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INFRARED DETERMINATION OF INORGANIC SULFATES AND
CARBONATES BY THE PELLET TECHNIQUE

by

David E. Chasan
George Norwitz

November 1969

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**DEPARTMENT OF THE ARMY
FRANKFORD ARSENAL
Philadelphia, Pa. 19137**

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Project - Materials Testing Technology

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Quality Assurance Directorate
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I. SUMMARY

The infrared spectra of sulfates and carbonates in the solid state are discussed.

Methods are proposed for the determination of the following single sulfates by the pellet technique: barium, strontium, sodium, and potassium sulfates. The sample is weighed into a tared mortar using a semimicro balance and is mixed with 300 mg of potassium bromide. The pellet is then formed and the peak heights are determined at the appropriate peak. The peaks recommended for barium and strontium sulfates are 983 cm^{-1} and 993 cm^{-1} , respectively. Sodium and potassium sulfates are both measured at 619 cm^{-1} .

A procedure is proposed for the determination of barium and strontium sulfates in the presence of each other by measurements at 983 cm^{-1} and 993 cm^{-1} , respectively.

Methods are proposed for the determination of the following single carbonates by the pellet technique: barium, strontium, and calcium carbonates. Measurements for the barium, strontium, and calcium carbonates are made at 693 cm^{-1} , 704 cm^{-1} , and 712 cm^{-1} , respectively. The procedure cannot be used for the determination of sodium or potassium carbonates because of the hygroscopicity of these compounds.

A procedure is described for the determination of barium, strontium, and calcium carbonates in the presence of each other by measuring the peak heights at 693 cm^{-1} , 704 cm^{-1} (or 698 cm^{-1}), and 712 cm^{-1} , respectively.

The methods for the determination of barium and strontium sulfates in the presence of each other, and barium, strontium, and calcium carbonates in the presence of each other can be used down to a concentration of 5% for the minor constituent. For lower percentages the errors are rather large.

II. RECOMMENDATIONS

It is recommended that the methods in this report be included in MIL-STD-286 (Military Standard, Propellants, Solid: Sampling, Examination, and Testing) and MIL-STD-650 (Military Standard, Explosive: Sampling, Inspection, and Testing).

III. INTRODUCTION

The object of this report was to investigate the application of the pellet technique to the quantitative determination of various inorganic sulfates (singly and together) and various inorganic carbonates (singly and together).

Very little has appeared in the literature concerning the quantitative determination of inorganic sulfates by infrared methods. Tai and Underwood (18) developed a method for the determination of total sulfate ion by combining freeze drying with the potassium bromide technique. The method involves addition of potassium bromide to an aqueous solution of the sample, removal of the water by shell freezing with a mixture of acetone and dry ice, evacuation overnight with a vacuum pump, and formation of the pellet. The method was subsequently applied (2, 3) to the determination of sulfate in water and reagent chemicals, after first passing the sample or the solution of the sample through an exchange column to remove interferences. The method used the peak at approximately 1130 cm^{-1} and the optimal range was 30 to 80 micrograms of sulfate ion. A disadvantage of the method is that it is time-consuming and requires special apparatus. Also, it is so sensitive that it can not readily be applied to many analytical problems.

Underwood, Miller, and Howe (19) determined sulfate directly in aqueous solutions using an Irtran-2 cell. The sulfate peak at approximately 1130 cm^{-1} was used and the optimal range was 10 to 50 mg per ml. A disadvantage of this method is that it is lacking in sensitivity and selectivity.

No method has appeared in the literature for the quantitative determination of inorganic carbonates by infrared.

In an earlier report (1) the authors developed a method for the determination of various inorganic nitrates, singly and in the presence of each other by the pellet technique. In the present report, the same method of approach is used for determining sulfates and carbonates.

IV. STUDY

A. SPECTRA OF INORGANIC SULFATES IN THE SOLID STATE

The infrared spectra of inorganic sulfates have been described (4, 5, 11, 12, 13, 14, 15, 17).

Free sulfate ion is of tetrahedral symmetry and should have four fundamental frequencies as discussed by Hertzberg (8) and shown in Table I.

Most sulfates vary from these calculated frequencies to one degree or another. In the solid state infrared spectra, the forbidden ν_2 frequency is invariably present. These indications point to a deviation from the ideal tetrahedral symmetry. Three possible reasons for the lowering of symmetry in solid sulfates have been considered by Hezel and Ross (11, 15):

- (a) Distortion of the SO_4^{--} tetrahedron in the crystal lattice.
- (b) Covalent bonding of the sulfate to the metal through one or more oxygen atoms.
- (c) A non-uniform field due to water molecules around the cation.

Without entirely discounting the possibility of coordination, Hezel and Ross show the spectra of solid state sulfates to be consistent with the site symmetry of the anion. These investigators state that the only reliable criterion for the detection of coordination in MSO_4 compounds is the discovery of an M-O frequency. None has been substantiated for the compounds studied. These investigators also found that water was not in itself a strong perturbing influence. Extinction coefficient data showed that fully hydrated compounds have more symmetrical spectra than their partially hydrated or anhydrous analogues. The greatest influence responsible for the deviations from the free-ion symmetry appears to be the nature of the crystal structure.

The four sulfates dealt with in this report (BaSO_4 , SrSO_4 , Na_2SO_4 , and K_2SO_4) all belong to the space group D_{2h}^{16} , with the sulfate ions on C_s sites. The C_s sites provide for up to nine internal vibrations

as opposed to the two infrared-allowed fundamental frequencies shown in Table I. The ν_1 and ν_2 vibrations become infrared-allowed and the degeneracies are removed from ν_2 , ν_3 , and ν_4 . Only seven of the nine permitted vibrations have been observed.

B. DEVELOPMENT OF METHODS FOR THE INFRARED DETERMINATION OF INORGANIC SULFATES BY THE PELLET TECHNIQUE

1. Single Sulfates

As indicated in the Introduction, previous investigators used the very sensitive sulfate peak at approximately 1130 cm^{-1} for the quantitative determination of inorganic sulfate by the pellet technique. This limited the solid state method to microgram quantities for which freeze-drying equipment with its accompanying disadvantages was necessary. It seemed to the present investigators that it would be very advantageous to use a less sensitive peak in order to be able to work with samples which could be weighed on a semimicro balance.

The spectra obtained for barium, strontium, sodium, and potassium sulfates by the pellet technique are shown in Figures 1, 2, 3, and 4, respectively. A suitable peak for quantitation, the ν_1 vibration, was observed at 983 cm^{-1} for BaSO_4 and at 993 cm^{-1} for SrSO_4 . For Na_2SO_4 and K_2SO_4 the ν_4 vibration, found at 619 cm^{-1} in the spectra of both, may be used.

In order to obtain accurate results in the quantitative pellet method, the samples of sulfate were weighed directly into a mortar to avoid any losses that might be incurred if a transfer from a balance pan were involved. The sulfate was then ground with 300 mg of potassium bromide for 7 minutes to ensure adequate mixing and pulverizing. (Grinding under a solvent such as chloroform was not used since residual trace amounts of solvent remained adsorbed to the sulfate - KBr mix after evaporation of the solvent and this resulted in some interference with the sulfate spectrum). The sulfate - KBr mix was then transferred quantitatively to the die and pressed. It was found that by using a flat edged microspatula and a brush, 99.8% of the sample could be transferred to the die. Therefore, no compensation measurements or corrections of the weights were necessary. The discs produced were 13 mm in diameter and 0.8 mm thick.

A calibration curve was prepared by carrying 0.1 to 1.4 mg portions of each inorganic sulfate through the procedure and plotting absorbance against milligrams of the inorganic sulfate.

It was felt that the accuracy achieved for the method could not be significantly improved by the addition of an internal standard. The practical difficulties that are involved in using an internal standard for such a small sample heavily outweigh the value of any slight improvement in reproducibility that might result.

The feasibility of determining inorganic sulfates in the presence of carbonates or nitrates was investigated. The following systems were studied: barium sulfate in the presence of barium carbonate or barium nitrate; strontium sulfate in the presence of strontium carbonate or strontium nitrate; sodium sulfate in the presence of sodium nitrate; potassium sulfate in the presence of potassium nitrate. Preliminary work had established that neither sodium nor potassium sulfate could be determined in the presence of sodium or potassium carbonate because of the hygroscopicity of the latter compounds.

The spectra of barium carbonate, strontium carbonate, barium nitrate, strontium nitrate, sodium nitrate, and potassium nitrate are shown in Figures 6, 7, 10, 11, 12, and 13, respectively. It is seen that the spectra of barium carbonate, strontium carbonate, barium nitrate, and strontium nitrate do not display significant absorption between 1000 cm^{-1} and 980 cm^{-1} , the region for measuring the peak for the determination of barium and strontium sulfates; also, that the spectra of sodium and potassium nitrates do not display significant absorption between 800 and 600 cm^{-1} , the region for measuring the peak for the determination of sodium and potassium sulfates. No interference was expected, therefore, for the determinations in question.

It was found that accurate results for the individual sulfates could be obtained for mixtures containing as low as 5% of the sulfate in the presence of 95% of the carbonate or nitrate using approximately 1-mg samples. For lower concentrations of sulfate the ν_3 absorption band at 1130 cm^{-1} might be used.

Presumably, the above procedure for the infrared determination of inorganic sulfates would be applicable to inorganic sulfates which fulfill the following criteria:

(a) There is no anion exchange between the inorganic sulfate and the potassium bromide during preparation of the disc.

(b) The sulfate is in the anhydrous form. Any water present will facilitate anion exchange with the potassium bromide.

(c) The sulfate is not hygroscopic. Hygroscopicity can cause fogging of the discs, in addition to facilitating anion exchange.

Experiments showed that the method could not be applied to the determination of calcium or lithium sulfates because of the hygroscopicity of these compounds.

