

SPECTROSCOPIC STUDY ON THE LINE INTENSITY OF SOME TRACE ELEMENTS IN SILICON DIOXIDE MATRIX

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Abstract

In this work, a study is presented handling different electrode shapes, different buffer types and different mixing ratios to one of the most common matrices. The matrix silicon dioxide was selected because it shares as a major constituent in different soils, minerals, ores and rocks. Elements were selected to represent different volatilities i.e. volatile, medium volatile and involatile. As a result, this study helps the spectroscopist to predict and choose the proper electrode shape, the proper buffer type and the proper mixing ratio for samples which has silicon oxide as a major component.

Introduction

Spectroscopic investigation of trace elements can be handled with widely different techniques. In general, there is no standard technique that covers all elements in different types of sample. The analysis is faced with many parameters that influence the rate of volatilization of test materials. Available data from literature allow only rough predictions. For that reason, Boumans[1] recommended and experiment only to decide the most appropriate parameters that provide the favourable circumstances for analysis. The addition of spectroscopic buffers used with dc arc to control the excitation conditions and the influence of varying the mixing ratios of some buffer compounds were discussed in many references [2-11].

Preliminary Preparations

a) Apparatus

Spectrograph	: Carl Zeiss medium quartz Q24
Dispersion	: 1.3 nm at 310 nm.
Slit width	: 0.01 mm.
Slit length	: 1.0 mm.
Filter	: no filter
Projector	: Carl Zeiss SP2
Photometer	: Carl Zeiss rapid photometer
Plates	: ORWO blue extra hard (9 x 24 cm).

Processing	: thermostatically at 20 ± 2 C° for 5 minutes.
Developer	: ORWO 1 freshly diluted (1:5) before each operation.
Fixer	: Hypo for 10 minutes.
Excitation	: DC arc, anode, 220 volts
Current	: 7 amperes
Gap	: 3 mm
Exposure time:	150 seconds.

b) Sample

Silicon dioxide matrix used was from Johnson Matthey spec pure chemicals. To this matrix, Johnson Matthey specromel No. 1 powder was mixed in the ratio (1 : 100) on two steps by weight. Spectromel powder contains 53 elements, each is with concentration 1.18%. Elements representing different volatilities are given in table (1). The wave lengths were selected from Seidel et al. [12] and boiling points from Torok et al. [13]

Table (1)
Specifications of elements under study

Element	Wave length nm	Volatility	Boiling point °C
Cu	282.437	Volatile	2595
Pb	283.306	"	1751
Sn	286.333	"	2687
Fe	259.939	Medium volatile	3070
Mn	293.306	"	2095
Ni	300.249	"	2800
B	249.677	Involatile	3900
Be	234.86	"	2477
V	318.3406	"	3380

Experimental :

Line intensity is the unique evidence to judge the suitability of any parameter. In the following the change in line intensity resulting from changing each studied parameter is represented.

A. Electrode shape

Buffer used : Lithium carbonate

Mixing ratio : (1:1)

In this work, three shapes of electrodes were prepared from Ringsdorf RWO free boron graphite rods with diameter 5.6 mm. The counter electrode used with all types was 5.6 mm diameter and 30 mm long with cone at one end. The three shapes were needle, normal and cup shapes.

I. The needle electrode was cut to be 30 mm long 3 mm external diameter and 15 mm needle length. The carter was 1 mm width and 10 mm depth. Thus the charge capacity of such type is:

$$\pi r^2 h = (22/7) \times (0.5)^2 \times 10 = 7.85 \text{ mm}$$

- II. The normal electrode was cut with length 30 mm and external diameter 5 mm. The crater was 3 mm width and 3 mm depth. Hence the charge capacity is:

$$\pi r^2 h = (22/7) \times (1.5)^2 \times 3 = 21.2 \text{ mm}$$

- III. The cup electrode was cut with length 30 mm, and external diameter 5 mm. The cup length was 5 mm. The crater was 3 mm width and 3 mm depth. Thus the charge capacity is:

$$\pi r^2 h = (22/7) \times (1.5) \times 3 = 21.2 \text{ mm}$$

Results and Discussion :

The relation between the measured line intensity and different electrode shapes under study are shown in fig. (1).

