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DETERMINATION OF LORANDITE AND REALGAR IN MINERAL MIXTURES USING INFRARED SPECTROSCOPY

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Abstract: The appearance, in the infrared spectrum of lorandite, $Tl_2As_2S_4$, of a band at 401 cm^{-1} (well above the bands appearing in the spectrum of realgar) made it possible to use infrared spectroscopic methods not only to detect the presence of small quantities of lorandite in realgar but also to estimate its content even when it was as low as 0.5%. The methods of infrared spectroscopy were, furthermore, used to detect the presence of realgar impurities in the mechanically separated lorandite minerals and to determine their contents. This was possible because a band at 359 cm^{-1} present in the spectrum of realgar lies outside the regions masked by lorandite bands. The sensitivity was lower than in the previous case and the limit of detection was around 4% realgar in lorandite.

Key words: Infrared spectra, lorandite, realgar, quantitative determination, minerals, Alšar mine.

INTRODUCTION

It was shown quite some time ago (Freedman et al., 1976) that the thallium mineral lorandite, $Tl_2As_2S_4$, found in the Alšar mine in Macedonia could be used as a geochemical detector for solar neutrinos. However, lorandite is, as a rule, accompanied by other minerals present in the same locality (such as realgar, As_4S_4, and orpiment, As_2S_3) and if it is to be used as a solar neutrino detector, it must be separated from its undesirable companions.

Because of this, it is necessary to be able to detect the presence of mineral impurities and to determine (or, at least, estimate) their content. On the other hand, in order not to lose the precious lorandite, it is advisable to know whether the minerals rejected as impurity still contain lorandite. In this respect is the analysis of lorandite-realgar mixtures is particularly important because of the resemblance of the two minerals.

When the content of realgar in lorandite (or vice versa) is *low*, the frequently used experimental techniques are either unable to provide satisfactory results (e.g. X ray diffraction) or are time-consuming (microscopic studies). In such cases, infrared spectroscopy can be put to efficient use. The samples

used to record the infrared spectra are small and the duration of the analysis is short.

As with other spectrometric methods, the infrared are based on the measurement of the intensity of selected bands in the spectrum of the sample studied. These bands (known as analytical bands) should appear in spectral regions in which the other constituents of the system studied do not exhibit appreciable absorption. The study of the infrared spectra of lorandite and realgar (Trajkovska et al., 1990, 1992) has shown that analytical bands do exist in the spectra of both minerals. In the spectrum of lorandite such is the band at 401 cm^{-1} which appears in a frequency region well above the one where the bands of realgar are found (Trajkovska et al., 1990, 1992). On the other hand, in the spectrum of realgar there is also a band (at 359 cm^{-1}) which is not appreciably overlapped by the lorandite bands. The existence of such bands makes it possible to use the study of the infrared spectra to quantitatively determine small amounts of lorandite in realgar or vice versa - to make determination of the realgar impurities in mechanically separated lorandite crystals.

EXPERIMENTAL

All the minerals studied were from the Alšar deposit near Kavadarci in Macedonia. They were carefully hand-picked under a microscope from the ore samples in which they were found.

Artificial mixtures of lorandite and realgar were prepared by simply mixing appropriate amounts of pure minerals. The total mass of the samples taken for analysis was 2 mg. In obtaining the calibration curve subsequently used to determine the amount of lorandite in its mixtures with realgar, the mass fraction of lorandite varied from 0 to 0.5 (this corresponds to

masses of lorandite ranging from 0 to 1 mg). In the opposite case, the mass fraction of realgar ranged from 0.1 to 0.5 (10 to 50 %), corresponding to realgar masses of 0.2-1 mg. The mixtures of lorandite and realgar were dispersed in 250 mg of KBr and a pellet was made using standard procedures. From these KBr pellets the infrared spectra were recorded on a Perkin-Elmer 580 spectrophotometer. Using the method of base lines, the relative intensities of the analytical bands were measured and used to construct the calibration diagrams. The intensities were expressed as $\log(I_0/I)$.