2. Two Sulfates in the Presence of Each Other

As stated earlier in this report, there is a variation in the spectra of various inorganic sulfates. These variations are associated with a lowering of the unperturbed tetrahedral sulfate ion symmetry. These dissimilarities in the spectra may be turned to the chemist's advantage, for they allow simultaneous qualitative and quantitative analyses of certain systems of sulfates. Metals with otherwise similar chemical and physical properties may be analyzed simultaneously as the sulfates, without any long involved separations. Qualitative information may be obtained simply by comparison with a collection of known sulfate spectra. Quantitative analyses may be conducted as described below on 1-mg samples. The method thus becomes particularly valuable when only minute quantities of samples are available for analysis.

This laboratory investigated barium sulfate-strontium sulfate mixtures. The spectra of 1.9 mg of a 1:1 mixture of barium and strontium sulfates is shown in Figure 5. The ν_1 peaks at 983 cm^{-1} for BaSO_4 and 993 cm^{-1} for SrSO_4 were selected for the quantitative investigation because their intensities fell in a workable absorbance range. The peaks were sharp enough that the 10 cm^{-1} split between them was sufficient to reduce any mutual overlapping to the nominal range.

To determine the absorbance more easily and more accurately, the abscissa (frequency) recordings were expanded to four times the standard size. This increased the recorded band width and separation between the peaks.

The calibration curves for barium and strontium sulfates were prepared by use of mixtures containing various percentages of these salts. It is essential that these standards be well mixed; therefore,

a mechanical vibrating ball mill (i. e., Wig-L-Bug) was used. Catch weight amounts of each of the mixtures weighing 0.9 - 1.4 mg were then sampled, mixed with KBr, ground, and pressed into discs as described above.

Mixtures containing varying amounts of sulfates were prepared and analyzed. Mixtures containing the two sulfates and nitrates and carbonates were also analyzed. Once again, the nitrates and carbonates were found not to interfere with the sulfate determinations. Accurate results were obtained for the mixed sulfates down to a percentage of 5% of one in the presence of 95% of the other. For lesser ratios, the errors are rather large.

The above method for mixed sulfates could be used for the quantitative analysis of other combinations of sulfates if the criteria listed in the previous section are met. In addition, an extra qualification is necessary. There must be a large enough separation between the specific sulfate peaks involved to allow measurement of the intensities of each individually. Expansion of the recorded abscissa (frequency) can be of great assistance in meeting this requirement. However, even with expansion, the method could not be applied to the determination of mixtures of sodium and potassium sulfates because the spectra of these two salts were too similar.

C. RECOMMENDED METHODS FOR THE INFRARED DETERMINATION OF SINGLE INORGANIC SULFATES BY THE PELLET TECHNIQUE

1. Apparatus and Reagents

Perkin-Elmer Model 621 Infrared Spectrophotometer.

Semimicro balance capable of weighing 1.00 mg to ± 0.01 mg.

Mechanical vibrating ball mill (Wig-L-Bug, Crescent Dental Manufacturing Co., Chicago, Ill.)

Evacuatable potassium bromide die (Model 186-0025, Perkin-Elmer Corp., Norwalk, Conn.).

Adapter for mounting KBr discs on spectrophotometer.

Twenty-ton hydraulic press.
Vacuum pump.
Mortars (O.D. 50 mm) with pestles.
Flat edged microspatula.
Camel's hair brush, shed-proof, No. 4.
Anhydrous barium nitrate, reagent grade.
Anhydrous strontium nitrate, reagent grade.
Anhydrous barium sulfate, reagent grade.
Anhydrous strontium sulfate, reagent grade.
Anhydrous barium carbonate, reagent grade.
Anhydrous strontium carbonate, reagent grade.
Anhydrous calcium carbonate, reagent grade.
Anhydrous sodium sulfate, reagent grade.
Anhydrous potassium sulfate, reagent grade.
Anhydrous sodium nitrate, reagent grade.
Anhydrous potassium nitrate, reagent grade.
Potassium bromide, infrared grade (Harshaw Chemical Co., Cleveland, Ohio).

2. Determination of Barium Sulfate

a. Preparation of calibration curve

Prepare in duplicate, discs containing approximately 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, and 1.4 mg of barium sulfate using the

following technique: Weigh the mortar to ± 0.01 mg and add the desired amount of sulfate to the mortar with a clean microspatula. Weigh the mortar plus sulfate to ± 0.01 mg. Subtract the weight of the mortar to determine the exact weight of sulfate taken. Weigh 300 mg of potassium bromide onto an aluminum balance pan. Add the potassium bromide to the mortar in four increasing portions, grinding well after each addition. The total grinding time should be no less than 7 minutes. When the grinding is completed, brush any powder adhering to the pestle back into the mortar. Use a clean, flat-edged microspatula to scrape the mix loose from the mortar. Transfer as much of the mix as possible to the die with the microspatula. Brush any powder left in the mortar into the die. Scrape the mortar surface a second time to loosen any remaining powder. Transfer this, too, into the die by brushing. Brush any powder that might have spilled around the opening of the die into the die. Level the sample as well as possible with the microspatula and insert the plunger. Evacuate the die for 5 minutes with a vacuum pump without applying pressure, then apply 18,000 pounds pressure with a hydraulic press for 7 minutes.

Disassemble the die and push out the potassium bromide disc with a gentle application of the hydraulic press. Mount the disc immediately on an adapter and record the spectrum from 1020 to 820 cm^{-1} . The following settings were used on the Perkin-Elmer Model 621 infrared spectrophotometer: slit program, 1000; gain, 5.1; attenuator speed, 1100; scan drive, 10; scan time, 20; suppression, 0; scale, 4x abscissa expansion; source current, 0.8.

Scan the region of 1020 to 820 cm^{-1} and determine the absorbance for each disc at 983 cm^{-1} . Make the peak measurements by measuring the transmittance at the tangent to the horizontal portion of the top right arm of the peak, I_0 , and the transmittance of the bottom of the peak, I . The absorbance, $\log I_0/I$ is then calculated. (The use of transmittance paper is preferred because it can be read more accurately than absorbance paper at higher concentration ranges). Plot absorbance against milligrams of barium sulfate present.

b. Procedure

Weigh, in duplicate, 0.9 - 1.4 mg of sample containing the barium sulfate to ± 0.01 mg as described under Preparation of calibration curve. Prepare the potassium bromide discs as described and measure

the absorbance at 983 cm^{-1} . Convert the readings of absorbance to milligrams of barium sulfate by referring to the calibration curve. Calculate the percent barium sulfate.

3. Determination of Strontium Sulfate

Proceed as described for barium sulfate but prepare the calibration curve with strontium sulfate and use the peak at 993 cm^{-1} .

4. Determination of Sodium Sulfate

a. Preparation of calibration curve

Prepare in duplicate, discs containing approximately 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 mg of sodium sulfate, using the technique described for Preparation of calibration curve for barium sulfate. Scan the region 820 cm^{-1} to 600 cm^{-1} and determine the absorbance for each disc at 619 cm^{-1} . Calculate the absorbance by using the transmittance of the tangent to the horizontal portion of the top left arm of the peak as I_0 . Plot absorbance against milligrams of sodium sulfate present.

b. Procedure

Weigh, in duplicate, 0.7 - 1.0 mg of sample containing the sodium sulfate to $\pm 0.01\text{ mg}$ as described above. Prepare the potassium bromide discs and record the spectrum from 820 cm^{-1} to 600 cm^{-1} . Calculate the absorbance at 619 cm^{-1} and convert the readings of absorbance to milligrams of sodium sulfate by referring to the calibration curve. Calculate the percent sodium sulfate.

5. Determination of Potassium Sulfate

Proceed as described for sodium sulfate but prepare the calibration curve with potassium sulfate.

D. RECOMMENDED METHOD FOR THE INFRARED DETERMINATION OF BARIUM AND STRONTIUM SULFATES IN THE PRESENCE OF EACH OTHER BY THE PELLET TECHNIQUE

a. Preparation of calibration curve

Prepare seven standard mixtures containing approximately the following amounts of sulfates:

	<u>BaSO₄ (grams)</u>	<u>SrSO₄ (grams)</u>
1	0.90	0.10
2	0.60	0.20
3	0.40	0.20
4	0.30	0.30
5	0.20	0.40
6	0.20	0.60
7	0.10	0.90

In preparing the above mixtures, weigh the indicated portion of barium sulfate to ± 0.1 mg in the aluminum balance pan and transfer to the vial of a vibrating ball mill (Wig-L-Bug). Brush out any remaining sulfate from the pan to the vial. Repeat with the proper amount of strontium sulfate. After both sulfates have been added to the vial, add the ball and mix for at least six 20-second portions. Repeat this procedure for each of the seven combinations.

Weigh, in duplicate, 0.9 - 1.4 mg of each of the above standard mixes into the mortar as described under preparation of calibration curve for barium sulfate. Prepare the pellet and record the spectrum from 1020 to 820 cm^{-1} , using a 4x abscissa (frequency) expansion.

Determine the absorbance of the peak at 983 cm^{-1} for barium sulfate and plot absorbance vs. milligrams of barium sulfate present. Determine the absorbance at 993 cm^{-1} for strontium sulfate and plot absorbance vs. milligrams of strontium sulfate present.

Repeat with each of the standard mixes and draw the calibration curves for barium and strontium sulfates.

b. Procedure

Weigh in duplicate 0.9 to 1.4 mg of sample containing barium and strontium sulfates to ± 0.01 mg into the mortar as described under preparation of calibration curve for barium sulfate. Prepare the potassium bromide pellets as described and measure the absorbances at 983 cm^{-1} for barium sulfate and 993 cm^{-1} for strontium sulfate. Convert the readings to milligrams of barium sulfate and milligrams of strontium sulfate by referring to the calibration curves. Calculate the percent barium and strontium sulfates.

