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Profiles of the Distribution of Atoms in the Nitrous Oxide-acetylene Flame

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The distributions of neutral atoms in the nitrous oxide–acetylene flame have been measured by nebulizing aquo ions of the following sixteen elements into the flame; cadmium, nickel, zinc, copper, lead, cobalt, manganese, iron, chromium, molybdenum, calcium, tin, gallium, indium, titanium, and boron. The distributions have been figured on the response surfaces on which the changes in distribution are expressed as functions of the flame height and the acetylene flow rate. The response surfaces for the temperature and the OH radical were also investigated. The response surfaces for the atomic absorptions of the elements can be related to the thermodynamic properties of the oxides of the elements. The results have then been used for the discussion of the atomization processes of the elements in the flame. In addition, the sensitivities of absorption spectrometry in the nitrous oxide–acetylene flame have been compared to those in the air–acetylene flame.

In atomic absorption spectrometry, it is important to know the atomization processes of analytical elements, which are reflected in the distribution of atoms in the flame. The distribution of atoms depends on the condition of the flame, particularly on the composition of the flame, which is usually expressed by the ratio of the fuel to the supporting gas.[1–6] However, the relation between the atomic distribution and the properties of the flame has not been well established. Hence, in a previous work a detailed investigation of the atomic distributions of fourteen elements in the air-acetylene flame has been carried out.[7]

In the present study, the absorbances of atoms in the nitrous oxide–acetylene flame are measured as the function of two variables, the acetylene flow rate and the height above the burner, while keeping the flow rate of nitrous oxide constant. The results are shown as a map of the distribution of the atoms, where the abscissa indicates the flow rate of acetylene, and the ordinate the height above the burner. This map of distribution will be refered to as "the response surface" hereafter. The present authors have investigated the response surfaces for atoms of sixteen elements, the OH radical and the temperature, and have discussed the mechanism of atomization in the nitrous oxide-acetylene flame.

Experimental

Reagents. All the reagents used were of an analytical grade and were purchased from the Wako Pure Chemical Ind. Ltd. Sample solutions of metal ions were prepared by dissolving the nitrates of Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ca^{2+}, Cr^{3+}, In^{3+}, Ga^{3+}, Cd^{2+}, and Pb^{2+} into distilled water containing 0.2% nitric acid. The solutions of ammonium molybdate and boric acid were prepared by dissolving the respective salts into water. The titanyl sulfate was dissolved into a 0.2 N sulfuric acid solution, while the stannic chloride was dissolved into a 0.2% nitric acid solution. The analytical concentrations of the elements are listed in Table 1.

Table 1. Sample solutions and analytical lines

Reagent	Concentration of metal ions (μg/ml)	Analytical line (nm)
$Cd(NO_3)_2\cdot 8H_2O$	2	228.8
$Ni(NO_3)_2\cdot 6H_2O$	20	352.4
$Zn(NO_3)_2\cdot 6H_2O$	1	213.8
$Cu(NO_3)_2\cdot 3H_2O$	5	327.4
$Pb(NO_3)_2$	20	283.3
$Co(NO_3)_2\cdot 6H_2O$	20	243.2
$Mn(NO_3)_2\cdot 4H_2O$	20	403.0
$Fe(NO_3)_3\cdot 7H_2O$	20	271.9
$Cr(NO_3)_3\cdot 9H_2O$	20	427.4
$SnCl_4\cdot 5H_2O$	500	286.3
$Ga(NO_3)_3$	20	287.4
$In(NO_3)_3$	20	303.9
$Ca(NO_3)_2\cdot 4H_2O$	5	422.6
$(NH_4)_2MoO_4$	20	313.2
$TiOSO_4$	200	364.2
H_3BO_3	1000	249.8

Apparatus. The Hitachi 207 Atomic Absorption Spectrophotometer was used after somewhat modifying the focussing of the light beam so that a single light path with a beam 2—3 mm in diameter was produced at the measuring position in the flame. The details of this modification have already been reported elsewhere.[4]

Most of the hollow cathode lamps which were used in the experiments were produced by Hitachi Ltd.; one for gallium was produced by Westinghouse, and one for tin by Varian Tectron Pty., Ltd., Australia. As the continuous light source, a 200 W deuterium discharge tube, Model HS 200 DS from Dr. Körn Gmbh and Co. was used. For the temperature measurements, a 250 W tungsten lamp, Halogen-bellaphot 64653, of the Osram Co. Ltd., was used as the incandescent light source; a mechanical chopper made by the K. K. Ewig Co. and an optical pyrometer, Model 201 N_1, of the Hokushin Electric Works were also used.