RESULTS AND DISCUSSION

Lorandite in realgar

The infrared spectra of mixtures of lorandite with realgar are shown in Fig. 1. As can be seen, the increase in the lorandite content results in an augmentation of the 401 cm^{-1} band intensity. As shown in Fig. 2, the relationship between the two quantities is linear, the regression analysis leading to the equations

$$\log(I_0/I) = 2.4520 \cdot 10^{-3} + 1.4010 \cdot 10^{-3} \cdot w(\text{lorandite})$$

(with a correlation coefficient $r = 0.9992$) or

$$w(\text{lorandite}) = 712.6451 \cdot \log(I_0/I) - 1.7235$$

(with $r = 0.9992$).

By measuring the intensities of the 401 cm^{-1} band in ten mixtures with the same mass fractions of lorandite (or, alternatively, of realgar), the precision of the method (expressed as the relative standard deviation, s_r) was estimated. It was found that s_r is in the range 1.3-15.7%. For the studied range of lorandite content, the precision can be considered satisfactory. By determining the standard deviations of the sample with minimal value for the lorandite mass fraction, the limit of detection (taken to be equal to 3 s) was found to be 0.5 %.

The procedure described above was further checked by the method of standard additions. In a sample from the Alšar deposit, the content of lorandite was determined and the sample was then divided into a number of smaller samples. To each of these, varying (but precisely known) amounts of lorandite were added, KBr pellets were prepared and the infrared spectra were recorded.

From the intensities of the 401 cm^{-1} band, using the second of the equations given above, the mass of lorandite in each of the samples was determined. The results are summarized in Table I where R denotes the

ratio of the mass found in this way and the mass of the added lorandite. As can be seen, R is in the range 0.942-0.979 (94.2-97.9 %). The high values for R confirm the suitability of infrared spectroscopic methods for determining the lorandite content in its mixtures with realgar.

Table I

Calculated and found values for the lorandite mass m, using the method of standard additions

m(added)/mg	m(calculated)/mg	m(found)/mg	R
-	-	0.228	-
0.100	0.328	0.309	0.9421
0.200	0.428	0.419	0.9790
0.300	0.528	0.506	0.9583

Realgar in lorandite

The infrared spectra of lorandite samples containing realgar are shown in Fig. 3. As can be seen, the increase in the realgar content causes an increase in the intensity of the 359 cm^{-1} band. As shown in Fig. 4, the relationship between $\log(I_0/I)$ and the mass fraction of realgar appears to be linear. The regression analysis led to the equations

$$\log(I_0/I) = -2.890 \cdot 10^{-4} + 1.120 \cdot 10^{-4} \cdot w(\text{realgar})$$

(with $r = 0.99394$) or

$$w(\text{realgar}) = 8809.832 \cdot \log(I_0/I) + 2.874$$

(with $r = 0.99394$).