E. SPECTRA OF INORGANIC CARBONATES IN THE SOLID STATE

The infrared spectra of inorganic carbonates in the solid state have been described (6, 7, 10, 12, 14, 16, 20, 21).

Free carbonate ion exhibits D_{3h} symmetry and should have the four fundamental frequencies calculated by Herzberg (9) shown in Table II.

As was the case with sulfates, deviations from the ideal carbonate ion spectra are observed and the forbidden ν_1 transition is once again evident in some spectra. Goldsmith and Ross (6) propose the following factors as being relevant to the deviations from carbonate ion spectra:

(a) Coordination to the metal, either by formation of a carbonate complex or by interaction with a cation of high polarizing power

(b) Perturbation of the anion by water or hydroxyl ion.

(c) Lowered site symmetry.

The effects of polarization of the cation appear to be negligible and there is no correlation between the amount of perturbing species (water or hydroxyl) present and the intensity of ν_1 . Hence they conclude that the major factor determining the carbonate spectra is the site symmetry of the carbonate ion. There are three possible structures for the simple carbonates, those of calcite, aragonite, and vaterite. The symmetry class for calcite type carbonates is D_3 , for aragonite type carbonates C_2 and for vaterite carbonates C_3 (unknown). The calcite spectrum should be close to that of the unperturbed carbonate ion shown in Table II. For aragonite, six internal frequencies of CO_3^{--} are permitted in the infrared as opposed to the three shown in Table II. Two additional frequencies are derived from the removal of the degeneracy of the ν_3 and ν_4 stretching modes and one from the ν_1 mode which becomes infrared-active.

The three carbonates used in this report are $BaCO_3$, $SrCO_3$, and $CaCO_3$. The $CaCO_3$ is in the calcite form and the $BaSO_4$ and $SrSO_4$ are in the aragonite form.

F. DEVELOPMENT OF METHODS FOR THE INFRARED DETERMINATION OF INORGANIC CARBONATES BY THE PELLET TECHNIQUE

1. Single Carbonates

The spectra obtained for barium, strontium, and calcium carbonates by the pellet technique are shown in Figures 6, 7, and 8, respectively. A suitable peak for quantitation for each of these carbonates was observed in the region of 720 - 690 cm^{-1} . The peaks occur at 693 cm^{-1} for $BaCO_3$, 704 cm^{-1} or 698 cm^{-1} for $SrCO_3$, and 712 cm^{-1} for $CaCO_3$.

Calibration curves were prepared as described for single sulfates.

The feasibility of determining an inorganic carbonate in the presence of sulfates or nitrates was investigated. The spectra of barium sulfate, strontium sulfates, barium nitrate, and strontium nitrate are shown in Figures 1, 2, 10, and 11, respectively. (Calcium

sulfate and calcium nitrate could not be used due to their hygroscopicity). It is seen that none of these spectra contain any significant absorption between 720 cm^{-1} and 690 cm^{-1} ; therefore, no interference would be expected with the carbonate analysis. This was borne out by experiment. Accurate results were attained for mixtures with as low as 5% carbonate and 95% nitrate or sulfate. For lower concentrations of carbonate, the major absorption band at approximately 1430 cm^{-1} might be used.

The same criteria listed for single sulfates would govern the feasibility of applying this technique to other carbonates. The authors attempted to analyze sodium and potassium carbonates according to the above technique, but their hygroscopicity caused fogged pellets and erratic results.

2. Two or Three Carbonates in the Presence of Each Other

This laboratory investigated barium carbonate-strontium carbonate-calcium carbonate mixtures. The spectra of 2.5 mg of a 1:1:1 mixture of barium, strontium, and calcium carbonates is shown in Figure 9. The ν_4 vibration region is seen to yield suitable peaks for quantitation. Barium carbonate can be measured at 693 cm^{-1} and calcium carbonate at 712 cm^{-1} . Strontium carbonate yields two peaks in this region, one at 704 cm^{-1} and one at 698 cm^{-1} . The peak at 704 cm^{-1} is preferred because of its larger extinction coefficient. However, in the presence of significant amounts of CaCO_3 (>10%) the peak at 698 cm^{-1} should be used because of a slight contribution by CaCO_3 to the absorbance at 704 cm^{-1} .

Calibration curves were prepared using mixtures containing various percentages of BaCO_3 , SrCO_3 , and CaCO_3 . As with sulfates abscissa expansion was used to aid in recording the spectra. Mixtures of the two or three carbonates were then analyzed.

Accurate results were obtained for the mixed carbonate method down to as low as 5% of either carbonate in approximately 1-mg samples.

This method should be applicable to the simultaneous quantitative analysis of any combination of two or three carbonates if the criteria mentioned in Section IV. B are met.

G. RECOMMENDED METHODS FOR THE INFRARED DETERMINATION OF
SINGLE INORGANIC CARBONATES BY THE PELLET TECHNIQUE

1. Determination of Barium Carbonate

Proceed as described for barium sulfate, but use barium carbonate for the preparation of the calibration curve, scan the region 740 to 640 cm^{-1} . Use the peak at 693 cm^{-1} and calculate the absorbance by using the transmittance of the tangent to the horizontal portion of the top left arm of the peak as I_0 .

2. Determination of Strontium Carbonate

Proceed as described for barium carbonate but prepare the calibration curve with strontium carbonate. Use the peak at 704 cm^{-1} and calculate the absorbance by using the transmittance of the tangent to the horizontal portion of the top left arm of the peak as I_0 .

3. Determination of Calcium Carbonate

Proceed as described for barium carbonate but prepare the calibration curve with calcium carbonate. Calculate the absorbance at 712 cm^{-1} by using the transmittance of the tangent to the horizontal portion of the top left arm of the peak as I_0 .

H. RECOMMENDED METHOD FOR THE INFRARED DETERMINATION OF
BARIUM, STRONTIUM, AND CALCIUM CARBONATES IN THE
PRESENCE OF EACH OTHER BY THE PELLET TECHNIQUE

a. Preparation of calibration curve

Prepare six standard mixtures containing approximately the following amounts of carbonates:

	<u>BaCO₃ (grams)</u>	<u>SrCO₃ (grams)</u>	<u>CaCO₃ (grams)</u>
1	0.90	0.05	0.05
2	0.05	0.90	0.05
3	0.05	0.05	0.90
4	0.50	0.25	0.25
5	0.25	0.50	0.25
6	0.25	0.25	0.50

In preparing the above mixtures, weigh the indicated portion of barium carbonate to ± 0.1 mg in the aluminum balance pan and transfer to the vial of a vibrating ball mill (Wig-L-Bug). Brush out any remaining carbonate from the pan to the vial. Repeat with the proper amounts of strontium and calcium carbonates. After all the carbonates have been added to the vial, add the ball and mix for at least six 20-second portions. Repeat this procedure for each of the six mixes.

Weigh, in duplicate, 0.9 to 1.4 mg of each of the above standard mixes into the mortar as described under preparation of calibration curve for barium sulfate. Prepare the pellet and record the spectrum from 740 to 640 cm^{-1} , using a 4x abscissa (frequency) expansion.

Determine the absorbance of the peak at 693 cm^{-1} for barium carbonate and plot absorbance vs. milligrams of barium carbonate present. Determine the absorbance at both 704 and 698 cm^{-1} for strontium carbonate and plot absorbances vs. milligrams of strontium carbonate present. Determine the absorbance at 712 cm^{-1} for calcium carbonate and plot absorbance vs. milligrams of calcium carbonate present.

Repeat with each of the standard mixes and draw the calibration curves for barium, strontium (2 curves), and calcium carbonates.

b. Procedure

Weigh in duplicate 0.9 to 1.4 mg of sample containing barium, strontium, and calcium carbonates to ± 0.01 mg into the mortar as

described under preparation of calibration curve for barium sulfate. Prepare the potassium bromide pellets as described and measure the absorbances at 693 cm^{-1} for barium carbonate and 712 cm^{-1} for calcium carbonate. If a significant amount of calcium carbonate is present (i.e. over 10 percent) use the peak at 698 cm^{-1} for strontium carbonate; otherwise, use the peak at 704 cm^{-1} for strontium carbonate. Convert the absorbance readings to milligrams of barium, strontium, and calcium carbonates by referring to their respective calibration curves. Calculate the percent barium, strontium, and calcium carbonates.

I. APPLICATION OF THE METHODS TO SPECIFIC PROBLEMS

The methods can obviously be applied to the determination of mixtures of salts.

For application to specific materials such as explosives, it is first necessary to separate the salts by an appropriate means.

The methods can be used for the determination of barium and strontium in the presence of each other by converting the barium and strontium to sulfates (by treating with sulfuric acid, evaporation to dryness, and ignition at about 500°C) and then applying the infrared method.

J. RESULTS

The results for barium and strontium sulfates singly in the presence of carbonates and nitrates are shown in Table III. The results for sodium and potassium sulfates singly in the presence of nitrates are shown in Table IV. The results for barium and strontium sulfate mixtures are shown in Table V. The results for barium and strontium carbonates singly in the presence of sulfates or nitrates are shown in Table VI. The results for barium, strontium, and calcium carbonate mixtures (two or three together) are shown in Table VII.

In all cases the results were satisfactory. The standard deviation of the methods is in the order of 2%.

