A SPECTROGRAPHIC STUDY OF THE MINOR ELEMENT CONTENT OF DIAMOND

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Abstract

A rapid spectrographic method for the quantitative assessment of trace element constituents in diamond is described. Of the fourteen elements looked for in twenty-five diamond specimens only eight made their appearance, with Si, Mg, Al, Ca, Fe and Cu the most important.

The color of diamond is linked, at least in part, with the presence of Fe and Cu. Type I diamonds are found, in general, to be more impure than Type II diamonds. Very little difference is observed as regards the nature and amounts of the impurities in Types II*a* and II*b* diamonds.

Introduction

It has long been a subject of considerable interest as to what minor elements, if any, are contained in diamond and to what extent these impurities are responsible for the color of diamonds, fluorescence, semiconductivity, etc.

Unfortunately, very little work has been done in this connection up to the present and of the few incomprehensive references existing in the literature, only that of Chesley (1) is of any significance. No work, from a quantitative point of view, has been reported. This lack of information must be attributed to the difficulty of obtaining diamond specimens for research purposes, especially in view of the fact that the stones have to be partially destroyed in order to glean the required information.

The Diamond Research Laboratory has devoted much time to diamond analysis on a quantitative basis and has developed a method which, besides obviating time consuming measurements, has proved to be very satisfactory.

Experimental Procedure

The first requirement is for standard mixtures to be made up in order to establish working curves whereby the respective amounts of the trace constituents can be assessed. In these standards it is essential to introduce an internal standard since its presence constitutes the basis of our analysis. This internal standard is some suitable element or compound, added to the standards or diamond samples to be analyzed in a fixed proportion, so that a relationship between the densities of selected spectral lines of this element and those of the elements being determined can be established. The presence of the internal standard furthermore permits spectra of the standards and the diamond samples to be carried on different plates, and source variations, etc., can be readily compensated for. Cobaltosic oxide in found to be very suitable.

To prepare the strongest standard, 0.1 gm. of the summation weight of a mixture of elements most likely to be present in diamond is mixed with pre-determined weights of exceptionally pure Johnson, Matthey & Co., Ltd., Cat. No. *JM 2B* graphite power and cobaltosic oxide to result in a standard containing 1% of each trace element constituent and 5% cobaltosic oxide as internal standard.

From this 1% standard, subsequent dilutions with the base (*JM 2B* graphite powder with 5% admixed cobaltosic oxide) are made in steps of $1:\sqrt{10}$, *i.e.* 0.316 gm. of each mixture is diluted with 0.684 gm. base (2). In this way a series of standard mixtures is obtained having graphite as matrix material and containing each individual trace element in amounts of 10,000 parts per million, 3160 p.p.m., etc., down to 1 p.p.m.

A 3.5 mg. portion of each standard is carefully weighed out and mixed with its own weight of pure graphite powder, and the whole used to fill the cavity in the specially shaped cathode shown in Fig. 1. This cathode has been advocated by various investigators such as Mitchell (2), and has proved most successful. It is shaped from pure *JM 2B* graphite rod 6.5 mm. in diameter, 25 mm. long and reduced in diameter over the upper 15 mm. to 2.8 mm. The boring is 0.8 mm. in diameter, and 8 mm. deep and can be filled expeditiously by slipping a tight fitting cellophane collar over the narrow portion of the electrode. A length of the same 6.5 mm. graphite rod is used as anode.

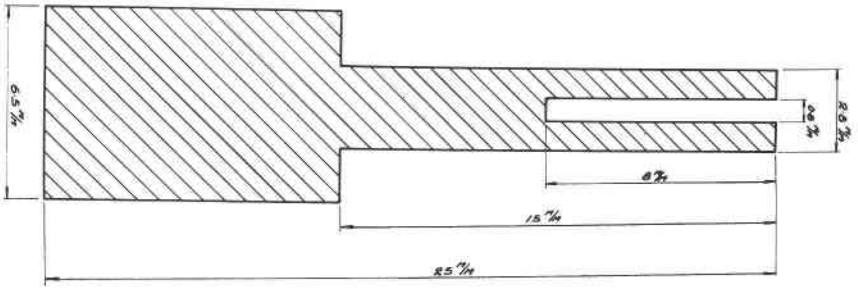

FIG. 1

The spectrograph in use is the Hilger Model *E.492*. A 150 volt D.C. source with variable resistance and inductance in series is used for excitation purposes. The samples are ignited at a current of 6±0.3 amps and an electrode separation of 5 mm. A slit width of 0.01 mm., slit height of 8 mm. and shutter aperture of 8 mm. are found advantageous. Following the cathode layer arc technique (2) exposures are made in the 3175–8000 A.U. and 2380–3290 A.U. ranges for 120 secs. and 180 secs. respectively on Ilford Thin Film Half Tone Plates and the same development procedure strictly adhered to throughout, *i.e.* 4½ minutes in *I.D. 2* metol-hydroquinone developer at full strength and a temperature of 18° C.

