very poorly defined ones such as those for potassium silicate, No. 32; monobasic magnesium phosphate, No. 69; and monobasic potassium orthoarsenate, No. 75. It seems to be characteristic of the phosphates, and especially of their monobasic and dibasic modifications, to have ill-defined spectra. The reason for this is not clear, but it may be due to lack of a single, well-ordered crystal structure.

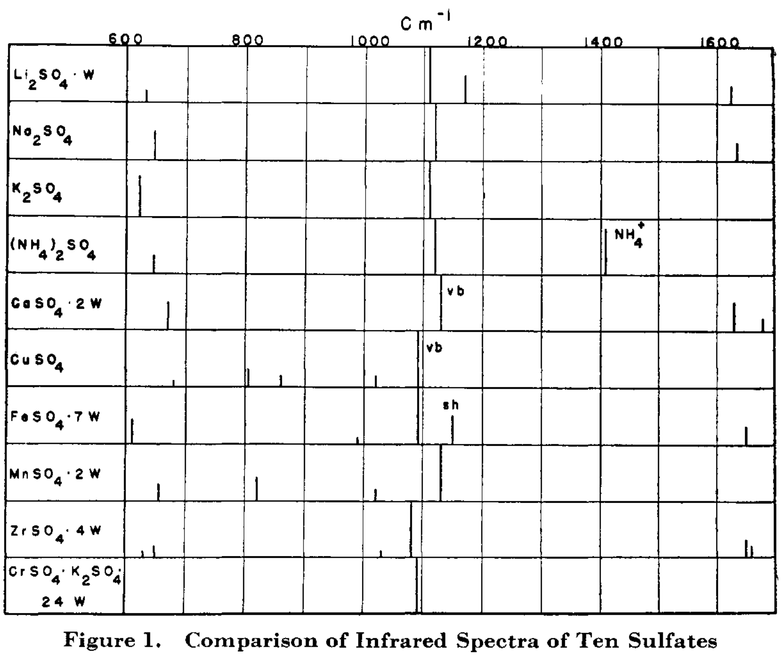


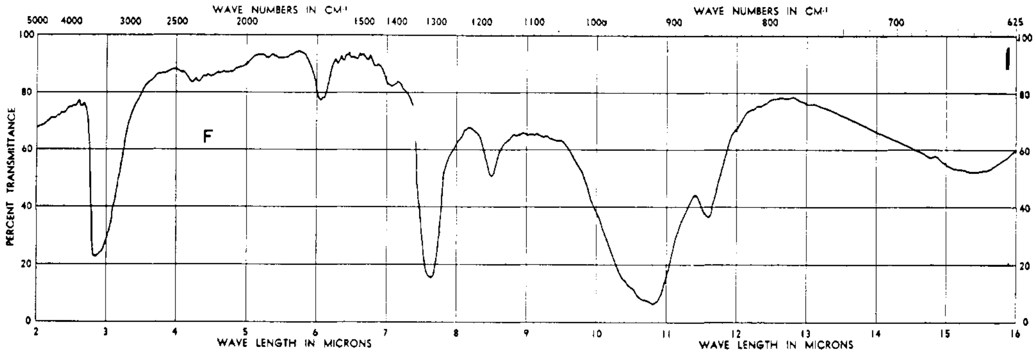
Figure 1. Comparison of Infrared Spectra of Ten Sulfates

W. Water
vb. Very broad
sh. Shoulder

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.

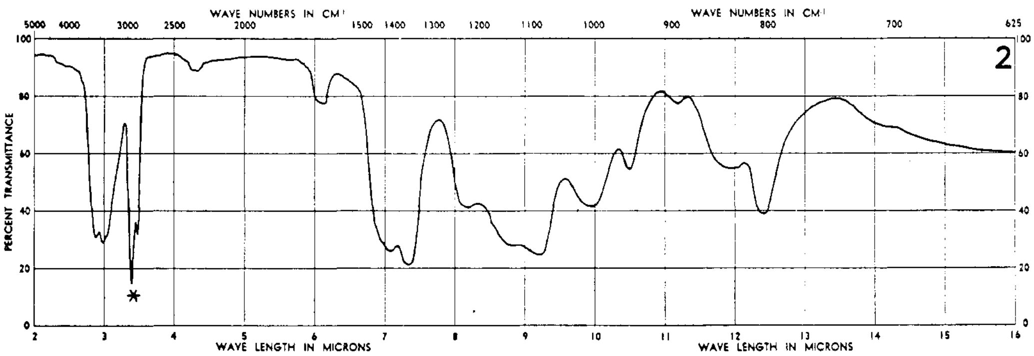
The different charges and radii of the various positive ions produce different electrical fields in the various salts. These doubtless affect the vibrational frequencies of the negative ions.

(*Continued on page 1292*)



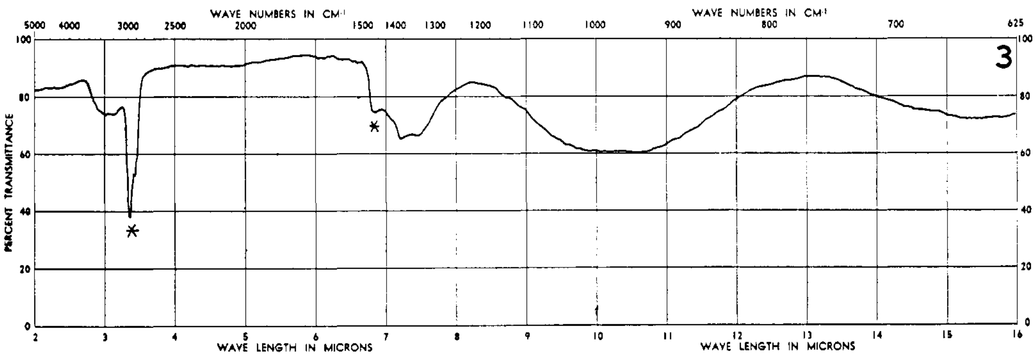
Sodium metaborate, $NaBO_2$

C.P.



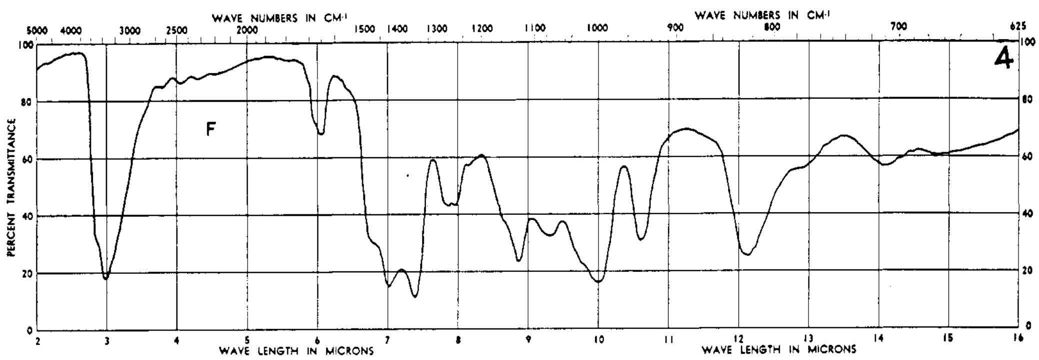
Magnesium metaborate, $Mg(BO_2)_2.8H_2O$

C.P.



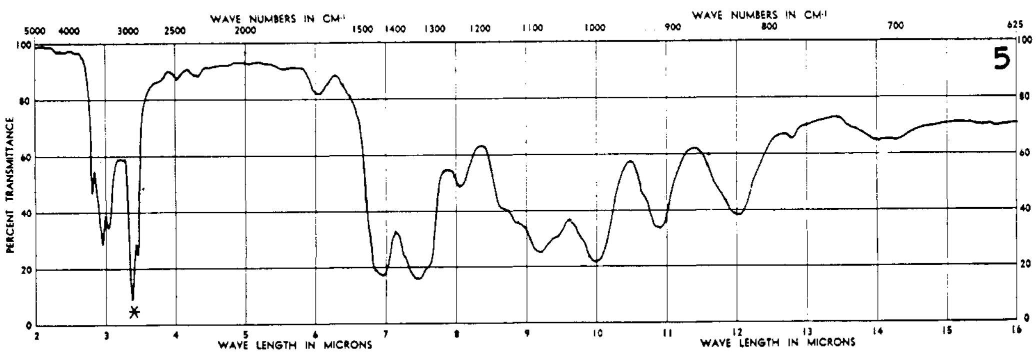
Lead metaborate, $Pb(BO_2)_2.H_2O$

C.P.



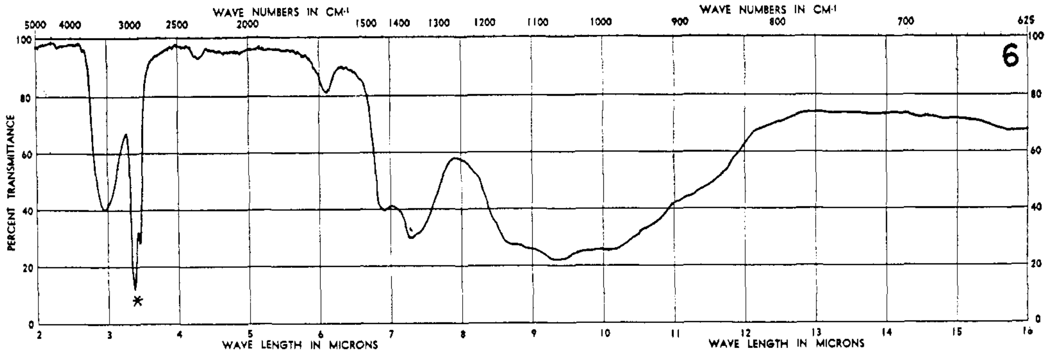
Sodium tetraborate, $Na_2B_4O_7.10H_2O$

C.P.



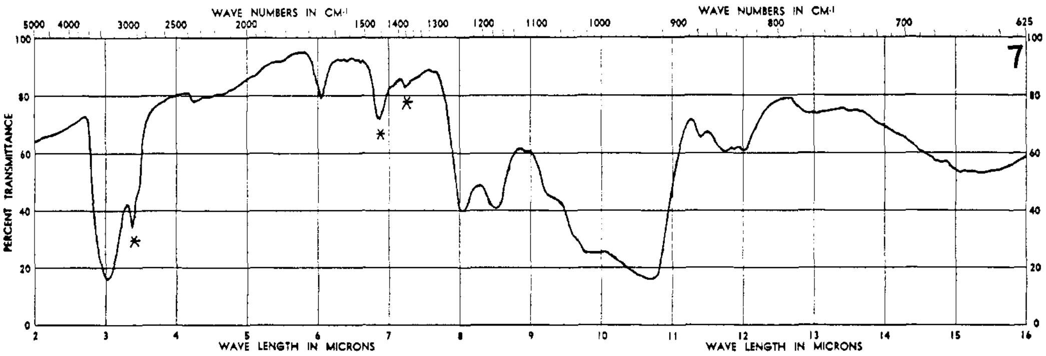
Potassium tetraborate, $K_2B_4O_7.5H_2O$

C.P.



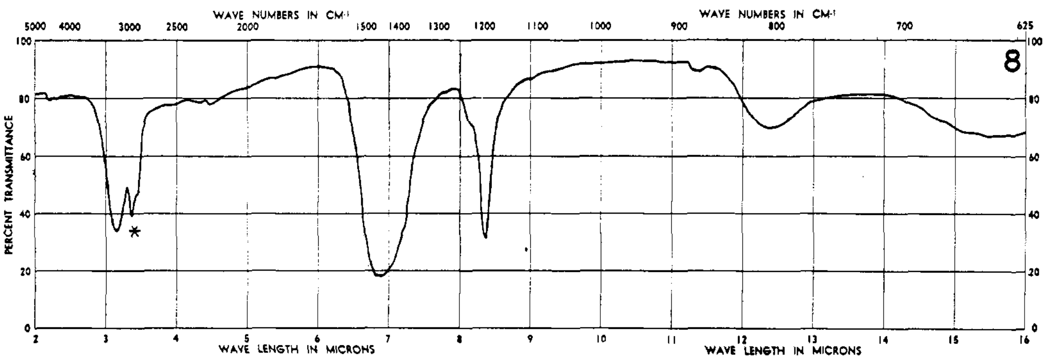
Manganese tetraborate, $MnB_4O_7.8H_2O$

C.P.



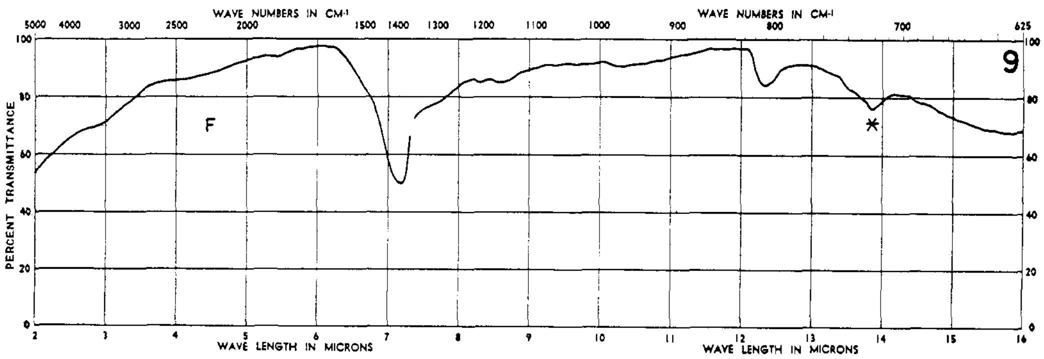
Sodium perborate, $NaBO_3.4H_2O$

C.P.



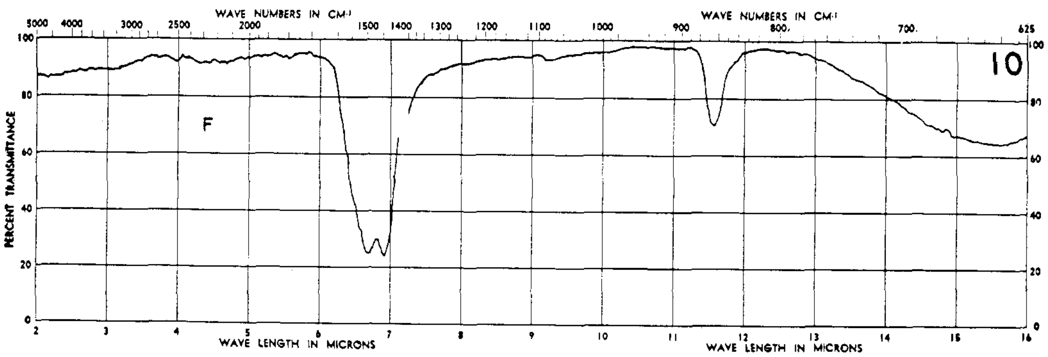
Boric acid, H_3BO

C.P.



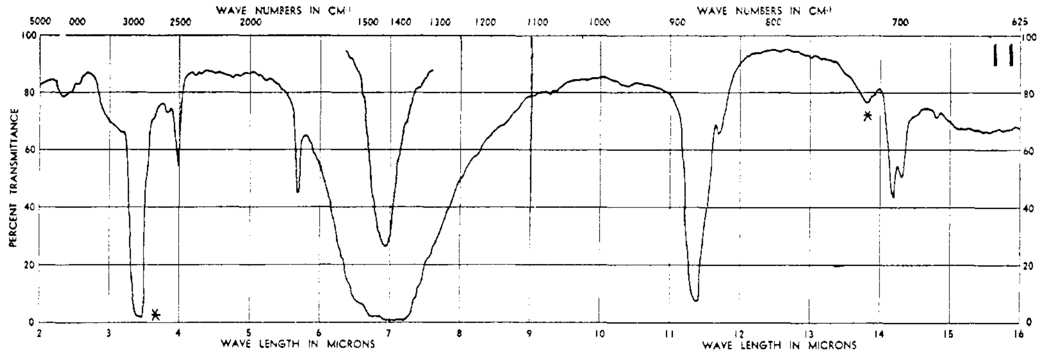
Boron nitride, BN

Pure



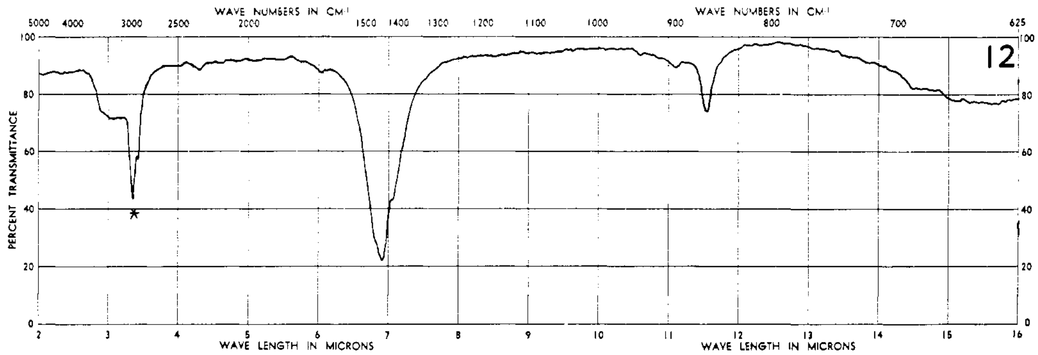
Lithium carbonate, Li_2CO_3

AR



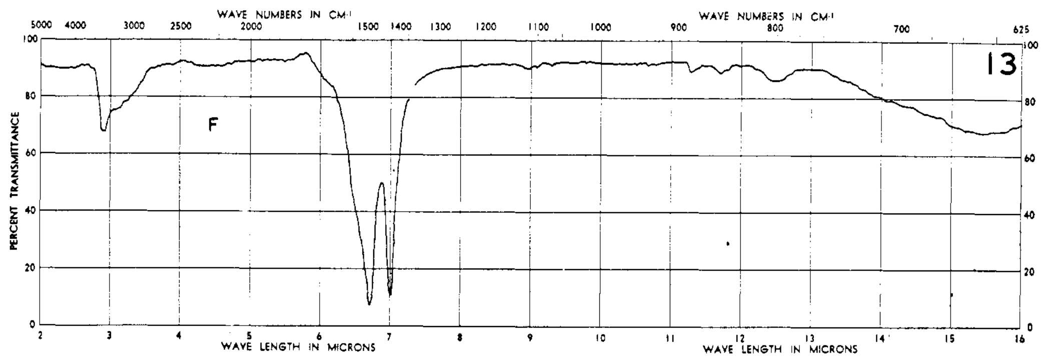
Sodium carbonate, Na_2CO_3

AR



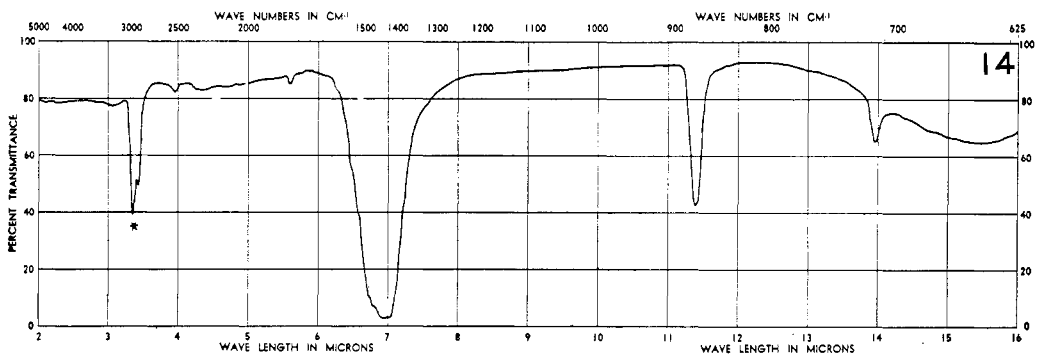
Potassium carbonate, K_2CO_3

AR



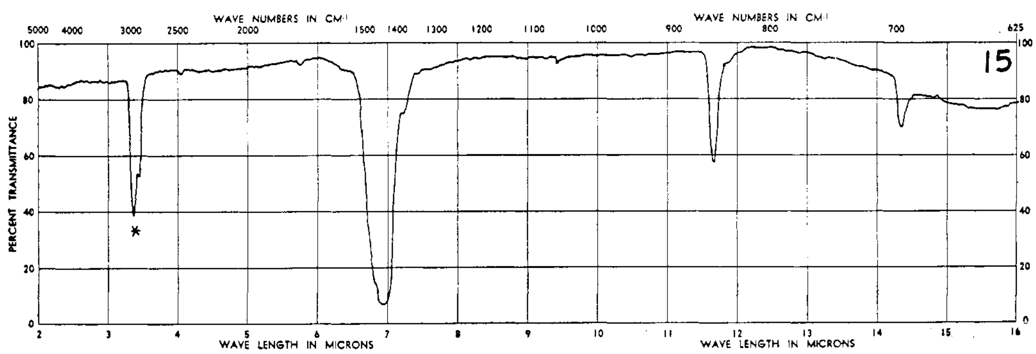
Magnesium carbonate, basic, $3MgCO_3\text{-}Mg(OH)_2.3H_2O$

Unk.



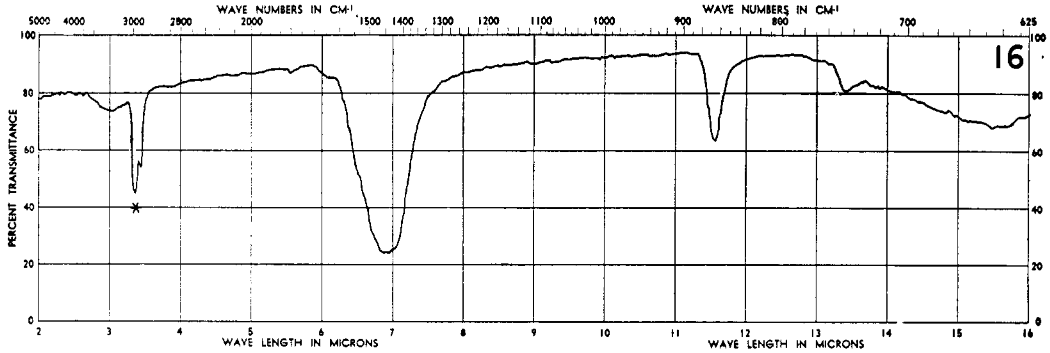
Calcium carbonate, $CaCO_3$

AR



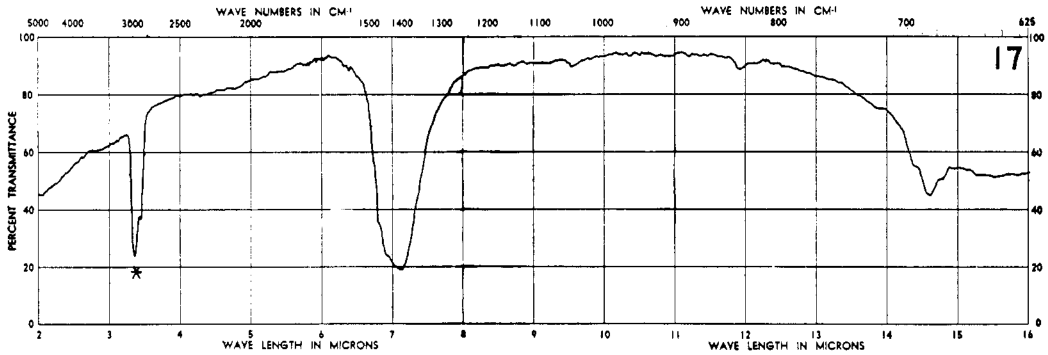
Barium carbonate, $BaCO_3$

AR



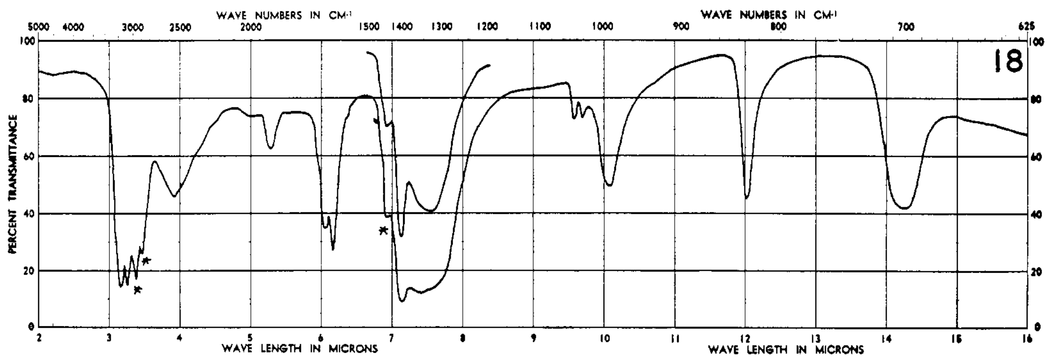
Cobaltous carbonate, $CoCO_3$

Unk.



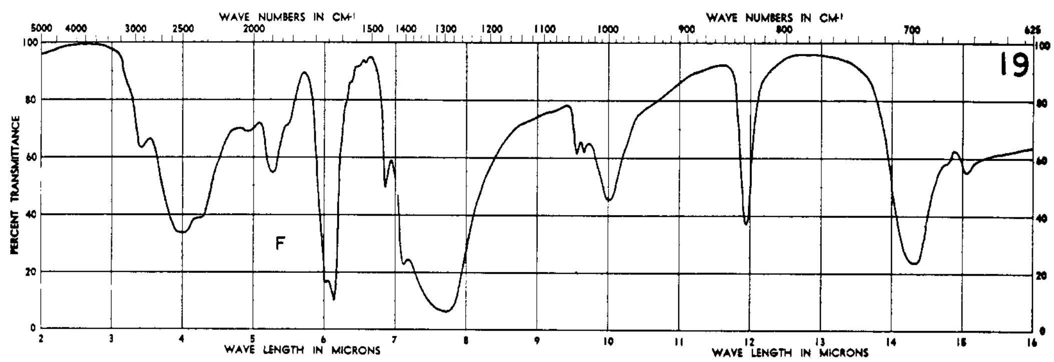
Lead carbonate, $PbCO_3$

Unk.



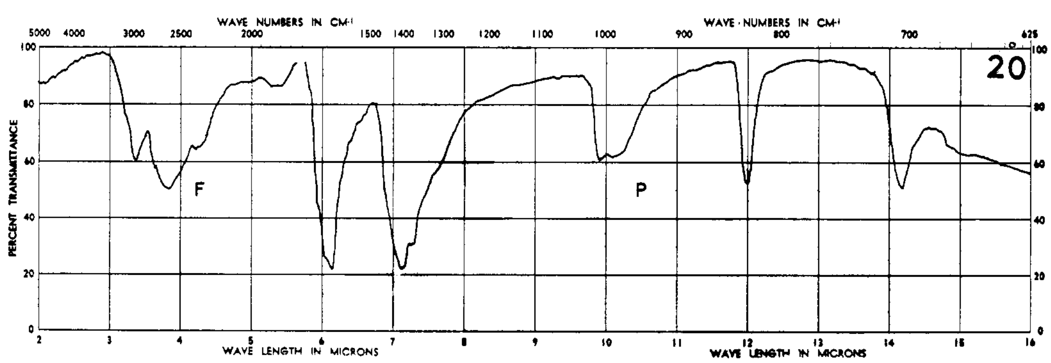
Ammonium bicarbonate, NH_4HCO_3

C.P.



