

VISUAL ARC SPECTROSCOPIC DETECTION OF HALOGENS, RARE EARTHS AND OTHER ELEMENTS BY USE OF MOLECULAR SPECTRA¹

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ABSTRACT

Cl, F, Br, Y, Sc, La, B, Al, Be, Ca and Zr may be detected in minerals by visual arc spectroscopic observation of molecular or band spectra. The versatility of the simple bunsen spectroscope is greatly enhanced through the application of molecular spectroscopy. A reference chart showing the most characteristic spectra of the visible region is included.

INTRODUCTION

The usefulness of visual-arc spectroscopy in determinative mineralogy has been described recently by Peterson, Kauffman and Jaffe.³ The marked superiority of the spectroscopic technique over the usual blow-pipe and wet reagent qualitative tests for most elements has been further emphasized by Garbriel, Jaffe and Peterson⁴ and by Vreeland.⁵ The methods described in these papers were concerned largely with the detection of the cationic constituents of minerals by means of atomic or line spectra. Subsequently, an investigation was made of the molecular or band spectra of the visible region in order to determine whether any additional anions could be detected by this means. The study revealed that chlorine could be readily detected in minerals by observation of the CaCl bands. It was also determined that several of the cationic constituents emit band spectra which are in some instances more useful than the line spectra of the same elements. All of the molecular spectra described in this paper are classified according to Pearse and Gaydon.⁶

GENERAL

Arc excitation of the various elements gives rise to a change of electronic state, which in turn gives rise to line spectra for excited atoms and band spectra for excited molecules. In most instances, line spectra are

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³ Peterson, M. J., Kauffman, A. J., Jr., and Jaffe, H. W., The spectroscope in determinative mineralogy: *Am. Mineral.*, **32**, 322-335 (1947).

⁴ Gabriel, A., Jaffe, H. W., and Peterson, M. J., Use of the spectroscope in the determination of the constituents of boiler scale and related compounds: *Proc. A.S.T.M.*, **47**, 1111-1120 (1947).

⁵ Vreeland, F. K., A direct reading analytical spectroscope: *Am. Mineral.*, **33**, 600-611 (1948).

⁶ Pearse, R. W. B., and Gaydon, A. G., *The Identification of the Molecular Spectra*: New York, John Wiley and Sons, Inc. (1941).

of sufficient abundance and intensity to serve for detecting most of the elements occurring in minerals. In the case of fluorine, chlorine, boron and other elements, it becomes necessary to resort to a study of molecular or band spectra. These elements do not provide atomic or line spectra, in the visible region, of sufficient intensity to permit their detection by normal spectroscopic procedures. They do, however, give molecular spectra which may be easily identified. Study of the band spectra of other elements that do show sensitive line spectra is also helpful in that these give the simple bunsen spectroscope a much greater versatility. For example, the only sensitive spectral lines of Al in the visible region lie at 3961.5 Å and 3944.0 Å in the violet region of the spectrum. A sensitive band resulting from AlO,⁶ however, is situated in the blue green region of the spectrum, with its head at 4842.1 Å. By moving the telescope arm of the spectroscope to the blue-green region and observing the AlO band it is also possible to identify the line spectra of other elements that may be volatilizing at the same time and have spectral lines in the vicinity of the AlO band. The mineral beryl is a good example. Be and Al will volatilize at approximately the same time. Both elements give sensitive bands in the blue and blue-green region, but Be does not in the violet region. Although it is a simple matter to move the telescope arm back and forth, this may sometimes be avoided. Where trace constituents are being sought along with major constituents of like volatility, it is highly desirable to focus on one portion of the spectrum rather than to shift about, risking loss of detection of the trace constituent.