A water-cooled burner with a 50 mm slot was used for the nitrous oxide–acetylene flame.

Procedure. A sample solution was nebulized into the burner at a rate of about 3 ml/min. The light beam was passed through the center of the flame just above the slot of the burner. The absorbances were measured at the positions in the flame, with intervals of 2.5 mm; the positions were adjusted by moving the burner vertically. The conditions of the flame were changed by varying the acetylene flow rate by 0.5 l/min., while the flow rate of nitrous oxide was kept constant at 6 l/min.

The atomic absorption lines for the elements are listed in Table 1.

Temperature Measurement: Temperature of the flame was measured by the sodium 5889 Å line-reversal method.[8,9] Two pin holes were set along the light path, one for obtaining a narrow light beam from the incandescent light source, and the other, behind the flame, for excluding the extra emission of the flame. The current of the incandescent lamp was controlled by an auto-transformer, while the temperature of the tungsten filament in the lamp was measured by means of the optical pyrometer at the reversal point of absorption and emission. In this measurement, an aqueous solution of 1000 μg Na/ml was nebulized into the flame. The reproducibility of the measurements was within 10 °C.

OH Radical Measurement: The concentration of the OH radical was measured by the molecular absorption method as follows. The luminous intensity of the deuterium discharge was almost constant in the range from 305.0 to 306.7 nm while the flame was not ignited. The absorption spectra of the flame were, therefore, measured by scanning the wavelengths in the above range continuously, and the relative concentrations of OH radicals were evaluated in terms of 305.8 and 306.4 nm. In this measurement, distilled water was nebulized into the flame.

Results

The experimental data for the flame temperature, the concentrations of the OH radical, and the atomic absorptions of Cd, Ni, Zn, Cu, Pb, Co, Mn, Fe, Mo, Ca, Cr, Sn, Ga, In, Ti, and B, which were observed as functions of two variables, such as the acetylene flow rate and the height above the burner, have been indicated in the response surface.

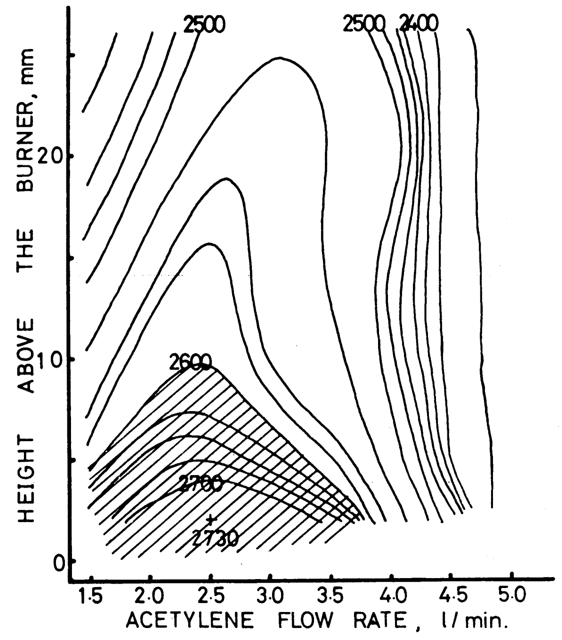

Fig. 1. Response surface of temperature.
Temperature in the hatched region is higher than 2600 °C.