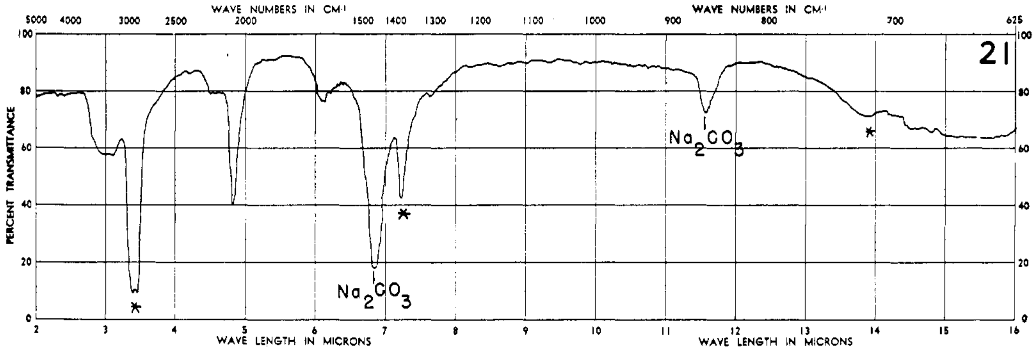
Sodium bicarbonate, $NaHCO_3$

C.P.



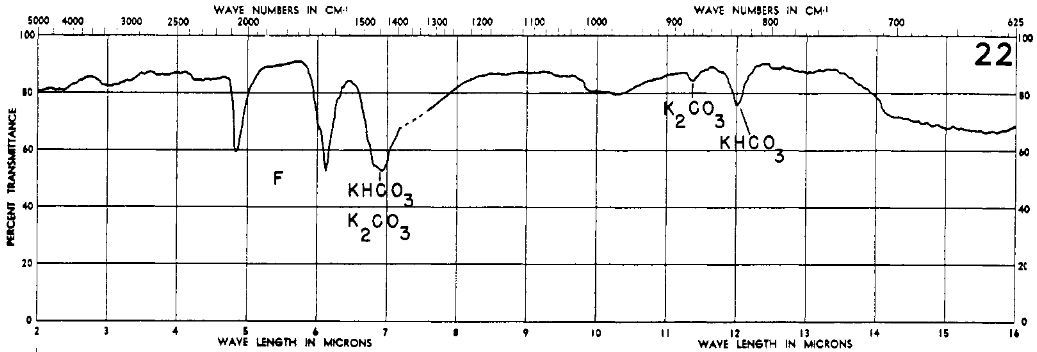
Potassium bicarbonate, $KHCO_3$

C.P.



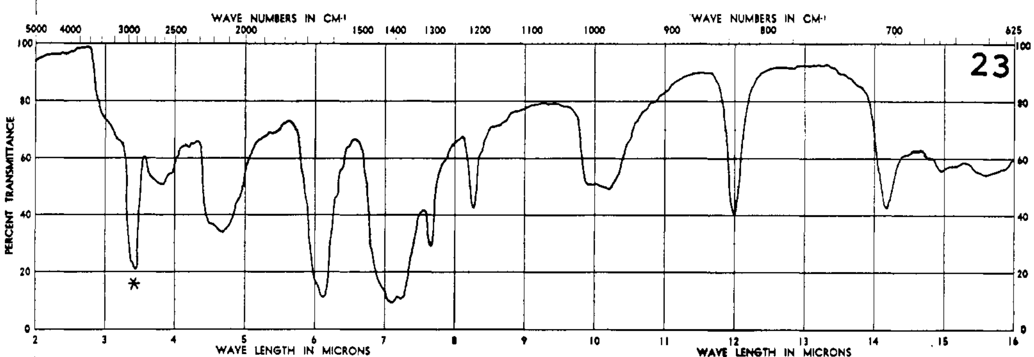
Sodium cyanide, NaCN

Na_2CO_3 impurity



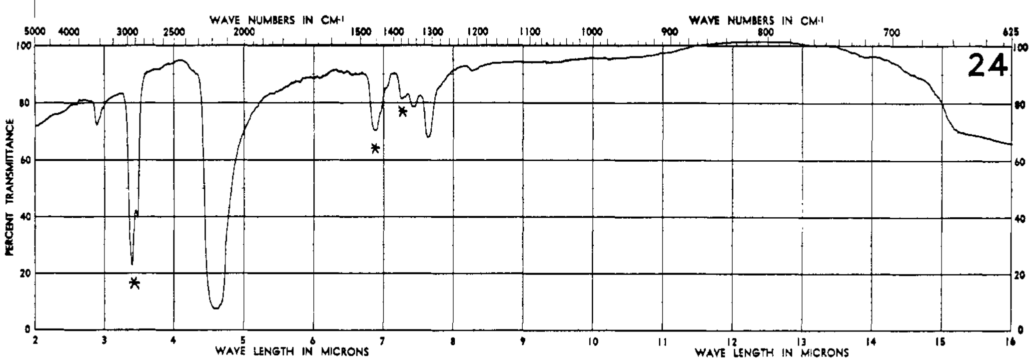
Potassium cyanide KCN

$KHCO_3$ and K_2CO_3 impurities



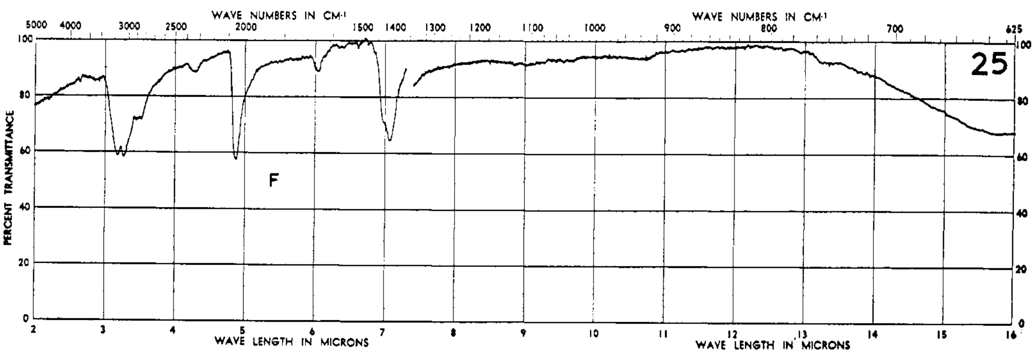
Potassium cyanate, KOCN

Considerable KHCO impurity



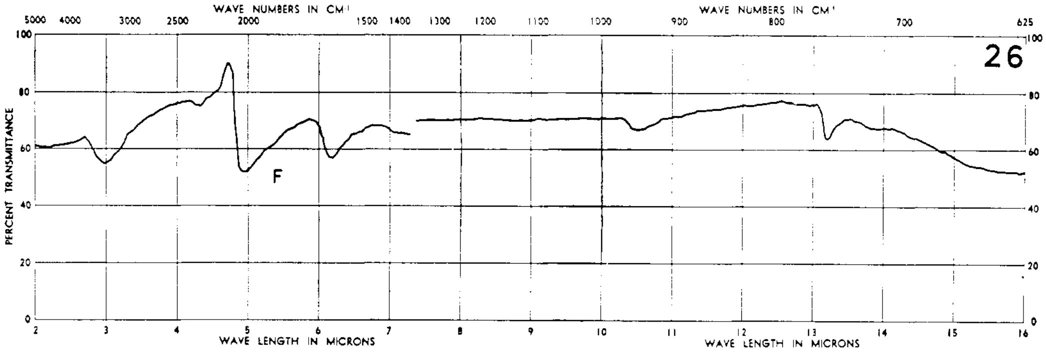
Silver cyanate, AgOCN

"Highest purity"



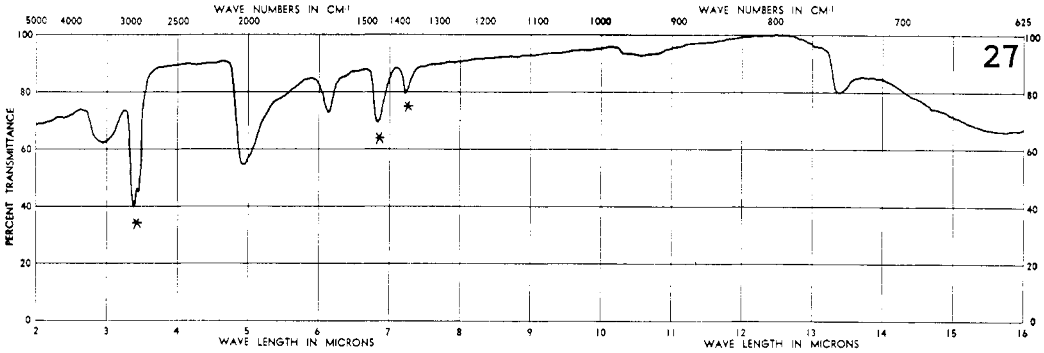
Ammonium thiocyanate, NH_4SCN

AR



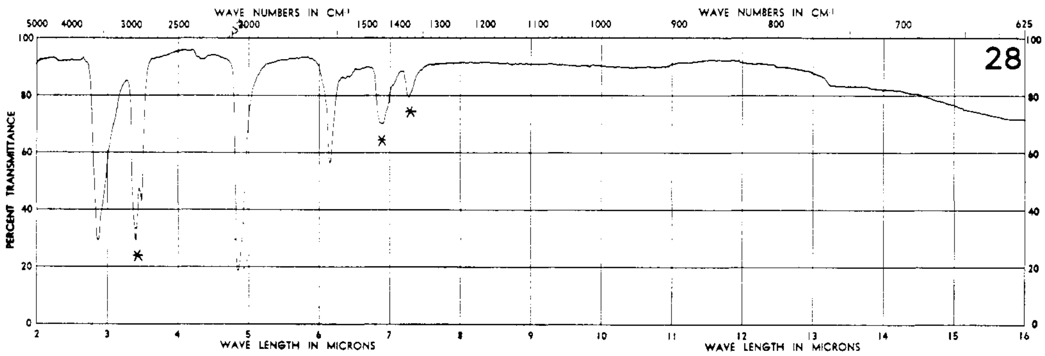
Sodium thiocyanate, NaSCN

Unk.



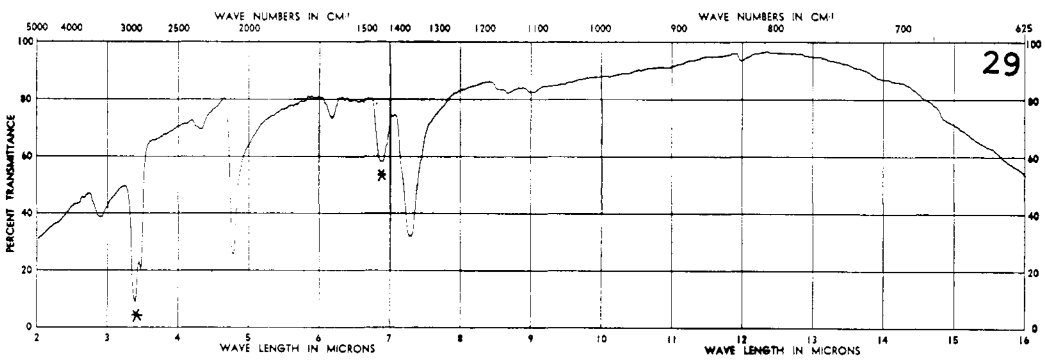
Potassium thiocyanate, KSCN

AR



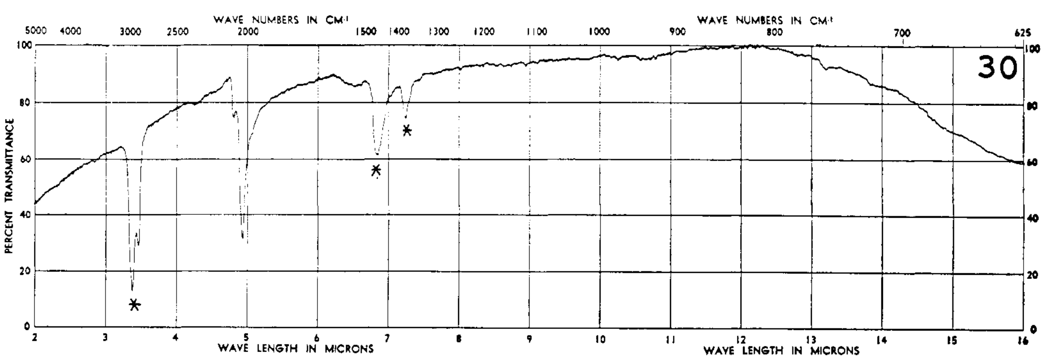
Barium thiocyanate, $Ba(SCN)_2.2H_2O$

C.P.



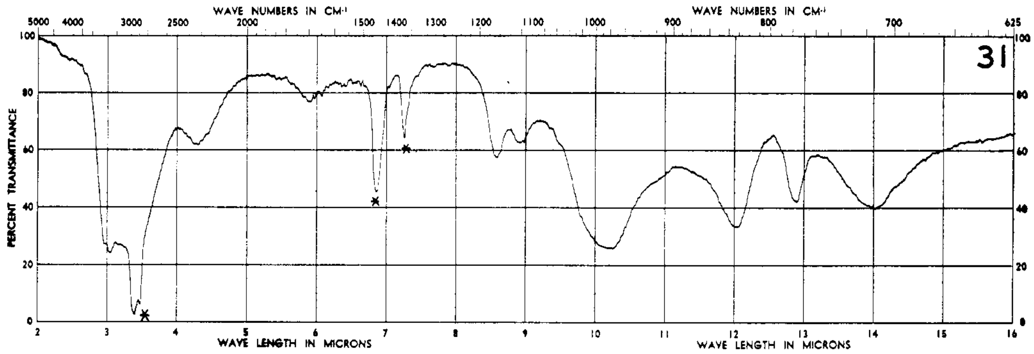
Mercuric thiocyanate, $Hg(SCN)_2$

Pure



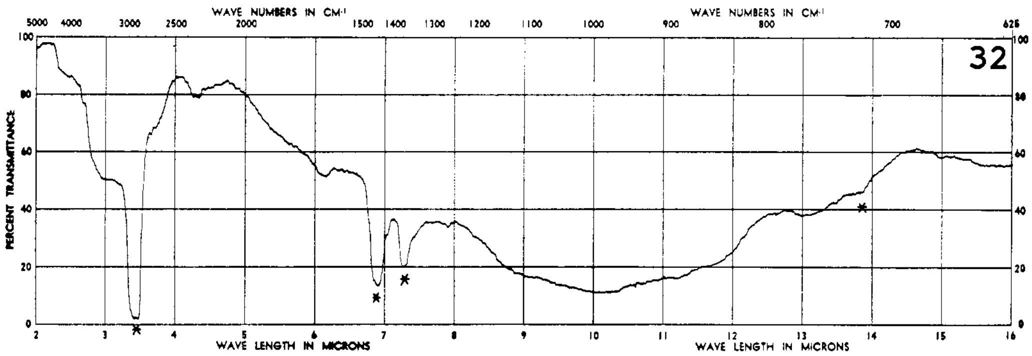
Lead thiocyanate, $Pb(SCN)_2$

C.P.



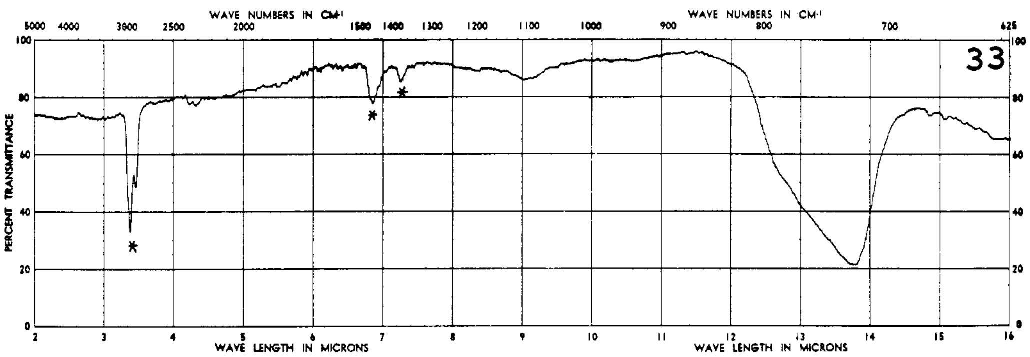
Sodium metasilicate, $Na_2SiO_3.5H_2O$

C.P.



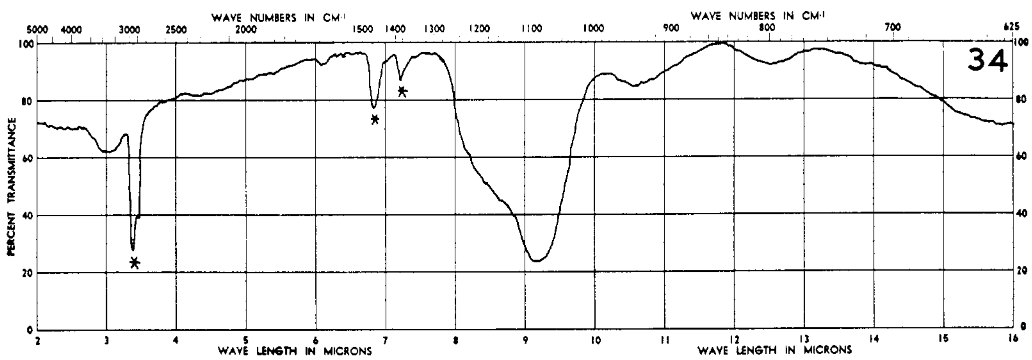
Potassium metasilicate, K_2SiO_3

C.P.

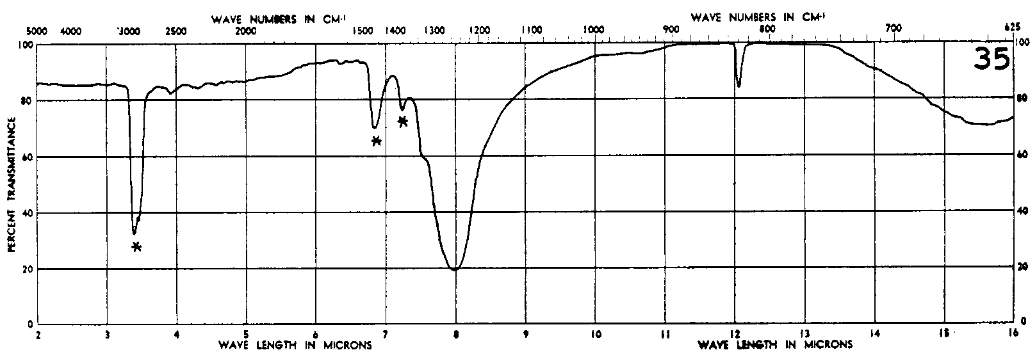


Sodium silicofluoride, Na_2SiF_6

C.P.

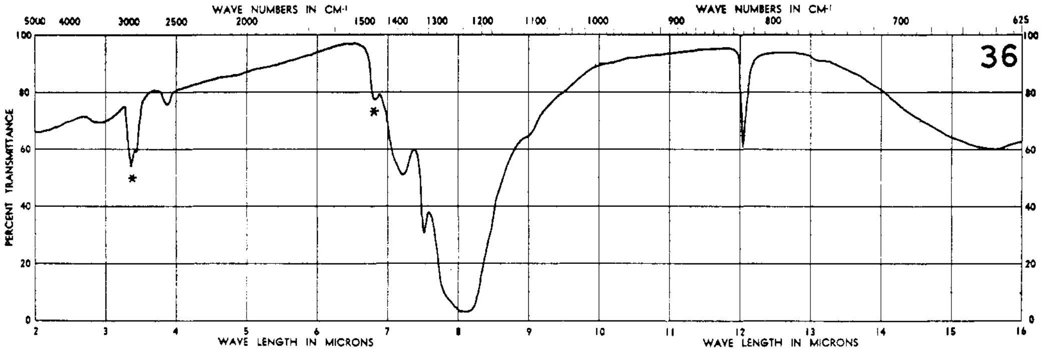


Silica gel, $SiO_2.xH_2O$



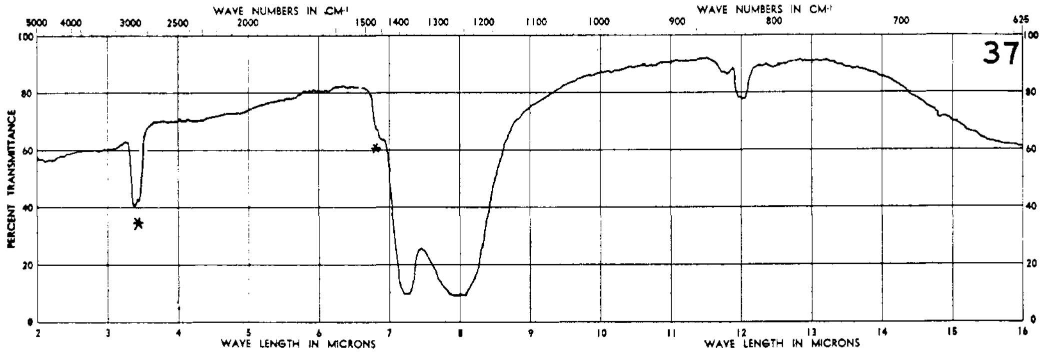
Sodium nitrite, $NaNO_2$

C.P.



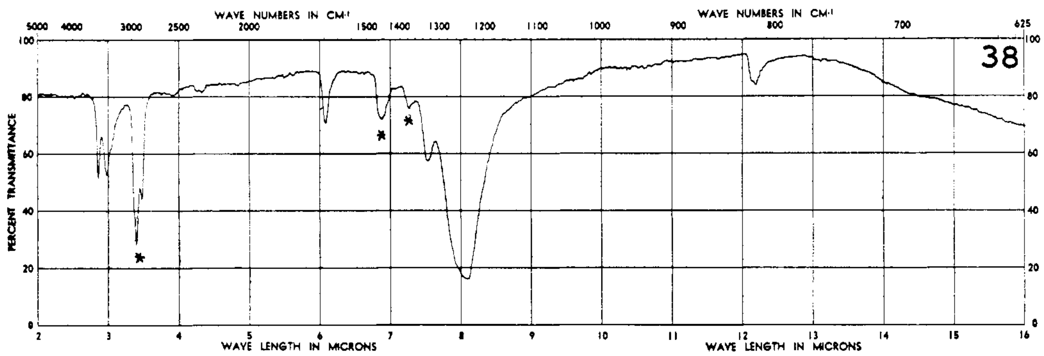
Potassium nitrite, KNO_2

C.P.



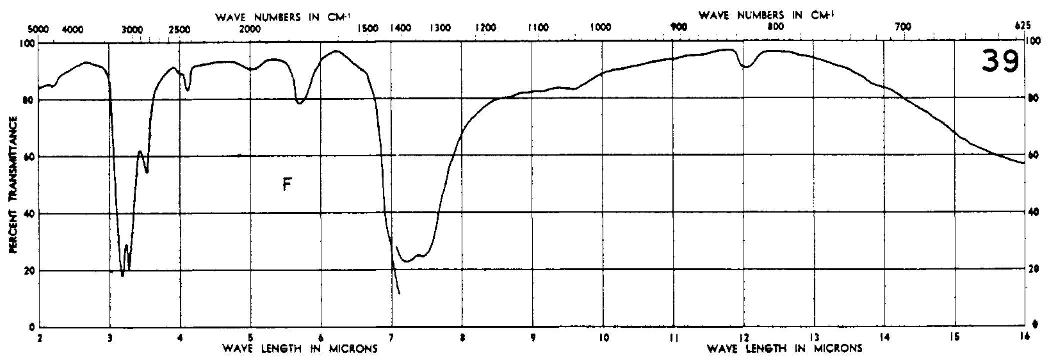
Silver nitrite, $AgNO_2$

C.P.



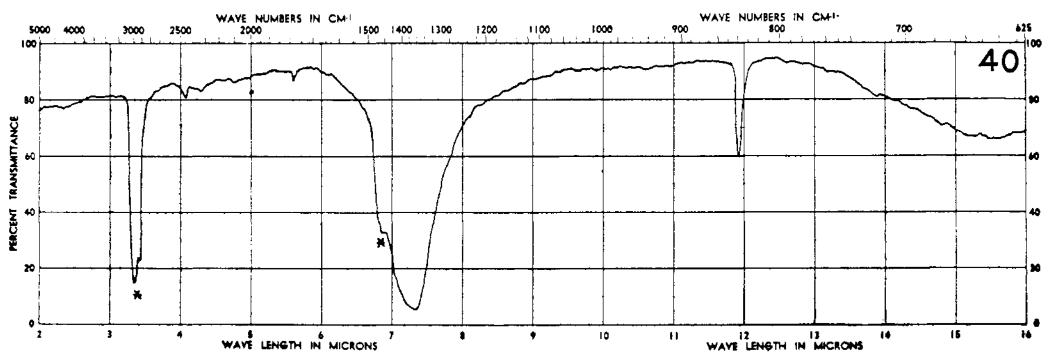
Barium nitrite, $Ba(NO_2)_2.H_2O$

C.P.



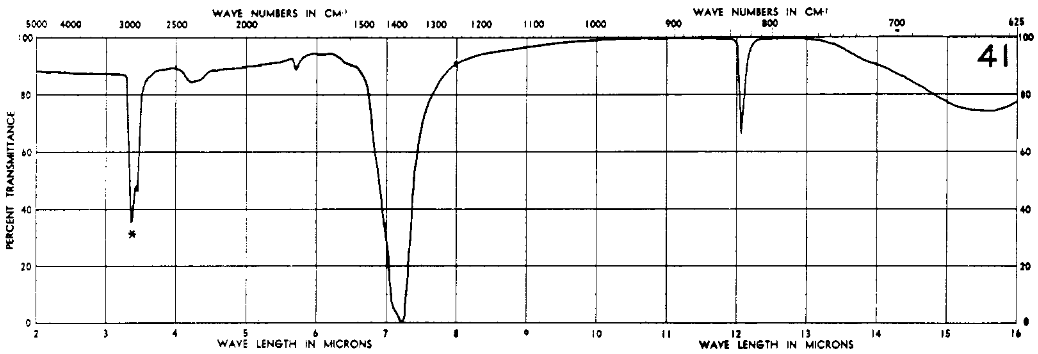
Ammonium nitrate, NH_4NO_3

C.P.



