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TABLE OF ATOMIC AND
MOLECULAR LINES FOR
SPARK SOURCE MASS SPECTROMETRY
OF
COMPLEX SAMPLE-GRAPHITE MIXES

R. A. BURDO AND G. H. MORRISON

Department of Chemistry
Cornell University, Ithaca, N.Y.

ABSTRACT

A detailed table of atomic and molecular mass spectral lines has been prepared to aid in the interpretation of interferences and assignment of spectral lines in complex spectra arising from the spark source analysis of natural insulating powders blended with graphite to sustain the RF spark. The compilation consisting of 3000 listings is particularly useful for multielement trace analysis of geological and biological solids. Included are carbides, oxides, polymers, multiply-charged ions, and other molecular species of several or more major and minor elements as well as a large number of trace elements.

INTRODUCTION

Spark source mass spectrometry is a useful technique for multielemental trace analysis of geological and biological solids. Such insulating materials are usually powdered and mixed with graphite to produce strong and conducting electrodes. However, the sparking of complex graphite mixes yields complicated spectra containing the carbides, oxides, polymers, multiply-charged ions, and other molecular species of several or more major and minor elements as well as a large number of trace elements.

The primary purpose of the following table is to aid in the interpretation of interferences and assignment of spectral lines in complex spectra arising from the spark source analysis of natural insulating powders in a graphite matrix. In a secondary sense, the table may also be applied to other sample types or even to other fields of mass spectrometry such as ion probe analysis where molecular species become relatively more important.

There are indeed other excellent mass tables available for general use, but they are limited for application to the specific problem as stated. More explicitly, the table of Owens and Sherman (1) is arranged by individual element with comprehensive coverage for certain kinds of species excluding carbides, oxides, and many molecular species. The table of Guthrie and Heath (2), albeit arranged by mass, excludes carbides, most oxides, charge-exchange species, and other species of interest. The aim herein is to include those species omitted in preceding tables but of possible interest in complex graphite systems, to arrange the table in order of ascending mass values, to include the relative abundance of each species listed, to indicate the theoretical resolution required to separate a listed species from a line of analytical value, and finally to be concise in format but comprehensive in scope. The latter requirement has resulted in approximately 3000 listings each containing four data words and producing a text of approximately 12,000 words on a physical format of only thirteen pages.

The entire table was manually calculated, compiled, and typed and is therefore not meant as a manual of supercritical mass and abundance data, but merely as an interpretive and useful guide. The user must assume any liability of any kind incurred in the employment of this table. Further, no claim is made as to the existence or nonexistence of any species listed herein, nor to that of any species accidentally or purposely omitted.

EXPLANATION OF TABLE

Each listing consists of a row of four words starting with the name of the species and followed by the mass, abundance, and resolution requirement of the named species respectively.

I. NOMENCLATURE OF SPECIES

The usual chemical notation is used to identify the elemental constituents of the species. A leading superscript refers to the nominal mass of the species and a trailing superscript refers to the positive charge of the species. The plus signs of the charge superscripts are omitted since all species are ions of positive charge. The charge superscript is omitted entirely for species having a single positive charge. A special two-digit charge superscript indicates a charge-exchange species where the first digit is the initial charge of the species before a charge-reducing collision and the second digit gives the resulting or final charge after collision. The general nomenclature and the special meaning of the nominal mass superscript are best illustrated by example.

I.A. Elementally Homogeneous Species

- (a) ^{12}C : a singly-charged ion of carbon 12
- (b) $^{12}\text{C}^3$: a triply-charged ion of carbon 12
- (c) $^{12}\text{C}_2$: a homo-isotopic dimer of carbon and the only combination of carbon isotopes having a nominal mass of 24. (Absence of superscript = +1).
- (d) $^{25}\text{C}_2^3$: a hetero-isotopic dimer of carbon having a +2 positive charge and containing all combinations of carbon isotopes having a nominal mass of 25. (Only one combination in this case).
- (e) $^{86}\text{Si}_3$: a trimer of silicon containing all combinations of silicon isotopes giving a nominal mass of 86, ie, $^{86}\text{Si}_3 = (^{28}\text{Si}_2 + ^{30}\text{Si}) + (^{28}\text{Si}_1 + ^{28}\text{Si}_2)$, where the parentheses indicate the combinations having the same nominal mass.
- (f) $^{12}\text{C}^{32}$: a charge-exchange species of carbon 12 where the initial charge is +3 and the final charge is +2.