In Fig. 1, the response surface for the flame temperature is shown. The temperatures were measured at 48 positions in the nitrous oxide-acetylene flame; the observed values are plotted in the response surface map. Thus, the isothermal contour lines are obtained with an interval of 25 degrees. In Fig. 1, the areas with a temperature range from 2300 to 2730 °C are shown. The maximal temperature is found at a height of 2 mm and with an acetylene flow rate of 2.5 l/min. The hatched area refers to when the flame temperature is higher than 2600 °C.

In Fig. 2, the response surface for the OH radical is shown. In this case, the absorbances of the molecular absorption of OH at 80 positions in the flame are plotted in the figure; the iso-absorbances are shown as contour lines with an interval of 0.012. The maximal absrobance of OH, 0.036, is found at the position with an acetylene flow rate of 1.5 l/min and a height of 5—20 mm. The absorbance in the hatched region is larger than 0.032.

In Figs. 3—7, the response surfaces for 16 elements are shown in the same way. The absorbances for those elements were measured at 40—72 positions of the

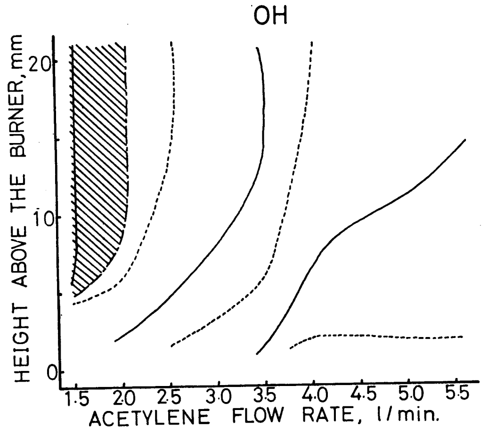

Fig. 2. Response surface of OH radical absorbance.
The absorbance in the hatched region is higher than 0.032.

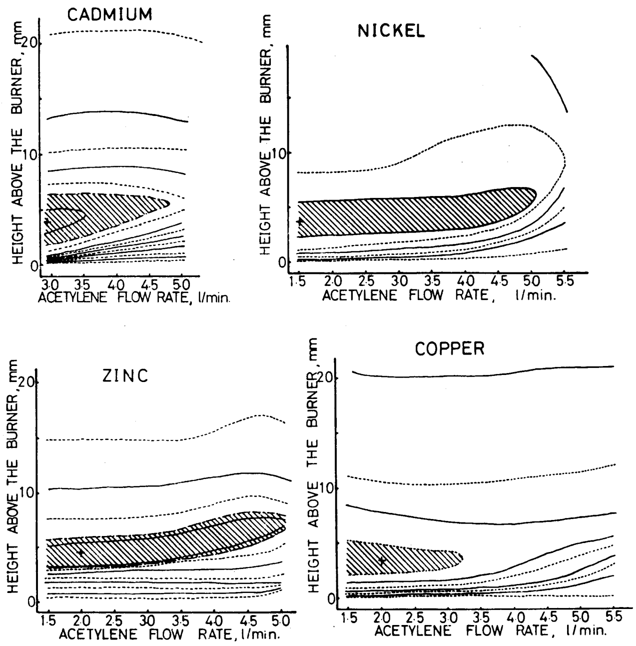

Fig. 3. Response surfaces of absorbances of cadmium, nickel, zinc, and copper.
The absorbances in the hatched regions are higher than 0.056, 0.036, 0.040, and 0.042 for cadmium, nickel, zinc and copper, respectively. The cross point indicates the position that gives the maximal absorbance.

