

## **INFRARED SPECTROPHOTOMETRIC STUDY OF THE EGYPTIAN ECONOMIC BEACH MINERALS AS WELL AS THEIR ALTERNATION AND WEATHERING PRODUCTS**

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### **ABSTRACT**

An infrared spectrophotometric method is indicated by which the quantitative mineralogy of any beach black sand sample can be quickly, accurately and reproducibly determined regardless of the degree of alternation or the degree of weathering the sample has undergone.

From standard calibration curves obtained by using individual pure minerals, and with the aid of a synthetic mixture of the diagnostic minerals, the quantities and types of minerals present in the unknown samples can be rapidly determined.

### **INTRODUCTION**

The importance of the Egyptian delta beach sands stems from the presence of several economic minerals by appreciable tenors and the large extension of the deposit. These minerals are garnet, zircon, monazite, rutile, ilmenite, magnetite and hematite. The average frequencies of these minerals are: garnet 3.25%, zircon 3.5%, monazite 0.16%, rutile 1.25%, ilmenite 39%, magnetite 15%, and hematite 4%. The rest are gangue minerals composed mainly of green silicates, quartz, and feldspars [WASSEF, 1965, 1973].

The use of the infrared absorption spectrophotometer has found added usage in the mineralogical fields [KELLER *et al.*, 1952; LAUNER, 1952; TUDDENHAM and LYON, 1959; MONTEL, 1971]. The method has several distinct advantages. The sample can be taken directly in powdered form, excellent spectra can be obtained with samples that would be judged amorphous by X-ray diffraction, the petrography of a sample can be determined even if that sample is a small grain or rock chip. Moreover, certain mineral impurities are clearly detectable in the spectra of some minerals to be determined.

### **EXPERIMENTAL**

1) The pure mineral samples were prepared from an ore-dressing concentrate sample. Every mineral sample is purified by passing on heavy liquid (bromoform) to separate the light contaminations and highly altered grains. Using the stereomicroscope the clean and pure mineral needed are removed by a needle and collected. The collected grains are rinsed by ethyl alcohol and thus made ready for the analysis.

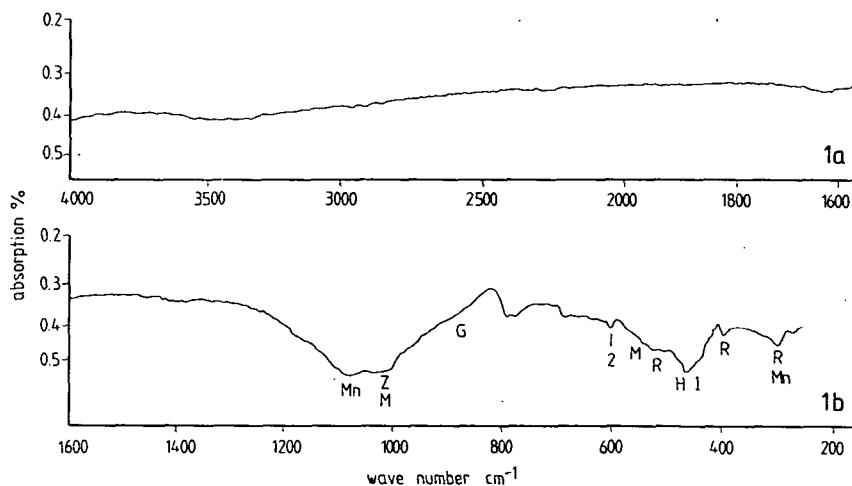
2) Infrared absorption spectra were obtained with KBr and CsI disks containing from 0.25 to 2% of the sample in question. These samples were preground under alcohol, mixing well with KBr or CsI in an electrical vibromill, weighing out enough of the blend to form a 12 mm diameter disk of the desired thickness and pressing under 12.5 tons pressure in a vacuum die. The absorption curves were obtained using

a Beckman Mod. 4240 double beam infrared spectrophotometer equipped with a dry air purge for the region  $400\text{--}200\text{ cm}^{-1}$ . The spectrum was measured in the range  $4000\text{--}200\text{ cm}^{-1}$ .

## RESULTS

*Figs. 1a and 1b* show the infrared spectrogram of the bromoform-sink Egyptian beach sample. Their absorption data are plotted in Table 1. It can be seen that the spectrum is very complicated especially with weak overtone and combination bands. The critical bands used for identification of each of the minerals are labelled (*Fig. 1*).