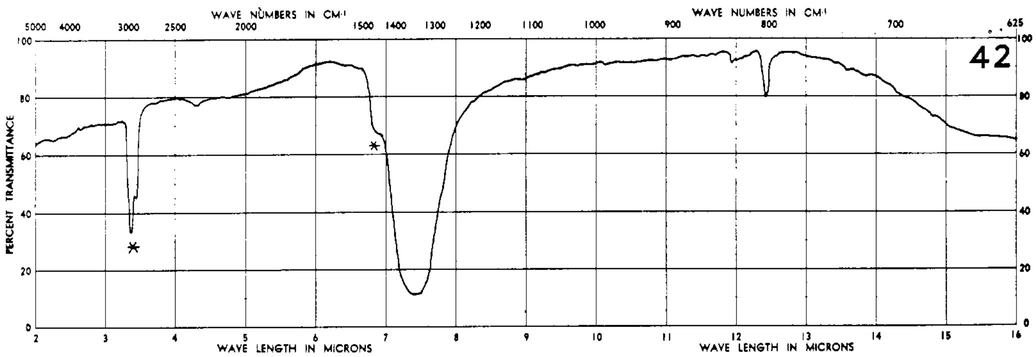
Sodium nitrate, $NaNO_3$

AR



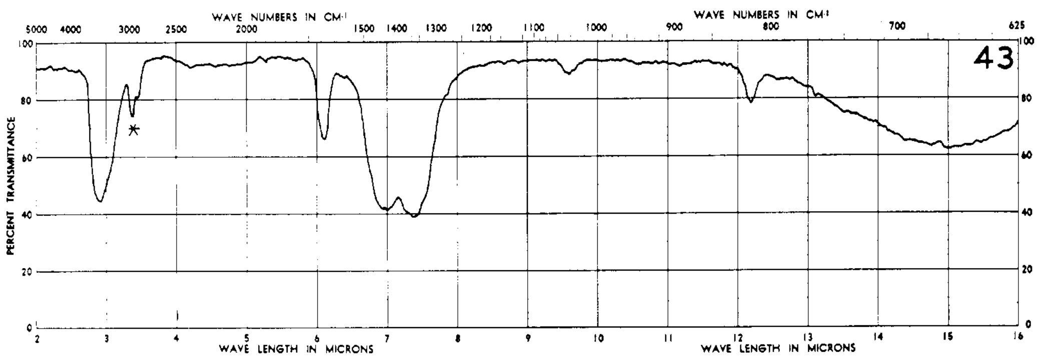
Potassium nitrate, KNO_3

AR



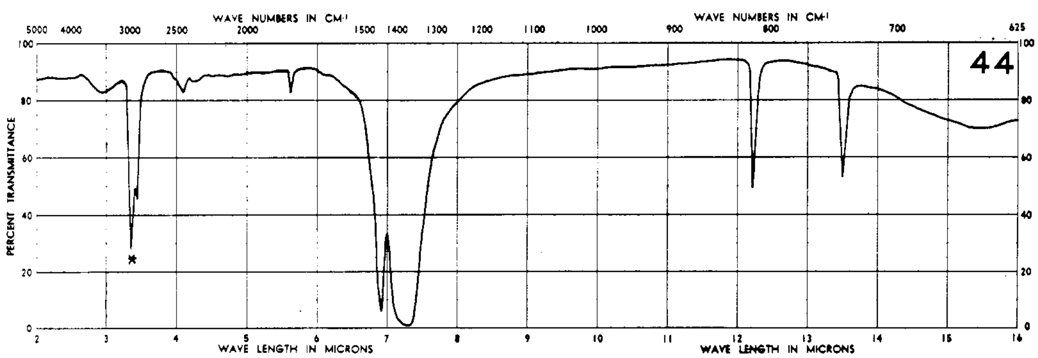
Silver nitrate, $AgNC_3$

C.P.



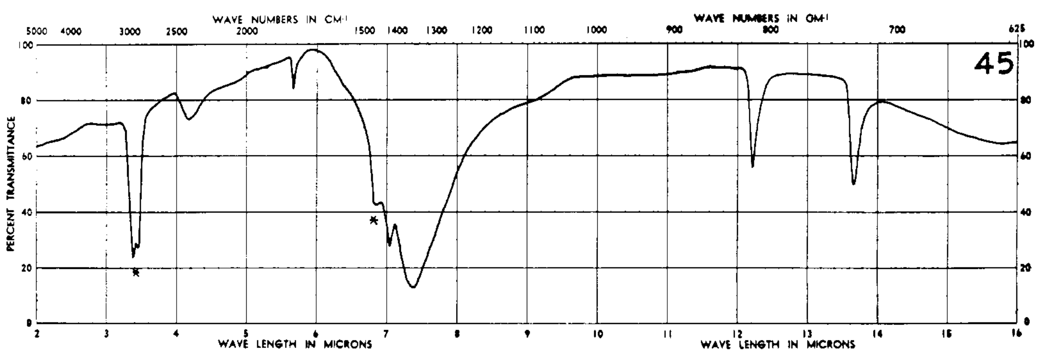
Calcium nitrate, $Ca(NO_3)_2$

C.P.



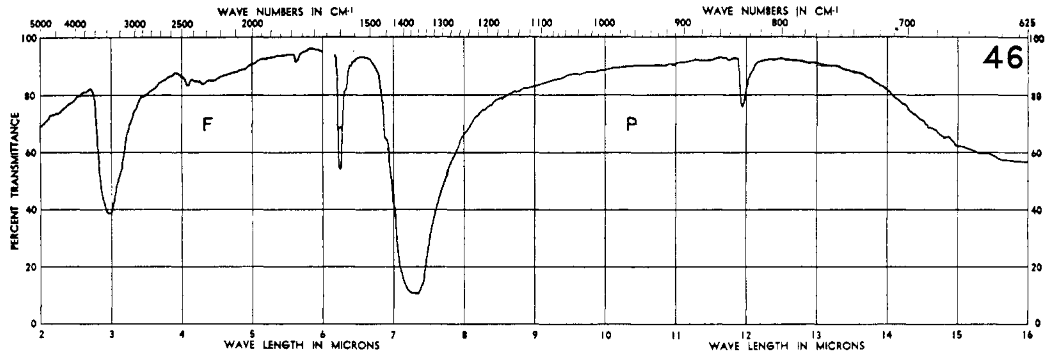
Strontium nitrate, $Sr(NO_3)_2$

Unk.



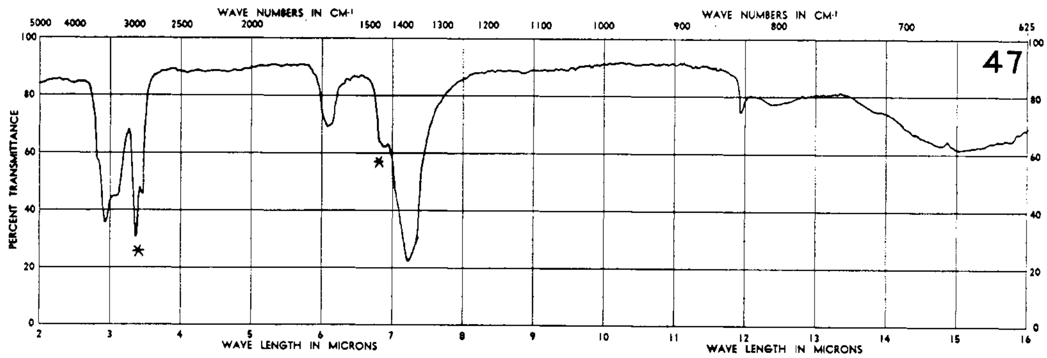
Barium nitrate, $Ba(NO_3)_2$

AR



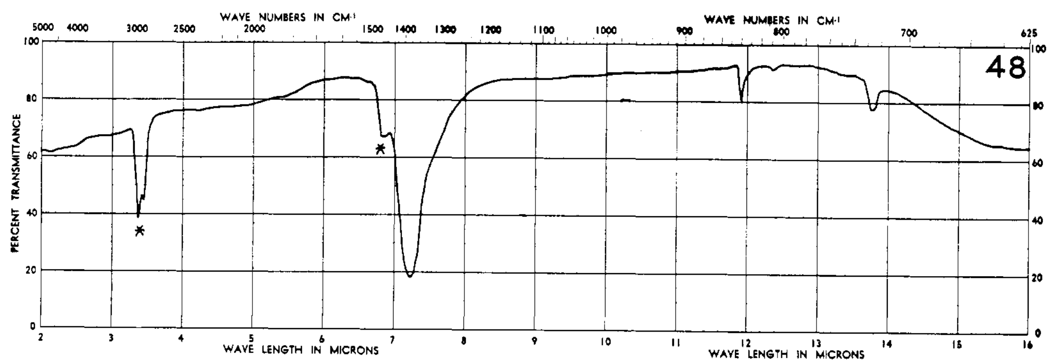
Cupric nitrate, $Cu(NO_3)_2.3H_2O$

C.P.



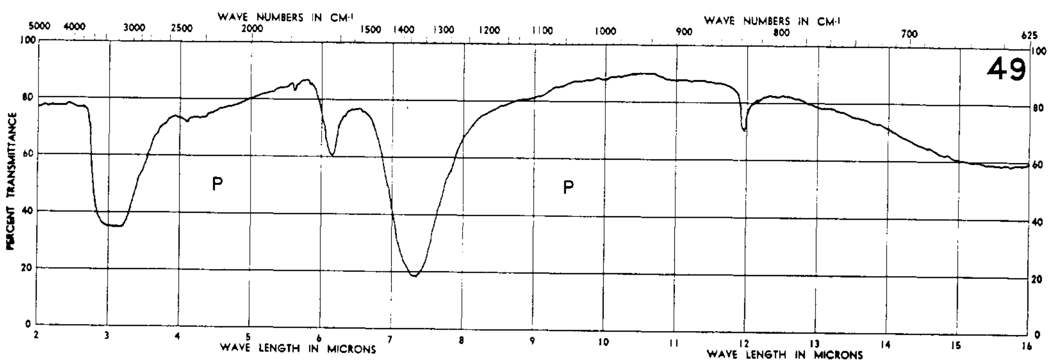
Cobaltous nitrate, $Co(NO_3)_2.6H_2O$

AR



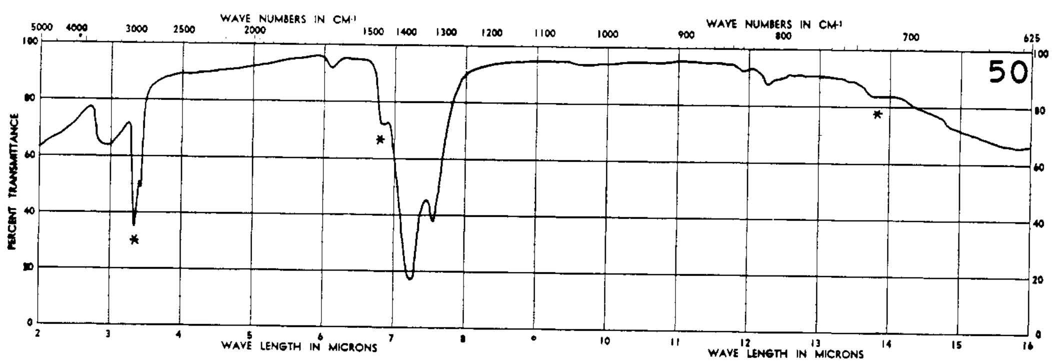
Lead nitrate, $Pb(NO_3)_2$

AR



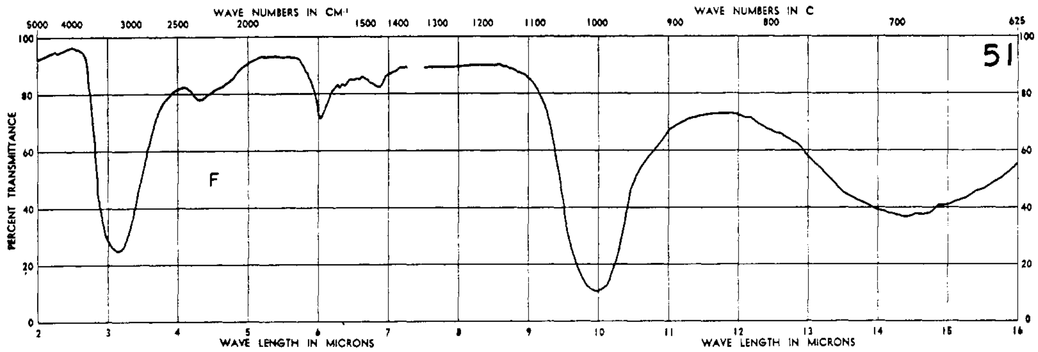
Ferric nitrate, $Fe(NO_3)_3.9H_2O$

AR



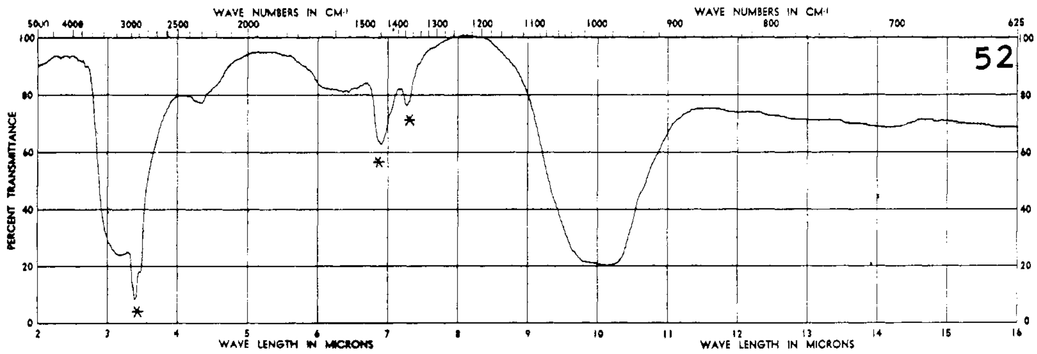
Bismuth subnitrate, $BiONO_3.H_2O$

Unk.



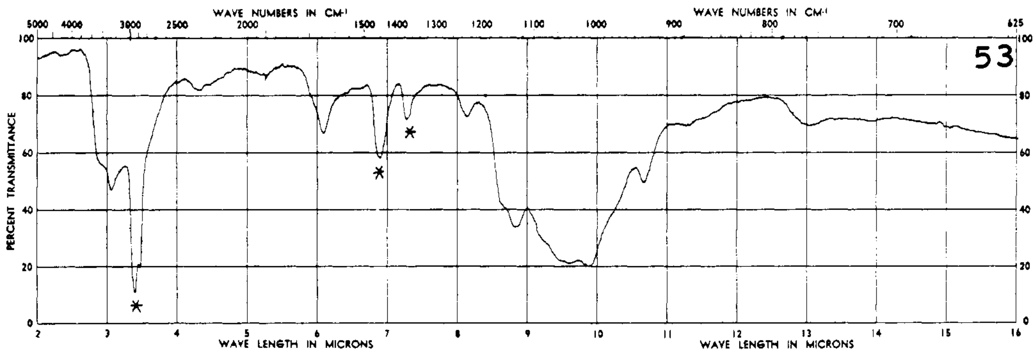
Sodium phosphate, tribasic, $Na_3PO_4.12H_2O$

AR



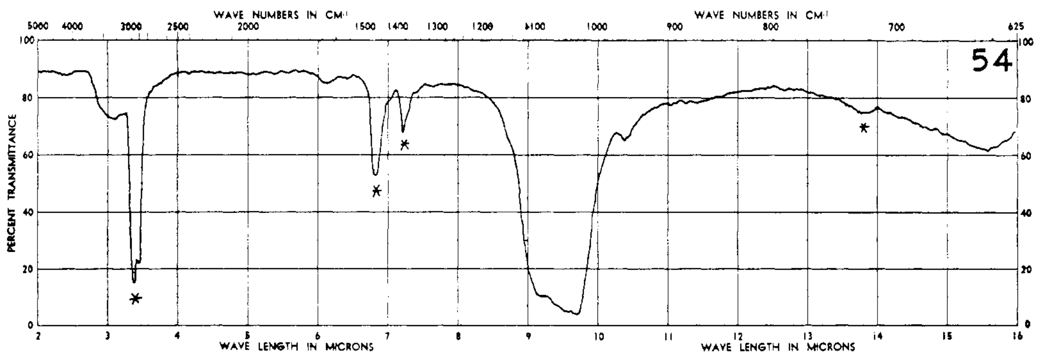
Potassium phosphate, tribasic, K_3PO_4

C.P.



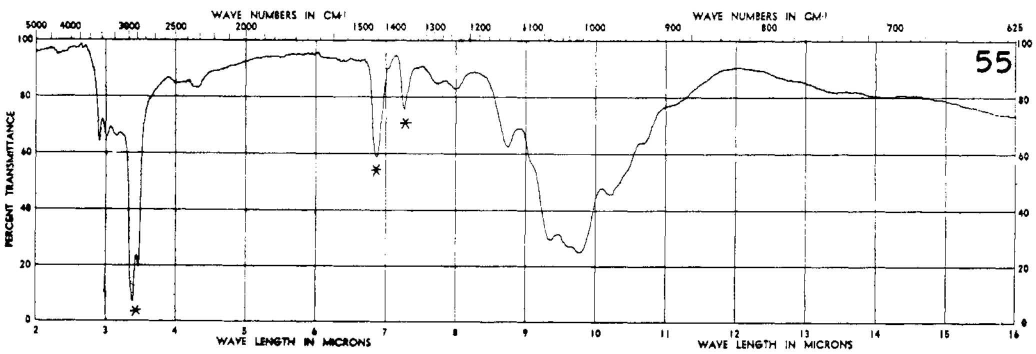
Magnesium phosphate, tribasic, $Mg_3(PO_4)_2.4H_2O$

C.P.



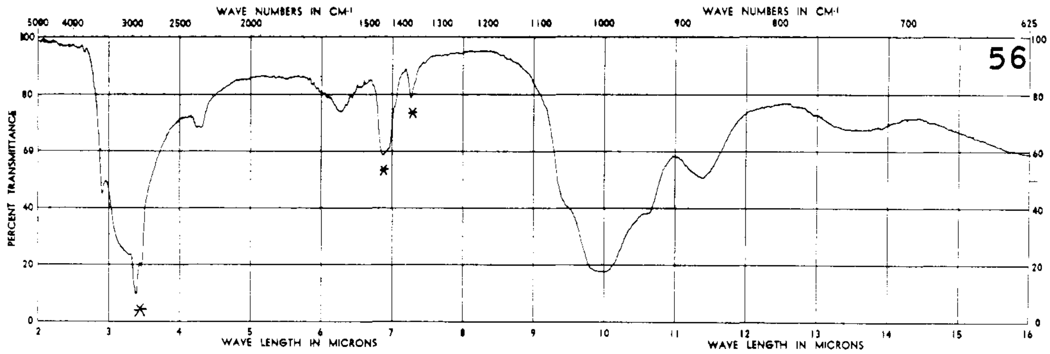
Calcium phosphate, tribasic, $Ca_3(PO_4)_2$

C.P



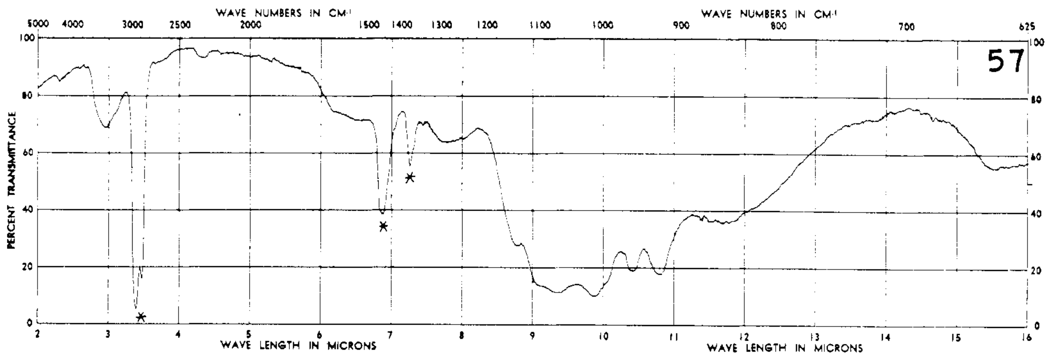
Manganese phosphate, tribasic, $Mn_3(PO_4)_2.7H_2O$

C.P.



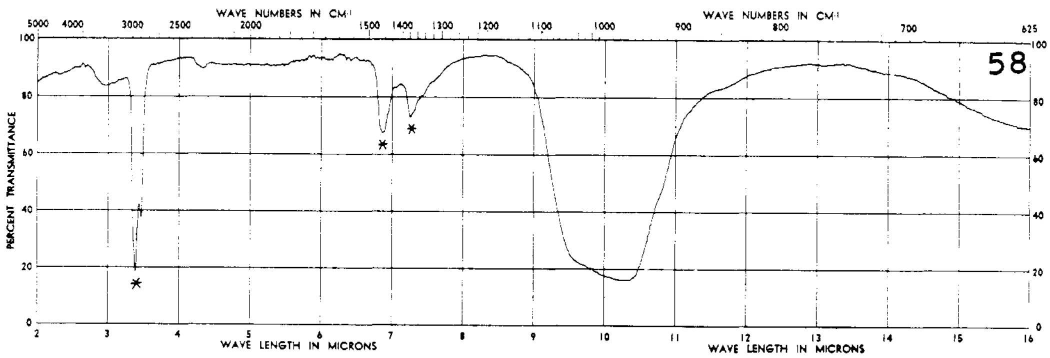
Nickel(ous) phosphate, tribasic, $Ni_3(PO_4)_2.7H_2O$

C.P.



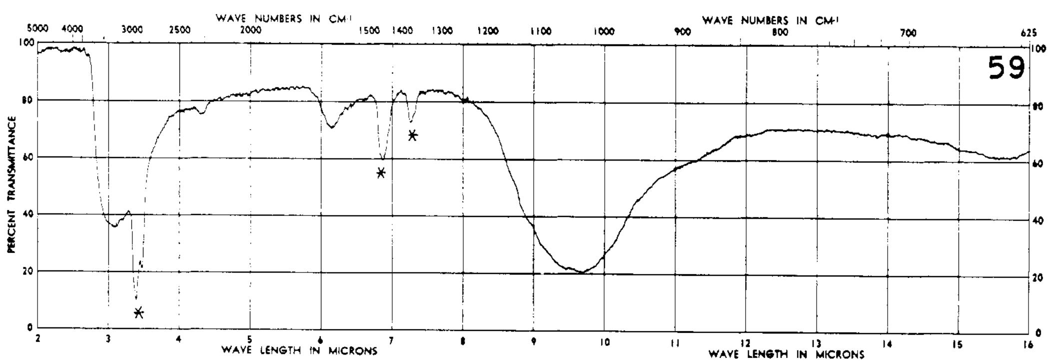
Copper(ic) phosphate, tribasic, $Cu_3(PO_4)_2.3H_2O$

C.P.



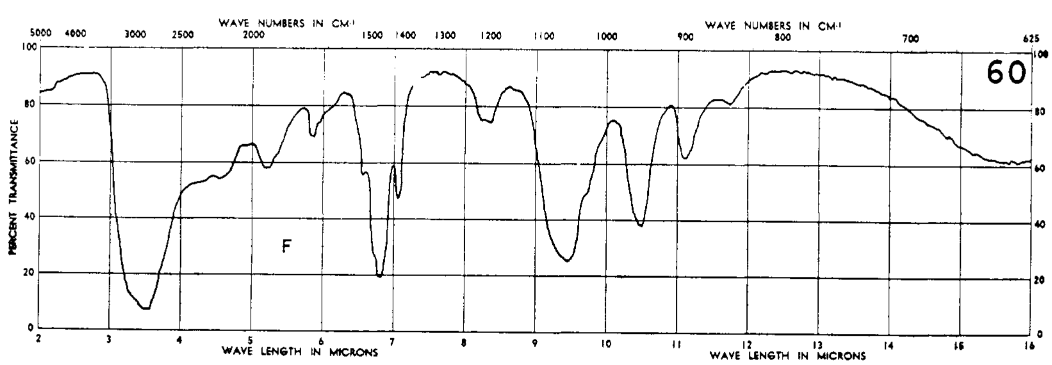
Lead phosphate, tribasic, $Pb_3(PO_4)_2$

C.P.



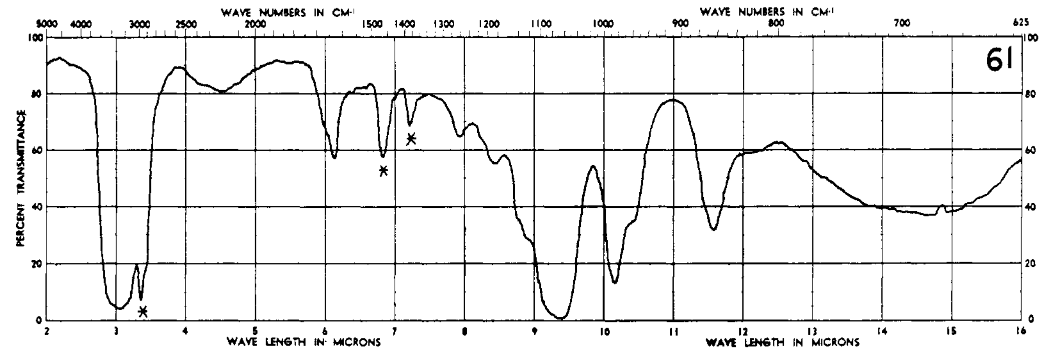
Chromic phosphate, tribasic, $CrPO_4.H_2O$

C.P.



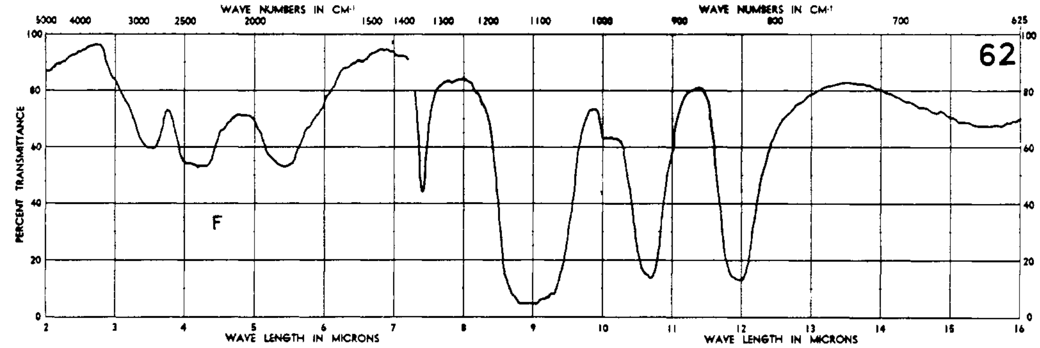
Ammonium phosphate, dibasic, $(NH_4)_2HPO_4$

C.P.