From Fig. (1), it is clear that the cup shape produced the highest line intensity. The needle type showed the lowest values, whilst the normal type gave values of middle intensity.

The result for the needle type could be explained because the charge capacity of such electrode (7.85 mm) is about one third of either cup or normal shapes (21.2 mm).

The highest intensity realized by the cup shape in comparison with normal shape (of the same charge capacity) could be explained as follows. Through the electrode cavity, a great heat intensity is attained because the electrode diameter is considerably decreased below the cavity, and as a result, heat conduction is lowered. Thus materials of difficult volatilization (similar to our silicate sample) can be arced more successfully.

B) Buffer type :

Electrode shape used : cup shape

mixing ratio : (1:1)

In this work five different buffers were tried.

- i) Ammonium chloride $\text{NH}_4 \text{Cl}$.
- ii) Lithium carbonate $\text{Li}_2 \text{CO}_3$.
- iii) Mixture (1:1) ammonium chloride : graphite
- iv) Mixture (1:1) lithium carbonate : graphite
- v) Graphite.

Arc temperature and electron pressure

Arriving to the suitable shape of electrode and to find out the suitable buffer it was necessary to measure both arc temperature and electron pressure. The arc temperature was measured using the two spectral line method. Zinc (307.6 nm & 328.2 nm) was used as thermometric element. The electron pressure was measured using the intensity ratio of ion-atom line pair of magnesium (279 nm & 285.2 nm) which was used as manometric element. The measurements were carried out following Bouman's formula (1966) [1].

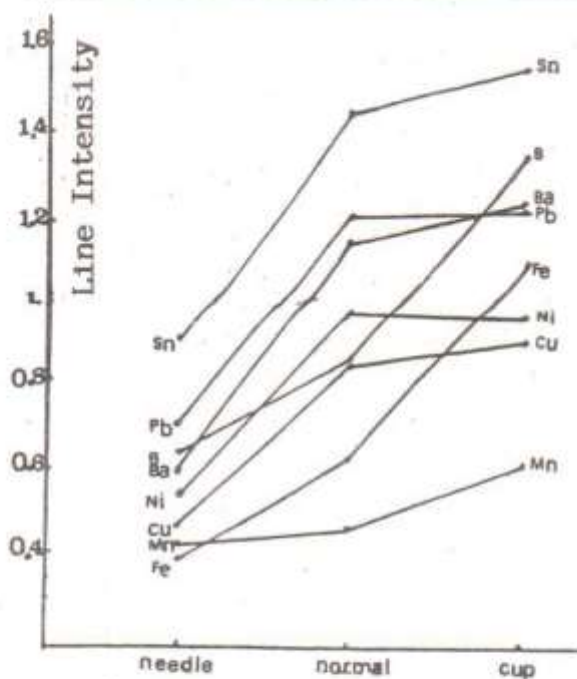
Results and Discussion

Generally, natural occurring silicates are very badly behaved during arcing. Using anode excitation with unmixed silicates, molten bead of involatile elements is formed during arcing. Such a bead may be lost early. Another disadvantage is that for silicates the arc behaves erratically. For the above reasons, the use of an appropriate buffer is indispensable.

Buffers are used to serve four main purposes :

- 1) To smooth out the volatilization differences.
- 2) To keep the source temperature as uniform as possible.
- 3) To obtain good compromise of detection limits.
- 4) To select satisfactory internal standard.

Fig (2) shows the relation between line intensity of elements under study and different buffer types. The figure shows that either ammonium chloride or lithium carbonate produces the least line



(Fig.1)