The spectroscopic assembly used in this laboratory has already been described in detail in other papers.^{3,4} Inasmuch as glass prisms are employed in place of the grating, the dispersion is nonlinear. For any one arbitrary field of view, the following portions of the visible spectrum may be observed:

	<i>Field of view</i>	<i>Range covered</i>
Red end	± 7800 to 6940 Å	± 860 Å
	6940 to 5520	1420
	5520 to 4830	690
	4830 to 4400	430
	4400 to 4120	280
	4120 to 3930	190
Violet end	3930 to ± 3880	± 50

The differences in the spectral range covered for each field of view illustrates the marked nonlinear dispersion of the prism-equipped spectroscope. The pros and cons of prism versus grating for *spectrographic* work

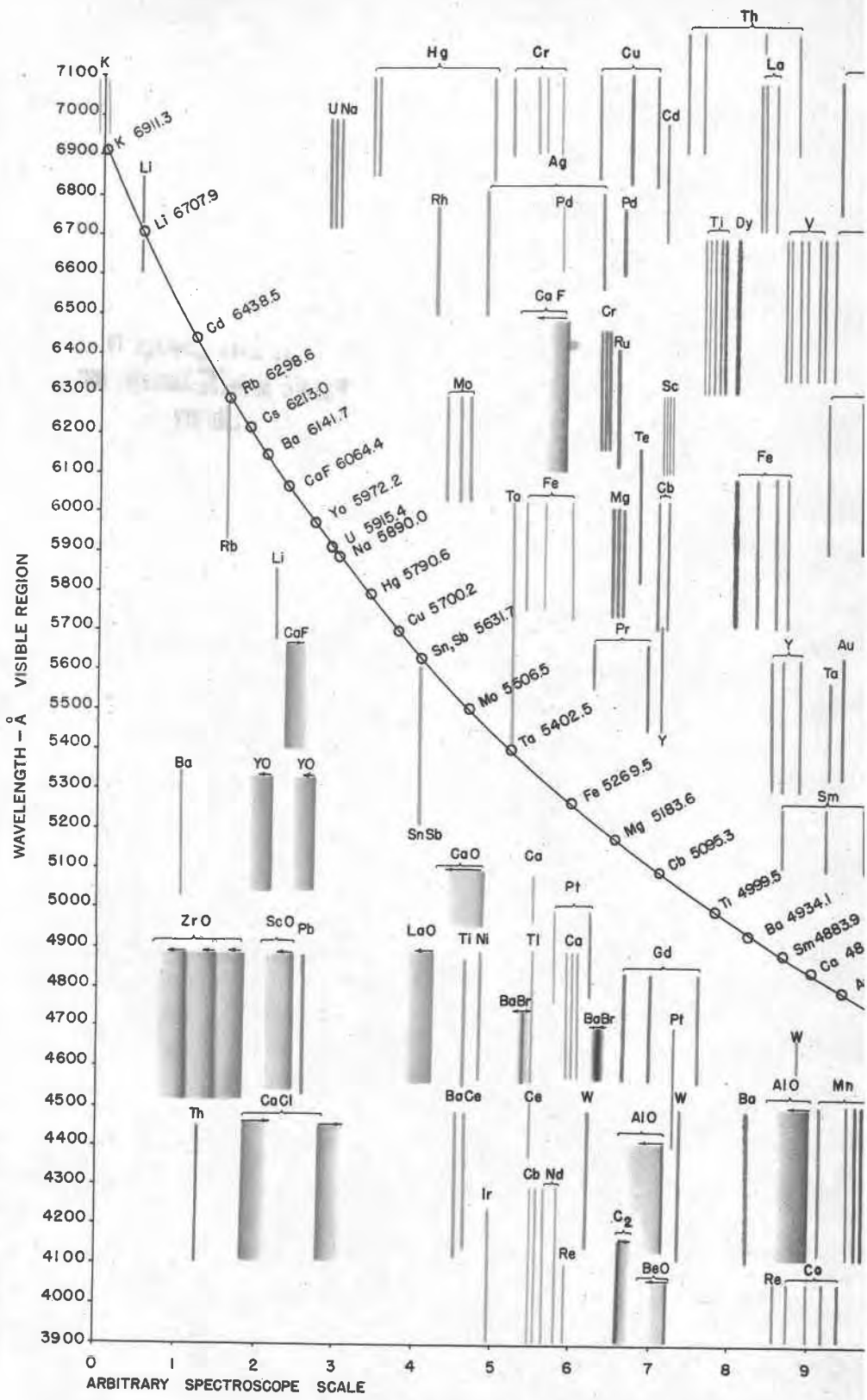
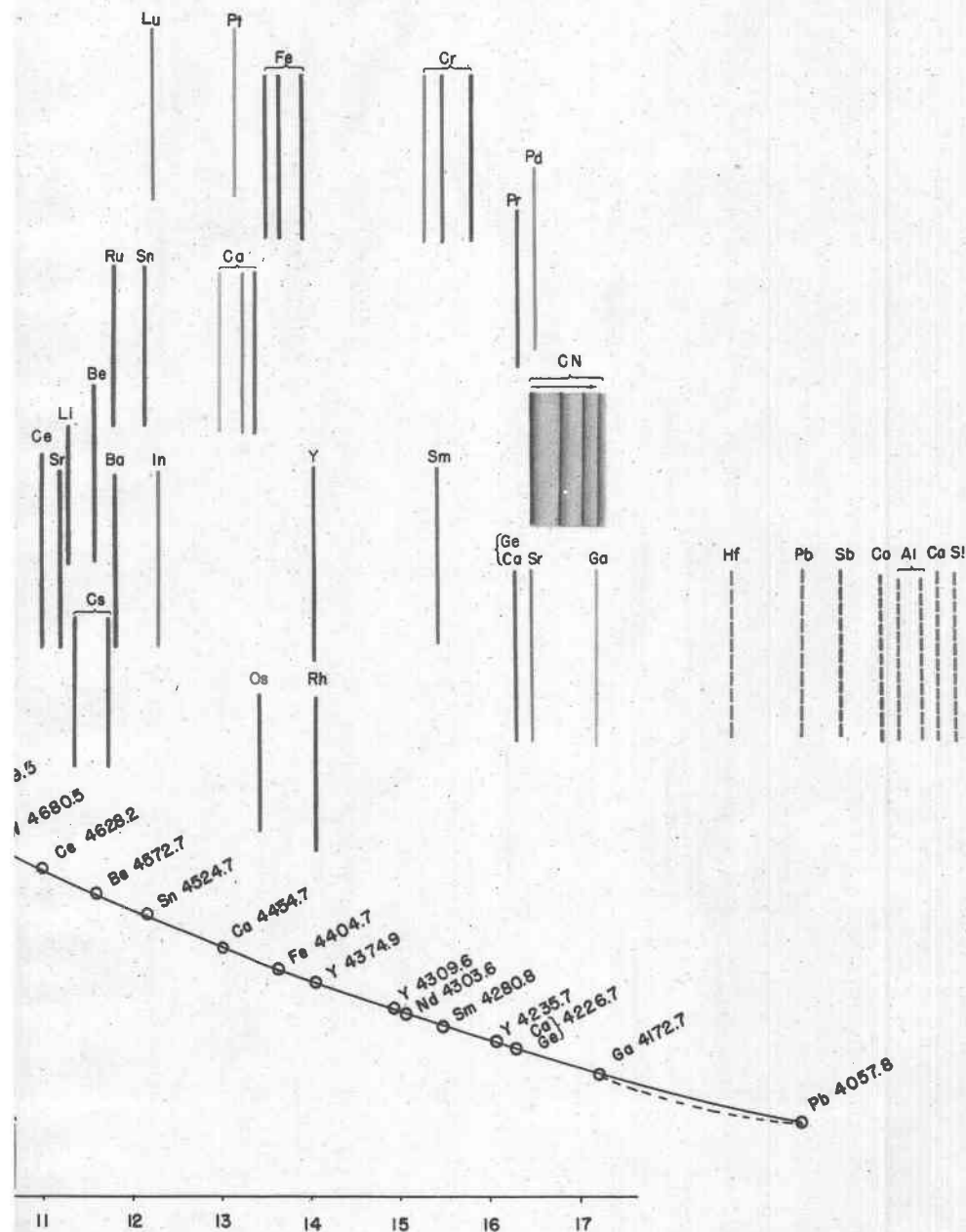