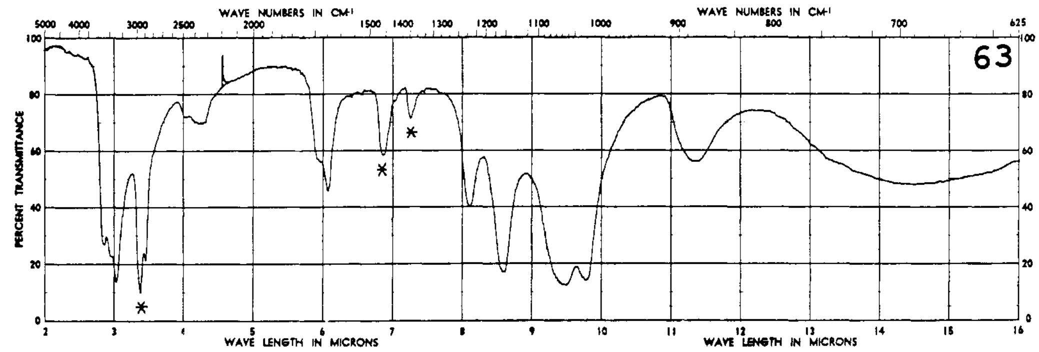
Sodium phosphate, dibasic, $Na_2HPO_4.12H_2O$

C.P.



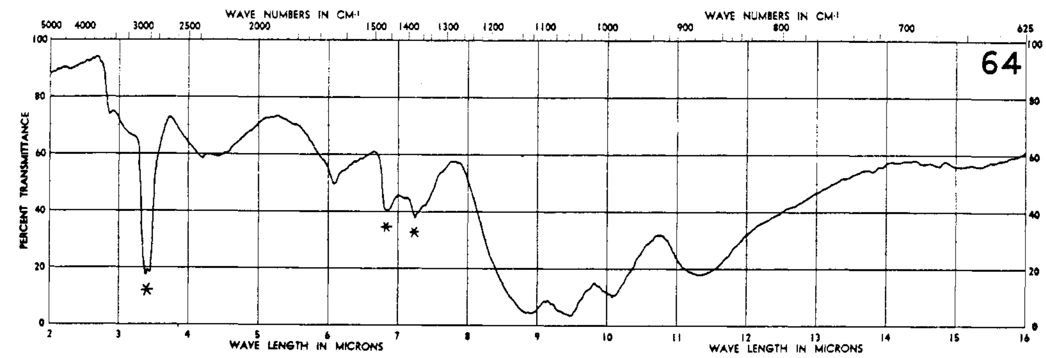
Potassium phosphate, dibasic, K_2HPO_4

C.P.



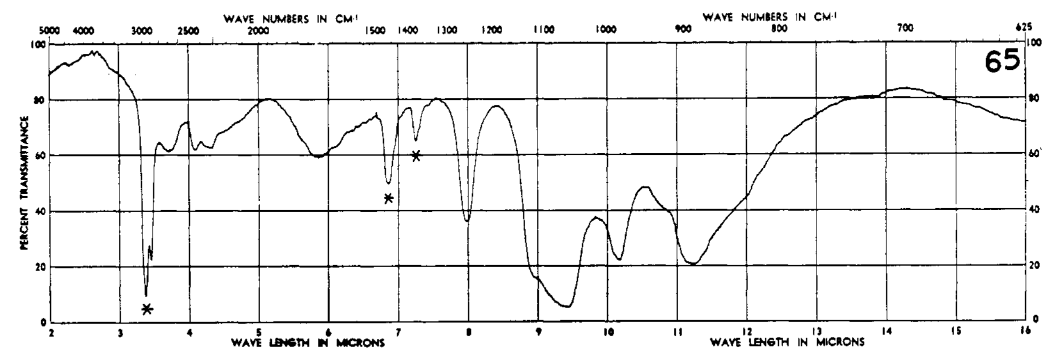
Magnesium phosphate, dibasic, $MgHPO_4.3H_2O$

C.P



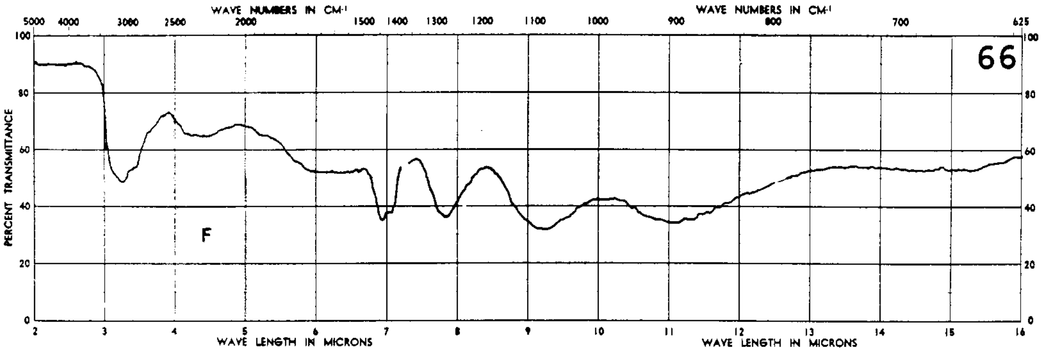
Calcium phosphate, dibasic, $CaHPO_4.2H_2O$

C.P.



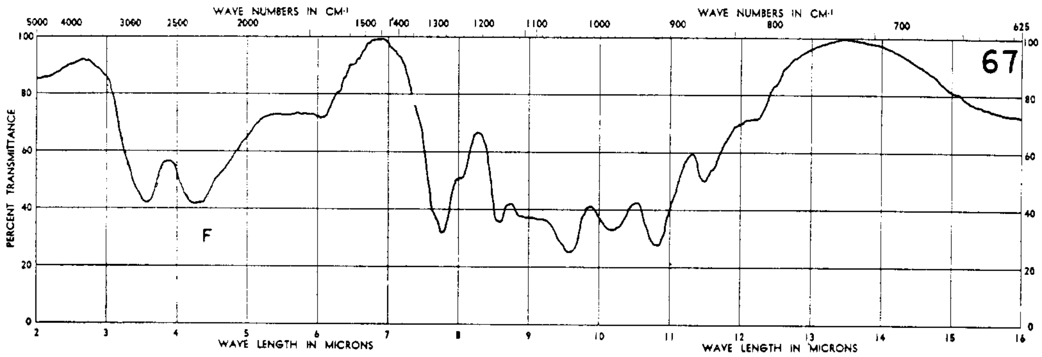
Barium phosphate, dibasic, $BaHPO_4$

C.P.



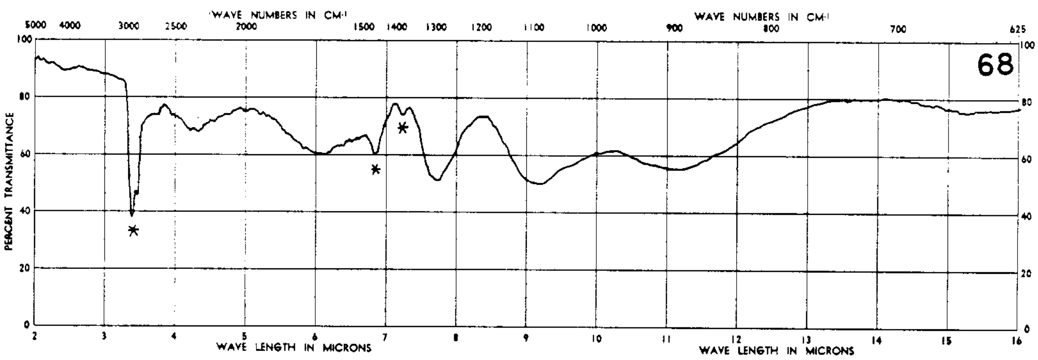
Ammonium phosphate, monobasic, $NH_4H_2PO_4$

AR



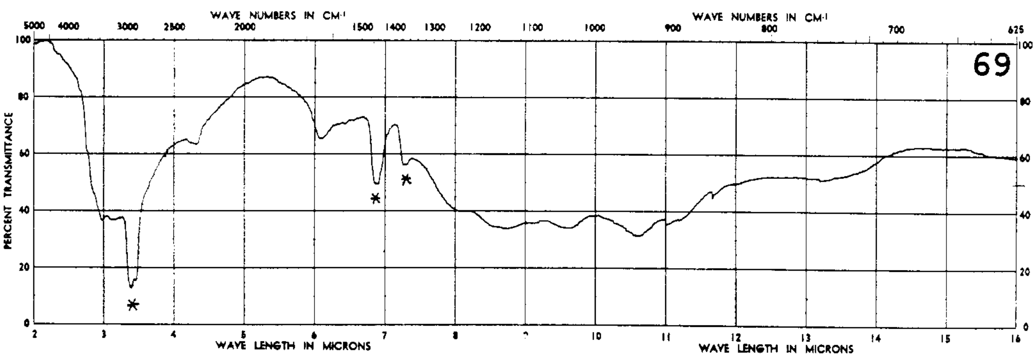
Sodium phosphate, monobasic, $NaH_2PO_4 . H_2O$

C.P.



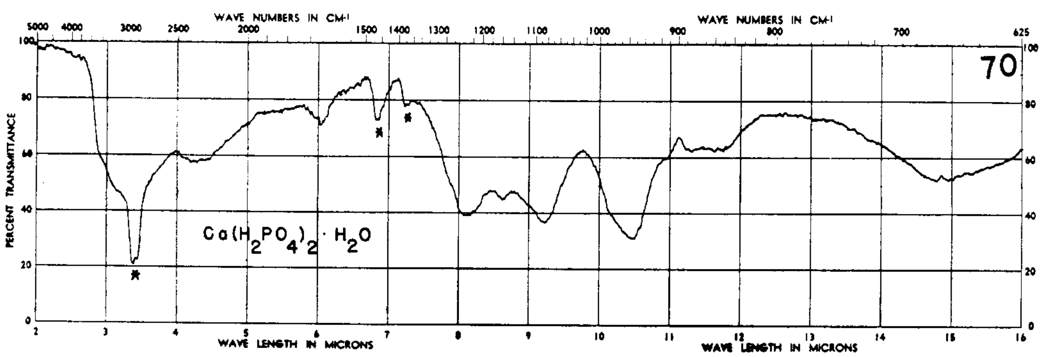
Potassium phosphate, monobasic, KH_2PO_4

C.P.



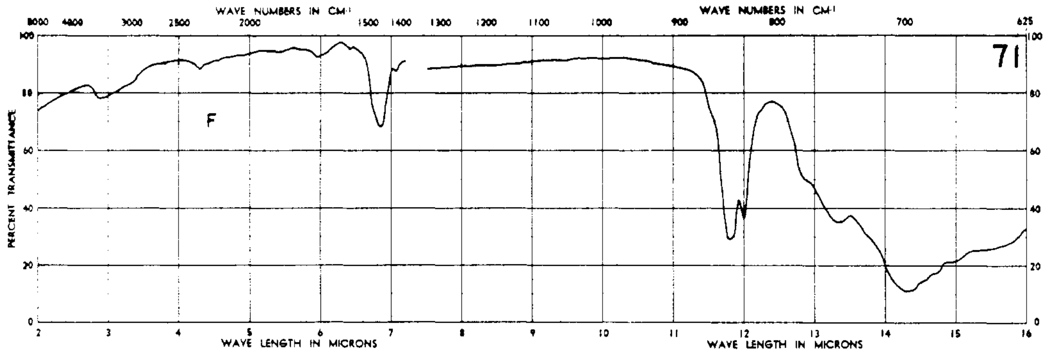
Magnesium phosphate, monobasic, $Mg(H_2PO_4)_2$

C.P.



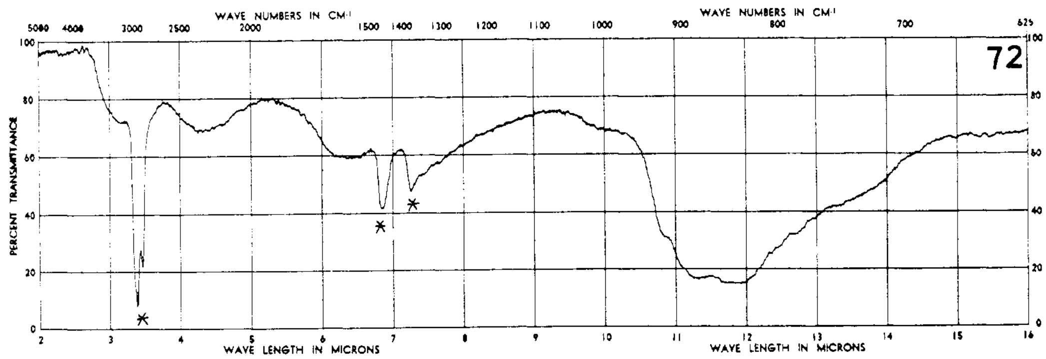
Calcium phosphate, monobasic, $Ca(H_2PO_4)_2 . H_2O$

AR



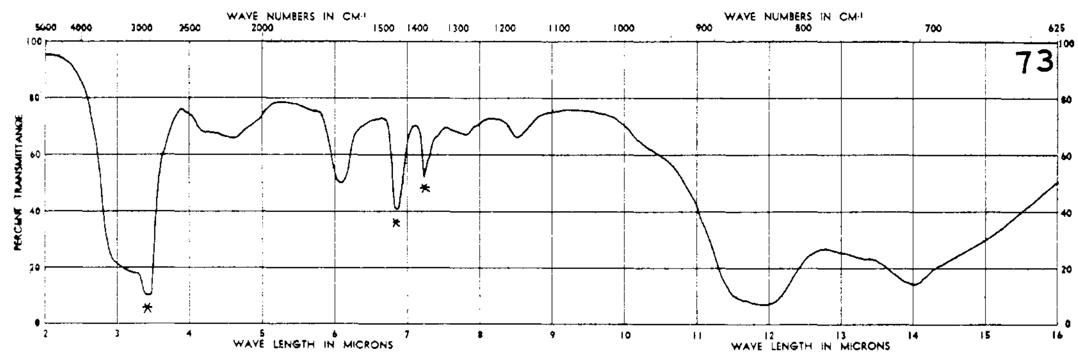
Sodium metaarsenite, $NaAsO_2$

AR



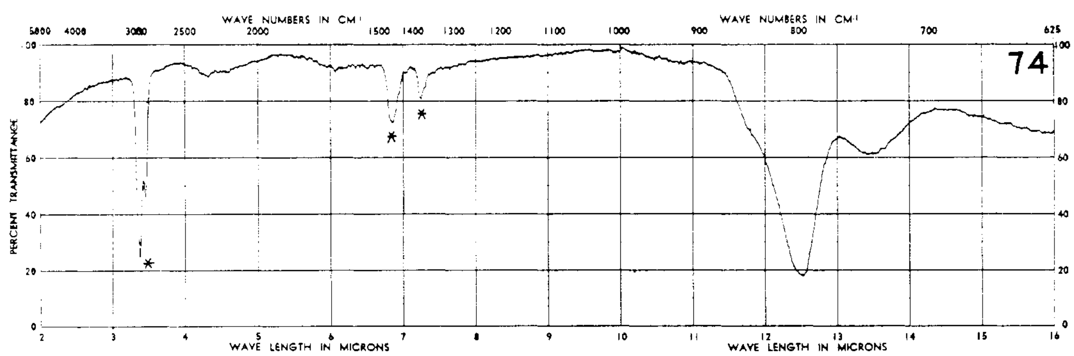
Calcium orthoarsenate, tribasic, $Ca_3(AsO_4)_2$

C.P.



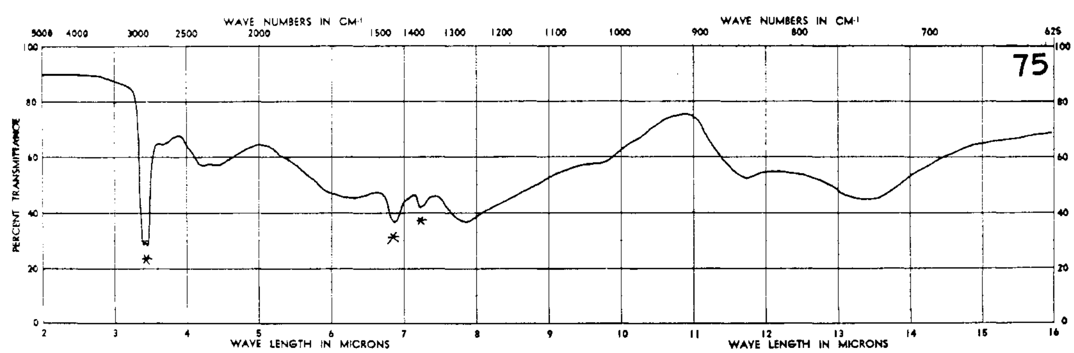
Sodium orthoarsenate, dibasic, $Na_2HAsO_4.7H_2O$

Unk.



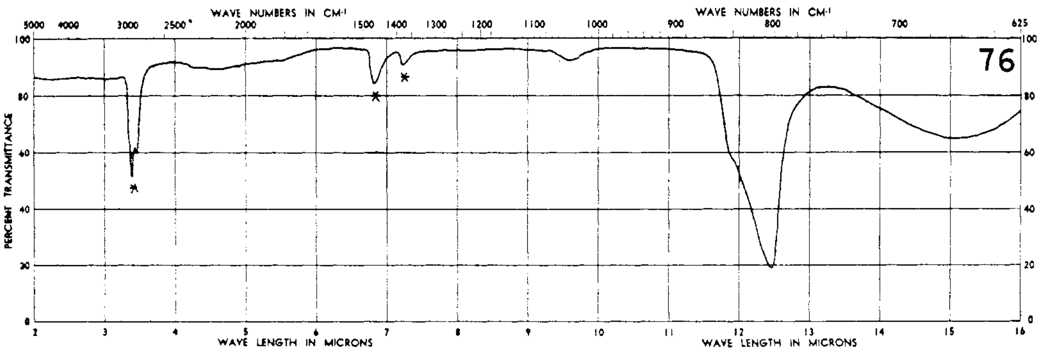
Lead orthoarsenate, dibasic, $PbHAsO_4$

C.P.



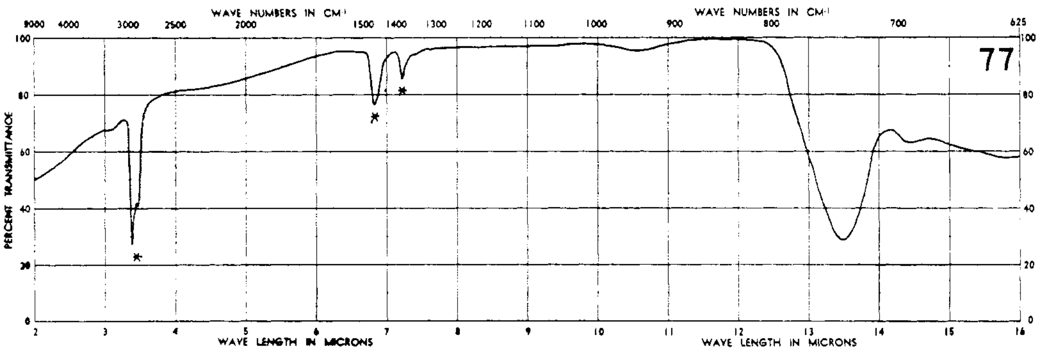
Potassium orthoarsenate, monobasic, KH_2AsO_4

AR



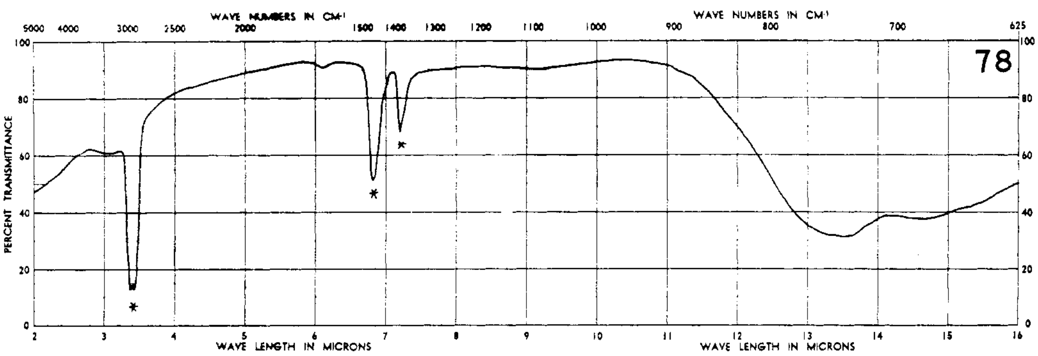
Arsenic trioxide, As_2O_3

Unk.



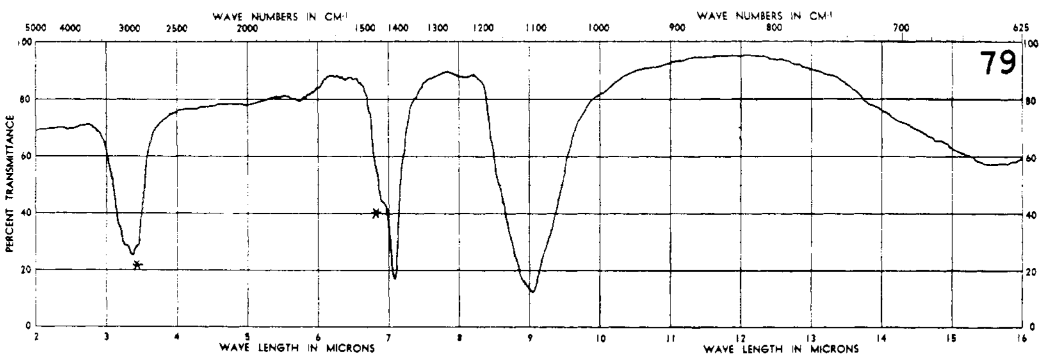
Antimony trioxide, Sb_2O_3

Unk.



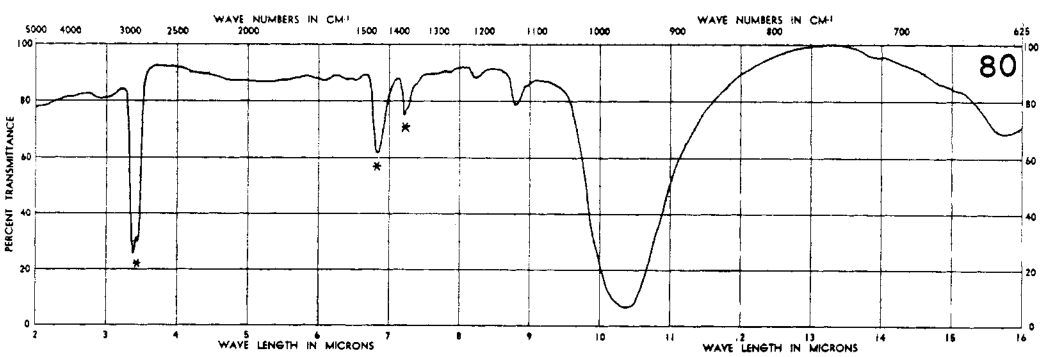
Antimony pentoxide, Sb_2O_5

C.P.



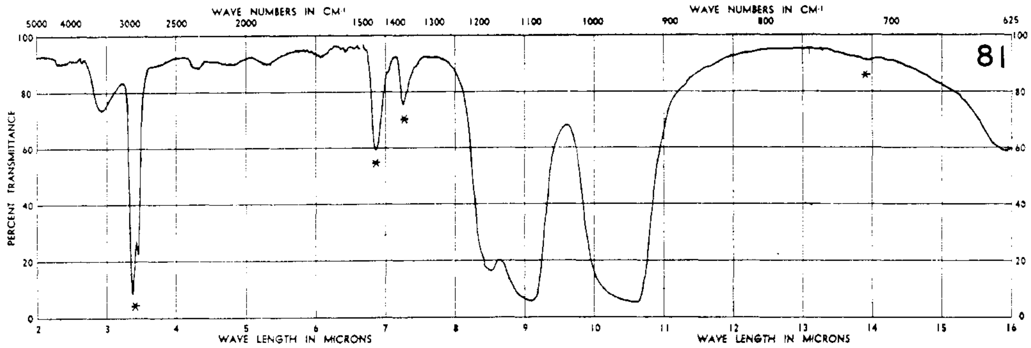
Ammonium sulfite, $(NH_4)_2SO_3.H_2O$

Unk.



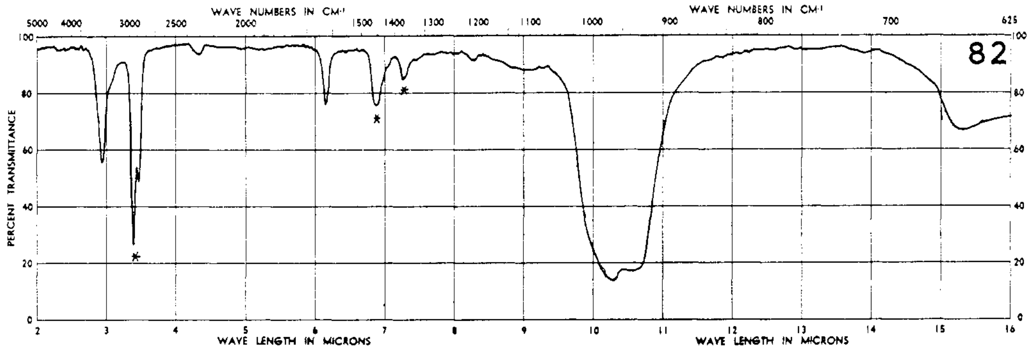
Sodium sulfite, Na_2SO_3

AR



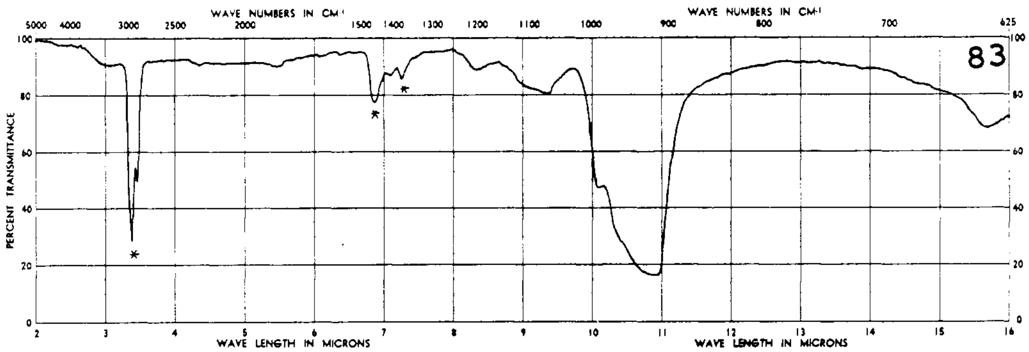
Potassium sulfite, $K_2SO_3.2H_2O$

C.P.