As in the previous case, the precision of the method (measured by the value of the relative standard deviation s_r) was estimated. It was found that the value
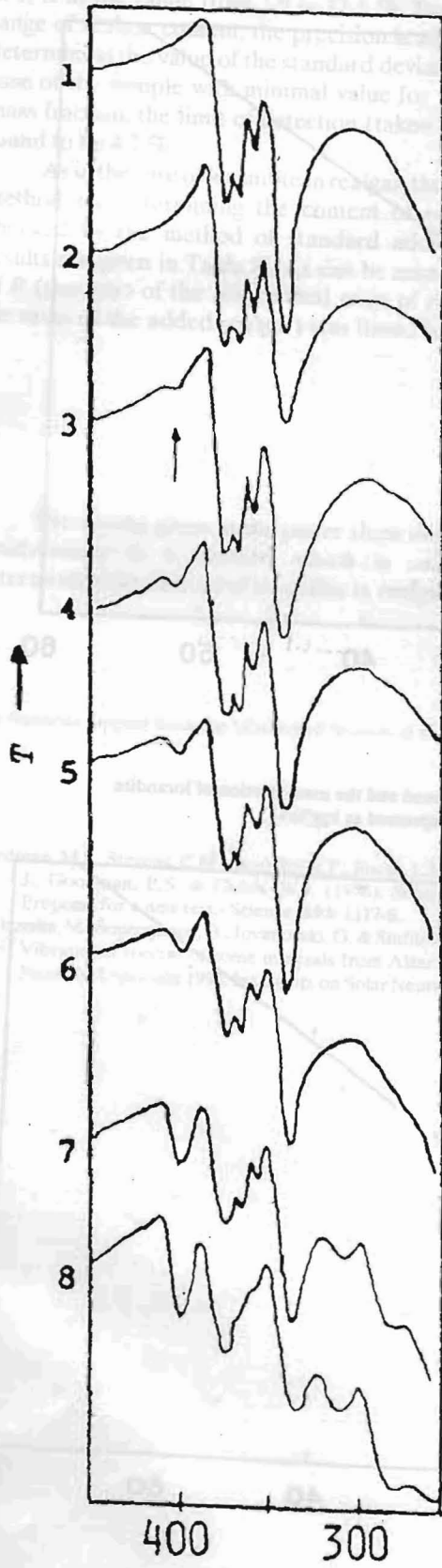
Fig.1. Infrared spectra of lorandite-realgar mixtures (the lorandite content increases on passing from curve 2 to curve 8)
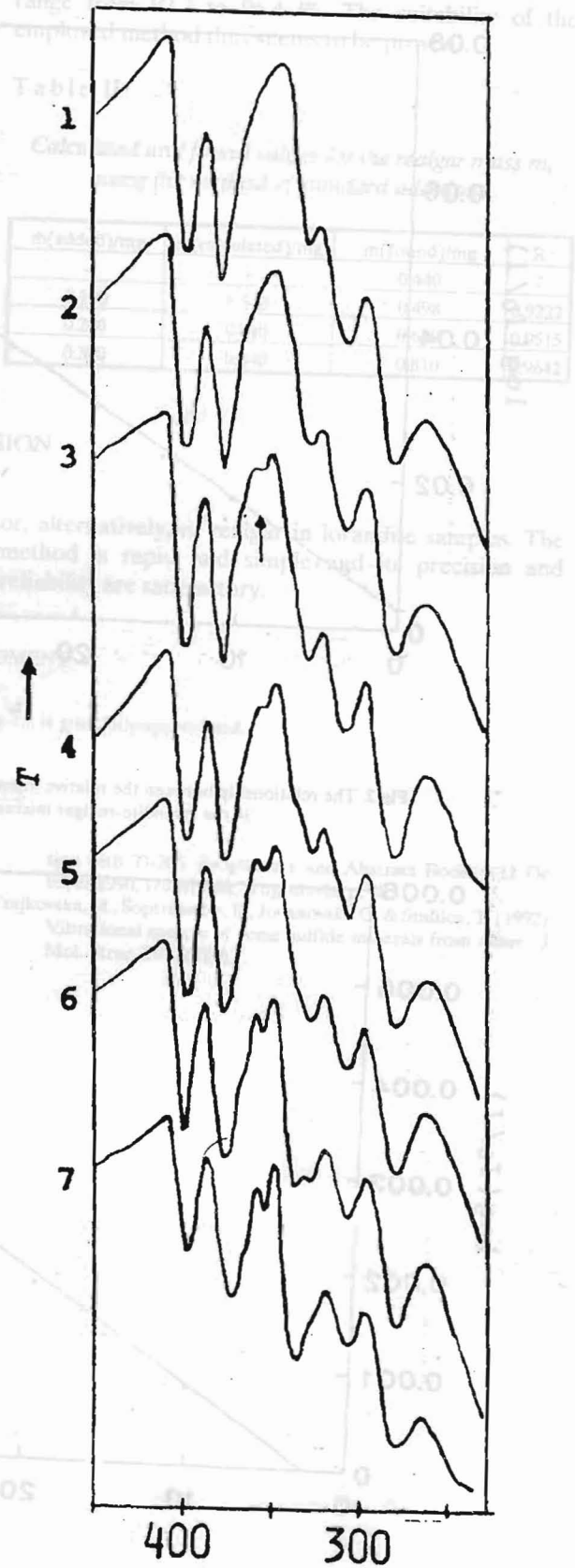