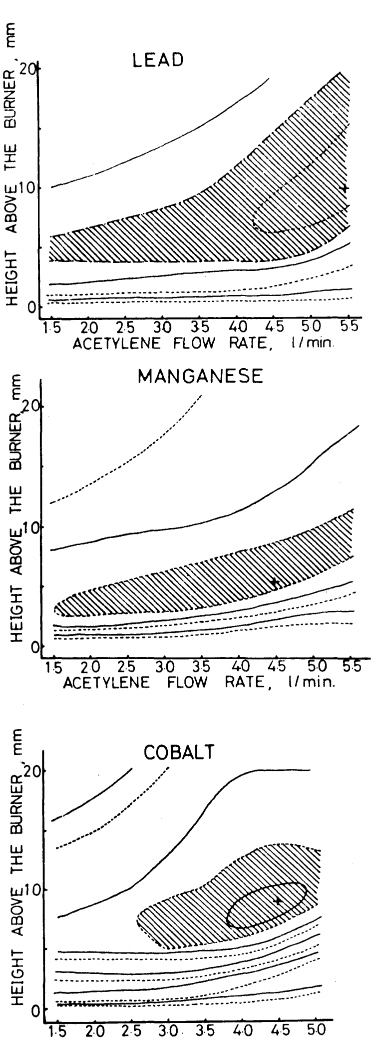

Fig. 4. Response surfaces of absorbances of lead, cobalt and manganese.
The absorbances in the hatched regions are higher than 0.028, 0.054, and 0.030 for lead, cobalt and manganese, respectively. The cross point indicates the position that gives the maximal absorbance.

flame. The response surfaces are classified into 5 groups. The basis of this classification will be described later. The maximal absorbances obtained in the nitrous oxide–acetylene flame are summarized in Table 2. The hatched regions in Figs. 3—7 refer to those giving an absorbance larger than nine-tenth of the maximal one. The contour lines giving the highest absorbance in the response surfaces of each element are summarized in Fig. 8.

Discussion

In the normal conditions of the flame in the present experiment system, the acetylene flow rate has been set at 4.0 l/min. This actually corresponds to the ratio of acetylene to nitrous oxide of 2 to 3 in volume. The region where the acetylene flow rate is larger than the normal condition of the flame is conventionally referred to as an acetylene-rich flame, and the smaller one, as an acetylene-lean flame.

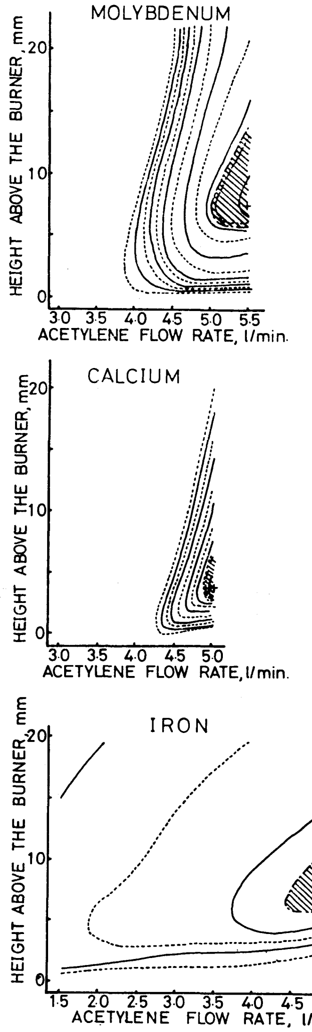

Fig. 5. Response surfaces of absorbances of calcium, molybdenum and iron.
The absorbances in the hatched regions are higher than 0.055, 0.065, and 0.028 for calcium, molybdenum and iron, respectively. The cross point indicates the position that gives the maximal absorbance.

Temperature in the Nitrous Oxide–acetylene Flame. The nitrous oxide–acetylene flame has been known as a high temperature flame. In fact, the temperature of this flame, as measured by the method reported previously, is about 300 degrees higher than that in the air–acetylene flame, the range of which is from 1900 to 2300 °C.[7] It should be noted that the highest temperature in the nitrous oxide–acetylene flame, 2730 °C, is observed in the lower part of the acetylene-lean region, and that the flame temperature decreases towards the upper part and the acetylene-rich region.

No distinct correlation in distribution between atoms and temperature in the response surfaces is observed. The sensitive regions of Cu, Ni, Cd, Zn, Co, Pb, and Mn spread from the region with the lowest temperature to that with the highest temperature. In the other elements, the sensitive regions are apart from the highest-temperature region.