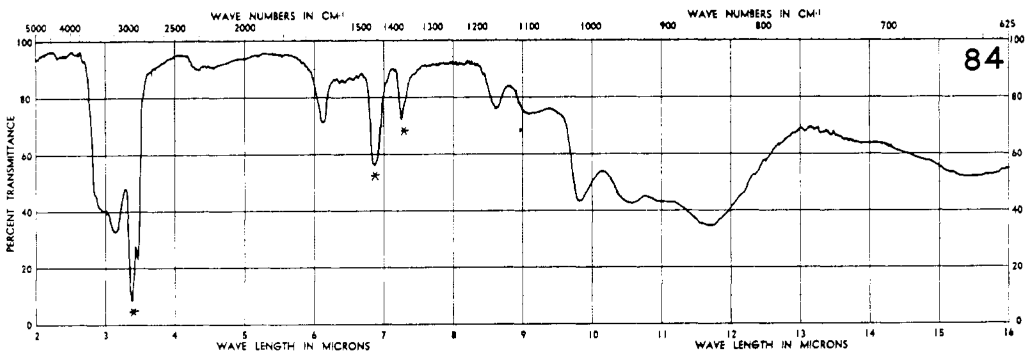
Calcium sulfite, $CaSO_3.2H_2O$

C.P.



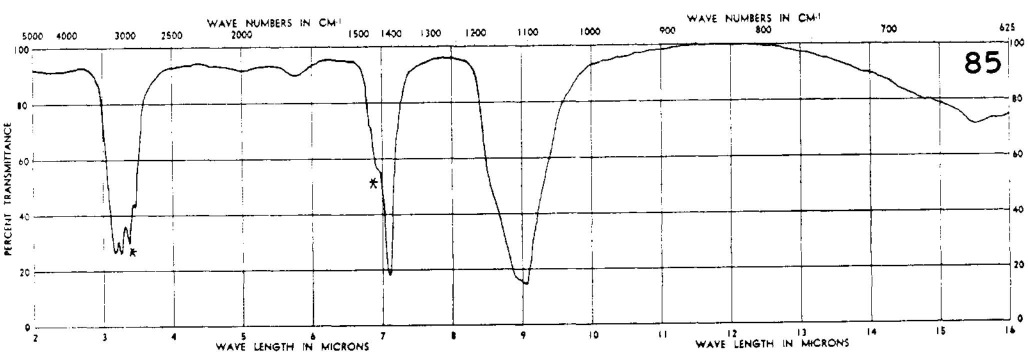
Barium sulfite, $BaSO_3$

C.P.



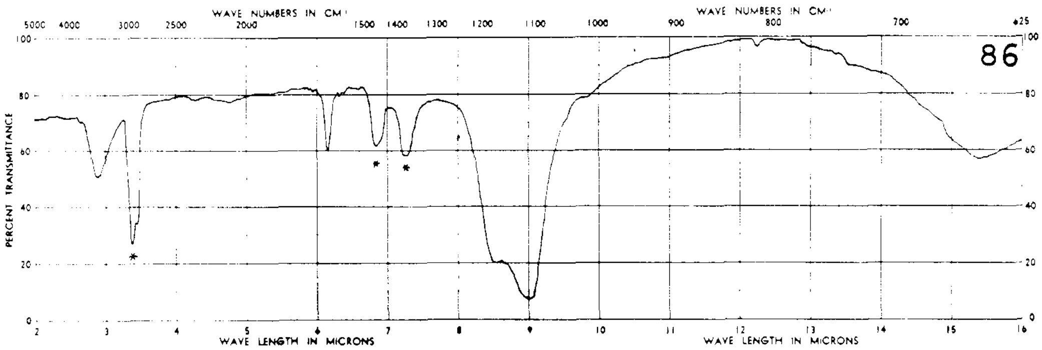
Zinc sulfite, $ZnSO_3.2H_2O$

C.P.



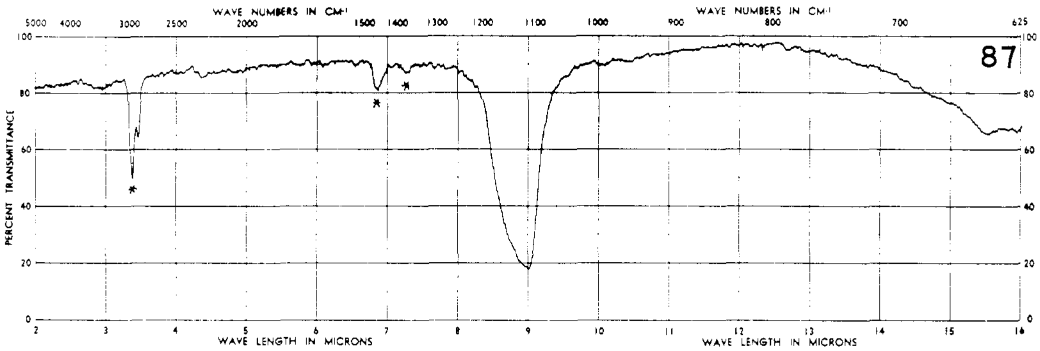
Ammonium sulfate, $(NH_4)_2SO_4$

Unk.



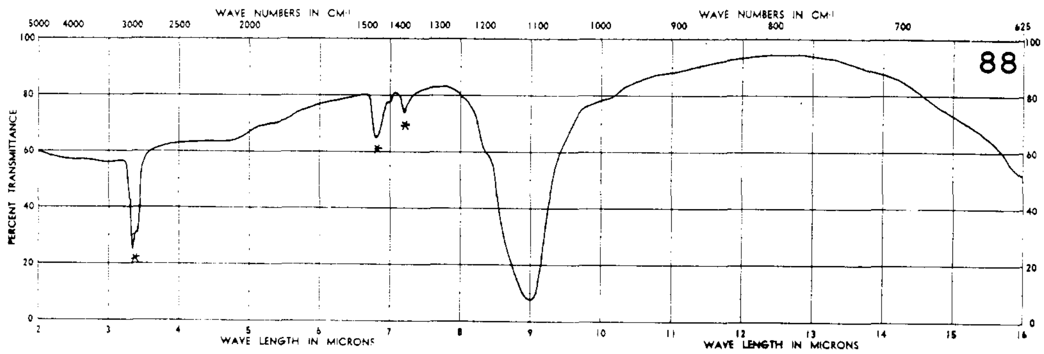
Lithium sulfate, $Li_2SO_4.H_2O$

Unk.



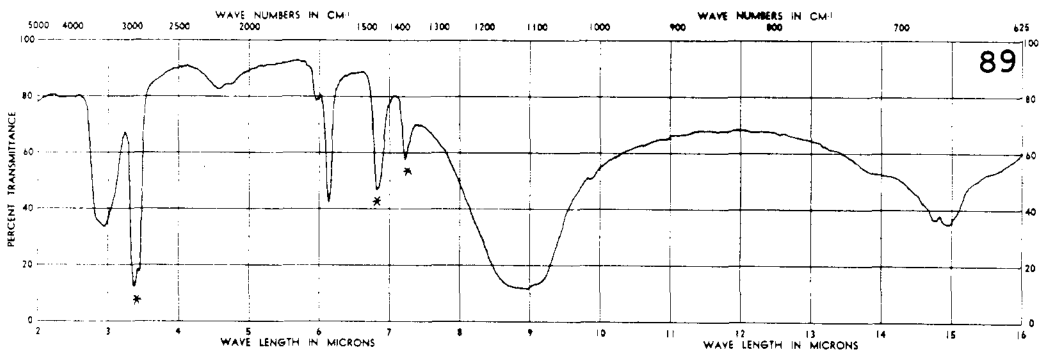
Sodium sulfate, Na_2SO_4

AR



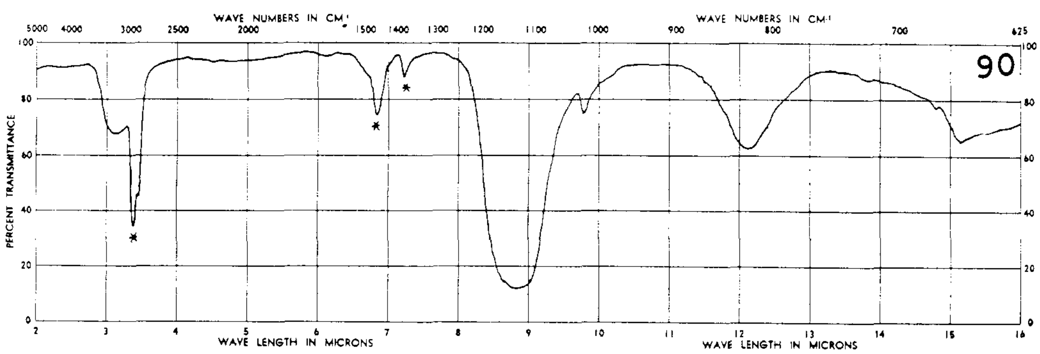
Potassium sulfate, K_2SO_4

AR



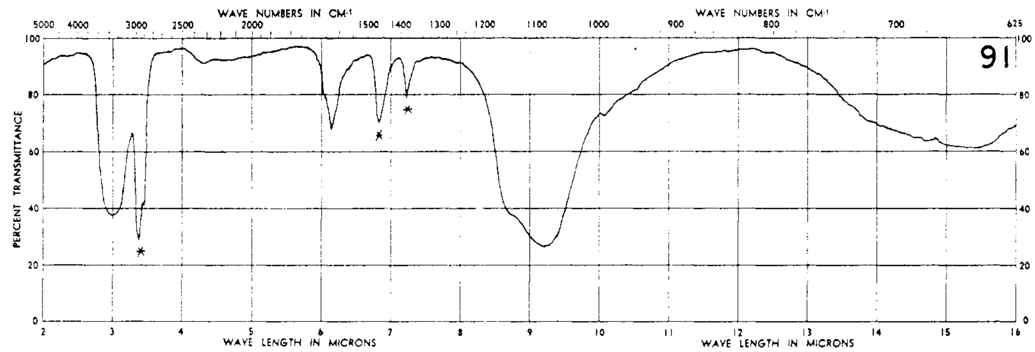
Calcium sulfate, $CaSO_4.2H_2O$

AR



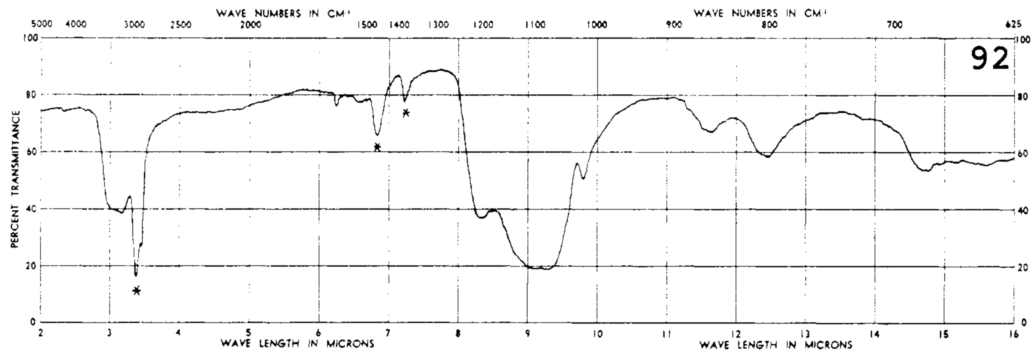
Manganese sulfate, $MnSO_4.2H_2O$

C.P.



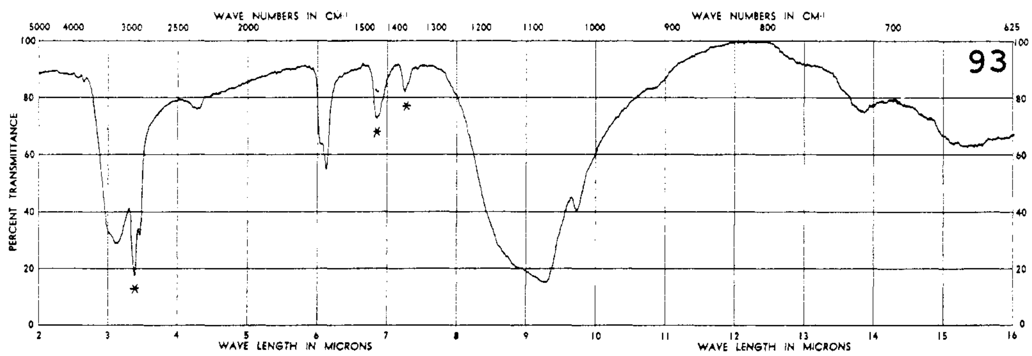
Ferrous sulfate, $FeSO_4.7H_2O$

Unk.



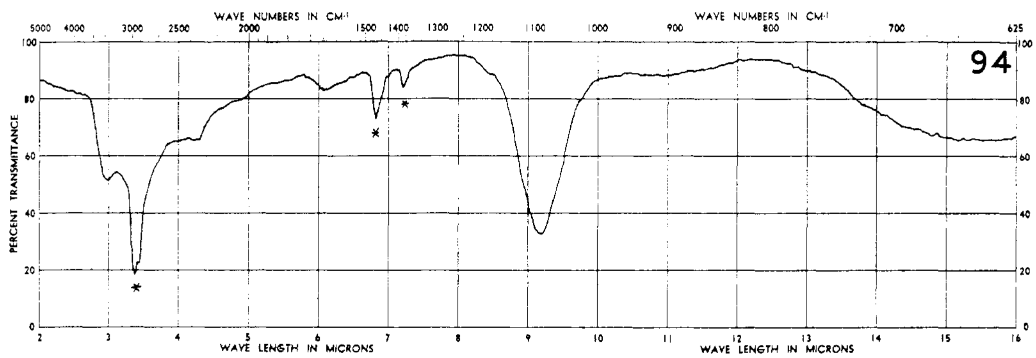
Copper sulfate, $CuSO_4$

AR



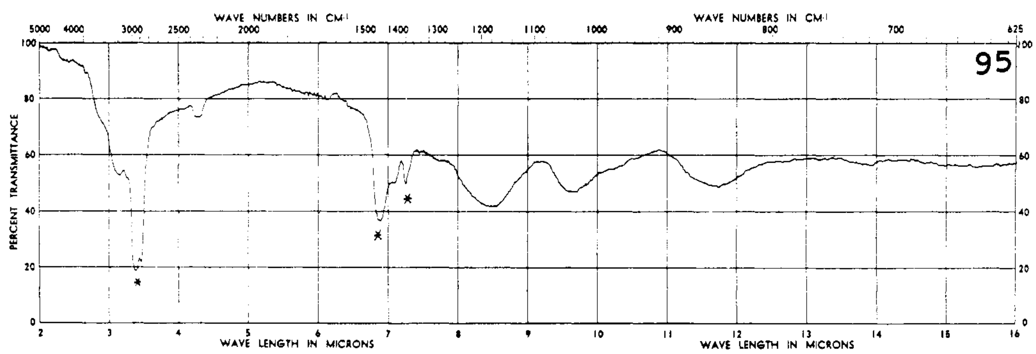
Zirconium sulfate, $ZrSO_4.4H_2O$

C.P.



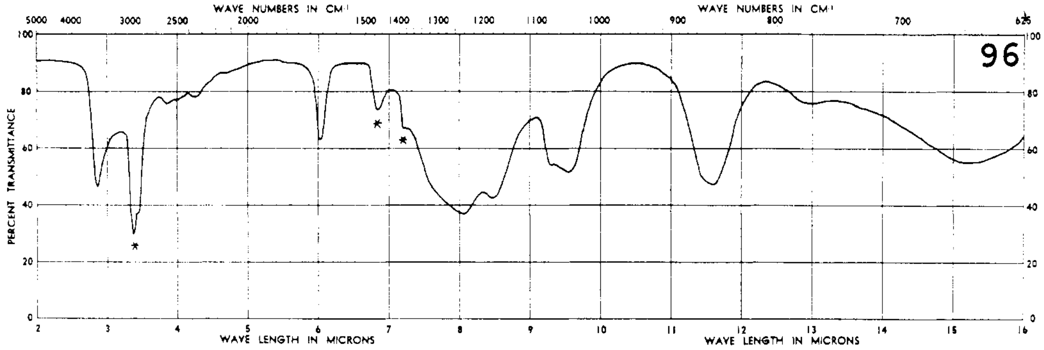
Chromium potassium sulfate, $Cr_2(SO_4)_3.K_2SO_4.24H_2O$

Unk.



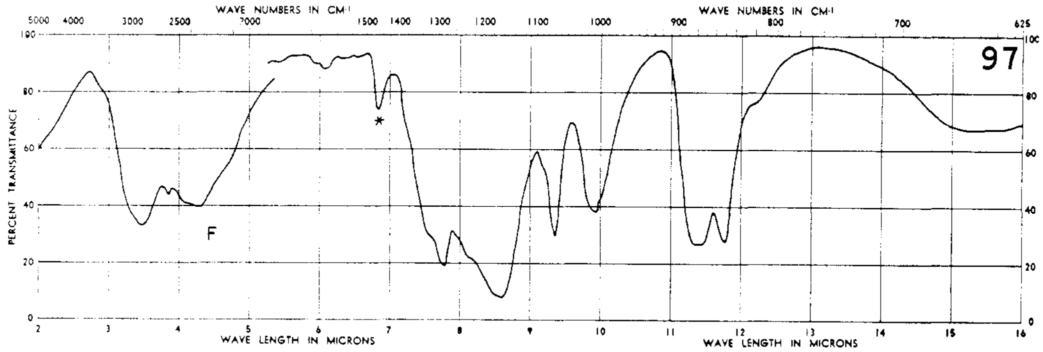
Ammonium bisulfate, NH_4HSO_4

C.P.



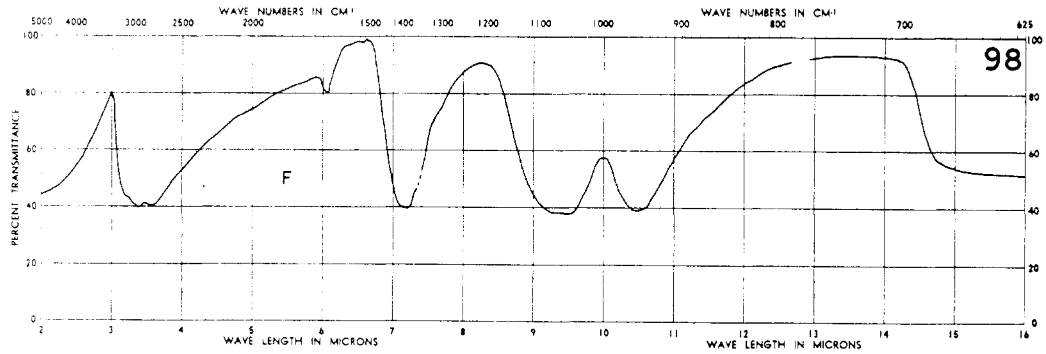
Sodium bisulfate, $NaHSO_4$

AR



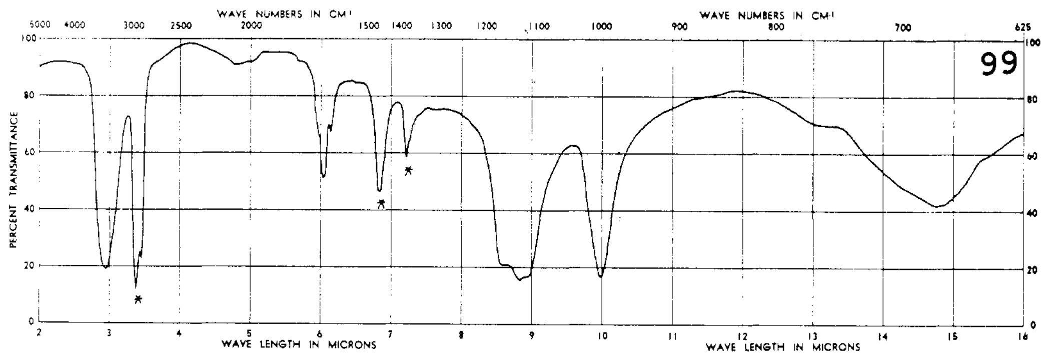
Potassium bisulfate, $KHSO_4$

AR



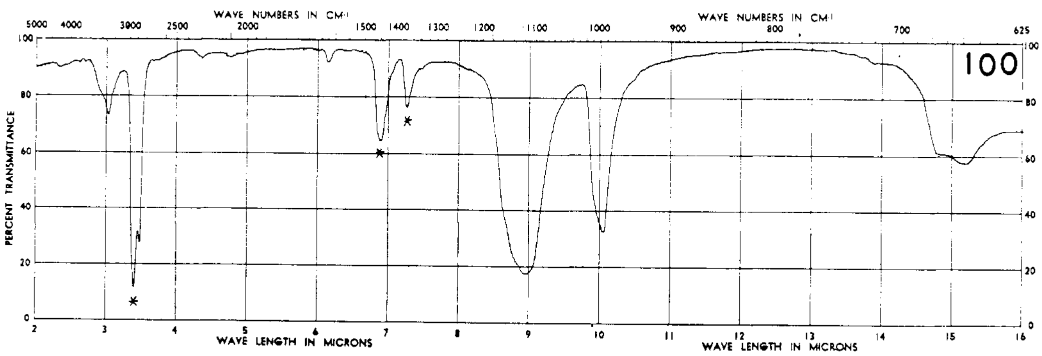
Ammonium thiosulfate, $(NH_4)_2S_2O_3$

C.P



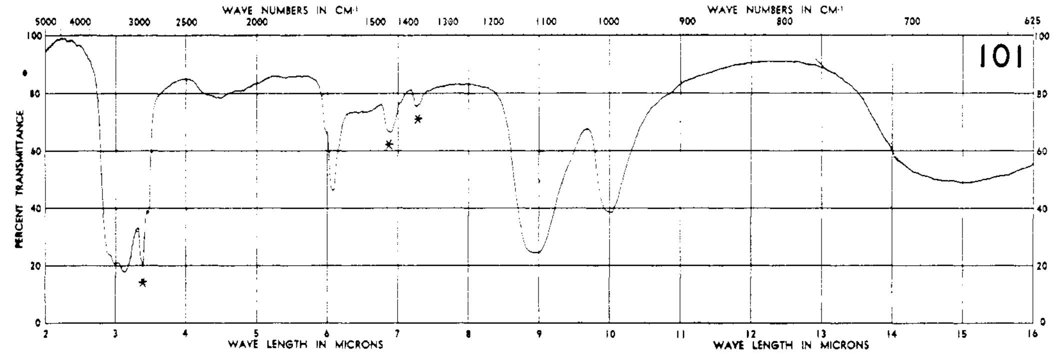
Sodium thiosulfate, $Na_2S_2O_3.5H_2O$

AR



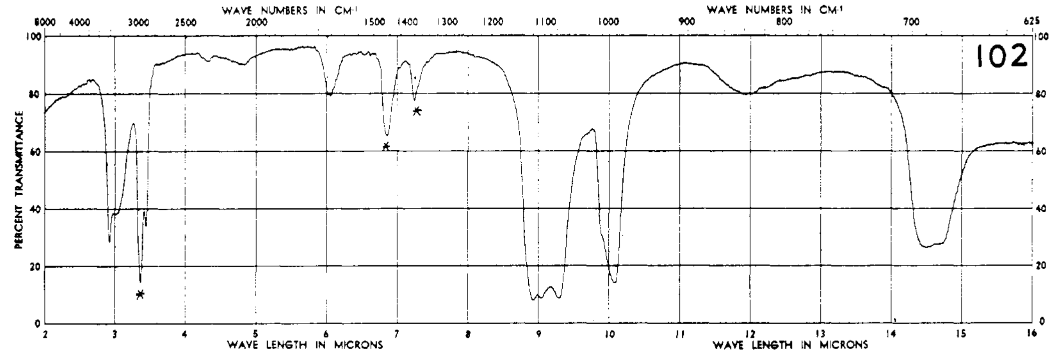
Potassium thiosulfate, $K_2S_2O_3.H_2O$

C.P.



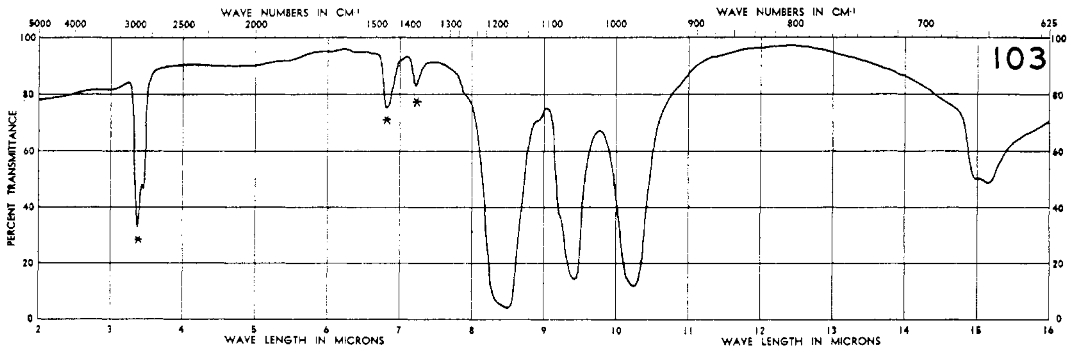
Magnesium thiosulfate, $MgS_2O_3.6H_2O$

C.P.



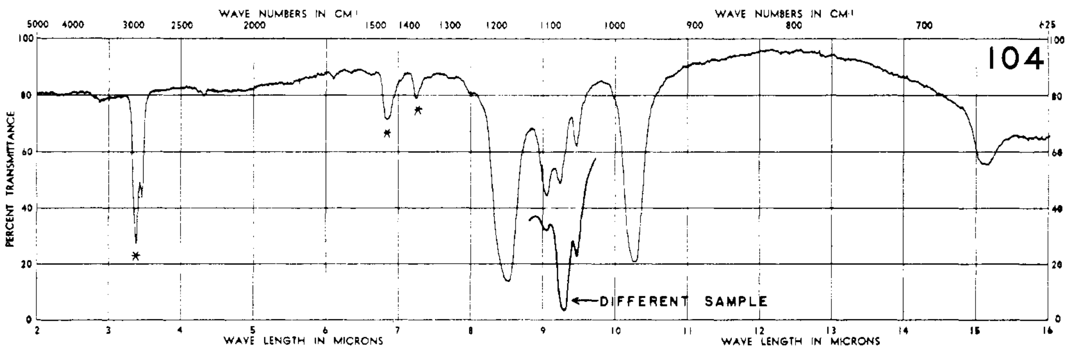
Barium thiosulfate, $BaS_2O_3.H_2O$

C.P.



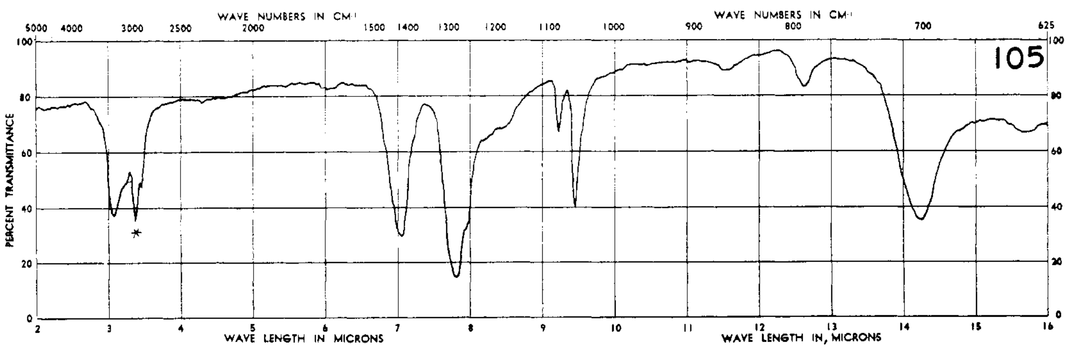
Sodium metabisulfite, $Na_2S_2O_5$

Unk.