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VI. TABLES

Table I. Fundamental Vibrations of the Sulfate Ion (8)

Type	ν_1	ν_2	ν_3	ν_4
Species	A ₁	E	F ₂	F ₂
Activity	Raman	Raman	IR, Raman	IR, Raman
Frequency (cm ⁻¹)	981	451	1104	613
Assignment	Symmetric stretching	Bending Deformation (doubly degenerate)	Assymmetric stretch (triply degenerate)	Bending Deformation (triply degenerate)

Table II. Fundamental Vibrations of the Carbonate Ion (9)

Type	ν_1	ν_2	ν_3	ν_4
Species	A ₁ '	A ₂ ''	E'	E'
Activity	Raman	IR	IR, Raman	IR, Raman
Frequency (cm ⁻¹)	1063	879	1415	680
Assignment	Symmetric stretching	Out-of-plane bending	Assymmetric stretching (doubly degenerate)	In-plane bending (doubly degenerate)

Table III. Results for Barium and Strontium Sulfates Singly
in the Presence of Carbonates or Nitrates

<u>Run</u>	<u>Added (mg)</u>	<u>Found (mg)</u>
1	0.98 BaSO ₄ + 0.49 Ba(NO ₃) ₂	0.96 BaSO ₄
2	0.88 BaSO ₄ + 0.44 Ba(NO ₃) ₂	0.85 BaSO ₄
3	0.78 BaSO ₄ + 0.39 Ba(NO ₃) ₂	0.77 BaSO ₄
4	0.24 BaSO ₄ + 0.96 BaCO ₃	0.24 BaSO ₄
5	0.26 BaSO ₄ + 1.03 BaCO ₃	0.26 BaSO ₄
6	0.29 BaSO ₄ + 1.12 BaCO ₃	0.31 BaSO ₄
7	0.43 SrSO ₄ + 0.85 Sr(NO ₃) ₂	0.45 SrSO ₄
8	0.44 SrSO ₄ + 0.86 Sr(NO ₃) ₂	0.46 SrSO ₄
9	0.47 SrSO ₄ + 0.93 Sr(NO ₃) ₂	0.49 SrSO ₄
10	0.43 SrSO ₄ + 0.81 SrCO ₃	0.43 SrSO ₄
11	0.54 SrSO ₄ + 1.00 SrCO ₃	0.55 SrSO ₄
12	0.52 SrSO ₄ + 0.96 SrCO ₃	0.51 SrSO ₄

Table IV. Results for Sodium and Potassium Sulfates
Singly in the Presence of Nitrates

<u>Run</u>	<u>Added (mg)</u>	<u>Found (mg)</u>
1	0.13 Na ₂ SO ₄ + 0.81 NaNO ₃	0.12 Na ₂ SO ₄
2	0.14 Na ₂ SO ₄ + 0.84 NaNO ₃	0.14 Na ₂ SO ₄
3	0.12 Na ₂ SO ₄ + 0.75 NaNO ₃	0.11 Na ₂ SO ₄
4	0.45 Na ₂ SO ₄ + 0.50 NaNO ₃	0.51 Na ₂ SO ₄
5	0.48 Na ₂ SO ₄ + 0.52 NaNO ₃	0.54 Na ₂ SO ₄
6	0.36 Na ₂ SO ₄ + 0.40 NaNO ₃	0.37 Na ₂ SO ₄
7	0.13 K ₂ SO ₄ + 0.73 KNO ₃	0.17 K ₂ SO ₄
8	0.15 K ₂ SO ₄ + 0.87 KNO ₃	0.14 K ₂ SO ₄
9	0.11 K ₂ SO ₄ + 0.67 KNO ₃	0.11 K ₂ SO ₄
10	0.59 K ₂ SO ₄ + 0.31 KNO ₃	0.58 K ₂ SO ₄
11	0.70 K ₂ SO ₄ + 0.37 KNO ₃	0.72 K ₂ SO ₄
12	0.59 K ₂ SO ₄ + 0.31 KNO ₃	0.57 K ₂ SO ₄

Table V. Results for Barium and Strontium Sulfate Mixtures

<u>Run</u>	<u>Added (mg)</u>	<u>Found (mg)</u>
1	0.04 BaSO ₄ + 1.20 SrSO ₄	0.02 BaSO ₄ + 1.22 SrSO ₄
2	0.04 BaSO ₄ + 1.22 SrSO ₄	0.06 BaSO ₄ + 1.23 SrSO ₄
3	0.04 BaSO ₄ + 1.14 SrSO ₄	0.03 BaSO ₄ + 1.13 SrSO ₄
4	0.14 BaSO ₄ + 1.22 SrSO ₄	0.17 BaSO ₄ + 1.19 SrSO ₄
5	0.13 BaSO ₄ + 1.10 SrSO ₄	0.17 BaSO ₄ + 1.13 SrSO ₄
6	0.15 BaSO ₄ + 1.29 SrSO ₄	0.18 BaSO ₄ + 1.26 SrSO ₄
7	0.47 BaSO ₄ + 0.89 SrSO ₄	0.47 BaSO ₄ + 0.88 SrSO ₄
8	0.50 BaSO ₄ + 0.96 SrSO ₄	0.51 BaSO ₄ + 0.93 SrSO ₄
9	0.51 BaSO ₄ + 0.98 SrSO ₄	0.55 BaSO ₄ + 0.97 SrSO ₄
10	0.88 BaSO ₄ + 0.44 SrSO ₄	0.88 BaSO ₄ + 0.46 SrSO ₄
11	0.98 BaSO ₄ + 0.49 SrSO ₄	0.97 BaSO ₄ + 0.51 SrSO ₄
12	0.87 BaSO ₄ + 0.44 SrSO ₄	0.85 BaSO ₄ + 0.44 SrSO ₄
13	1.12 BaSO ₄ + 0.13 SrSO ₄	1.13 BaSO ₄ + 0.15 SrSO ₄
14	1.20 BaSO ₄ + 0.14 SrSO ₄	1.19 BaSO ₄ + 0.14 SrSO ₄
15	1.30 BaSO ₄ + 0.15 SrSO ₄	1.28 BaSO ₄ + 0.17 SrSO ₄
16	1.31 BaSO ₄ + 0.04 SrSO ₄	1.32 BaSO ₄ + 0.05 SrSO ₄
17	1.08 BaSO ₄ + 0.03 SrSO ₄	1.02 BaSO ₄ + 0.04 SrSO ₄
18	1.35 BaSO ₄ + 0.04 SrSO ₄	1.39 BaSO ₄ + 0.04 SrSO ₄

Table V. Results for Barium and Strontium Sulfate Mixtures (cont'd)

<u>Run</u>	<u>Added (mg)</u>	<u>Found (mg)</u>
19	0.31 BaSO ₄ + 0.29 SrSO ₄	
	+0.29 Ba(NO ₃) ₂ + 0.29 Sr(NO ₃) ₂	0.30 BaSO ₄ + 0.26 SrSO ₄
20	0.34 BaSO ₄ + 0.32 SrSO ₄	
	+0.33 Ba(NO ₃) ₂ + 0.33 Sr(NO ₃) ₂	0.37 BaSO ₄ + 0.33 SrSO ₄
21	0.32 BaSO ₄ + 0.30 SrSO ₄	
	+0.32 Ba(NO ₃) ₂ + 0.31 Sr(NO ₃) ₂	0.31 BaSO ₄ + 0.27 SrSO ₄
22	0.42 BaSO ₄ + 0.44 SrSO ₄	
	+0.20 Ba(NO ₃) ₂ + 0.20 Sr(NO ₃) ₂	0.43 BaSO ₄ + 0.44 SrSO ₄
23	0.43 BaSO ₄ + 0.44 SrSO ₄	
	+0.21 Ba(NO ₃) ₂ + 0.20 Sr(NO ₃) ₂	0.45 BaSO ₄ + 0.45 SrSO ₄
24	0.42 BaSO ₄ + 0.43 SrSO ₄	
	+0.20 Ba(NO ₃) ₂ + 0.19 Sr(NO ₃) ₂	0.40 BaSO ₄ + 0.40 SrSO ₄

Table VI. Results for Barium and Strontium Carbonates Singly in the Presence of Sulfates or Nitrates

<u>Run</u>	<u>Added (mg)</u>	<u>Found (mg)</u>
1	0.27 BaCO ₃ + 0.99 BaSO ₄	0.28 BaCO ₃
2	0.28 BaCO ₃ + 1.04 BaSO ₄	0.30 BaCO ₃
3	0.22 BaCO ₃ + 0.80 BaSO ₄	0.21 BaCO ₃
4	0.75 BaCO ₃ + 0.19 BaSO ₄	0.80 BaCO ₃
5	0.92 BaCO ₃ + 0.23 BaSO ₄	0.95 BaCO ₃
6	1.04 BaCO ₃ + 0.26 BaSO ₄	1.04 BaCO ₃
7	0.19 BaCO ₃ + 0.93 Ba(NO ₃) ₂	0.20 BaCO ₃
8	0.22 BaCO ₃ + 1.04 Ba(NO ₃) ₂	0.22 BaCO ₃
9	0.20 BaCO ₃ + 0.99 Ba(NO ₃) ₂	0.19 BaCO ₃
10	0.22 SrCO ₃ + 0.71 SrSO ₄	0.23 SrCO ₃
11	0.25 SrCO ₃ + 0.80 SrSO ₄	0.25 SrCO ₃
12	0.36 SrCO ₃ + 1.16 SrSO ₄	0.40 SrCO ₃
13	0.75 SrCO ₃ + 0.40 SrSO ₄	0.77 SrCO ₃
14	0.63 SrCO ₃ + 0.34 SrSO ₄	0.65 SrCO ₃
15	0.66 SrCO ₃ + 0.36 SrSO ₄	0.66 SrCO ₃
16	0.20 SrCO ₃ + 0.85 Sr(NO ₃) ₂	0.20 SrCO ₃
17	0.24 SrCO ₃ + 1.03 Sr(NO ₃) ₂	0.26 SrCO ₃
18	0.23 SrCO ₃ + 0.97 Sr(NO ₃) ₂	0.25 SrCO ₃