Figure 1 LINE AND BAND SPECTRA OBSERVED WITH A BUNSEN SPECTROSCOPE

Source of excitation_____D. C. Arc

Dispersion system_____two 60° flint glass prisms 27 x 54 mm



have been discussed elsewhere by M. Slavin.⁷ For visual *spectroscopic* analysis, the advantages resulting from the use of the prism or grating vary with the nature of the problem being studied. For rapid spectroscopic analyses of minerals, the author prefers the prism-equipped instrument. When a grating is used, many of the spectral lines and bands are too spread out to be viewed rapidly by the operator. Use of the prism affords many tight groups of spectral lines and narrow bands that may be rapidly recognized. The disadvantage of the prismatic lack of resolution in the red and orange areas is negligible for this type of analysis.

REFERENCE CHART OF THE VISIBLE SPECTRA

To familiarize the reader with the characteristic spectra of the visible region, a reference chart (Fig. 1) has been prepared. The chart shows the most sensitive visible molecular and atomic spectra of 62 elements. For a complete description of the equipment used and the operating conditions by which these spectra were obtained, the reader is referred to "The spectroscope in determinative mineralogy"⁸. By using a reference chart of this type, the inexperienced operator can readily familiarize himself with the positions of the various lines and bands of the different elements. By laying a straightedge along any particular line or band head he may also detect the presence of any interfering lines. The most sensitive spectral bands referred to in this paper are shown in Fig. 1.

DETECTION OF HALOGENS

1. Chlorine—This element may best be detected visually by observation of the CaCl bands⁶ in the red-orange region with heads at 6211.6 Å. and 5934.0 Å. Both bands are degraded to the violet or shorter wavelengths. The band at 5934.0 Å. appears as a very narrow band with a bright head and is easier to detect in low Cl concentrations than the band at 6211.6 Å. Pearse and Gaydon⁶ give intensities of 10 (based upon a scale of 10 for strongest band heads) for both of these bands but these are the result of spectrographic measurements rather than visual spectroscopic observations. On occasion these relative intensities may vary for several reasons. One of these is the source of excitation used; the author used only the D.C. carbon arc. Additionally, the eye sensitivity to the various colors varies, as do the photographic sensitivities of different film emulsions used in spectrographic work. In Table 1 the author has estimated the visual spectroscopic intensities of these and other bands which are offered for comparison with the intensities listed by Pearse and Gaydon.

⁷ Slavin, Morris, Prism Versus Grating for Spectrochemical Analysis: Proc. Seventh Conference on Spectroscopy (1939), John Wiley and Sons, 1940, pp. 51-58.

TABLE 1. PERSISTENT BAND HEADS* (in Carbon Arc only)

Molecule	Wavelength in Å	Direction Degraded	Intensity Spectro- graphic	Intensity Spectro- scopic
AlO	4842.1	Red	10	10
BO	Weak, diffuse, broad bands in the green	—	—	1
BaBr	5360.1	Headless	Very weak	1
BaBr	5208.2	Headless	Very weak	1
BaCl	5240.5	Red	10	4
BaCl	5136.0	Red	10	4
BeO	5075.2	Red	7	7
BeO	4708.7	Red	10	10
CaCl	6211.6	Violet	10	9
CaCl	5934.0	Violet	10	10
CaF	6064.4	Violet	10	10
CaF	5291.0	Red	10	10
CaO	5473.0	Red	10	10
LaO	5599.9	Red	10	10
LaO	4418.1	Red	10	9
LaO	4371.9	Red	10	9
ScO	6036.2	Red	10	10
ScO	4857.8	Red	5	6
YO	6132.1	Red	10	9
YO	5972.2	Red	10	10
YO	4817.4	Red	10	10
ZrO	6473.7	Red	10	8
ZrO	6344.9	Red	9	8
ZrO	6229.4	Red	9	8

* Adapted from Pearse and Gaydon.⁶

Chlorine may also be detected by observation of the BaCl bands in the green, with heads at 5240.5 Å. and 5136.0 Å. Both bands are degraded to the red or shorter wavelengths. Both of these appear as narrow bands with fuzzy, rather indistinct heads. Pearse and Gaydon give intensities of 10 to both bands. Visually, however, both BaCl bands have an approximate intensity of 4. For visual spectroscopic detection of Cl, therefore, the CaCl bands are preferred. Other molecules containing chlorine, not studied by the author, are thoroughly described by Pearse and Gaydon.