OH Radical Distribution. The OH radical is produced by the oxidation of the fuel; it oxidizes the reductive component of the flame and also the metal

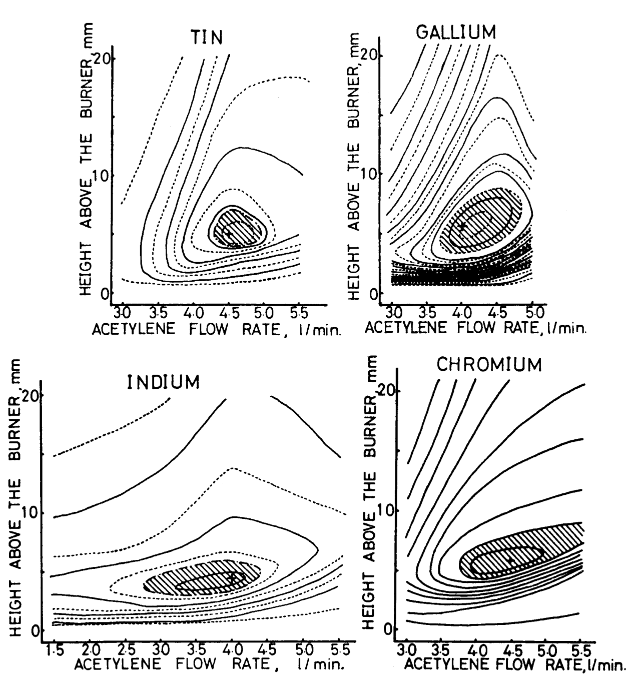

Fig. 6. Response surfaces of absorbances of tin, gallium, indium and chromium.
The absorbances in the hatched regions are higher than 0.050, 0.114, 0.044, and 0.108 for tin, gallium, indium and chromium, respectively. The cross point indicates the position that gives the maximal absorbance.

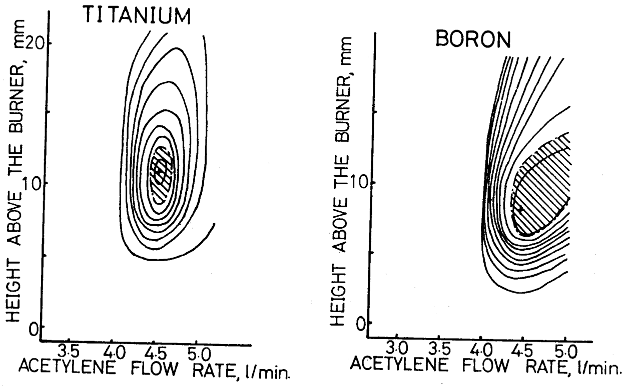

Fig. 7. Response surfaces of absorbances of titanium and boron.
The absorbances in the hatched regions are higher than 0.091 and 0.112 for titanium and boron, respectively. The cross point indicates the position that gives the maximal absorbance.

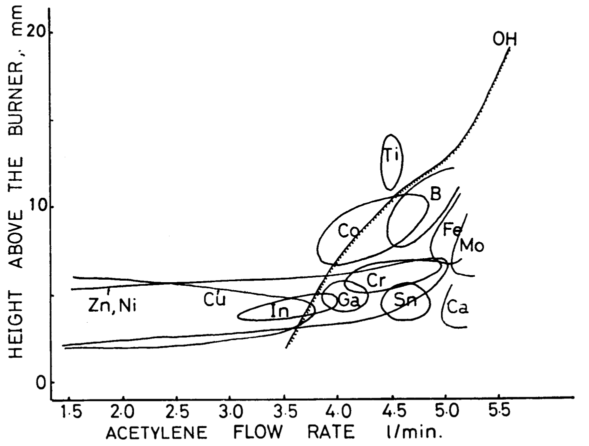

Fig. 8. Locations of higher sensitive regions of elements investigated.
The cited areas refer to those of higher sensitivities. The hatched line, ▥, denotes the OH concentration, *i.e.*, the area which is right-hand side of the line refers to that of low concentration, absorbance of OH is lower than 0.012.

atoms.[10] Hence, the relative concentration of the OH radical (shown in Fig. 2) has been used as an index of the oxidation potential of the flame. Its concentration becomes higher in the upper part of the acetylene-lean region. On the other hand, the atomic concentrations of all the elements become lower in this region. This suggests that the oxidative reactions are predominant in this region and that the atomization of the analyzed element is prevented by the formation of oxide.