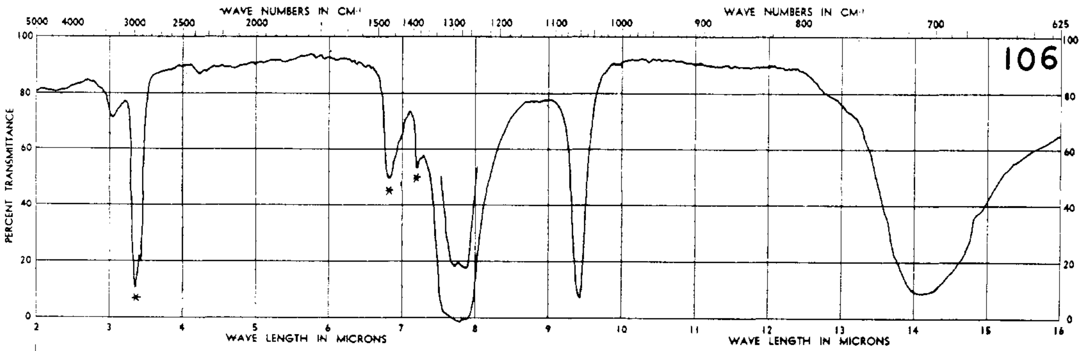
Potassium metabisulfite, $K_2S_2O_5$

AR



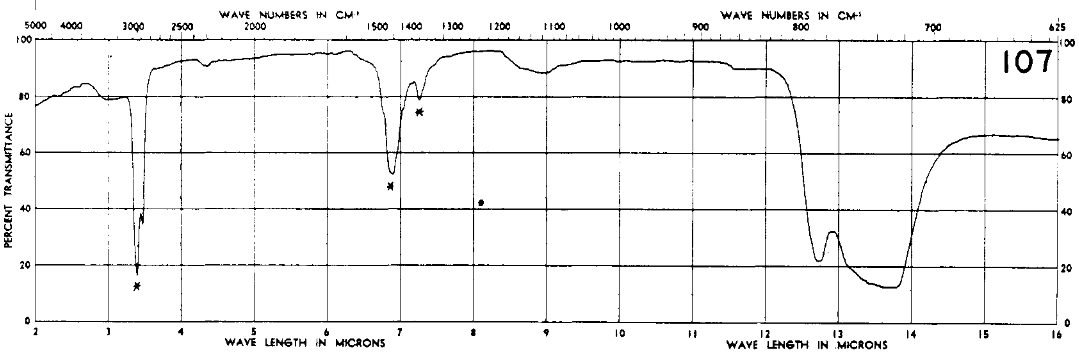
Ammonium persulfate, $(NH_4)_2S_2O_8$

AR



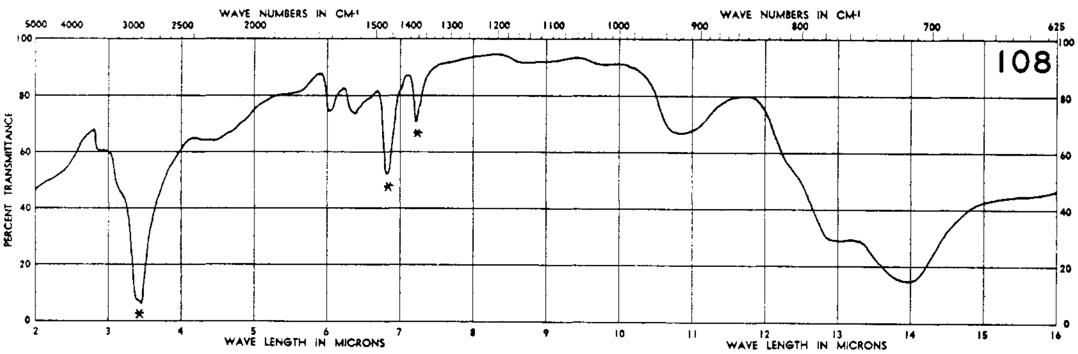
Potassium persulfate, $K_2S_2O_8$

C.P.



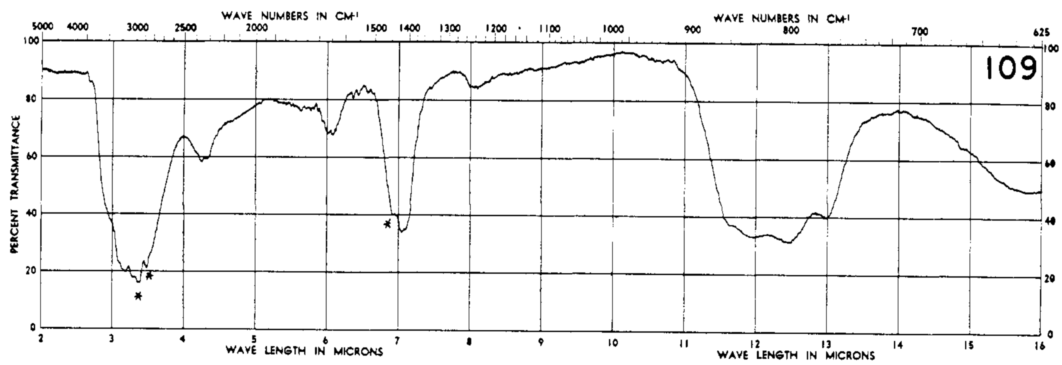
Sodium selenite, Na_2SeO_3

Pure



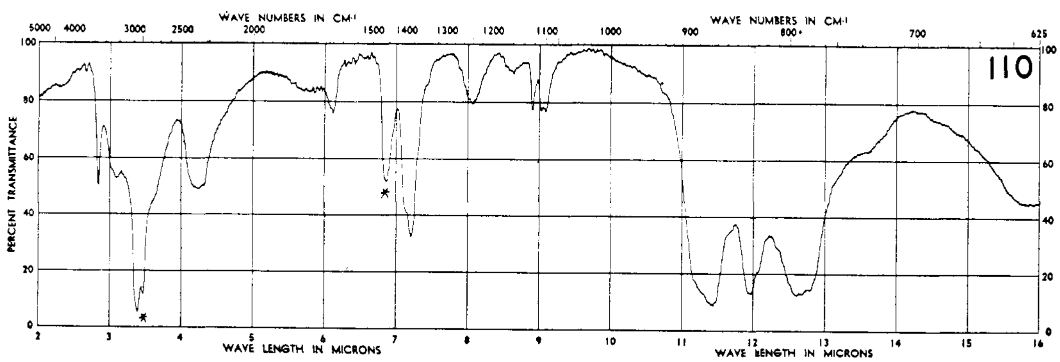
Copper selenite, $CuSeO_3.2H_2O$

Unk.



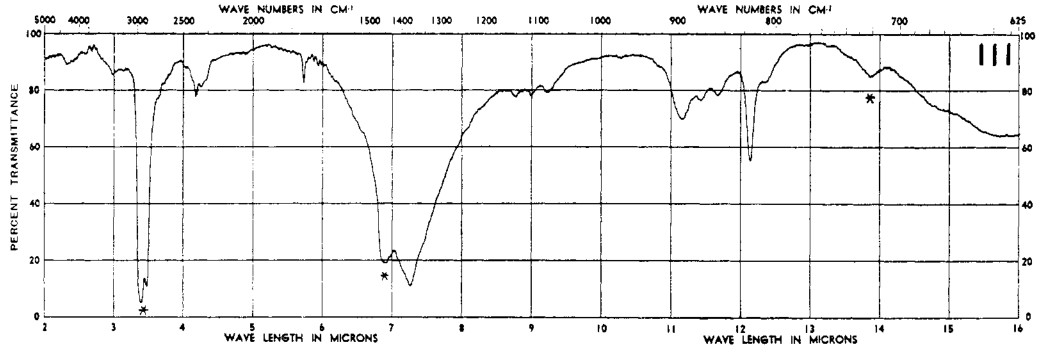
Ammonium selenate $(NH_4)_2SeO_4$

C.P.



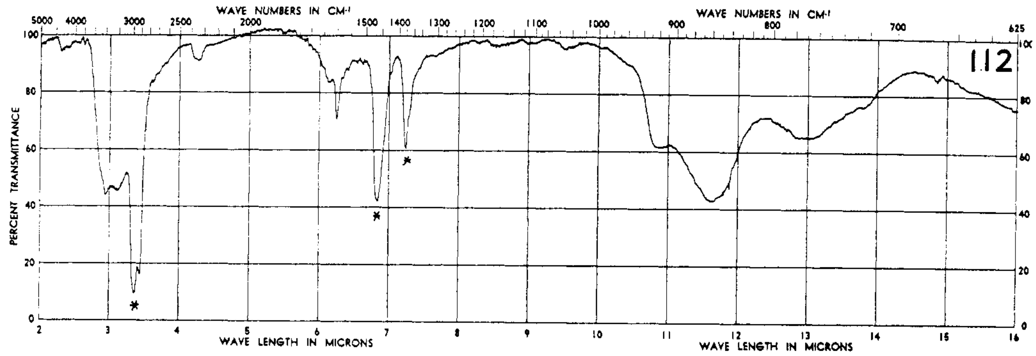
Sodium selenate, $Na_2SeO_4.10H_2O$

C.P.



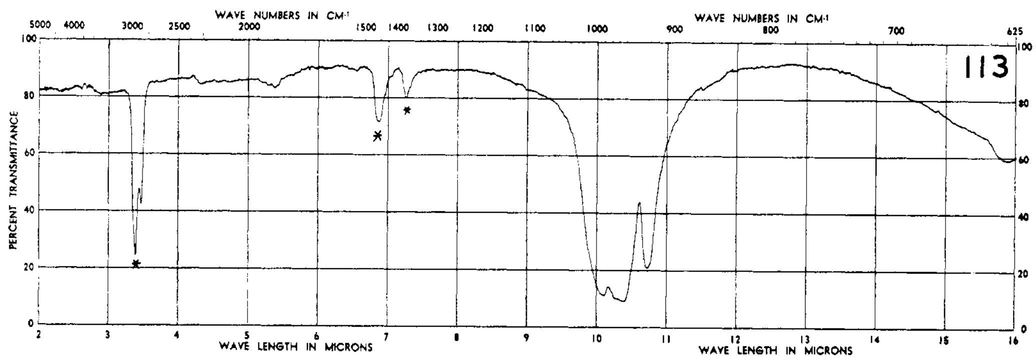
Potassium selenate, K_2SeO_4

C.P.



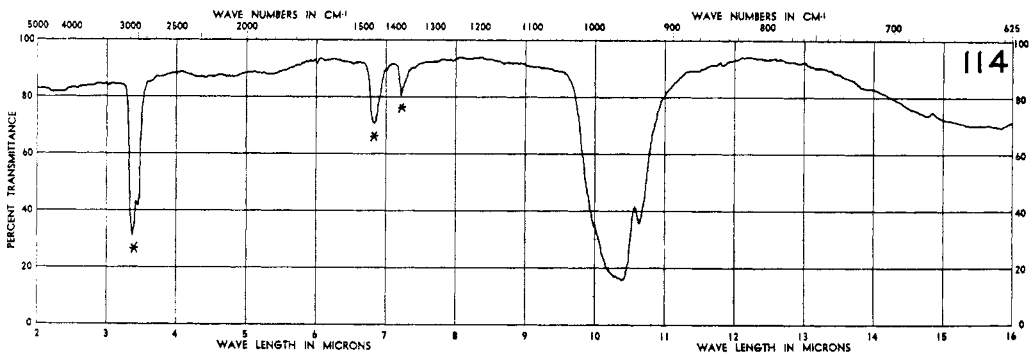
Copper selenate, $CuSeO_4.5H_2O$

C.P.



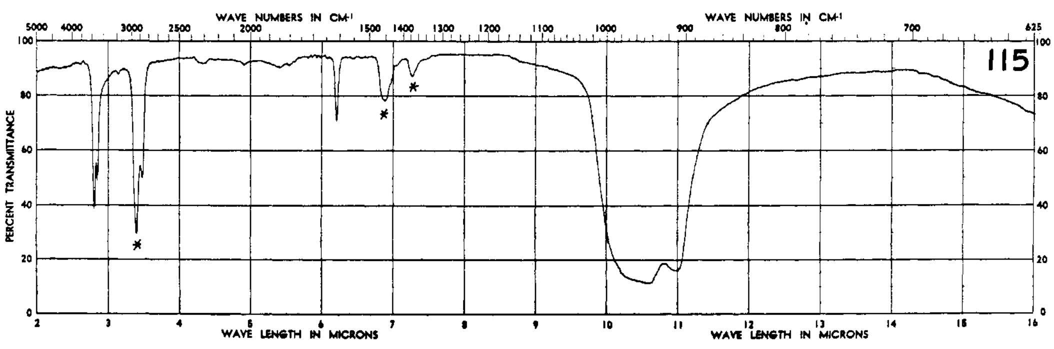
Sodium chlorate, $NaClO_3$

AR



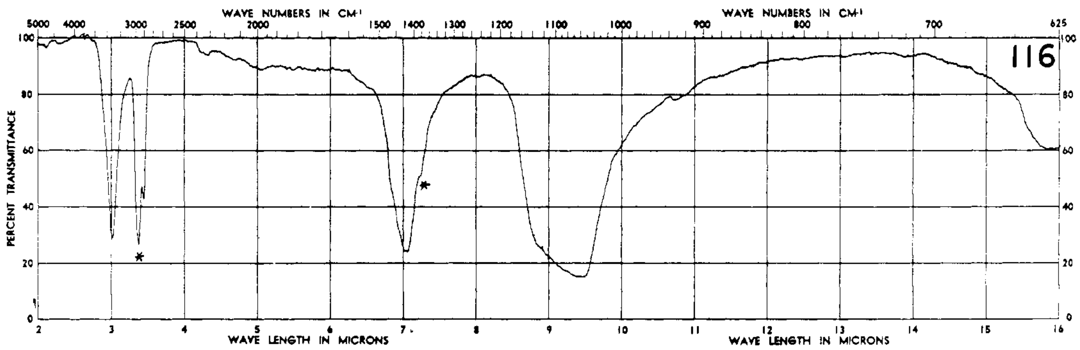
Potassium chlorate, $KClO_3$

AR



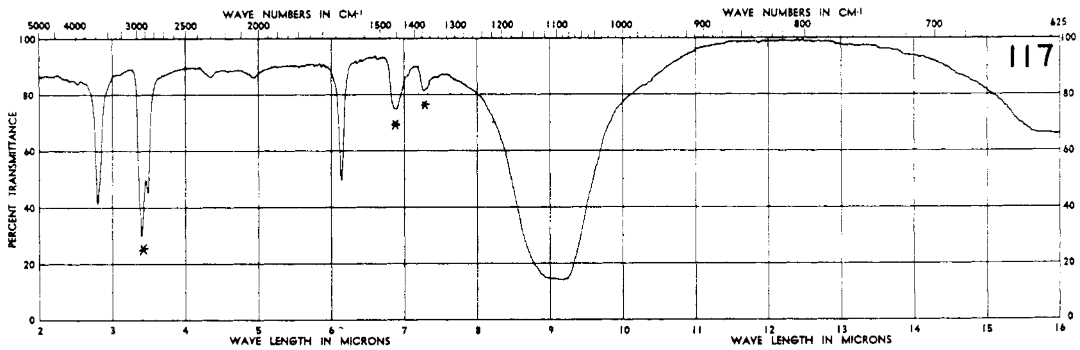
Barium chlorate, $Ba(ClO_3)_2.H_2O$

C.P.



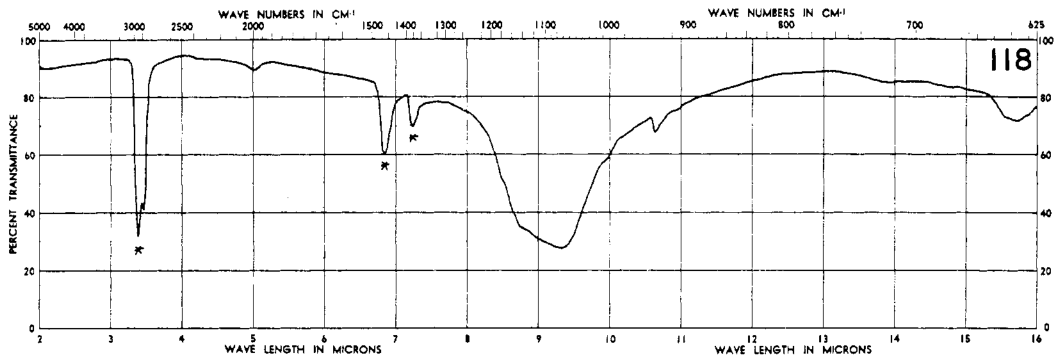
Ammonium perchlorate, NH_4ClO_4

C.P.



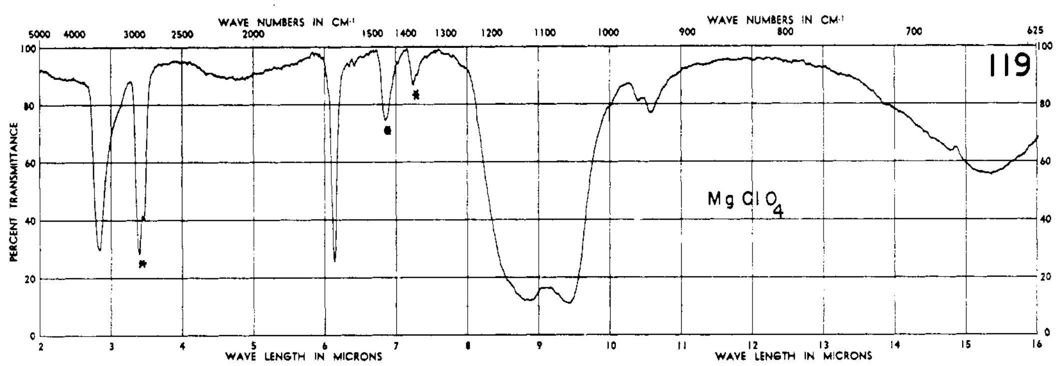
Sodium perchlorate, $NaClO_4.H_2O$

C.P



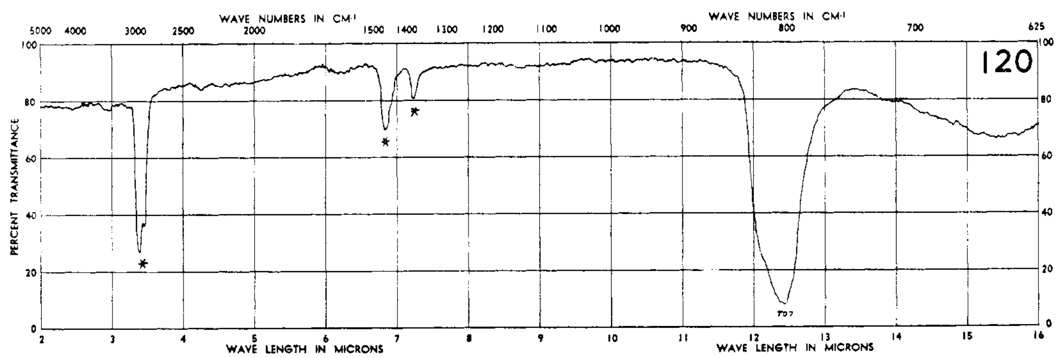
Potassium perchlorate, $KClO_4$

AR



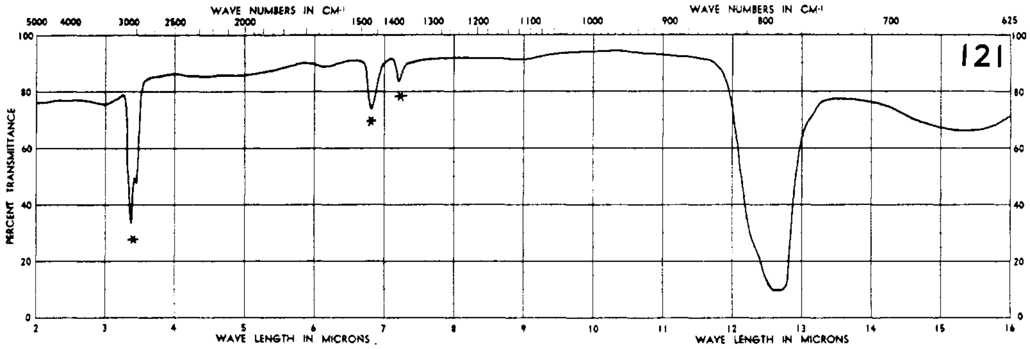
Magnesium perchlorate, $Mg(ClO_4)_2$

Unk.



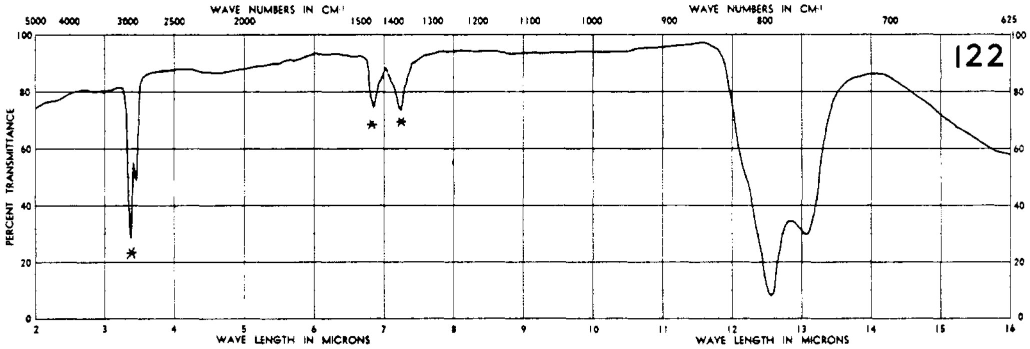
Sodium bromate, $NaBrO_3$

C.P



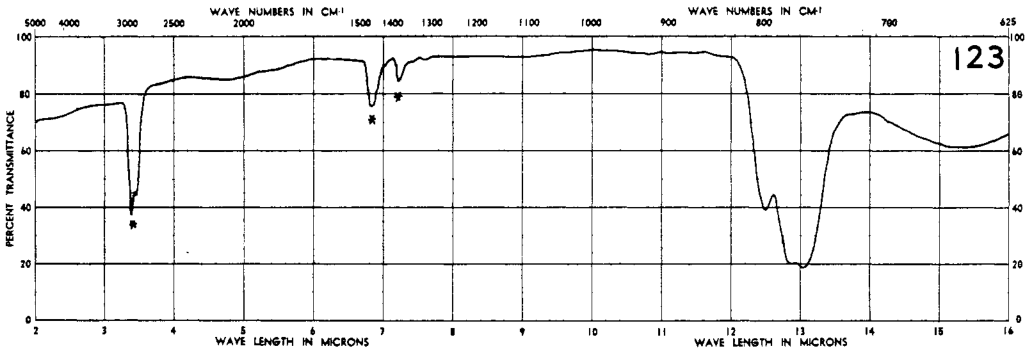
Potassium bromate, $KBrO_3$

AR



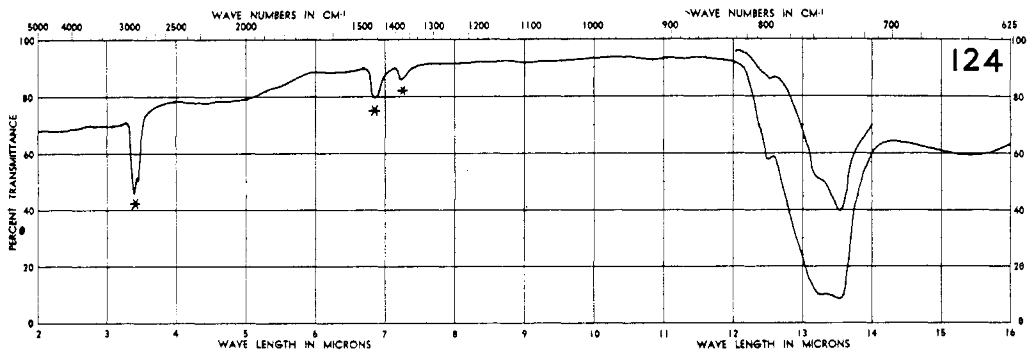
Silver bromate, $AgBrO_3$

C.P.



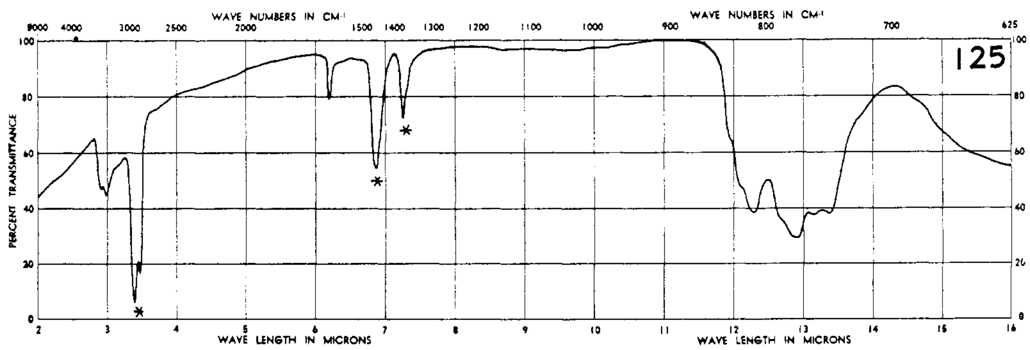
Sodium iodate, $NaIO_3$

C.P.



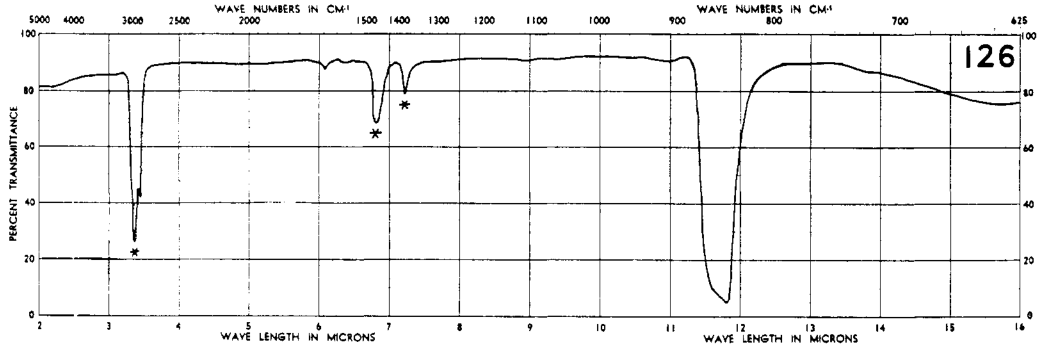
Potassium iodate, KIO_3

Unk.