Table VII. Results for Barium, Strontium,
and Calcium Carbonate Mixtures

Run	Added (mg)			Found (mg)		
	BaCO ₃	SrCO ₃	CaCO ₃	BaCO ₃	SrCO ₃	CaCO ₃
1	0.40	0.40	0.40	0.40	0.41	0.38
2	0.36	0.36	0.36	0.35	0.36	0.34
3	0.41	0.41	0.41	0.41	0.44	0.41
4	0.23	0.23	0.45	0.20	0.20	0.44
5	0.25	0.25	0.50	0.25	0.25	0.50
6	0.23	0.23	0.46	0.21	0.22	0.47
7	0.49	0.24	0.24	0.51	0.26	0.26
8	0.44	0.22	0.22	0.41	0.20	0.20
9	0.57	0.28	0.28	0.55	0.28	0.27
10	0.30	0.60	0.32	0.30	0.60	0.32
11	0.25	0.49	0.25	0.25	0.48	0.26
12	0.34	0.67	0.34	0.34	0.68	0.36
13	0.09	0.09	0.68	0.09	0.10	0.68
14	0.10	0.10	0.82	0.12	0.10	0.82
15	0.12	0.12	0.97	0.16	0.15	1.00
16	0.14	1.10	0.14	0.12	1.09	0.14
17	0.12	0.97	0.12	0.12	0.97	0.12
18	0.16	1.29	0.16	0.17	1.32	0.17
19	0.86	0.11	0.11	0.82	0.09	0.11
20	0.92	0.12	0.12	0.92	0.10	0.11
21	0.90	0.11	0.11	0.90	0.11	0.11
22	0.52	0.53	-	0.51	0.51	-
23	0.47	0.47	-	0.44	0.46	-
24	0.67	0.67	-	0.67	0.68	-
25	-	0.41	0.42	-	0.44	0.41
26	-	0.52	0.53	-	0.50	0.47

Table VII. Results for Barium, Strontium,
and Calcium Carbonate Mixtures (cont'd)

<u>Run</u>	<u>Added (mg)</u>			<u>Found (mg)</u>		
	<u>BaCO₃</u>	<u>SrCO₃</u>	<u>CaCO₃</u>	<u>BaCO₃</u>	<u>SrCO₃</u>	<u>CaCO₃</u>
27	-	0.53	0.53	-	0.54	0.49
28	0.69	-	0.69	0.70	-	0.69
29	0.63	-	0.63	0.65	-	0.64
30	0.71	-	0.71	0.74	-	0.72
31	0.05	0.05	0.90	0.05	0.05	0.94
32	0.06	0.06	1.11	0.08	0.08	1.14
33	0.06	0.06	1.08	0.09	0.08	1.07
34	0.06	1.00	0.06	0.06	1.02	0.05
35	0.04	0.73	0.04	0.03	0.75	0.04
36	0.05	0.85	0.05	0.05	0.82	0.06
37	0.91	0.05	0.05	0.94	0.05	0.05
38	1.12	0.06	0.06	1.11	0.07	0.08
39	1.21	0.07	0.07	1.21	0.08	0.07