On the other hand, as may be seen in Fig. 8, the absorption maxima of many elements can be observed in the region of the OH radical minimum. This region is actually reductive; this suggests that the reductive condition is favorable for the atomization of many elements in the nitrous oxide–acetylene flame.

Sensitivities of the Nitrous Oxide–acetylene Flame and the Air–acetylene Flame. In Table 2 the sensitivities for the analyzed elements in the nitrous oxide–acetylene flame and in the air–acetylene flame are compared; the sensitivity is expressed in terms of the ratio of maximal absorbance. The values in Table 2 refer to those obtained after the normalization with respect to

Table 2.

Element	Heat of formation of M_xO_y (Ref. 15) (eV)	Dissociation energy of MO (Ref. 12, 13, 14, 16) (eV)	Maximum absorbance	Ratio of max. absorbance in N_2O–C_2H_2 flame to that in air-C_2H_2 flame
Cd	CdO 2.6	3.8	0.063	0.61
Ni	NiO 2.5	3.9	0.041	0.34
Zn	ZnO 3.6	2.8	0.052	0.64
Cu	CuO 1.6	3.3—4.1	0.047	0.48
Pb	PbO 2.3	3.9	0.031	0.32
Co	CoO 2.5	—	0.062	0.65
Mn	MnO 4.0	4.0—4.2	0.033	0.46
Ca	CaO 6.6	4.1—4.7	0.064	0.53
Fe	Fe_2O_3 8.5	4.3—4.8	0.031	0.35
Mo	MoO_3 7.7	5.0	0.072	0.83
In	In_2O_3 9.6	3.3	0.049	0.46
Ga	Ga_2O_3 11.1	3.0	0.126	1.6
Sn	SnO_2 6.0	5.4	0.056	1.5
Cr	Cr_2O_3 12.9	4.4—4.9	0.125	1.0
Ti	TiO_2 9.5	6.8—7.2	0.091	a)
B	B_2O_3 13.1	8.0—8.3	0.130	a)

a) Absorbance is not obtained in the air–acetylene flame.

the length of the burner. Those of Ga, Sn, Cr, and B show the ratios larger than one. This indicates the higher sensitivity in the nitrous oxide–acetylene flame. All these elements, except Sn, form stable oxides whose heats of formation are larger than about 10 eV. The results obtained here suggest that the formations and the thermal decompositions of these oxides are essentially important processes for the atomization, which will be discussed later. Sn may form type of oxide other than SnO_2.[11)]

Classification of the Elements in Terms of the Response Surface Patterns. The profiles of the response surfaces for 16 elements are shown in Figs. 3—7. Some of the elements are similar to each other. The elements may be classified into the following five groups according to the similarity;

Group A: Cd, Cu, Zn, Ni (Fig. 3); Group B: Pb, Co, Mn (Fig. 4); Group C: Fe, Mo, Ca (Fig. 5); Group D: In, Ga, Cr, Sn (Fig. 6); Group E: Ti, B (Fig. 7).

The characteristics of each group can be summarized as follows.

Group A: The contour lines for the iso-absorbance are almost horizontal and parallel with each other. This indicates that the absorbances of these elements are almost independent of the composition of the flame, although they are slightly more sensitive in the very acetylene-lean region than in the acetylene-rich one.

Group B: The contour lines run from the lower-left to the upper-right, and sensitive regions, expressed by the hatched area, spread towards the acetylene-rich region.

Group C: The contour lines in the response surfaces form half-rounded loop, which open mouth towards the acetylene-rich part. Moreover, the hatched region is very narrow and is located in the most acetylene-rich region. It should be noted that the absorbances of these elements can be hardly detected in the acetylene-lean region. This suggests that the increase in the reductive components of the flame rather than a high temperature is necessary for the atomizations of these elements.