If a calcium-free mineral is to be checked for chlorine, a small amount of CaO or any other calcium salt may be added to the unknown to produce the CaCl molecular band. (Any such salt added should, of course, first be checked spectroscopically for purity.) Chlorine has been detected by the author in vanadinite, sodalite, apatite, sylvite, halite, atacamite,

calomel, pyromorphite and zunyite by observation of the two CaCl bands. The distinction of chlor-apatite from fluor-apatite is a simple one if this method is used. Such distinction can be made in less than 1 minute because both halogens volatilize very rapidly. Of five apatites examined, fluorine was a major constituent of four and a trace constituent of the other which contained major chlorine. Only one of the four fluor-apatites contained a trace of chlorine.

2. Fluorine—Visual spectroscopic detection of this halogen by observation of the yellow-green CaF band has previously been described by Peterson, Kauffman, and Jaffe³ and more recently by Jaffe.⁸ Spectrographic studies of this band were made by Papish, Hoag, and Snee,⁹ Pearse and Gaydon,⁶ Ahrens,¹⁰ and others. This band has its head at 5291.0 Å. and is degraded to the longer wavelengths. It is a broad band which culminates in a very sharp head rendering its detection a very simple matter. Less than 0.1 per cent of fluorine may be detected by visual observation of this very sensitive band. A second CaF band of equal prominence and sensitivity occurs in the red-orange region with its head at 6064.4 Å. This band is rather narrow, has a sharp head and is degraded to the shorter wavelengths. It may be used as an alternate when detection of the alkalies is being sought. Na, K, and Rb have their sensitive lines in this same portion of the visible region and like CaF, volatilize very rapidly. Both of the CaF bands appear to be brighter than those of any other molecule observed. To determine fluorine in calcium-free minerals, as with chlorine determinations, any pure salt of calcium may be added to the unknown.

3. Bromine—The only bands observed were those of the BaBr molecule.⁶ These occur in the yellow-green region with heads at 5360.1 Å. and 5208.2 Å. Both are very weak visually and do not show well-defined heads. Because of their poor sensitivity, they will not prove very useful for visual arc spectroscopic analysis of minerals.

4. Iodine—Although many molecules of this halogen give band spectra,⁶ none were observed in the visible region using the carbon arc as the source of excitation.

DETECTION OF RARE EARTHS

1. Yttrium—Although this element has several sensitive lines in the visible region, knowledge of its band spectra has proved useful, particularly when only a trace of this element is present. Yttrium is relatively

⁸ Jaffe, H. W., Reexamination of sphene (titanite): *Am. Mineral.*, **32**, 638 (1947).

⁹ Papish, J., Hoag, L. E., and Snee, W. E., Spectroscopic detection of fluorine: *Ind. and Eng. Chem.*, **2**, No. 3, 263-264 (1930).

¹⁰ Ahrens, L. H., The spectrochemical determination of fluorine in phosphate rock: *J. S. African Chem. Inst.*, **25**, 18-32 (1942).

refractory and one of the last elements to volatilize in some minerals. Where a spectroscopic trace is present, the atomic line and molecular band spectra will flash intermittently, particularly if the amperage is kept low. When only a few such flashes are to be observed, the broad conspicuous YO bands are easier to see than any of the Y lines. By observation of the YO bands in the red-orange region, the author can detect the yttrium commonly present in apatites; normally less than 0.5 per cent of Y_2O_3 . In other minerals, it has been detected in concentrations as low as 0.01 per cent.

Bands resulting from the YO molecule⁶ occur in the red-orange region with heads at 6132.1 Å. and 5972.2 Å. A third band with a head at 4817.4 Å. is situated in the blue. All three bands are degraded to the red or longer wavelengths. Inasmuch as many other refractory elements have lines and bands in the blue, especially titanium, it is better to use the red-orange bands in order to avoid interference.

2. Scandium—Although this element may not be as prevalent in minerals as other rare earths, a knowledge of its molecular spectra may prove helpful. Bands of ScO^6 occur in the red-orange and in the blue with heads at 6036.2 Å. and 4857.8 Å., respectively. Both are degraded to the longer wavelengths. The intensities favor the use of the red-orange band. Scandium has been observed in some micas, tourmalines and garnets where it occurs in concentrations of less than 0.1 per cent of Sc_2O_3 .