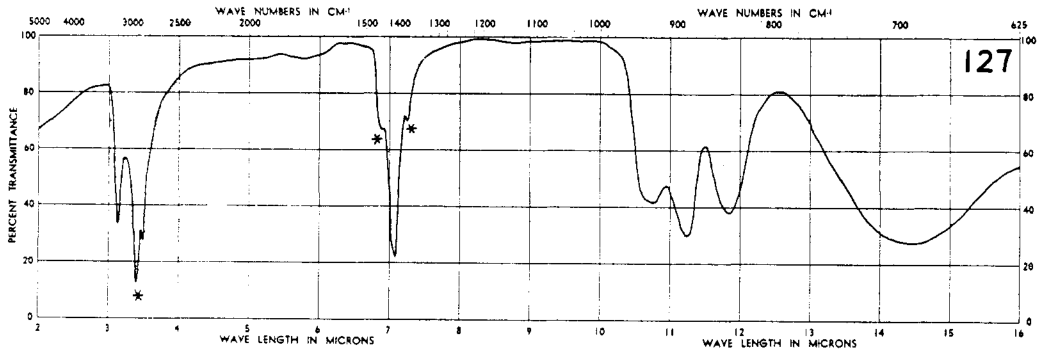
Calcium iodate, $CaIO_3.6H_2O$

C.P.



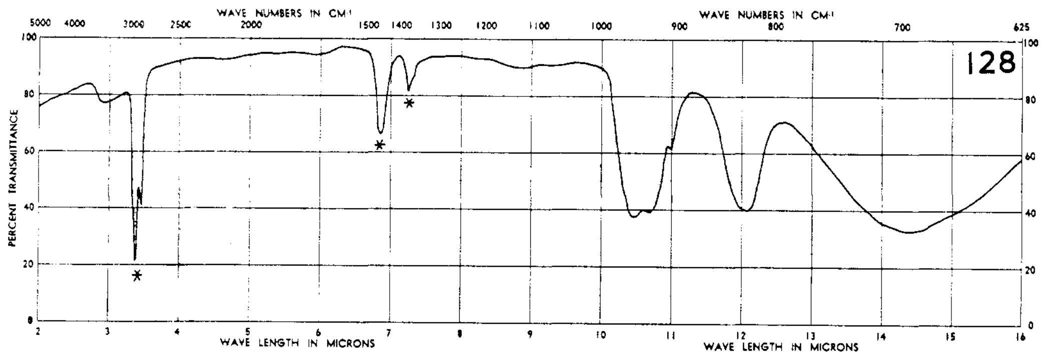
Potassium periodate, KIO_4

C.P.

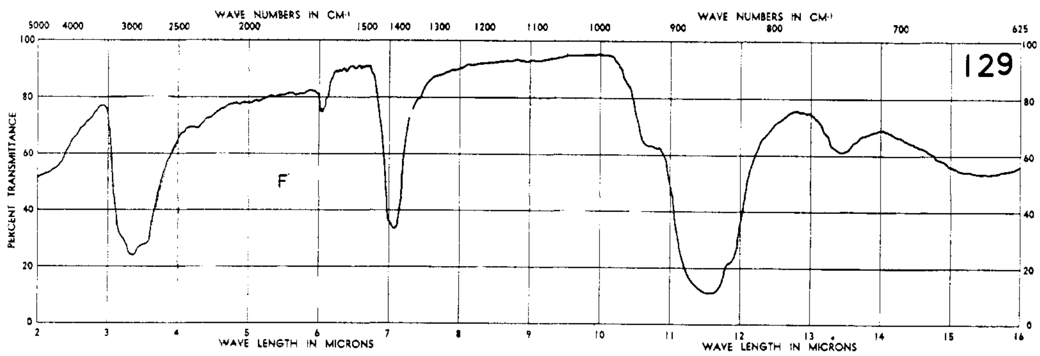


Ammonium metavanadate, NH_4VO_3

C.P.

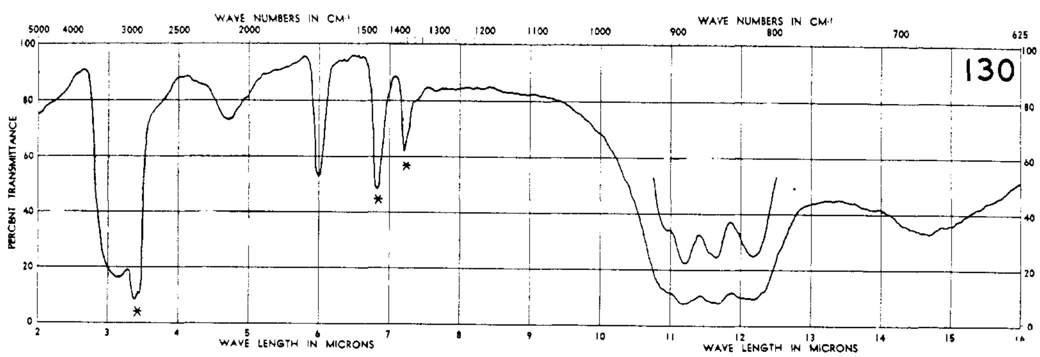


Sodium metavanadate, $NaVO_3.4H_2O$



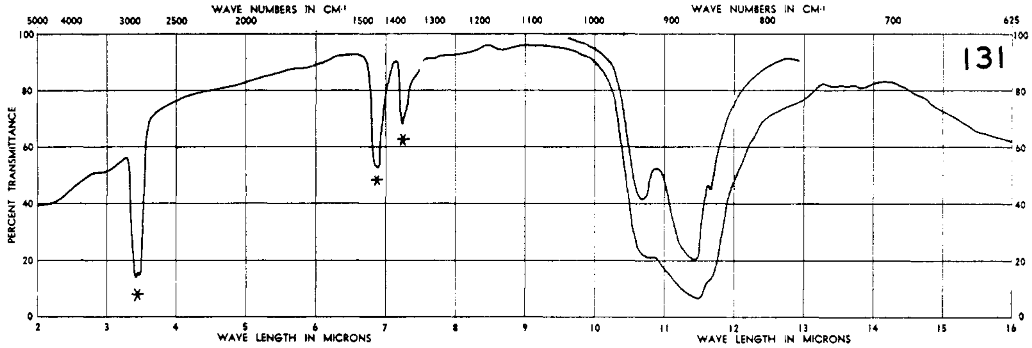
Ammonium chromate, $(NH_4)_2CrO_4$

Unk.



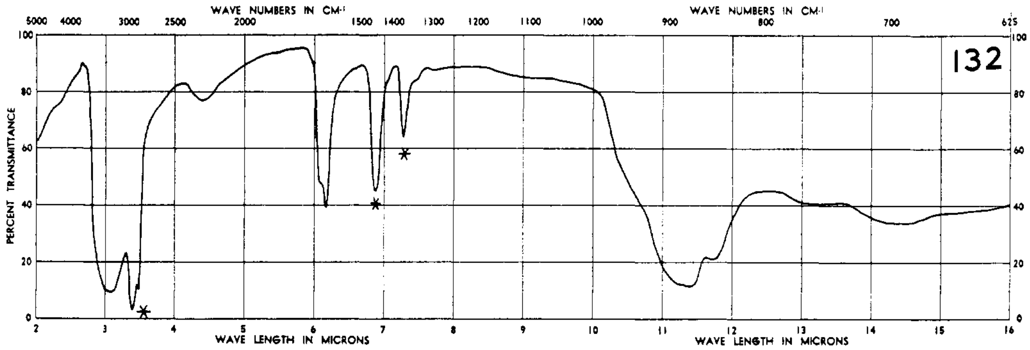
Sodium chromate, Na_2CrO_4

Unk.



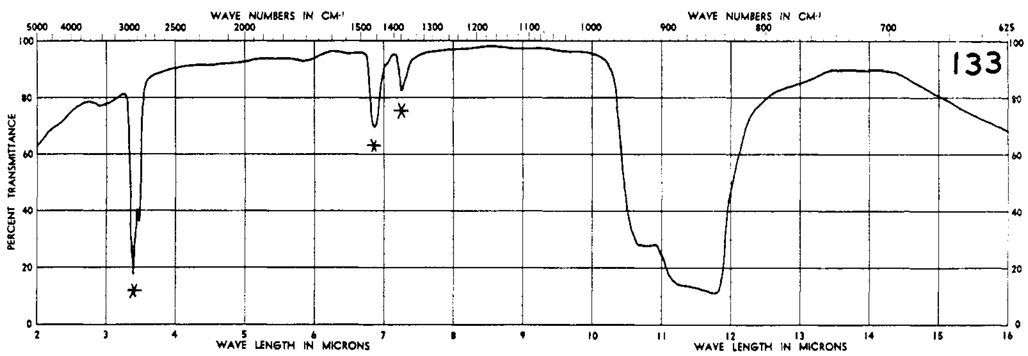
Potassium chromate, K_2CrO_4

AR



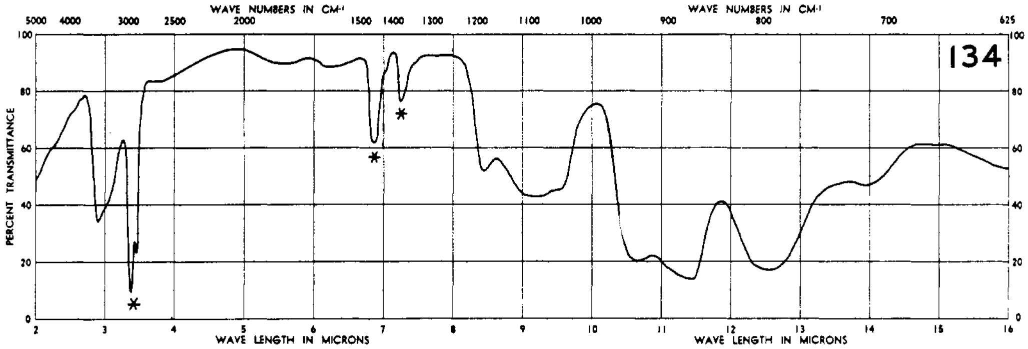
Magnesium chromate, $MgCrO_4.7H_2O$

C.P.



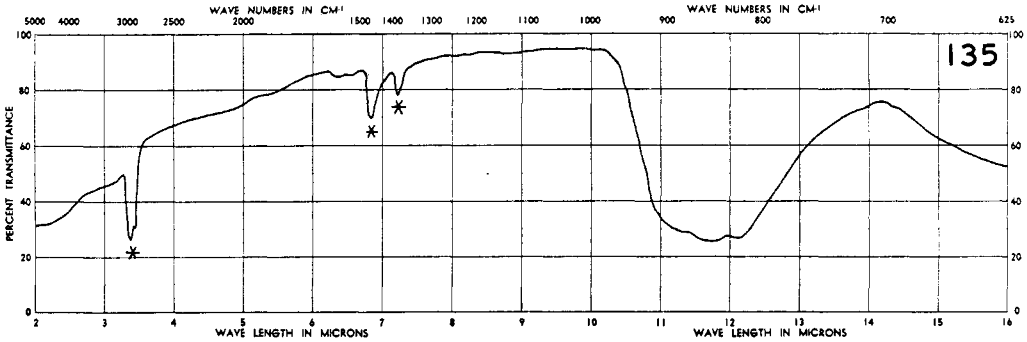
Barium chromate, $BaCrO_4$

C.P.



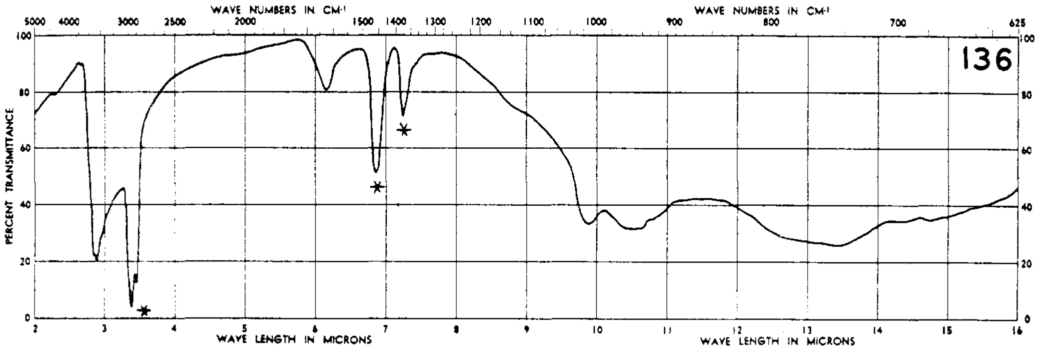
Zinc chromate, $ZnCrO_4.7H_2O$

C.P.



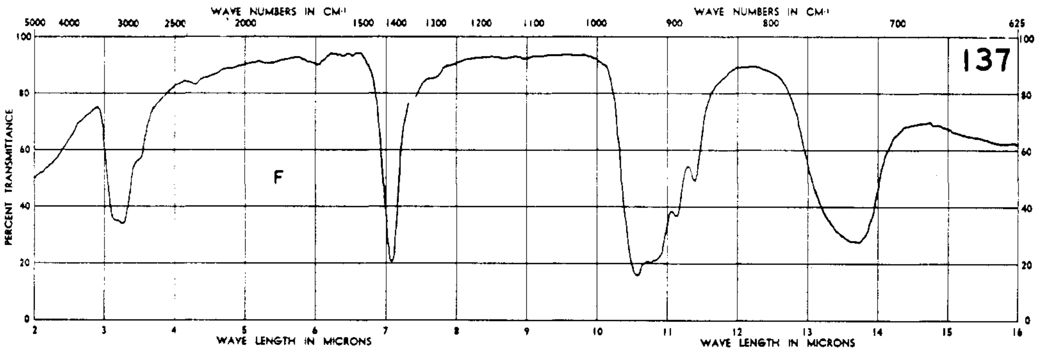
Lead chromate, $PbCrO_4$

C.P



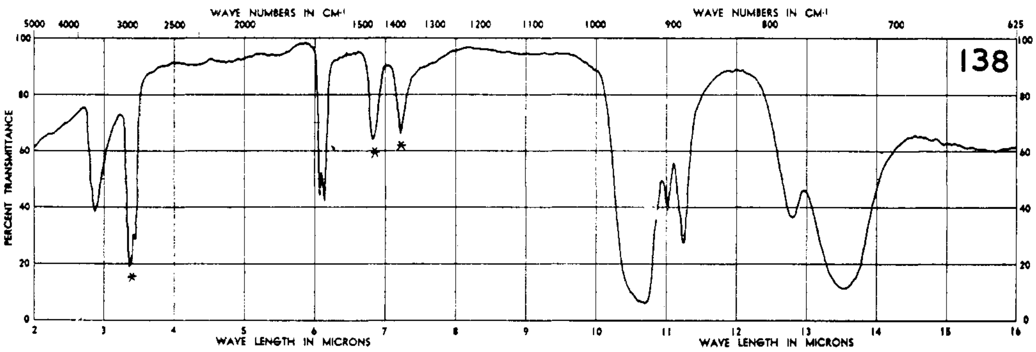
Aluminum chromate, $Al_2(CrO_4)_3$

C.P.



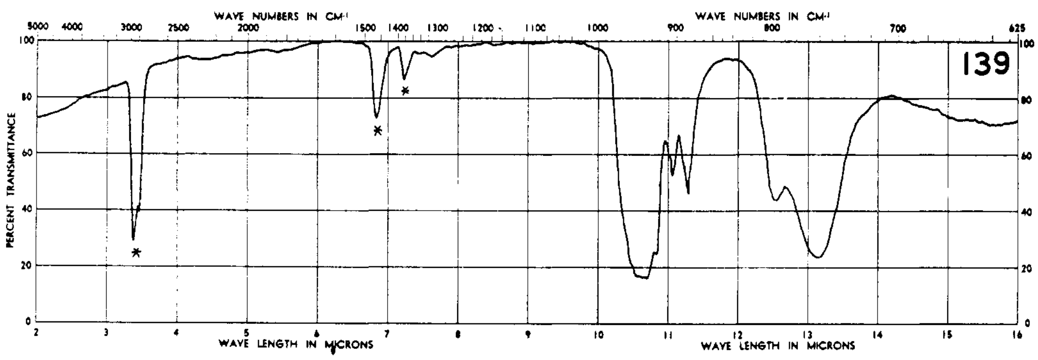
Ammonium dichromate, $(NH_4)_2Cr_2O_7$

C.P.



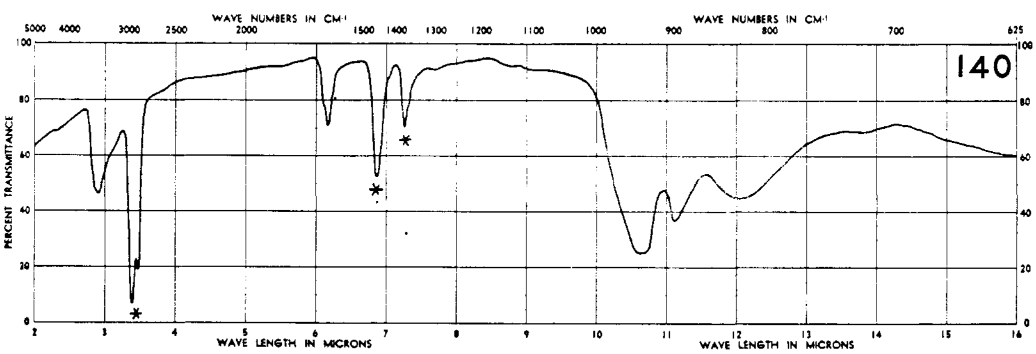
Sodium dichromate, $Na_2Cr_2O_7.2H_2O$

C.P.



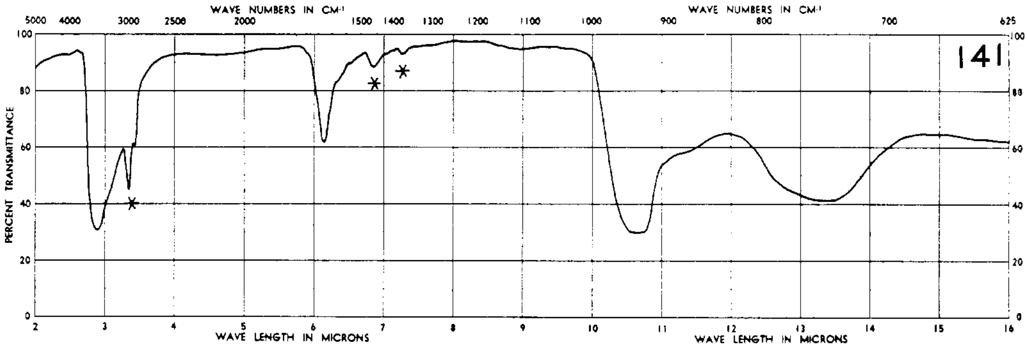
Potassium dichromate, $K_2Cr_2O_7$

Unk.



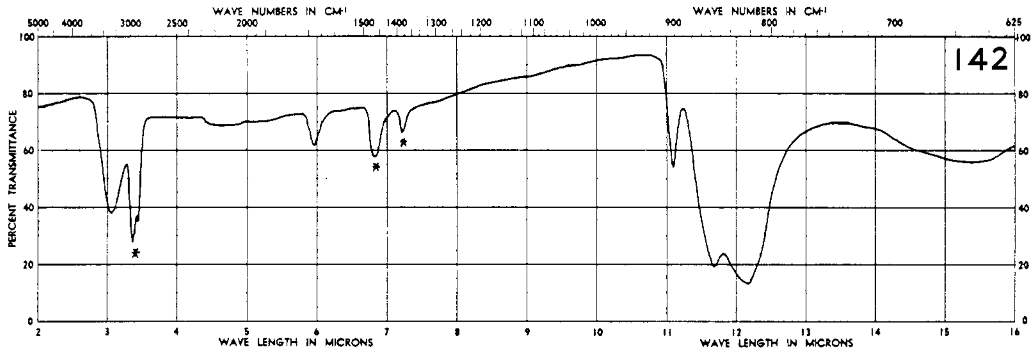
Calcium dichromate, $CaCr_2O_7.3H_2O$

C.P.



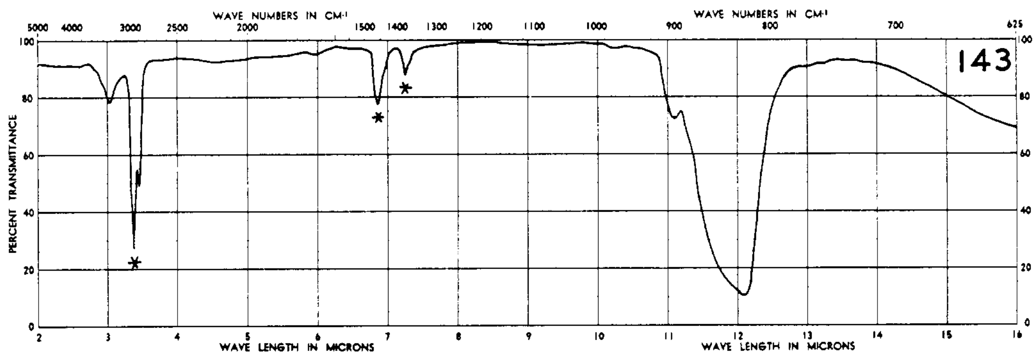
Copper dichromate, $CuCr_2O_7.2H_2O$

C.P.



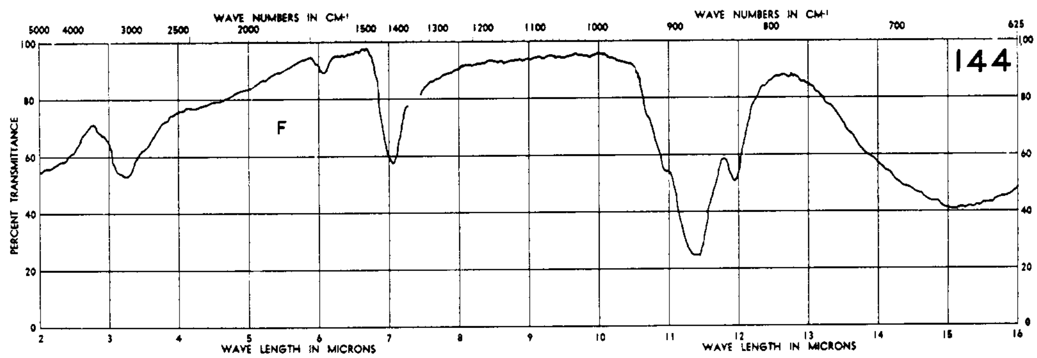
Sodium molybdate, $Na_2MoO_4.2H_2O$

AR



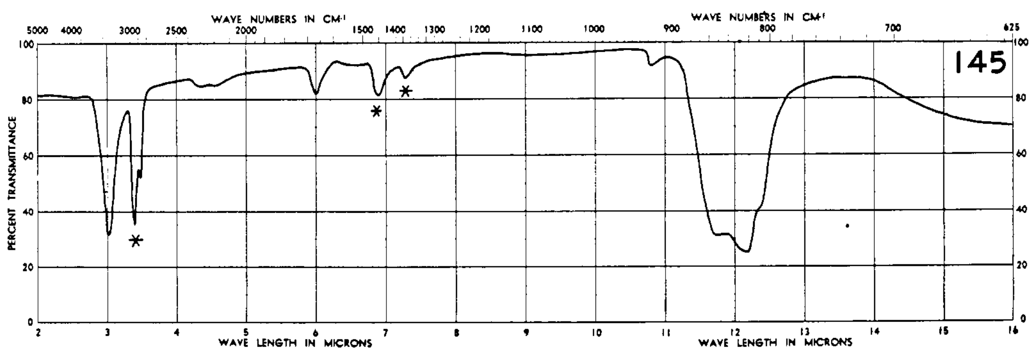
Potassium molybdate, $K_2MoO_4.5H_2O$

C.P.



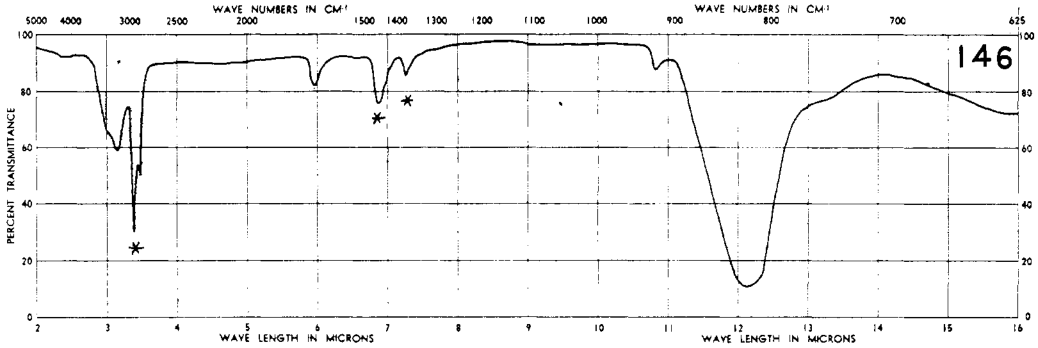
Ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}.4H_2O$

AR



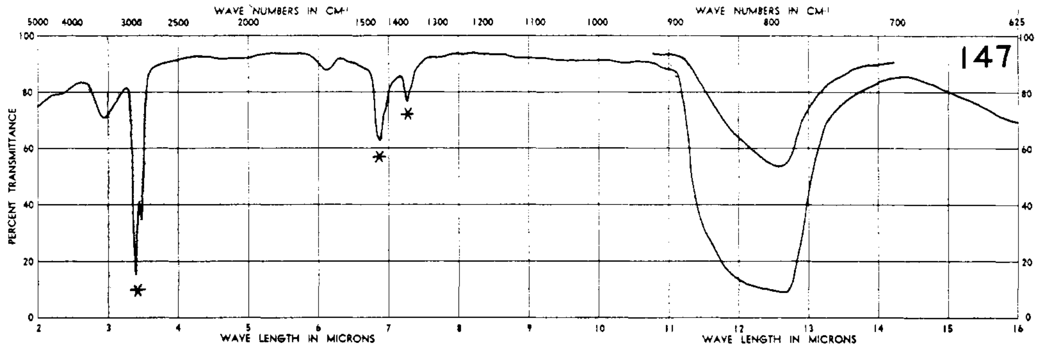
Sodium tungstate, $Na_2WO_4.2H_2O$

C.P.