Group D: The hatched regions are in a small circle of the contour line at the lower part of the flame height in the rather acetylene-rich region. The sensitivities of the elements in this group decrease in the relatively-lower-temperature part. This is characteristic of the elements whose oxides have large heats of formation as listed in Table 2.

Group E: The hatched regions are observed in longitudinally elongated loops of the contour lines in the acetylene-rich region. They are located at a upper position of flame height comparing to the other elements. The absorbances of these elements can be observed only in the extreme neighbourhood of the absorption maxima.

Atomization Processes. The thermodynamic properties, the heats of formation of the oxide, M_xO_y, and the dissociation energies of monoxides, MO, with respect to the elements are summarized in Table 2. They are concerned with the atomization processes of elements.

The patterns of the response surfaces obtained show that two different patterns of the atomization process exist. One is independent of the change in the nature of the flame. The response surface of *Group A* is typical of this pattern. The other is directly susceptible to the nature of the flame; *i.e.*, the atomization is promoted by an increase in the fuel flow rate. A typical pattern is *Group C*. *Group B* is intermediate between the former and the latter. For an explanation of this difference, the dissociation energy of the monoxide should be considered. The elements in *Group A* have small dissociation energies of monoxides, lower than 3.9 eV. Therefore, the monoxides of *Group A* elements are easily decomposed, and the monoxide formation does not actually interfere with the atomization of the element. In the case of *Group C*, whose monoxides have dissociation energies larger than 4.5 eV, the reduction of monoxide by the reduction components of the flame is an important process in the atomization. The energies of the monoxides of elements in *Group B* are between those of *Group A* and *C*, 3.9—4.2 eV; this explains why the response surface pattern of *Group B* is intermediate between those of *A* and *C*.

On the other hand, the locations of the sensitive region for the elements in *Group D* and *E* can not be interpreted only in terms of the dissociation energies of their monoxides. The hatched regions of Ga and In are located near the normal flame region, while the dissociation energies of their monoxides are very small. The hatched region of Sn is located in a less fuel-rich region than those of Fe and Mo, while the dissociation energy of SnO is larger than those of FeO and MoO. Those of Ti and B, whose monoxides have the largest dissociation energies among the elements investigated, do not appear in the most acetylene-rich region. It is noted that the sensitive regions of *Groups D* and *E* appear in a temperature region higher than those to be expected from the magnitudes of the dissociation energies of their monoxides. The fact mentioned above seems to be due to the formation of stable oxides, M_xO_y, of these elements in the flame. According to the description given in the previous section, the higher sensitivities are obtained in the higher-temperature flame for the elements whose oxides have heats of formation of more than about 10 eV. This fact suggests that the decomposition of the stable oxide proceeds under high-temperature conditions.

In the case of *Group E* elements, the oxides, TiO_2 and B_2O_3, and monoxides, TiO and BO, are all extremely stable compared to those of other elements. For the atomizations of these elements, a high temperature and a reductive atomosphere are indispensable. The atomic absorption spectrometry of these elements is difficult in the air–acetylene flame. This may be due to the facts that the temperature of the flame is as low as below 2100 °C in the fuel-rich region,[7)] and that their oxides are not decomposed. The atomic absorption spectrometry of these elements is also difficult in the hydrogen–oxygen flame even though the temperature of this flame is almost equal to that of the nitrous oxide–acetylene flame.[5)] We assume that the carbon components play an important role in the decomposition of the stable monoxide.

In summary, on the basis of the above discussions, the following atomization processes of the elements can be considered in the nitrous oxide–acetylene flame:

$$M(OH_2)_n{}^{m+} \longrightarrow M_xO_y \qquad (1)$$

$$M_xO_y \xrightarrow{\varDelta} MO \qquad (2)$$

$$MO + C \longrightarrow M + CO \qquad (3)$$

where $\varDelta$ represents the pyrolysis reaction; M, the atom of the analyzed element, and C, the carbon component in the flame. Reaction (2) expresses the pyrolysis of the oxides; it is important for the elements in *Group D* and *E*. Reaction (3) expresses the reduction of monoxide by means of the flame components. This must play a significant role in the atomizations of the elements in the *Group C* and *E*.

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