Since the instrument used in this study operates on the double beam principle, a synthetic mixture can be used in the reference beam and its absorption pattern will be removed from the final spectrogram of the unknown sample by simultaneous compensation. Thus, we can reproduce the individual curves for each of the seven minerals shown in *Fig. 2*. The amount of the calculated constituent minerals are: Garnet 3.0%, zircon 3.15%, monazite 0.14%, rutile 1.45%, ilmenite 42.0%, magnetite 13.5%, and hematite 5.4%. A detailed description of the individual infrared absorption spectral data have been given in Table 2.



*Fig. 1.* IR-spectra of the Egyptian beach heavy fraction minerals, Sp. G. > 2.85, in the range of  $4000\text{--}200\text{ cm}^{-1}$ . H: hematite, M: magnetite, I: ilmenite, R: rutile, Mn: monazite, Z: zircon and G: garnet

TABLE I

*Infrared absorption data of the Egyptian beach heavy fraction minerals. Sp. Gr.  $2.85\text{ g/cm}^3$*

Sample	Frequency ranges and absorption magnitudes
Bromoform sink Sp. Gr. $2.85\text{ g/cm}^3$	260 w, 300 w, 325 w, 330 w, 400 w, 450 w, 460 w, 530 w, 535 w, 545 w, 560 w, 577 w, 615 m, 625 wsh, 630 wsh, 655 w, 685 w, 855 s, 910 w, 930 w, 960 w, 1000 w, 1040 w, 1050 w, 1060 w, 1250 w, 1280 w, 1370 w, 1430 w, 1470 w, 1640 m, 1650 m, 1690 w, 1720 w, 1770 w, 1830 m, 1980 w, 2020 w, 2200 w, 2300 m, 2700 m, 3250 bs, 3250—4000 mb.

Absorption magnitudes; s (strong), m (medium), w (weak), sh (shoulder), b (broad).

TABLE 2

*Infrared absorption data from separated Egyptian economic beach minerals*

Mineral and symbol	Frequency ranges and absorption magnitudes ( $\text{cm}^{-1}$ )
Almandine-pyrop Garnet (G)	385 m, 460 s, 488 s, 577 s, 650 wsh, 885 s, 910 s, 975 s, 1000 wsh, 1060 wsh, 1100 vwsh, 1140 vwsh, 1420 w, 1450 w, 1625 w, 2738 w, 3380 mb.
Zircon (Z)	315 m, 385 m, 445 s, 600 m, 618 m, 860 sh, 910 s, 1000 bs
Monazite (Mn)	300 m, 495 sh, 545 m, 563 m, 590 wsh, 625 w, 910 w, 1050 xbs, 3000 b
Rutile (R)	300 m, 400 m, 460 sh, 535 s, 570 m, 1040 w.
Ilmenite (I)	325 m, 400 w, 420 w, 460 m, 485 w, 530 s, 570 sh, 590 sh, 630 sh, 760 sh, 810 w, 875 w, 1425 w, 1440 w, 1600 w, 2200 w, 3200–3600 w.
Magnetite (M)	490 m, 575 s, 1000 m, 2200 xbs.
Hematite (H)	333 w, 470 s, 560 s, 630 sh, 1060 w.

Absorption magnitudes; s (strong,) m (medium), w (weak), sh (shoulder), b (broad), x (extra), v (very).

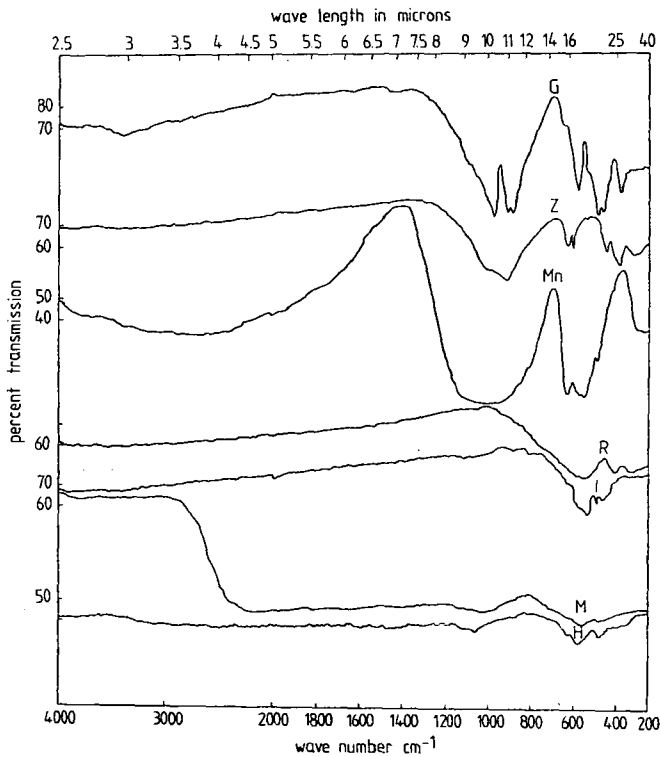


Fig. 2. IR-spectra of the Egyptian economic beach minerals. H: hematite, M: magnetite, I: ilmenite, R: rutile, Mn: monazite, Z: zircon and G: garnet

### *Almandine-Pyrope Garnet*

The free silicates ion has a tetrahedral symmetry and belongs to point group  $T_d$ . Its nine normal modes of vibration are, in HERZBERG's [1964] notation,  $\nu_1$  (non degenerated),  $\nu_2$  (doubly degenerated),  $\nu_3$  and  $\nu_4$  (each triply degenerated).