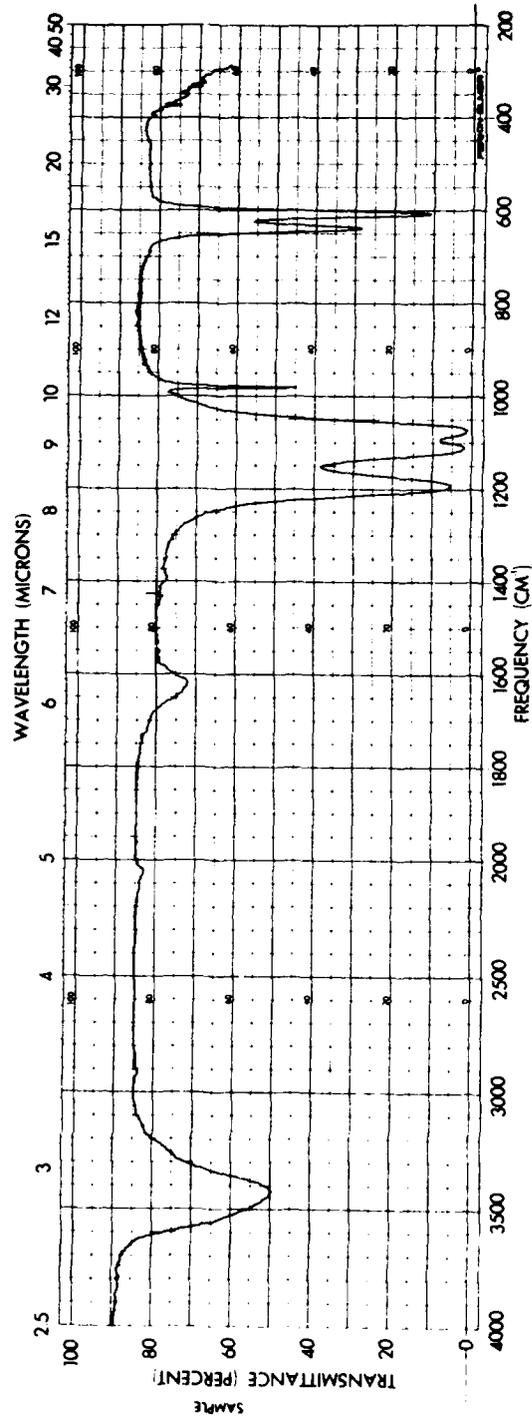


Figure 1. Spectrum of BaSO₄

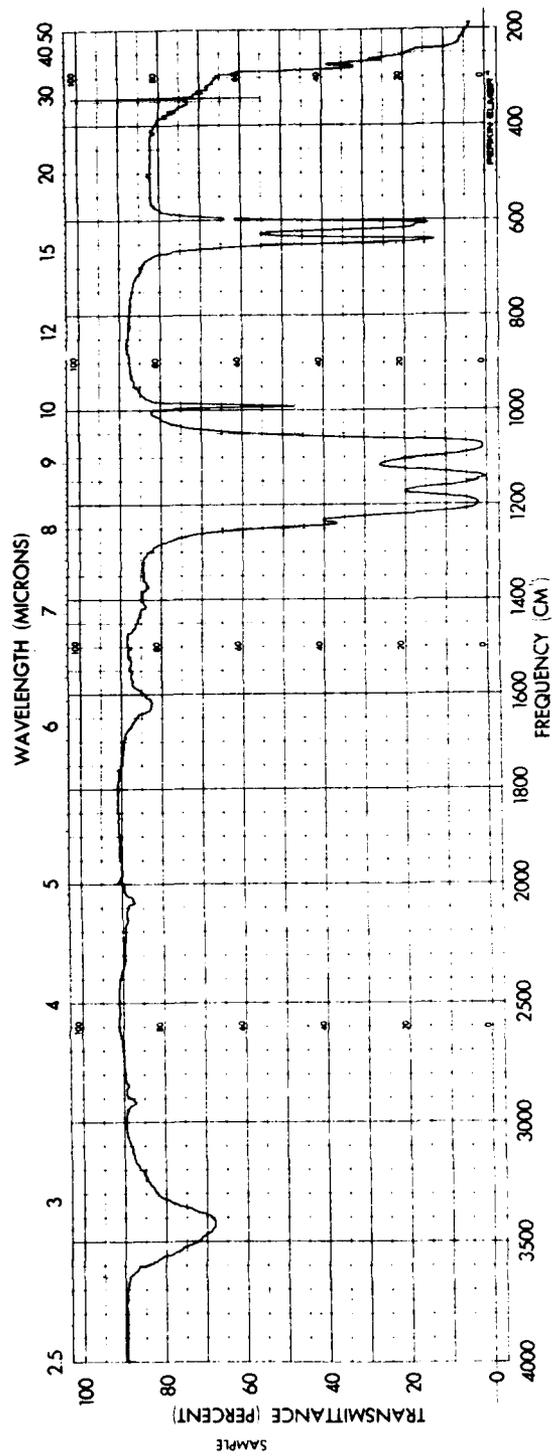


Figure 2. Spectrum of SrSO₄

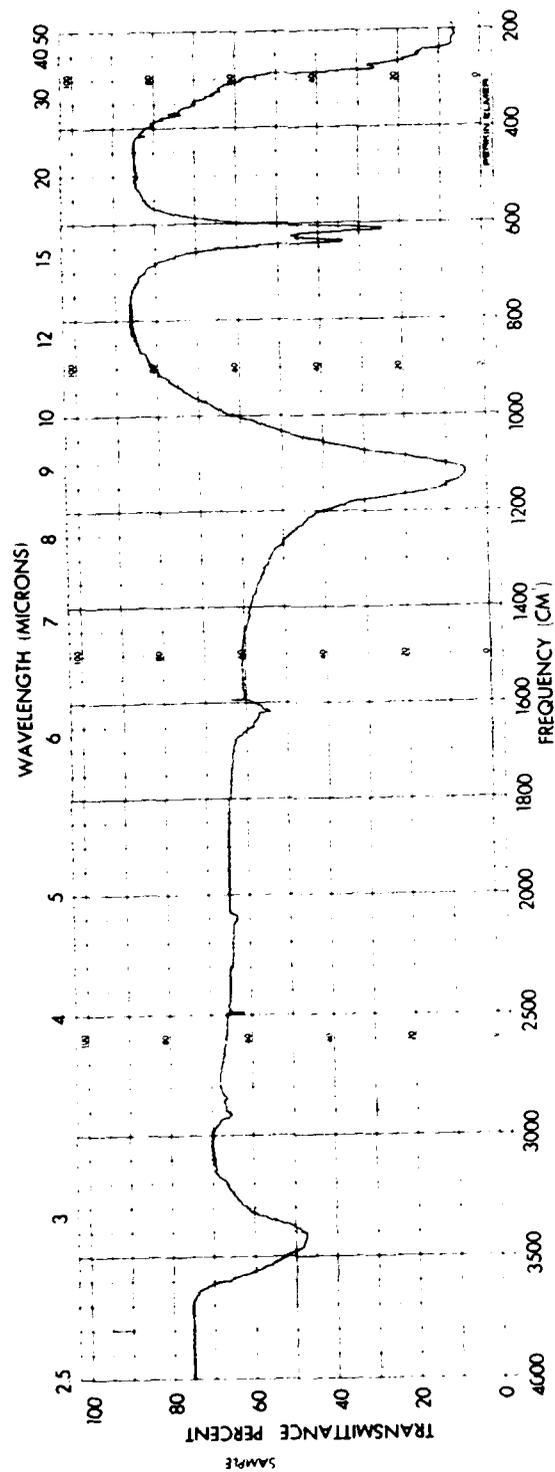


Figure 3. Spectrum of Na_2SO_4

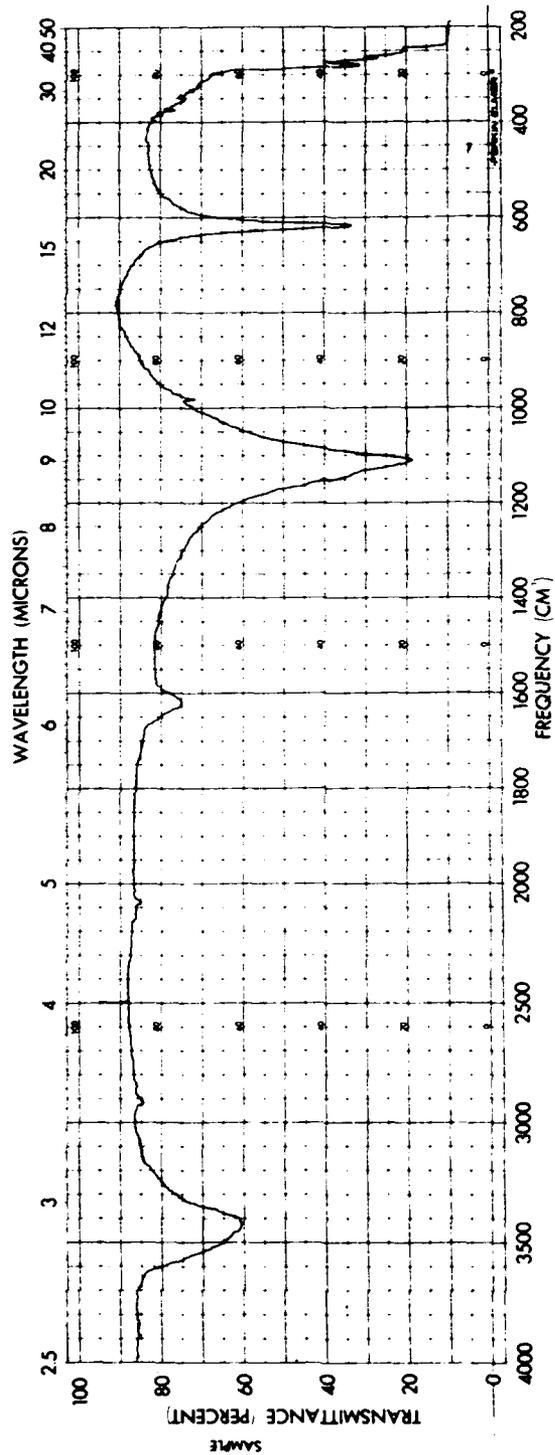


Figure 4. Spectrum of K_2SO_4

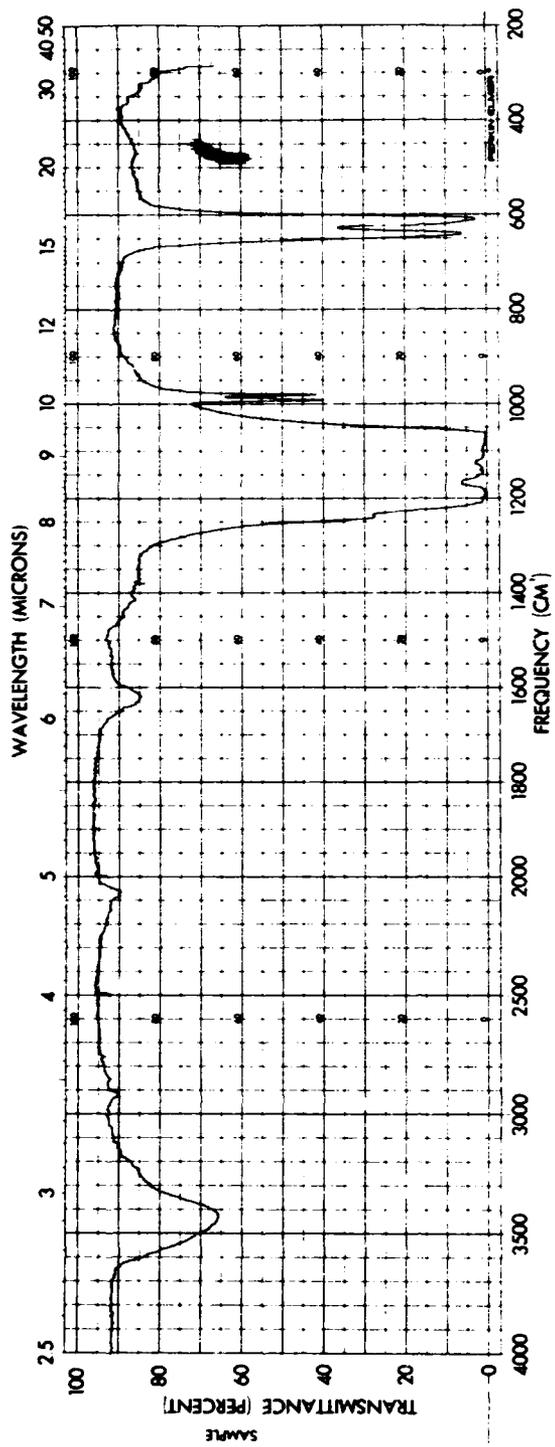


Figure 5. Spectrum of mixture of BaSO₄ and SrSO₄ (1 to 1)