Relation between line intensity & electrode shape

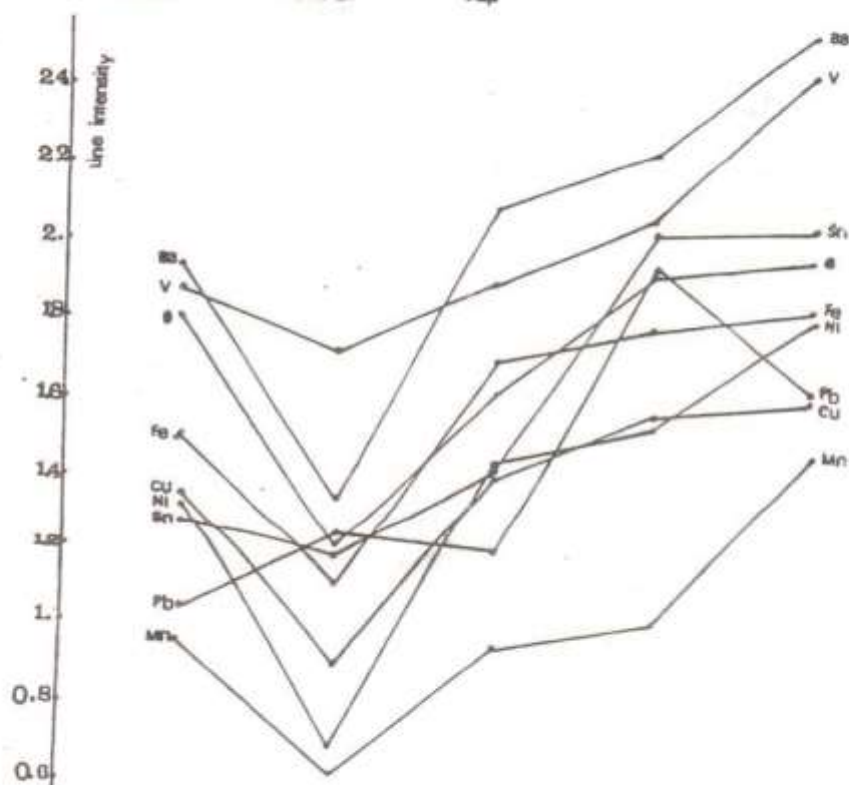


Fig.2 Relation between line intensity & type of buffer

intensity. Again in figure (2) it is clear that addition of graphite to ammonium chloride causes a slight enhancement of intensities. A remarkable sharp increase in line intensity is observed with the mixture of lithium carbonate and graphite.

The highest line intensity is resulted with the use of graphite only for all elements under study except for lead. The line intensity of lead is relatively higher when the buffer is a mixture of lithium carbonate and graphite than with graphite only. This behaviour could be explained due to the fact that lead possesses the lowest value of boiling point with respect to other elements. The boiling point for lead is 1751 ° (Mika & Torok, 1978) [13]. This means that the arc temperature resulted with the use of such a mixture is the most conducive to the emission intensity of the element lead.

The results of measured arc temperature and electron pressure are summarized in Table (II).

Table (II)

Arc Temperature & Electron Pressure of Different Buffers

Buffer	Arc temperature °K	electron pressure atm.
Ammonium chloride NH_4Cl	4809	1.579×10^{-3}
Lithium carbonate Li_2CO_3	5205	1.711×10^{-3}
Ammonium chloride+graphite	5005	1.646×10^{-3}
Lithium carbonate + graphite	5610	1.840×10^{-3}
Graphite	6403	2.107×10^{-3}

It is clear that in the presence of graphite admixture the arc burns more steadily and selective volatilization is less marked. The highest electron pressure and arc temperature attained due to the highest

ionization potential of graphite. Lithium carbonate and ammonium chloride show less arc temperature and electron pressure. This behaviour is due to their lowest values of ionization potential. Again it is worth to notice that the addition of graphite to these buffers increased both arc temperature and electron pressure.

The improvement of excitation condition is attributed to the enhanced electrical and thermal conductivity of graphite. In addition graphite assisted chemical reduction of oxides and prevented globule formation.

Statistical calculation of standard deviation and relative deviation

Replicate determination (11 times) of both arc temperature and electron pressure for the most suitable buffer (graphite) revealed the following values:

Arc temperature	6409 °K
Standard deviation S	= ± 58 °K
Relative deviation D	= ± 0.9 %
.	
Electron pressure	2.107×10^{-3} atm.
Standard deviation S	= ± 0.04×10^{-3} atm.
Relative deviation D	= ± 1.9%

C) Buffer Mixing Ratio :

Electrode used	: cup shape
Buffer	: graphite

In this work three mixing ratios of sample to buffer (graphite) were tried (1:1), (1:2) and (1:3).