In the garnet sample examined a medium peak at  $385\text{ cm}^{-1}$  shifted from  $415\text{ cm}^{-1}$  is due to the substitution of the larger ion of  $\text{Fe}^{2+}$  with the smaller  $\text{Mg}^{2+}$ ; this band is attributed in part to the  $\nu_2$  of  $\text{SiO}_4$  tetrahedra and an unspecified mode of  $\text{MgO}_6$  octahedra.

The strong band at  $460\text{ cm}^{-1}$  is due to  $\text{Fe}_2\text{O}_3$  [GORE, 1972]. This is clearly seen in the spectra of hematite, magnetite and ilmenite while the strong bands at  $488$  and  $577\text{ cm}^{-1}$  could be assigned to  $\nu_4$ .

Silicates absorb strongly in the range  $800\text{--}1100\text{ cm}^{-1}$  ( $\nu_3$ ). However, the shape of the absorption bands differ considerably between the different silicates. Thus, in case of garnet the peak at  $909\text{ cm}^{-1}$  splits into two peaks at  $885$  and  $910\text{ cm}^{-1}$ , respectively, and there is a strong peak at  $975\text{ cm}^{-1}$  while there are two small shoulders at  $1000$  and  $1060\text{ cm}^{-1}$ .

The infrared shifted spectrum suggests that the  $\text{SiO}_4$  tetrahedra in these silicates garnets are strongly affected by the metal oxide bonds and alteration products.

It is interesting to notice that the garnet spectrum herein matches that given by OMORI [1971] for almandine-pyrope garnet from Nijosan, Osaka Prefecture, Japan, except for the two carbonate bands at  $1420$  and  $1450\text{ cm}^{-1}$  which could be due to small alteration to calcite or the presence of calcite in the pitted garnet grains.

There is more than one way of fitting the hydroxyl ion as it is clear from the bands at  $1625\text{ cm}^{-1}$ ,  $2738\text{ cm}^{-1}$  and  $3380\text{ cm}^{-1}$  which may be due to alteration.

### *Zircon*

The bands at  $910$  and  $1000\text{ cm}^{-1}$  are transitions to crystal field split  $\nu_3$  levels. There is also a large crystal field splitting in  $\nu_4$  whose observed crystal levels are  $600\text{ cm}^{-1}$  and  $445\text{ cm}^{-1}$ .

The band at  $385\text{ cm}^{-1}$  is an external rotary mode in which the silicates ion executes partial rotation about the „a” axis while the band at  $315\text{ cm}^{-1}$  is an external or lattice mode involving the translatory motion of the positive zirconium ion with respect to the negative silicate ion.

The main difference between garnet and zircon as orthosilicate minerals is that the  $\text{SiO}_4$  tetrahedra in garnet share corners with an octahedron and edges with a dodecahedron [GIBBS and SMITH, [1965], whereas in zircon the tetrahedron and  $\text{ZrO}_6$  dodecahedra share edges [ROBINSON *et al.*, 1971].

### *Monazite*

In the spectrum of monazite an extra broad band occurs due to ionic phosphate vibration  $\text{PO}_4^{-3}$  with an absorption maximum at  $1050\text{ cm}^{-1}$  caused by P—O stretching vibration [COLTHUP *et al.*, 1964].

The  $625\text{ cm}^{-1}$ ,  $545\text{ cm}^{-1}$ ,  $495\text{ cm}^{-1}$  and  $300\text{ cm}^{-1}$  bands appear in the spectrum of the standard monazite sample and according to McDEVIT and WILLIAM [1964], this could be due to a group of rare earth oxides. The broad absorption band around  $3000\text{ cm}^{-1}$  may be due to hydrogen bound in water.

### *Rutile*

The spectrum of rutile shows a strong band at  $535\text{ cm}^{-1}$  and a medium one at  $400$  and  $300\text{ cm}^{-1}$  which is due to Ti—O stretching vibration. It is interesting that the weak band at  $1040\text{ cm}^{-1}$  is well defined in the spectrum of the synthetic rutile and hematite, and this may show exsolution intergrowth of rutile-hematite. A medium band at  $570\text{ cm}^{-1}$  may also confirm the presence of hematite.