Fig. 3. Infrared spectra of lorandite samples containing realgar (the realgar content increases on passing from curve 2 to curve 8)
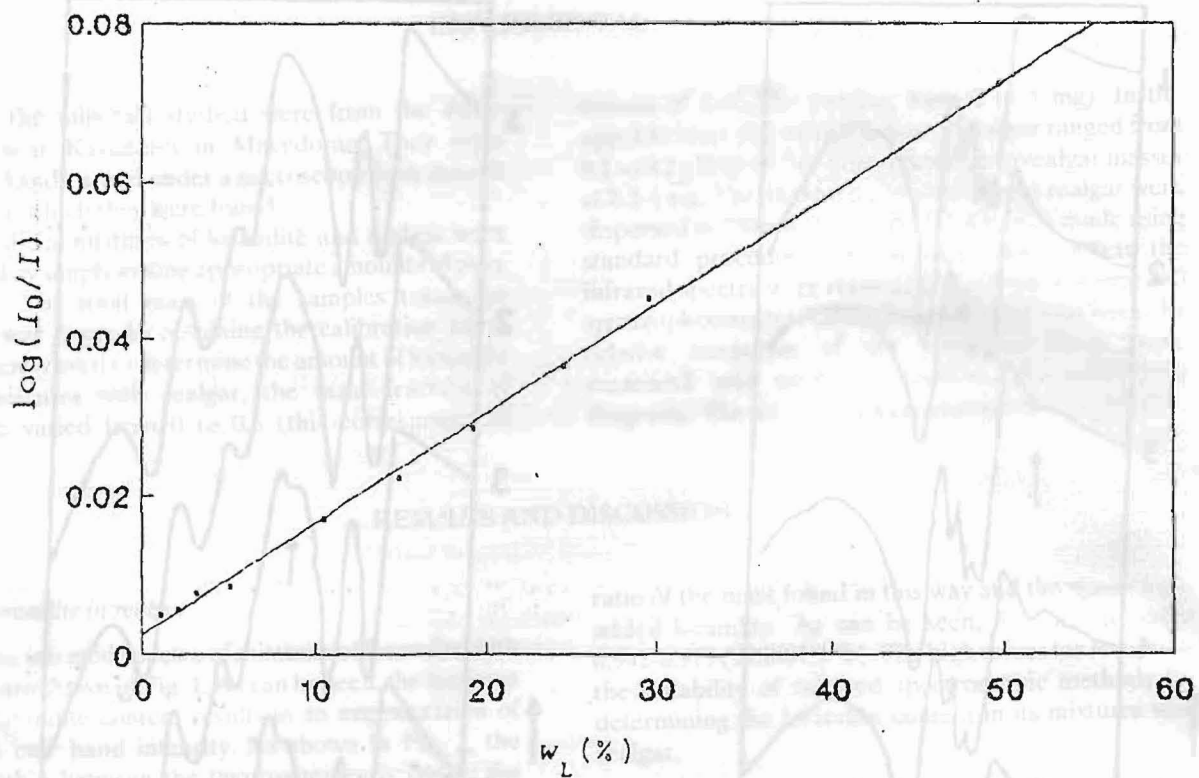
Fig.2. The relationship between the relative intensity of the 401 cm^{-1} band and the mass fraction of lorandite
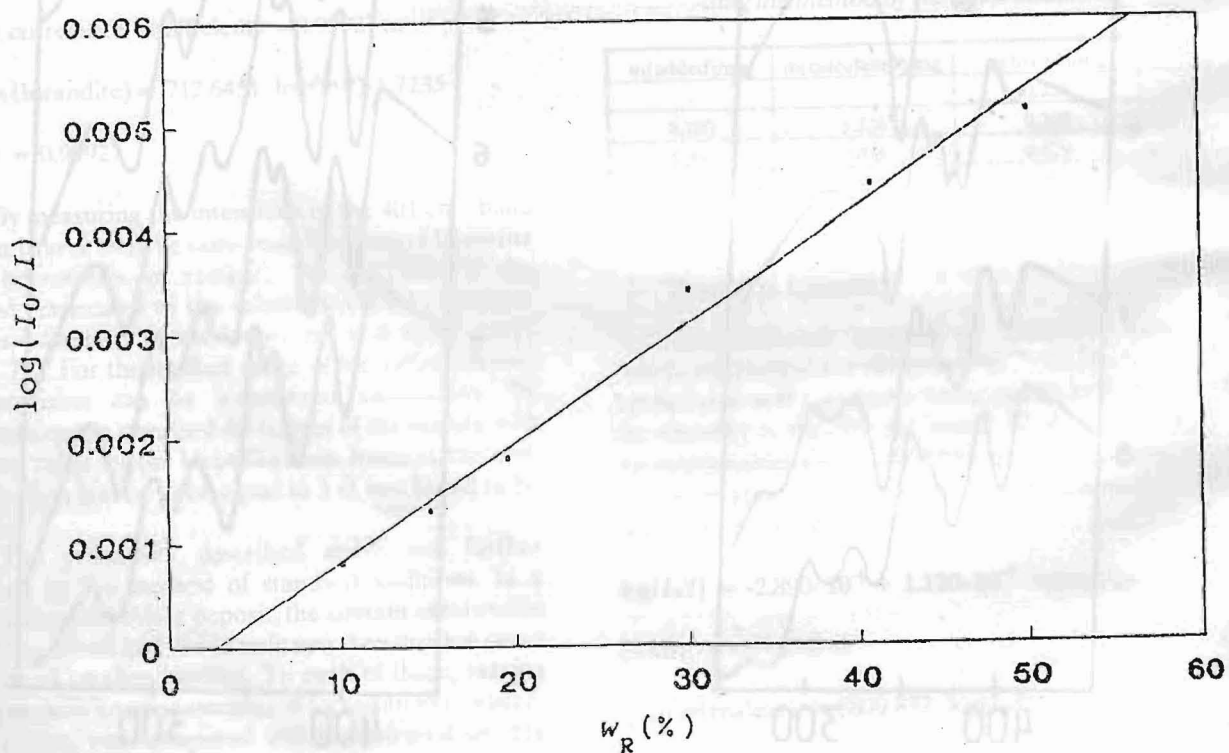in the lorandite-realgar mixtures. The intensity is expressed as log(I_0/I)