The most persistent lines of the various elements are easily identified and the ones selected for analysis are listed in Table 1.

TABLE 1

Element sought		Analysis line in A.U.	Element sought		Analysis line in A.U.
Aluminium	Al	3092.7	Magnesium	Mg	2852.1
Barium	Ba	4554.0	Nickel	Ni	3619.4
Calcium	Ca	3179.3	Silicon	Si	2516.1
Chromium	Cr	4254.3	Silver	Ag	3280.7
Copper	Cu	3274.0	Sodium	Na	3302.9
Iron	Fe	2599.4	Strontium	Sr	4607.3
Lead	Pb	2833.1	Titanium	Ti	3349.4

The densities of these lines for the various different concentrations of the standards are then carefully recorded by means of a Kipp recording microphotometer. The density of a line is taken as the logarithm of the opacity which, in turn, is defined as the ratio of the intensity of the light transmitted by the clear plate (I_0) to that transmitted by the line image (I). The value of I_0 is taken each time as the mean of several readings on both sides and close to the line to be measured. This procedure eliminates the need of background correction since the ratio of the galvanometer deflection obtained for line and background and background images gives, in fact, a value for the transmission of the line freed from background.

A plot of the densities measured in the above way as a function of the logarithm of the concentration provides our standard working curves.

It should be noted that the line densities and therefore the working curves of the different elements are obtained relative to the line densities of the cobalt 2663.5 and 3334.1 A.U. lines. With due care to experimental procedure the line densities of the latter exhibit remarkable constancy for the different exposures thereby indicating the absence of excessive source and other fluctuations.

To ascertain the amounts of trace constituents in diamond, a spectrogram is made of the stone as far as possible under precisely the same conditions as the standards. Since only a small piece of diamond is necessary for spectrum analysis, the general procedure adopted is to saw or cleave the diamond so as to provide two end pieces of approximately 50 mg. each and a middle piece, which on polishing, results in a specimen with optically parallel windows. This middle piece is then used for light absorption measurements with a *Model DU* Beckman spectrophotometer over the range 2000–10000 A.U. In this way it can be ascertained to what type the diamond belongs. The diamond type has been designated according to the following criterion.

Type II diamonds are transparent to about 2250 A.U. (3). This class of diamond has been further subdivided into Types II*a* and II*b* (4). Type II*b* diamonds are in general blue, and this color arises out of absorption lines in the near infra-red (5). They conduct electricity and behave as *p*-type semi-conductors (6). Type II*a* diamonds do not show these infra-red absorption lines and are non-conductors.

Type I diamonds show a secondary absorption edge at about 3200 A.U. The strength of this edge varies with the number of group *A* centers present which absorb at this wave length (5). The number of these centers may be assessed, in a qualitative way, from the wave length limit of transmission as measured on the spectrophotometer. Thus, in Table 2, we define:

Transmission limit equal to or larger than 3000 A.U.—Extreme Type I.
Transmission limit between 2800–3000 A.U.—Medium Type I.
Transmission limit between 2400–2800 A.U.—Weak Type I or Mixed Type.
Transmission limit between 2250–2400 A.U.—Type II.

The end pieces of the diamond are subjected to rigorous cleaning, first in "aqua regia" and then chromic acid at mild heat to remove all traces of surface impurities. The pieces are then transferred to a small impact crusher which has been buffed clean beforehand on an iron wheel, and are shattered by one sharp blow with a hammer.

The resulting powder is treated with 50% nitric acid followed by further treatment with 50% hydrochloric acid solution. It is washed by decantation with distilled water until completely free from chloride and dried at about 100°C.