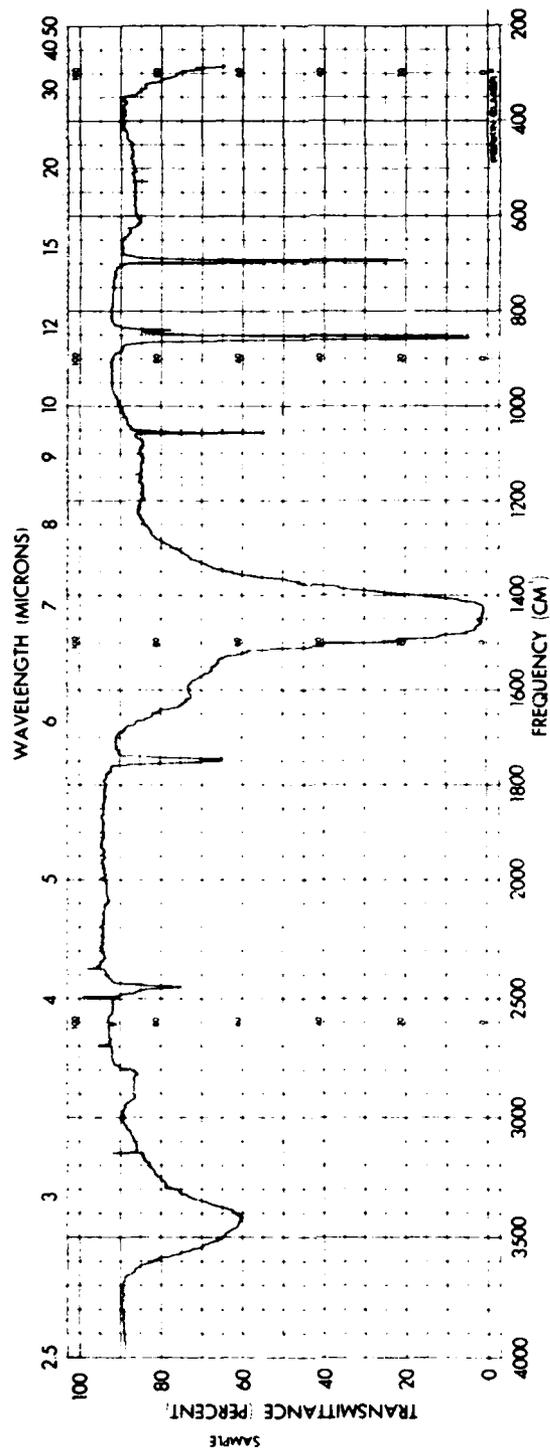


Figure 6. Spectrum of BaCO₃

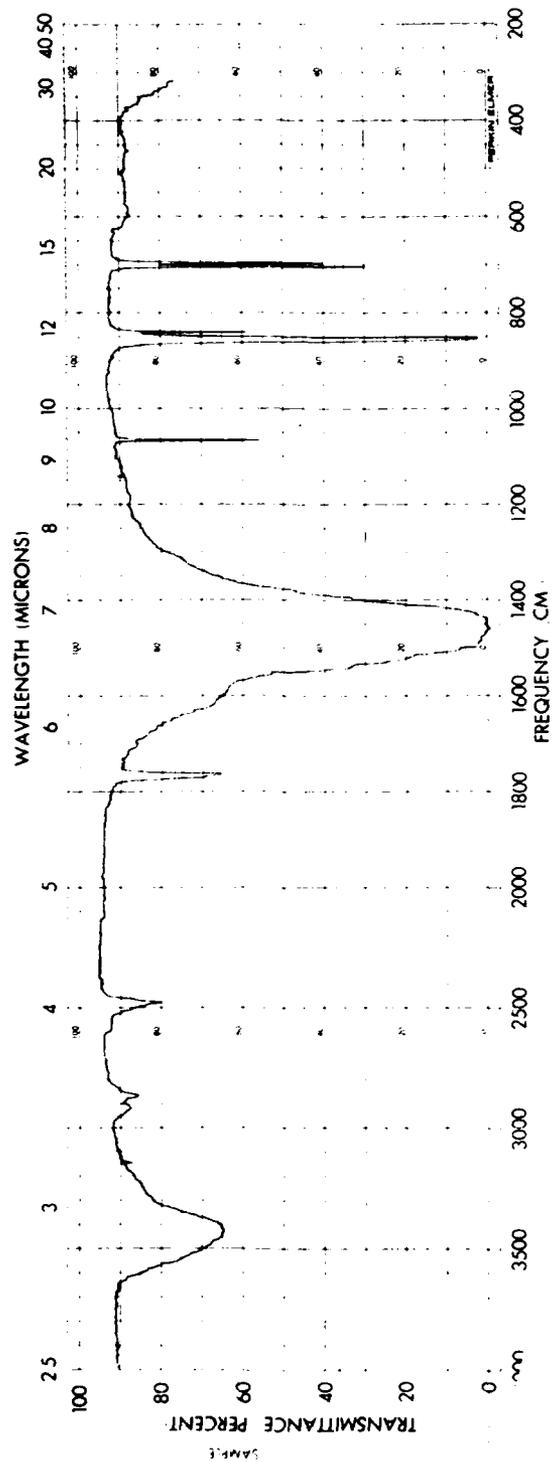


Figure 7. Spectrum of SrCO₃

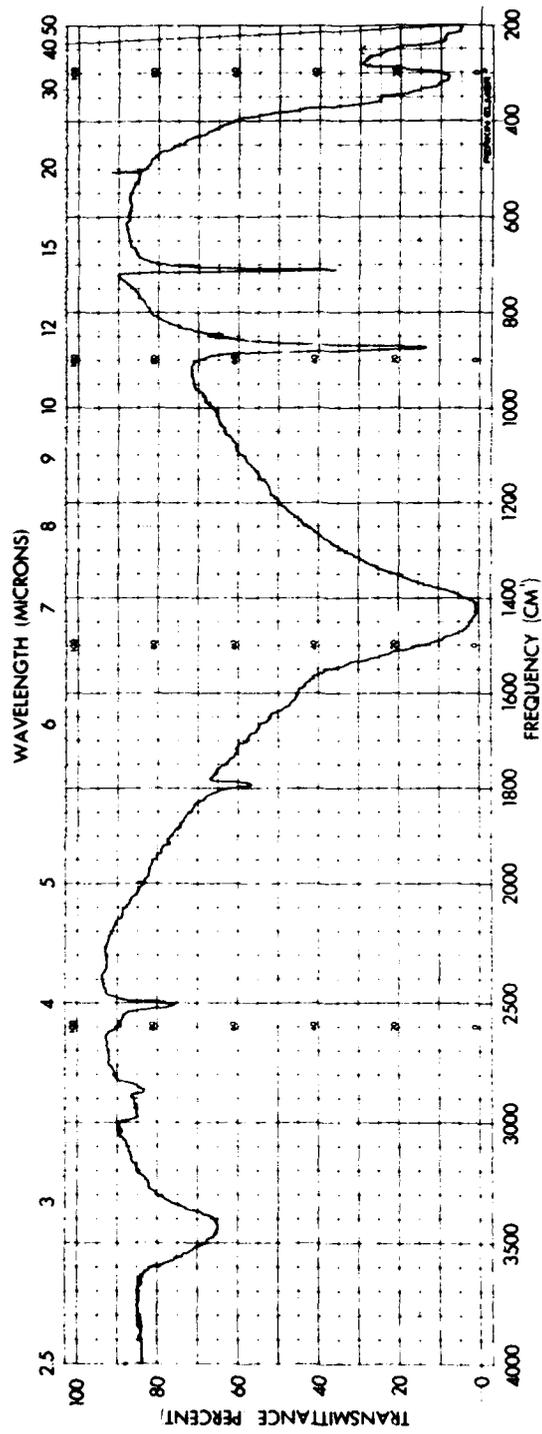


Figure 8. Spectrum of CaCO₃

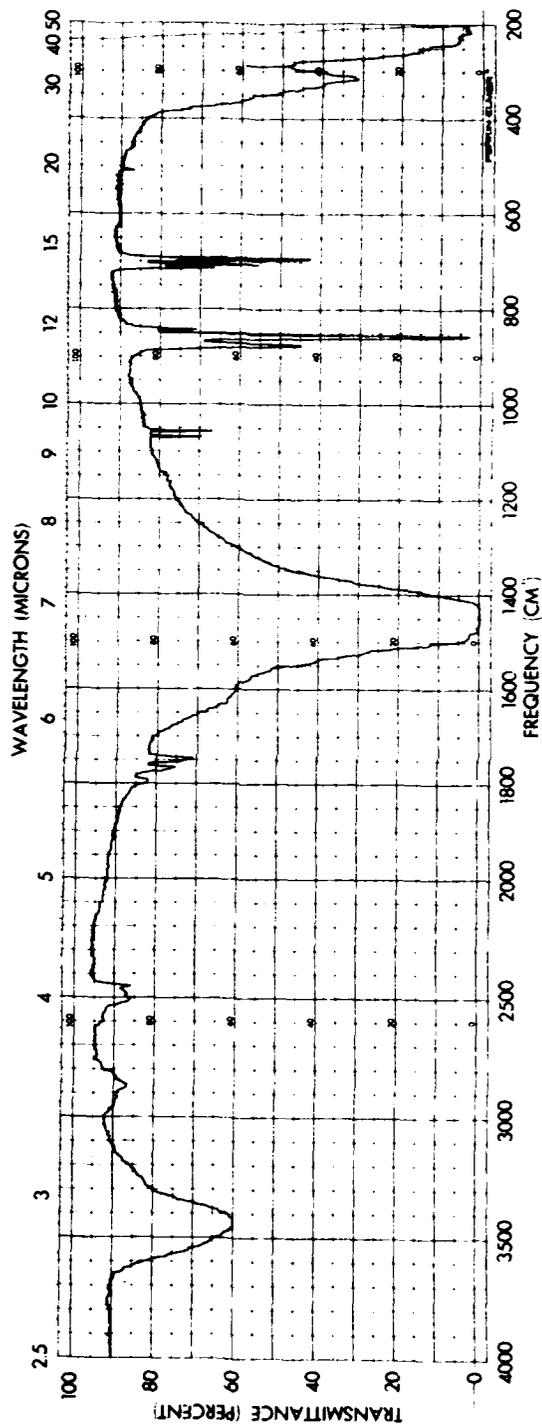


Figure 9. Spectrum of mixture of BaCO₃, SrCO₃, and CaCO₃ (1 to 1 to 1)