Fig.4. The relationship between the relative intensity of the 359 cm^{-1} band and the mass fraction of realgar
in the lorandite-realgar mixtures. The intensity is expressed as log(I_0/I).

of s_r is in the range from 1.9 to 12.1 %. For the given range of realgar content, the precision is adequate. By determining the value of the standard deviation s in the case of the sample with minimal value for the realgar mass fraction, the limit of detection (taken as 3 s) was found to be 4.2 %.

As in the case of lorandite in realgar, the described method for determining the content of realgar was checked by the method of standard additions. The results are given in Table II. As can be seen, the value of R (the ratio of the determined mass of realgar and the mass of the added realgar) was found to be in the range from 92.2 to 96.4 %. The suitability of the employed method thus seems to be proven.

T a b l e II

Calculated and found values for the realgar mass m, using the method of standard additions

m(added)/mg	m(calculated)/mg	m(found)/mg	R
-	-	0.440	-
0.100	0.540	0.498	0.9222
0.200	0.640	0.609	0.9515
0.300	0.840	0.810	0.9642

CONCLUSION

The results given in the paper show that infrared spectroscopy is a method which is suitable for determining the content of lorandite in realgar samples or, alternatively, of realgar in lorandite samples. The method is rapid and simple and its precision and reliability are satisfactory.

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