Results and Discussion :

Fig. (3) clarifies the relation between line intensity for elements under study and the three mixing ratios. From Fig. (3) it is clear that the proper mixing ratio of sample to graphite that produce the highest line intensity is (1:2). With the presence of silicon as a major constituent, it appears that the ratio (1:1) was not sufficient to prevent the bead formation. Regarding mixing ratio (1:3), certainly no bead is formed, but naturally the great dilution will lessen available elements concentration. Consequently, the occurring decrease in line intensity would be expected.

Conclusion

- 1) The cub shape electrode proved to be the most suitable shape for detecting trace elements in any silicate sample. This may be due to the fact that the decreased diameter below the electrode cavity causes lowering of heat conduction.
- 2) Graphite with its highest value of ionization potential (11.2 ev.) produces the highest value of arc temperature. This high temperature in turn produces the highest intensity for elements studied except for lead.
- 3) The element lead possesses a special character. Its intensity is high when the buffer used is a mixture of lithium carbonate and graphite with a mixing ratio (1:1).
The boiling point of lead (1751 c) is relatively in need to lower arc temperature. This temperature is realized by the above mixture than with graphite.
- 4) The proper mixing ratio of graphite as a buffer to silicate sample proved to be (1:2). One of the advantages is that graphite reduced elements oxide to elements only. The presence of elements in the arc in-turn creates the most favourable circumstances for the emission of line intensity.
- 5) It is clear from this paper, that using either lithium carbonate or ammonium chloride as buffer depress line intensity for all sharing elements. This behaviour could be useful when there is a need to get rid of self absorption of such elements.

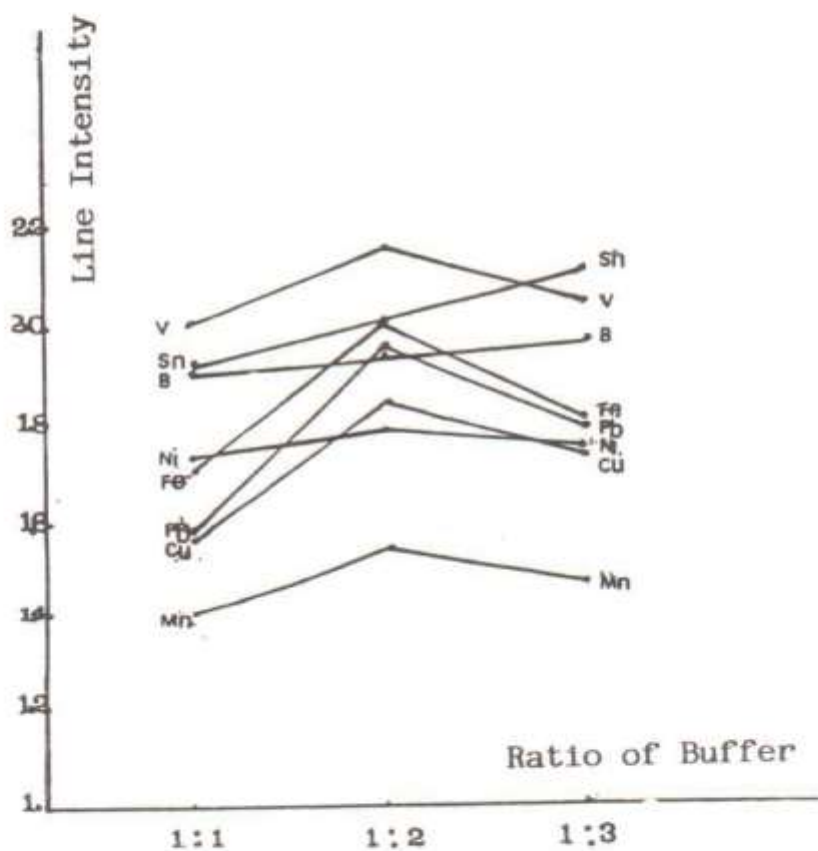


Fig.3 Relation between line intensity & ratio of buffer

- 6) The buffer graphite with mixing ratio (1:2) proved to be the most suitable buffer. Graphite produces the highest value of both arc temperature and electron pressure and consequently to the highest line intensity.

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