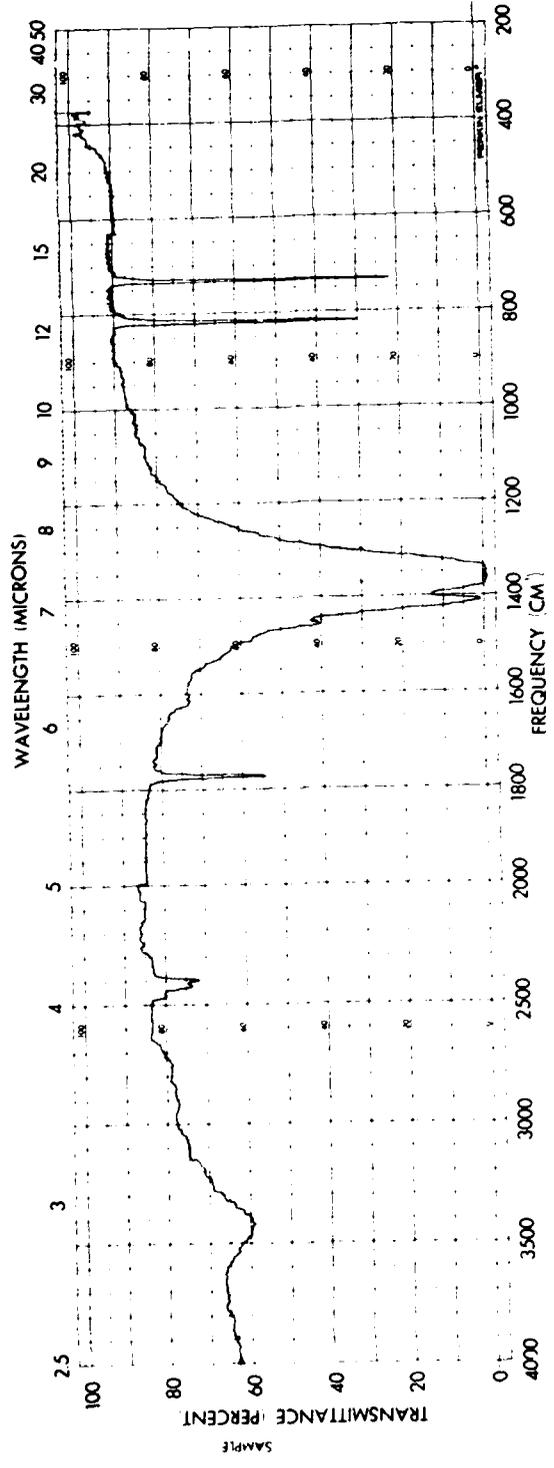


Figure 10. Spectrum of $Ba(NO_3)_2$

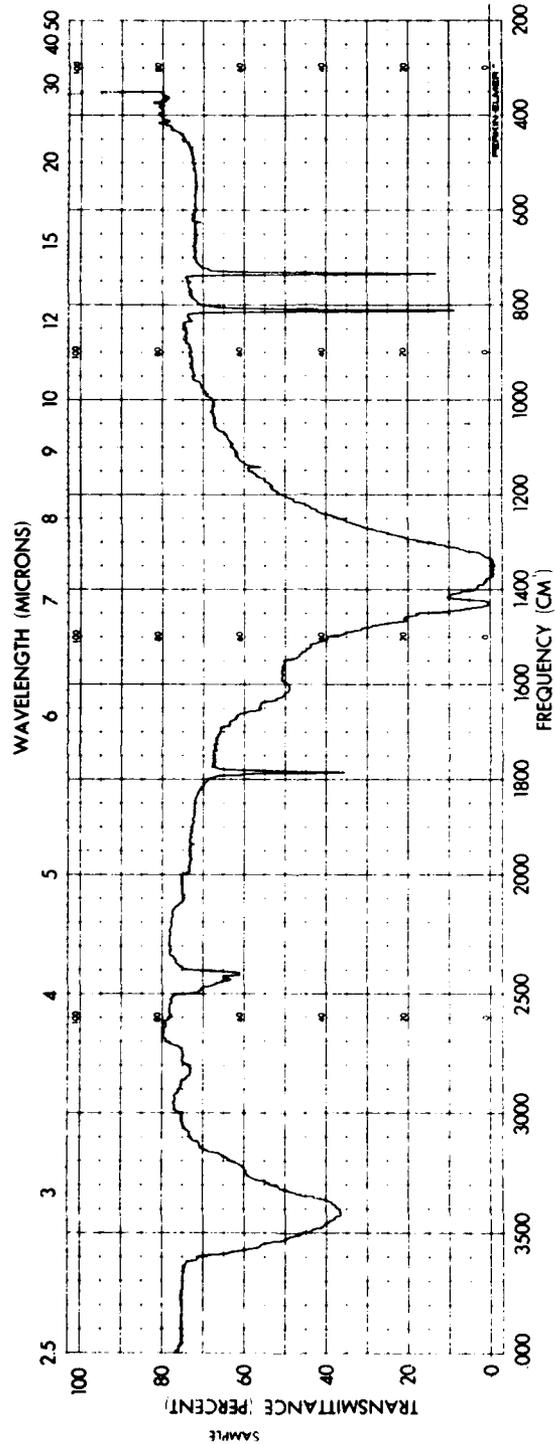


Figure 11. Spectrum of $\text{Sr}(\text{NO}_3)_2$

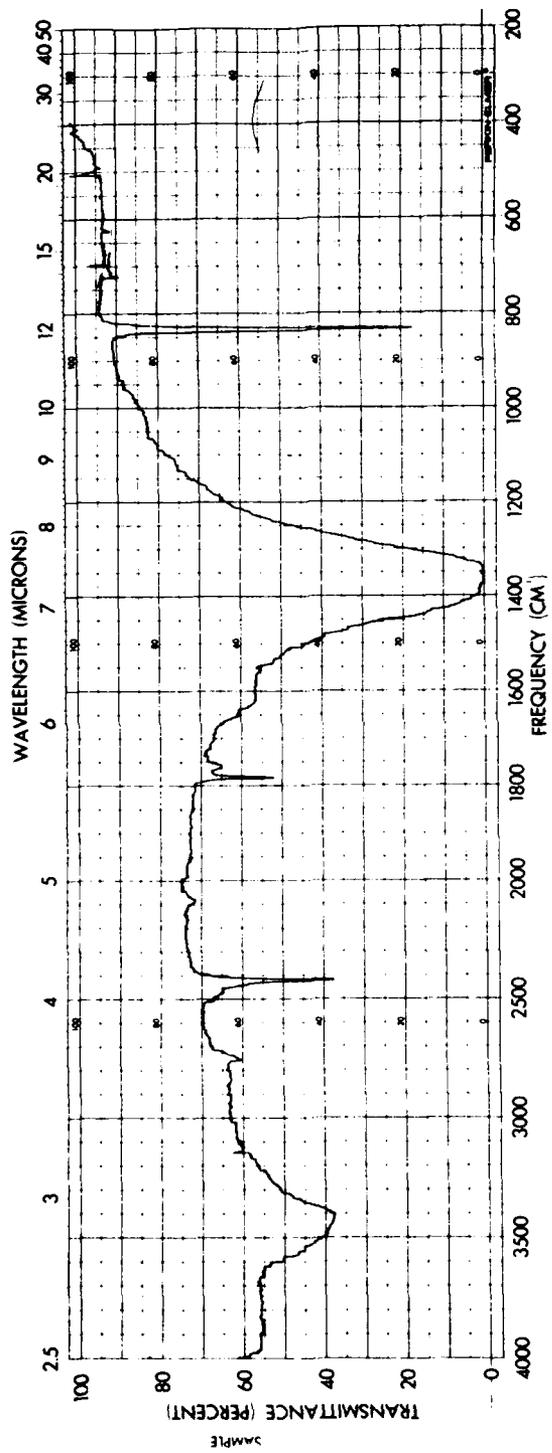


Figure 12. Spectrum of NaNO₃

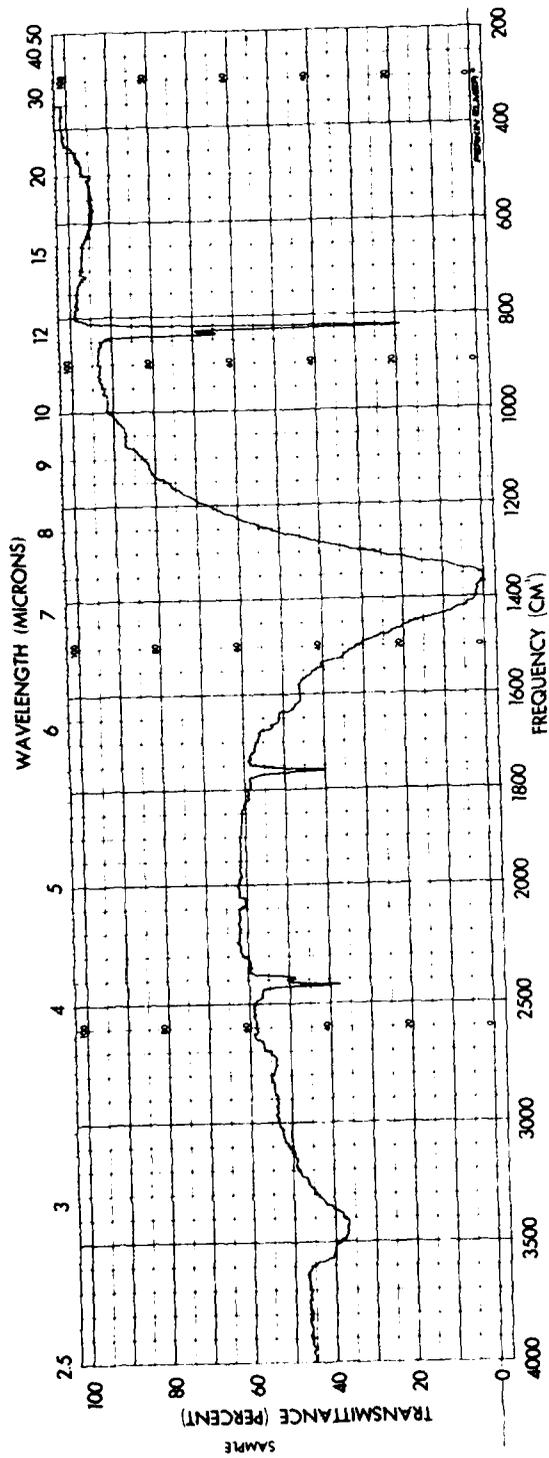


Figure 13. Spectrum of KNO₃

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

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13. ABSTRACT The infrared spectra of sulfates and carbonates in the solid state are discussed. Methods are proposed for the determination of single sulfates (barium, strontium, sodium, and potassium sulfates) by the pellet technique. The sample is weighed into a tared mortar using a semimicro balance and is mixed with 300 mg of potassium bromide. The pellet is then formed and the peak heights are determined at the appropriate peak. The peaks recommended for barium and strontium sulfates are 983 cm^{-1} and 993 cm^{-1} , respectively. Sodium and potassium sulfates are both measured at 619 cm^{-1} . A procedure is proposed for the determination of barium and strontium sulfates in the presence of each other by measurements at 983 cm^{-1} and 993 cm^{-1} , respectively. Methods are proposed for the determination of single carbonates (barium, strontium, and calcium carbonates) by the pellet technique. Measurements for the barium, strontium, and calcium carbonates are made at 693 cm^{-1} , 704 cm^{-1} , and 712 cm^{-1} , respectively. The procedure cannot be used for the determination of sodium or potassium carbonates because of the hygroscopicity of these compounds. A procedure is described for the determination of barium, strontium, and calcium carbonates in the presence of each other by measuring the peak heights at 693 cm^{-1} , 704 cm^{-1} (or 698 cm^{-1}), and 712 cm^{-1} , respectively. The methods for the determination of barium and strontium sulfates in the presence of each other, and barium, strontium, and calcium carbonates in the presence of each other can be used down a concentration of 5% for the minor constituent. For lower percentages the errors are rather large.			

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14. KEY WORDS	LINK A		LINK B		LINK C	
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Inorganic Sulfates						
Inorganic Carbonates						
Sodium Sulfate						
Potassium Sulfate						
Barium Sulfate						
Strontium Sulfate						
Barium Carbonate						
Strontium Carbonate						
Calcium Carbonate						
Infrared Spectra						