3. Lanthanum—This element has three LaO bands⁶ all degraded to the longer wavelengths. They culminate in relatively sharp heads at 5599.9 Å., 4418.1 Å. and 4371.9 Å. These are useful when the very sensitive La doublet at 4921.8 Å. and 4921.0 Å. is covered by interference from Fe or other lines. Lanthanum traces have been detected by the author in several apatites, where it commonly occurs in concentrations of less than 0.1 per cent of La_2O_3 .

Cerium, praeosodymium, samarium, neodymium and erbium all have spectral lines that are more conspicuous than any molecular bands observed. The author has not studied the other rare earths in any detail due to the difficulty of obtaining uncontaminated salts.

OTHER USEFUL BAND SPECTRA

1. Aluminum—The utility of the AlO band in the blue-green region has been discussed in the "General" section of this paper. It is a broad band, culminating in a sharp head at 4842.1 Å., and is degraded to the red. Other less sensitive bands occur in the green spectral region.

2. Boron—This element does not show any bright or conspicuous band heads in the visible region. It does, however, have a series of broad diffuse

bands which cloud the entire green region of the spectrum in a characteristic manner. This is attributed to the BO molecule.⁶ The veiled appearance, its early volatility and the green arc image color are diagnostic. Traces of boron cannot be detected visually but the element is readily detectable in tourmaline, axinite and other boron minerals.

3. Beryllium—This element has but one atomic spectral line in the visible region, at 4572.7 Å., which is usable. When this line is covered by interference, the BeO bands⁶ in the blue-green region are indispensable alternates. These have band heads at 5075.2 Å. and 4708.7 Å. Both are degraded to the longer wavelengths.

4. Calcium—This element has a very complicated system of CaO bands⁶ in the red-orange region. They are bright bands but overlap and for this reason are not too easily identified visually. A broad band in the yellow-green is easier to detect and is sometimes useful. The band head is at 5473.0 Å and is degraded to the red. It is interesting to note that, when a sample of fluorite is volatilized in the carbon arc, lines of Ca, bands of CaF and bands of CaO are all readily discernible. In apatites, the CaCl bands may also be present at the same time.

5. Zirconium—This element gives a very complex line spectrum in the visible region. The strong lines in the blue, however, are sometimes interfered with by lines of titanium, molybdenum and other refractory elements. Because of this, a trio of ZrO bands⁶ in the red are on occasion helpful. These culminate in distinct heads at 6473.7 Å., 6344.9 Å. and 6229.4 Å. All are degraded to the longer wavelengths.

6. Thorium—Pearse and Gaydon⁶ and other reference books do not list any molecular spectra of which thorium is a constituent. However, the element has a number of lines lying between 6408.6 Å. and 6416.1 Å. in the red portion of the spectrum. These lines are not resolved and are seen as a conspicuous narrow "band." The author has found this "band" to be more sensitive visually than any of the four individual thorium lines in the green and blue spectral region. Inasmuch as this element often occurs in minerals containing appreciable amounts of rare earths, which are of like volatility, it is difficult to detect the Th lines in the green and blue region. For example, lines of Ce, La, Y and Nd commonly interfere with the detection of thorium. By use of the "band" in the red region, however, the operator can avoid the otherwise serious effects of interfering lines. Thus far, thorium has been detected in every monazite examined, by observation of the "band." It could not be detected in several of these by use of other line spectra. The thoria content of different monazites, however, shows a marked variation.

The thorium lines are not nearly so sensitive as those of the rare earths and trace amounts cannot be detected by visual spectroscopy.

CONCLUSIONS

1. In visual spectroscopic work, F, Cl, Br and B may be identified in minerals only by observation of molecular or band spectra.
2. Molecular spectra are in some instances more useful than atomic or line spectra for the detection of some elements by means of visual arc spectroscopy. (E.g., the YO bands appear to be more sensitive than the Y lines.)
3. Where spectral lines of one element are hidden by interfering lines of another element, a knowledge of band spectra is indispensable. (E.g., use of the BeO bands when the only usable Be line is hidden.)

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