A 3.5 mg. portion of the diamond powder is weighed out and mixed with its own weight of base, which was specified under the heading "Experimental Procedure." Spectrograms of this mixture are obtained under the same conditions as those prevailing with the standards. Lines due to trace constituents, if any, are identified and the densities measured. Before assessing the amounts of constituents present the densities of the Cobalt 2663.5 and 3334.1 A.U. lines are first measured and compared with those of the working curves. If different, the line densities of the constituent elements are adjusted in accordance with this difference before interpolations are made on the working curves. In general, it is found that with due care in the duplication of experimental procedure, the densities of the reference cobalt lines do not show appreciable deviations from the standard values. This is a condition to be aimed at since the unknowns in the diamond might respond differently than the internal standard to voltage and current variations.

GEOGRAPHIC LOCATION AND COLOR OF STONES

In all, twenty-five diamonds were studied. Two of these, Nos. 1 and 2, came from Sierra Leone. No. 1 was colored a green-yellow whereas No. 2 had a pale green color.

Thirteen diamonds, Nos. 3–15, came from the Premier Mine, South Africa. Stones 3–8 were a natural blue and of the Type II*b* variety, while Nos. 9–15 were all colored various shades of brown. Of the brown variety three diamonds, Nos. 9–11, were of Type IIa while the rest, Nos. 12–15, belonged to the Type I classification.

Six diamonds, Nos. 16–21, were of a fine yellow color and originated from the Consolidated Diamond Mines in South West Africa.

Of the remainder, No. 22 was a white Type II*a* diamond from the Wesselton Mine, South Africa, No. 23 white, and Nos. 24 and 25 brown. Unfortunately, the sources of origin of the last three diamonds are not known.

RESULTS AND DISCUSSION

Quantitative spectrographical analysis is never an easy procedure and with diamond in particular it proves to be even more difficult, due to the nature of the material and the fact that the trace constituents are present to the extent of a few parts per million only. It is of essence, therefore, to be extremely meticulous in the handling and preparing of the samples, the conditions of exposure, etc., in order to get anything like reproducible results.

Quite often good duplication of results was found for duplicate samples and only four exposures were necessary, *i.e.*, two in the lower wave length bracket and two in the higher.

Sometimes, however, it was necessary to take some eight exposures of samples of the same diamond before any reliable duplication could be obtained. These contradictory findings could be due to minute inclusions in the diamond or it might well be that the impurities in diamond are localized and not uniformly distributed throughout the crystal. Berman, *et al.* (7) in their work on the thermal conductivity of diamond arrived at the conclusion that imperfections in diamond, the nature of which is not specified, occur in groups.

The results of the investigation are given in Table 2, together with

TABLE 2

Diamond No.	Geographic Location	Color	Type	P.P.M. of								Special Effects
				Si	Ca	Mg	Al	Fe	Ti	Cu	Cr	
1	Sierra-Leone	Green-yellow	Medium I	4 2	5 4	4 4	56 58	20 15	4 4	7 6	a a	BF
2	Sierra-Leone	Pale green	Medium I	3 2	1 2	3 2	3 16	10 17	4 5	7 10	trace a	BF
3	Premier	Natural blue	II(*b*)	4 2	a a	1 3	34 32	a a	a a	a a	a a	P. S-C
4	Premier	Natural blue	II(*b*)	2 4	a a	2 2	8 6	a a	a a	a a	a a	P. S-C
5	Premier	Natural blue	II(*b*)	4	a	4	10	a	a	a	a	P. S-C
6	Premier	Natural blue	II(*b*)	2 1	a a	4 3	4 3	1 2	a a	a a	a a	P. S-C
7	Premier	Natural blue	II(*b*)	1 2	a a	5 7	7 4	a a	a a	a a	a a	P. S-C
8	Premier	Natural blue	II(*b*)	1 2	a a	2 2	3 2	a a	a a	a a	a a	P. S-C
9	Premier	Brown	II(*a*)	2 2	a a	3 2	4 1	a a	a a	a a	a a	—
10	Premier	Brown	II(*a*)	5 10	a a	10 5	10 13	a a	a a	a a	a a	—
11	Premier	Brown	II(*a*)	a 1	a a	3 5	1 2	a 1	a a	2 a	a a	—
12	Premier	Brown	Medium I	6 3	20 6	3 2	4 10	9 13	8 7	6 6	a a	BF
13	Premier	Brown	Extreme I	51 40	15 7	15 5	79 47	10 13	a 3	3 4	a a	BF. Z
14	Premier	Light brown	Medium I	2 2	2 6	6 9	10 2	a 2	4 3	6 2	a a	BF. Z
15	Premier	Light brown	Medium I	1 3	a 2	3 4	9 10	24 29	4 3	5 3	a a	GF. Z
16	S.W.A.	Fine yellow	Extreme I	2 a	5 3	8 2	25 19	15 8	a 3	3 4	a a	YF
17	S.W.A.	Fine yellow	Extreme I	2 1	2 a	4 2	8 3	9 4	a 1	3 2	a a	BF
18	S.W.A.	Fine yellow	Weak I (Mixed?)	a a	a a	2 2	1 1	12 7	a a	3 4	a a	YF. Z
19	S.W.A.	Fine yellow	Extreme I	a a	a a	1 2	8 8	12 20	a a	2 a	a a	YF
20	S.W.A.	Fine yellow	Extreme I	1 a	4 6	a 3	13 10	12 18	a a	5 3	a a	YF
21	S.W.A.	Fine yellow	Extreme I	1 5	2 4	1 3	2 9	8 17	a a	4 2	a a	YF
22	Wesselton	White	II(*a*)	a a	2 2	1 1	4 3	a a	a a	a a	a a	—
23	Unknown	White	Medium I	a a	a a	2 2	10 2	a a	a a	2 2	a a	BF
24	Unknown	Brown	Medium I	1 1	2 2	4 1	6 3	10 16	1 2	a a	a a	BF. Z
25	Unknown	Mottled brown	Medium I	1 a	a a	4 3	a a	4 1	a a	5 3	a a	GF