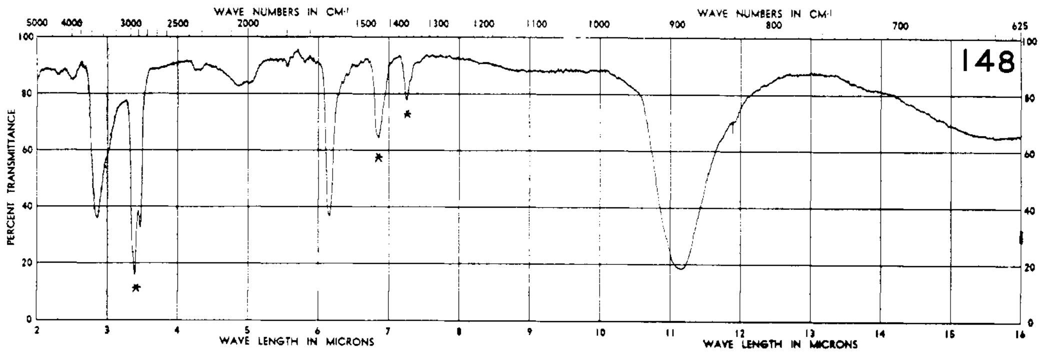
Potassium tungstate, K_2WO_4

C.P.



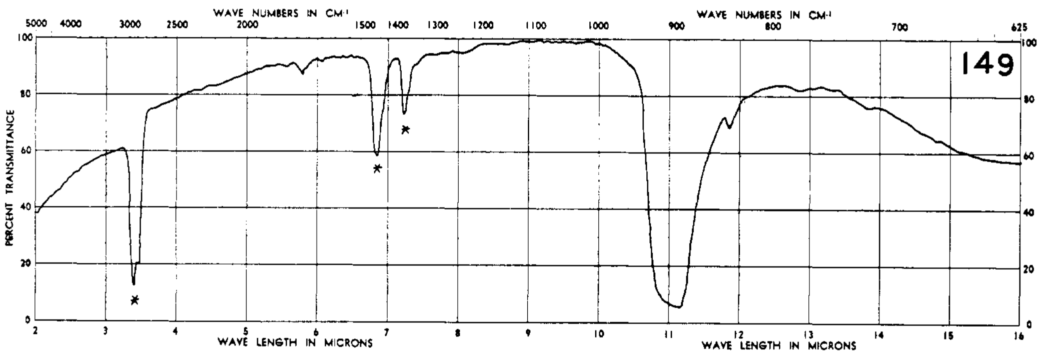
Calcium tungstate $CaWO_4$

Pure



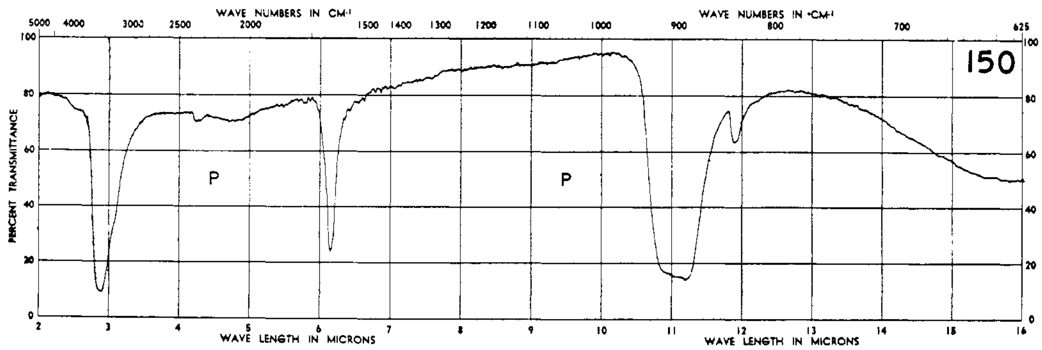
Sodium permanganate, $NaMnO_4.3H_2O$

C.P.



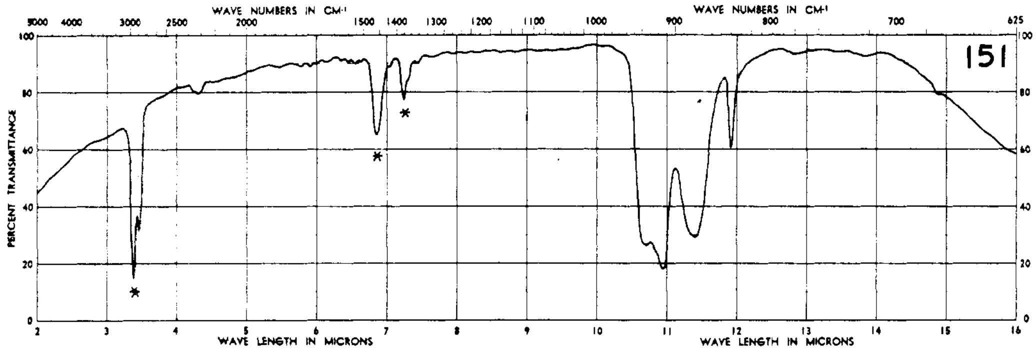
Potassium permanganate, $KMnO_4$

AR



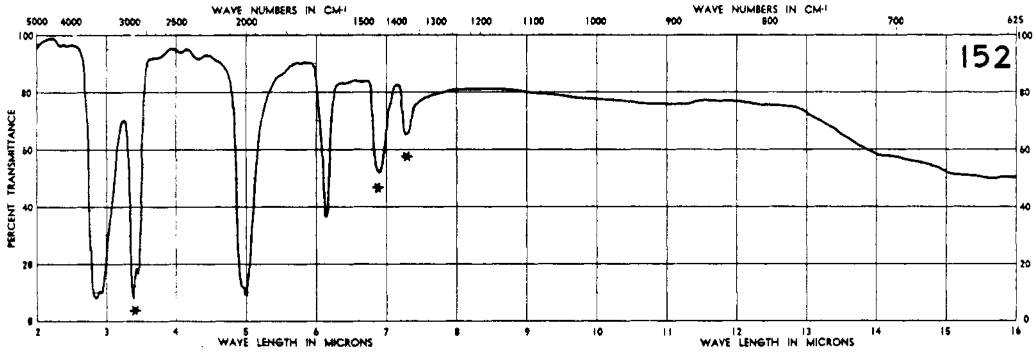
Calcium permanganate, $Ca(MnO_4)_2.4H_2O$

C.P



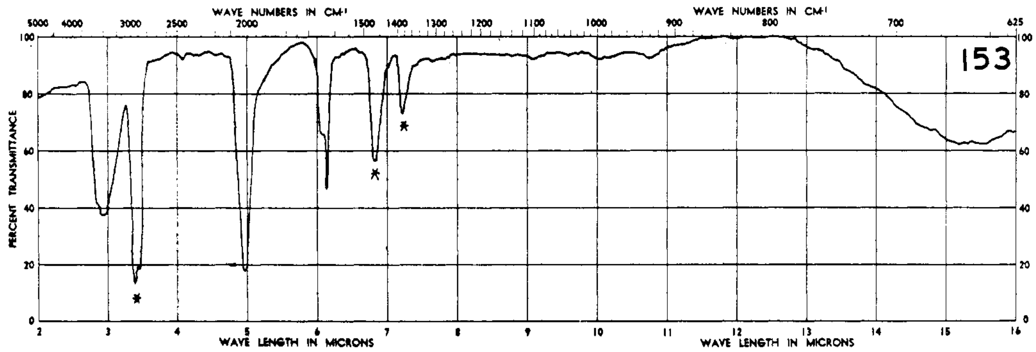
Barium permanganate, $Ba(MnO_4)_2$

C.P.



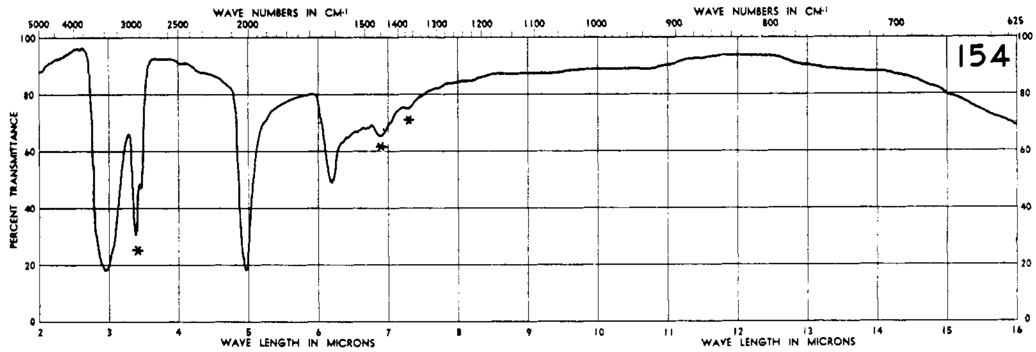
Sodium ferrocyanide, $Na_4Fe(CN)_6.10H_2O$

C.P.



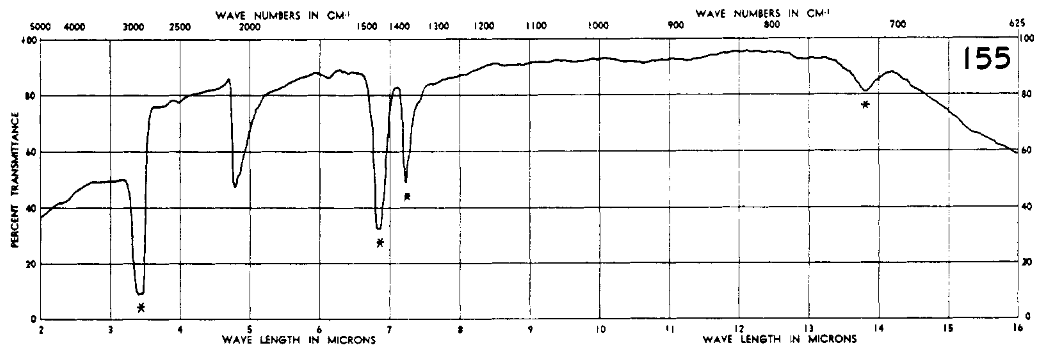
Potassium ferrocyanide, $K_4Fe(CN)_6.3H_2O$

AR



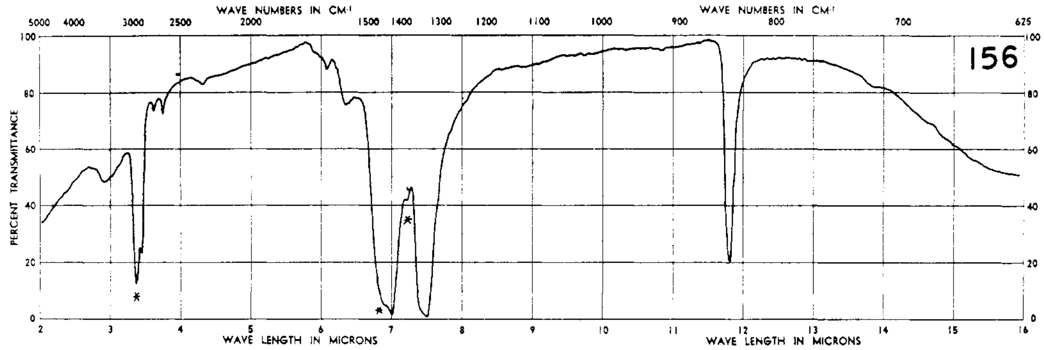
Calcium ferrocyanide, $Ca_2Fe(CN)_6.12H_2O$

Pure



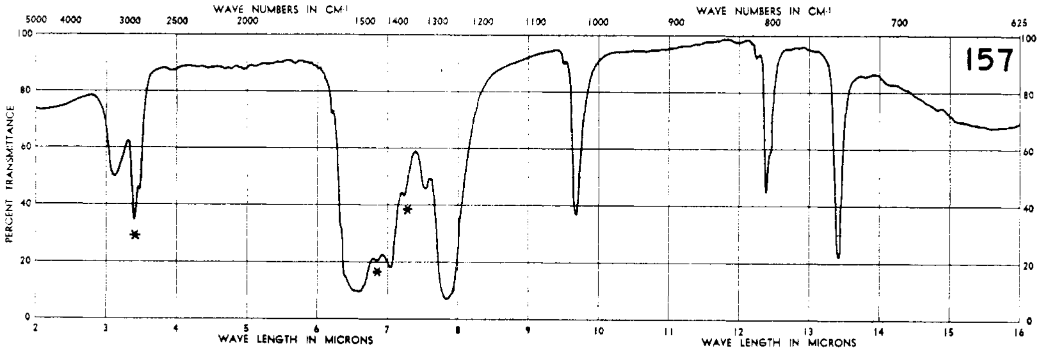
Potassium ferricyanide, $K_3Fe(CN)_6$

AR



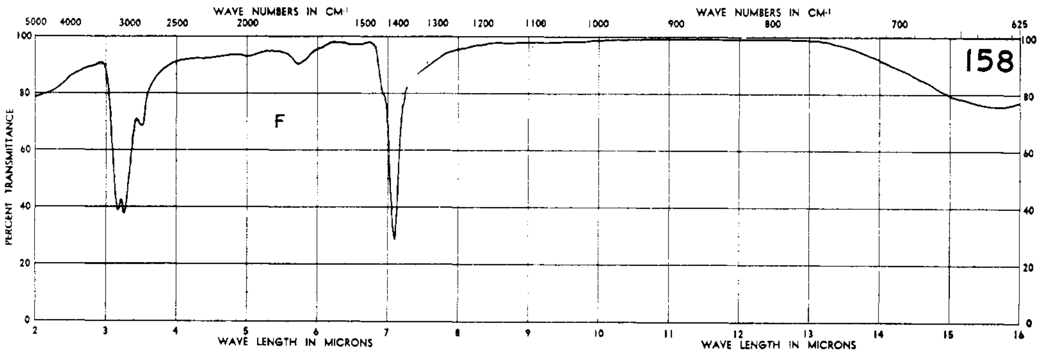
Sodium cobaltinitrite, $Na_3Co(NO_2)_6$

AR



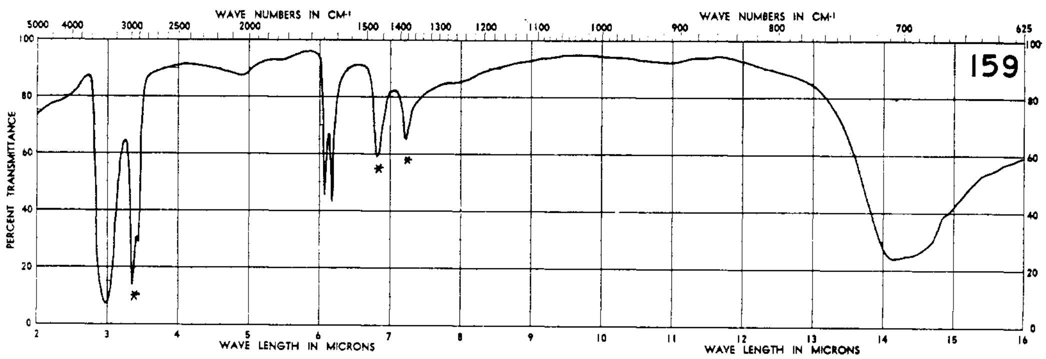
Ammonium hexanitratocerate, $(NH_4)_2Ce(NO_3)_6$

AR



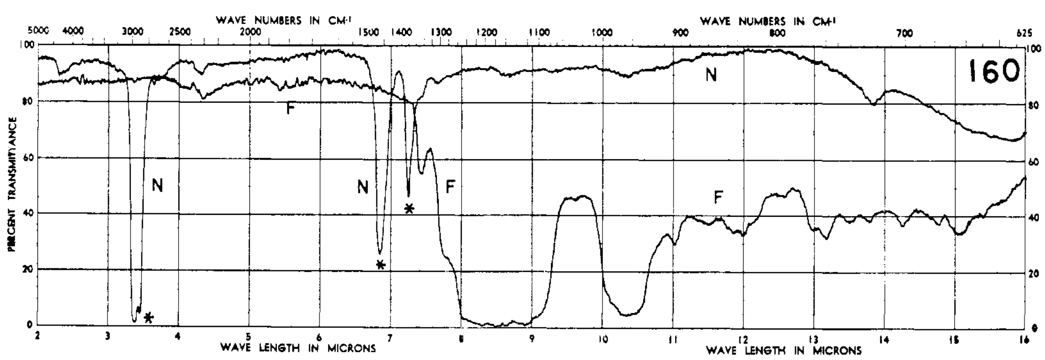
Ammonium chloride, NH_4Cl

AR



Barium chloride, $BaCl_2.2H_2O$

AR



Nujol (N); Fluorolube (F)

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 (5) 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

Table IV. Use of Infrared Spectra in Qualitative Analysis

No.	Independent Analyses: Emission	Independent Analyses: Infrared	Independent Analyses: X-ray	Final Combined Analysis	Actual Composition
1	Na K Ca	$NaHCO_3$	$NaHCO_3$ $CaCO_3$? KNO ?	$NaHCO_3$ $CaCO_3$ KNO_3	$NaHCO_3$ $CaCO_3$ KNO_3
2	Si B Pb Al	NH_4^+ NO_3^- SO_4^{--} Silica gel	NH_4NO_3 Very poor pattern	NH_4NO_3 SO_4^{--} Silica gel B Pb Al	NH_4NO_3 $CaSO_4$ 85% SiO_2–15% Al_2O_3 $Pb(BO_2)_2$
3 Yellow	Na K Cr Sulfide odor Pb ?	$K_2Cr_2O_7$ NaSCN or NH_4SCN $Mg(ClO_4)_2$	Nothing Very poor pattern	$K_2Cr_2O_7$ NaSCN $Mg(ClO_4)_2$? Pb ?	$K_2Cr_2O_7$ NaSCN KSCN $CaSO_4 \cdot 2H_2O$
4 Yellow	Cd Bi B Na ? C ??	$Na_2B_4O_7$	$Na_2B_4O_7 . 10H_2O$ CdS	$Na_2B_4O_7 . 10H_2O$ CdS $NaBiO_3$?	$Na_2B_4O_7 \cdot 10H_2O$ CdS $NaBiO_3$
5	As Pb Na B ?	Na_2SO_3 $NaAsO_2$	Na_2SO_3 $PbCO_3$? $BaCO_3$? $MgSO_4$?	Na_2SO_3 $NaAsO_2$ $PbCO_3$	Na_2SO_3 $NaAsO_2$ $Pb(BO_2)_2 . H_2O$
6	Mo Ca K Na ? Sr ??	$K_2S_2O_5$ $CaCO_3$ $PbCrO_4$ Na_2SO_3 ?	$K_2S_2O_5$ $CaCO_3$ Na_3PO_4 ? Na_2SO_3 ?	$K_2S_2O_5$ $CaCO_3$ Na_2SO_3 Mo in some form	$K_2S_2O_5$ $CaCO_3$ $Na_2MoO_4 . 2H_2O$
7	Sb Si P Ca C ??	$Ca_3(PO_4)_2$	$Ca_{10}O(PO_4)_6$ $CaSiO_3$??	$Ca_3(PO_4)_2$ $CaSiO_3$ Sb	$Ca_3(PO_4)_2$ Sb_2O_5
8	Ba Na V Al ? Sr ??	$NaVO_3$ A nitrate; probably $Ba(NO_3)_2$, possibly $NaNO_3$ Other component(s) Possibilities: Another nitrate, $NaBrO_3$, Na_2WO_4 or K_2WO_4, $NaMoO_4$ or $KMoO_4$	$Ba(NO_3)_2$ $PbSO_4$?	$NaVO_3$ $Ba(NO_3)_2$ Another component	$NaVO_3 \cdot 4H_2O$ $Ba(NO_3)_2$ $Na_2WO_4 \cdot 4H_2O$

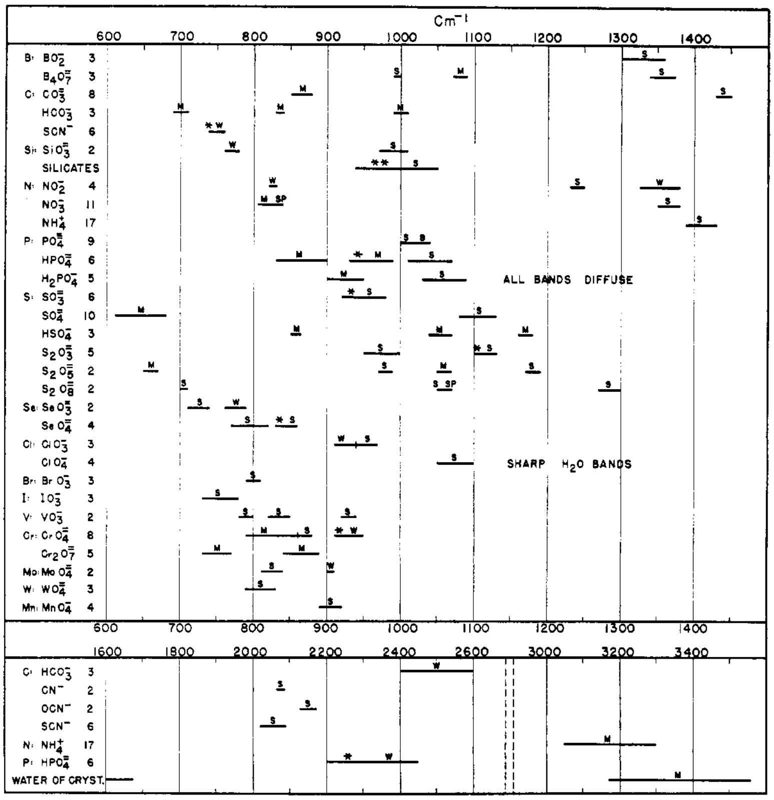


Figure 2. Characteristic Frequencies of Polyatomic Inorganic Ions

s, m, w. Strong, medium, weak
sp. Sharp
* In most, but not all, examples
** Literature value

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.

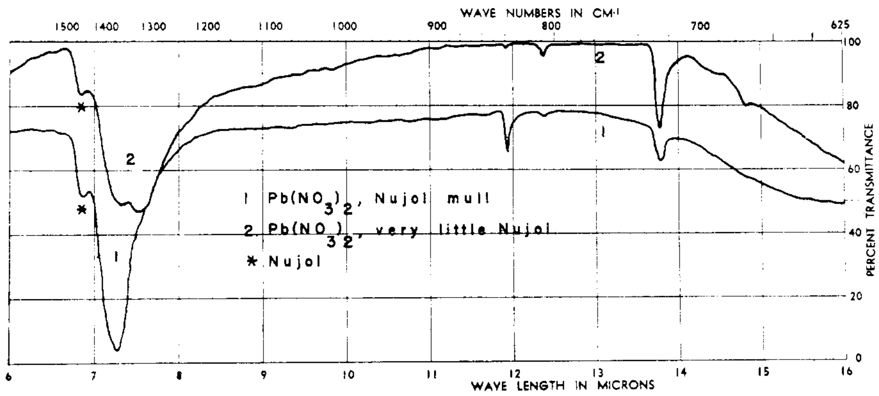


Figure 3. Portion of Infrared Spectrum of Lead Nitrate

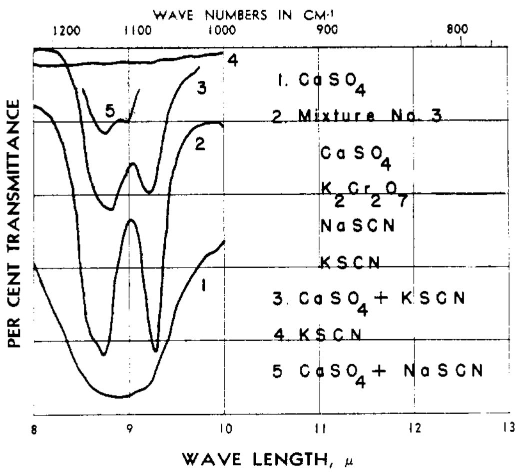


Figure 4. Anomalous Band in Unknown 3

In every case $CaSO_4$ should be written $CaSO_4.2H_2O$

Individual Techniques. X-ray analysis of a completely unknown sample becomes difficult when there are more than two components. It is not applicable to noncrystalline materials (cf. unknown 2) and runs into trouble with substances that gain or lose water of hydration readily. In both cases infrared is often a reliable tool.

Substances like metal oxides, hydroxides, and sulfides generally have no sharply defined infrared absorption from 2 to 16 microns aside from possible water and O—H bands. On the other hand, they are often good samples for x-ray analysis (cf. cadmium sulfide in unknown 4).

The principal fault with emission analysis is its great sensitivity; it is frequently difficult to distinguish between major components and impurities. This fact accounts for the surprising oversight of calcium in unknown 2, and tungsten in 8.

Infrared examination has advantages over wet chemistry for detecting the more unusual ions, such as BO_2^-, $B_4O_7^{--}$, $S_2O_3^{--}$, and $S_2O_5^{--}$, since these are not included in the usual schemes of analysis.

The proper sequence in using these techniques is the order emission, infrared, 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.

Polymorphism. 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, $K_2S_2O_5$, 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 mulled 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.$^{-1}$ is triply degenerate (*12*), and this may be a case of splitting of the degeneracy as a result of altering the crystal symmetry. Finally, potassium sulfate has exhibited a similar variability in this same band.

Table V. Characteristic Frequencies in Complex Ions

Complex Ion	Cm.$^{-1}$	Simple Ion	Cm.$^{-1}$
$Fe(CN)_6^{---}$	2100	CN^-	2070–80
$Fe(CN)_6^{----}$	~2010	CN^-	2070–80
$Fe(CN)_5NO^{--}$	2140	CN^-	2070–80
	1925	NO (gas)	1878
$Co(NO_2)_6^{---}$	847	NO_2^-	820–35
	1335		1235–50
	1430		1328–80
$Ce(NO_3)_6^{--}$	745	NO_3^-	725–40
	807		815–35
	1030		...
	1260		...
	1420		1350–80
	1530		...

It is much safer to base arguments on the identity of spectra than on their nonidentity. More empirical experience with the spectra of salts from many different sources should improve this situation.

Miscellaneous Observations. Anomalous Dispersion and Christiansen Filter Effects. These have been adequately described in the literature (*5, 9*). Examples will be seen in the steep-sided band of magnesium carbonate at 3 microns (No. 13), of sodium thiocyanate near 5 microns (No. 26), and of potassium ferricyanide near 5 microns (No. 155).

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.$^{-1}$), are striking. Apparently there is very little hydrogen bonding in these salts. It is interesting to note that ammonium perchlorate (No. 116), which forms no hydrate, has a high N—H stretching frequency. Other compounds with sharp water bands are barium chlorate (No. 115) and barium chloride (No. 159).

In bicarbonate there is a band at 2500 to 2600 cm.$^{-1}$, in bisulfate at 2300 to 2600 cm.$^{-1}$ (very broad), and in HPO_4^{--}, $H_2PO_4^-$, $HAsO_4^{--}$, and $H_2AsO_4^-$ at about 2300 cm.$^{-1}$ (very broad). There 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.$^{-1}$, which was totally unexpected but was confirmed on a second sample. It is not attributable to carbonate or bicarbonate, but may be due to a torsional motion of the water molecules in the lattice.

Complex Ions. The characteristic frequencies carry over moderately well into complex ions—for example, potassium ferricyanide has a band at 2100 cm.$^{-1}$, and each of the three ferrocyanides has one near 2010 cm^{-1}. This is obviously the stretching frequency of the CN^- group, which in simple cyanides is 2070 to 2080 cm.$^{-1}$ Other examples are shown in Table V.

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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