### *Ilmenite*

The curve has an absorption band around  $530\text{ cm}^{-1}$  which may be due to TiO linkage and two medium absorption bands at  $460\text{ cm}^{-1}$  and  $325\text{ cm}^{-1}$  which may be due to FeO linkage. The studied ilmenite also absorbs over a wide range starting at  $590\text{ cm}^{-1}$ . Thus there is a carbonate band at  $1425\text{ cm}^{-1}$  and  $1440\text{ cm}^{-1}$ . Hydroxyl lattice group bands appear at  $1600\text{ cm}^{-1}$  and  $2200\text{ cm}^{-1}$ . There is an amount of loosely bound water evidenced by the water band at  $3200\text{--}3600\text{ cm}^{-1}$ . These could be due to the beginning of ilmenite alteration to leucoxene.

### *Magnetite*

Magnetite shows a strong band at  $575\text{ cm}^{-1}$  which is due to  $\text{Fe}_3\text{O}_4$  linkage. The  $490\text{ cm}^{-1}$  and  $1000\text{ cm}^{-1}$  bands could be due to  $\text{Fe}_2\text{O}_3$  mineral impurity. Some alteration to hydrated minerals is evidenced by the OH lattice group vibration at  $2200\text{ cm}^{-1}$ .

### *Hematite*

The strong band at  $560\text{ cm}^{-1}$  is the mean value of bands of almost equal intensities reported by McDEVIT and WILLIAM [1964] at  $540\text{ cm}^{-1}$  and  $590\text{ cm}^{-1}$ . Another strong band appears at  $470\text{ cm}^{-1}$  which is due to  $\text{Fe}_2\text{O}_3$  [GORE, 1972], but the weak bands at  $333$ ,  $630$ , and  $1060\text{ cm}^{-1}$  could be due to some rutile impurity.

## CONCLUSION

Many of the beach samples given to the petrologist for identification are altered beyond recognition, but we now have a very powerful tool to aid in the rapid qualitative and quantitative determination of the mineralogy of such samples, as shown from the obtained results which are in harmony with the known black sands composition.

## REFERENCES

- COLTHUP, N. B., LAWRENCE, H. D., and WIBERIEG, S. E. [1964]: Introduction to infrared and Raman spectroscopy. Academic Press, New York, London.
- GIBBS, G. V., and SMITH, J. V. [1965]: Refinement of the crystal structure of synthetic pyrope. *Amer. Mineral.*, **50**, 2032—2039.
- GORE, R. C.: [1972]: Infrared spectral interpretation. *J. Hully Association* 112.
- HERZBERG, G. [1964]: Infrared and Raman spectra of polyatomic molecules. Princeton, Van Nostrand.
- KELLER, W. D., SPOTTS, J. H. and BIGGS, D. L. [1952]: Infrared spectra of some rock-forming minerals. *Am. J. Sci.*, **250**, 453—471.
- LAUNER, P. J. [1952]: Regularities in the infrared absorption spectra of silicate minerals. *Amer. Mineral.*, **37**, 774—784.
- MONTEL, G. [1971]: Sur les structures de quelques apatites d'interet biologique et leur imperfections, *Bul. Soc. Fr. Mineral. Cristallogr.*, **94**, 300—313.
- McDEVIT, T., and WILLIAM, L. [1964]: Infrared absorption study of metal oxides in the low frequency region ( $700\text{--}240\text{ cm}^{-1}$ ). *Spectrochimica Acta* **20**, 799—808.

- OMORI, K. [1971]: Analysis of the infrared absorption spectrum of almandine-pyrope garnet from Nijosan, Osaka Prefecture, Japan. *Amer. Mineral.*, **56**, 841—849.
- ROBINSON, K., GIBBS, G. V., and RIBBLE, P. H. [1971]: The structure of zircon: A comparison with garnet. *Amer. Mineral.*, **56**, 782—790.
- TUDDENHAM, W. M., and LYON, R. J. P. [1959]: Relation of infrared spectra and chemical analysis of some chlorites and related minerals. *Anal. Chem.*, **31**, 370—380.
- WASSEF, S. N. [1965]: Correlation of the sedimentation conditions of the Mediterranean beach east of Damietta to the Suez Canal by heavy minerals and isotopes applications. M. Sc. thesis, Faculty of Science, Ain Shams Univ., Cairo, Egypt.
- WASSEF, S. N. [1973]: Distribution of monazite in the black sands of Rosetta and Damietta and its conditions of sedimentation. Ph. D. Faculty of Science, Ain Shams Univ., Cairo, Egypt (1973).

*Manuscript received, 19 April, 1983*

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