BF = Blue fluorescence.
GF = Green fluorescence.
YF = Yellow fluorescence.
P = Phosphorescence.

S-C = Semi-conducting.
Z = Zoned i.e. fluorescence not uniform throughout the diamond but restricted to localized spots or zones.

P.P.M. = Parts per million
a = Absent (not detectable)

special effects such as semi-conductivity, fluorescence etc., observed for each diamond. Except for diamond No. 5 where the specimen was too small to permit duplication, the results are given in duplicate.

Of the fourteen elements looked for, only Si, Ca, Mg, Al, Fe, Ti, Cu and Cr made their appearance, with Ag, Ni, Pb, Na, Ba and Sr absent in all cases. However, the failure to detect these elements does not rule out their presence altogether. The limits of detection of some of these elements, notably Pb and Ba, are of the order of anything up to 10 p.p.m. and they might be present to an extent such that the most persistent lines are not detectable.

The presence of Co could of necessity not be established since it is used as the internal standard.

The main impurities in diamond seem to be Si, Ca, Mg, Al, Fe and Cu, with the Al predominating in most cases. This result is not surprising since the first five elements are found abundantly in nature and are readily detectable by the spectrograph.

The colored diamonds, *i.e.*, the South West African yellows, the two Sierra Leone stones and the brown diamonds with the exception of the II*a* diamonds all contain Fe, up to an appreciable amount in some cases. Cu also shows a tendency to be present in the colored stones with the exception of the II*a* diamonds again. Ti appears only when Fe is present. The theory of Sutherland and co-workers (8) to the effect that Type I diamonds are more impure than Type II diamonds seems, in general, to have credence although there are exceptions. Thus medium Type I diamond No. 23 has a total impurity content of 6–14 p.p.m. whereas Type II*a* diamond No. 10 contains 25–28 p.p.m.

On the whole, Type II*a* and II*b* diamonds appear to differ very little as regards impurity content. The impurities are, almost exclusively, Si, Mg, and Al with the latter predominant in most cases.

A current theory is that Al, by virtue of its being an electron-acceptor is, at least in part, responsible for the semi-conducting properties of Type II*b* diamonds. If this is the case the Al in Type II*b* diamonds may be accommodated differently in this type of diamond than in Type II*a* diamonds, since the amounts of Al are virtually the same in the two types. Alternatively, an excess of donor levels in Type II*a* diamonds may "quench" the *p*-type semi-conductivity.

Finally, although it is apparent from the results that impurities in diamond have an effect on the color it is by no means an established fact that they constitute the main contributing factors for the anomalous light absorption of diamond in the ultra-violet and infra-red, semi-conductivity, etc.

It looks rather at this stage as if impurities in conjunction with defects inherent in the diamond are responsible for these observed phenomena.

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