I.B. Elementally Heterogeneous Species

- (a) ^{28}SiC : a monocarbide of silicon 28 and the only significant* combination of carbon and silicon isotopes having a nominal mass of 40.
- (b) ^{41}SiC : all the combinations** of silicon and carbon isotopes having a nominal mass of 41, ie, $(^{28}\text{Si} + ^{12}\text{C})$ and $(^{28}\text{Si} + ^{13}\text{C})$.
- (c) $^{28}\text{Si}_3\text{C}_2$: the only significant* combination of silicon and carbon isotopes having a nominal mass of 108, ie, there is only one silicon trimer of nominal mass 84 and only one carbon dimer of nominal mass 24.
- (d) $^{109}\text{Si}_3\text{C}_2$: all the combinations** of silicon trimer and carbon dimer having a nominal mass of 109, ie, $(^{28}\text{Si}_3 + ^{12}\text{C}_2)$ and $(^{28}\text{Si}_3 + ^{28}\text{C}_2)$.

* The word 'significant' means that if a single combination of isotopes is cited, then it is either the only possible combination or a combination which accounts for 99.0% or more of the abundance of all possible combinations.

** The phrase 'all the combinations' means that the combinations included are either the only possible ones or that they cumulatively account for 99.0% or more of the abundance of all combinations.

The starred definitions have meaning in relation to the mass and abundance data following a cited species (see parts II and III).

II. MASS (second word)

The masses of singly-charged species are taken from the table of Guthrie and Heath (2) and are rounded to five decimal places. Some elements are known to less than five places while others are only approximated as indicated by a (/) following the last digit in the mass value. Polymeric and heterogeneous species have masses equal to the sum of

the individual contributing masses. Charge-exchange masses are obtained by multiplying the singly-charged mass by a factor (m/n^2) where (m) is the initial and (n) the final charge of the ion. Multiply-charged ions have masses equal to the singly-charged mass divided by the integral number of positive charges.

For species containing more than one combination of isotopes (eg., I.A.e, I.B.b, and I.P.d), the mass is that of the combination of isotopes which is the most abundant, as opposed to masses of single combinations which are unequivocal. The grouping of combinations of isotopes of the same elements to produce a species of the same chemical formula was performed to reduce the number of listings and is based on the fact that the combinations in a group are not resolvable with present commercial apparatus which have resolutions of 10,000 maximum and 5,000 or less practical.

III. ABUNDANCE (third word)

Isotopic abundances are based on Guthrie and Heath (2). Abundances apply only to species of the same kind (same chemical formula, same charge, but possibly different exact masses). For example, ^{28}SiC at mass 39.97693 comprises 91.19% of the total amount of silicon carbide formed from all combinations of silicon and carbon isotopes, ^{41}SiC at mass 40.97649 accounts for 5.67%, etc. The abundance of ^{28}SiC is that of a single combination while that of ^{41}SiC is the sum of the abundances of more than one combination.

The abundances of molecular species which are elementally homogeneous are calculated using the binomial expansion according to Hill (3) or the equivalent probability formula given by Owens and Sherman (1) for polyatomic clusters:

$$RA = (A^a B^b C^c \dots N^n)(M!)/(a! b! c! \dots n!) \quad 1.$$

where RA is the relative abundance of a given polyatomic cluster (a specified combination of isotopes) containing M total atoms of an element which has isotopes A', B', C', ..., N' with isotopic abundances A, B, C, ..., N respectively and where the number of atoms of each isotope contained in the cluster is a, b, c, ..., n respectively. The summation (a+b+c+...+n) is equal to M. This formula is applied to each specific combination of isotopes until all possible combinations are exhausted.

For clusters containing different elements, the above formula is applied to each element individually and the abundance of the heterogeneous cluster is taken as the product of the individual RA's for each element in the cluster.

The tabulated abundances are given in percent. The appearance of an (E) in the tabulated abundance indicates a negative exponential form so that 1.2E3, for example, means 0.0012%.

For species containing more than one combination (see I), the abundance is the sum of all combinations considered, whereas the mass is that of the most abundant combination.

IV. RESOLUTIONAL REQUIREMENT (fourth word)

Resolution is defined as $R = M_0/4M$. M_0 is indicated in the table by a series of five dashes for a line of interest at each nominal mass unit and at some half-mass units where appropriate. A negative value for R indicates that the listed species occurs at a lower mass than M_0 , the latter being indicated by the next dashed line. A positive value of R indicates a higher mass than M_0 which is defined as the first previous dashed line.

The appearance of an (E) in the resolution value indicates a positive exponential form so that 15E3, for example, means a resolution of 15,000. There are no exponential forms for resolutions less than 10,000 (= 10E3).

V. SCOPE

The number and kinds of species included for each element depends on its definition as a major, minor, or trace constituent in geological and biological samples. Carbon, being the matrix considered, is defined as a major element. Other defined majors are oxygen, sodium, silicon, phosphorus, sulfur, potassium, calcium, titanium, and iron. Minors are given as chromium, nickel, zinc, strontium, zirconium, and barium. Most other elements are defined as trace.

For trace elements the species considered are: singly-and-multiply charged ions up to +3, polymerization up to the dimer only, mono-and-dicarbides, and mono-and-di-oxides.

For minor elements the species are: singly-and-multiply charged ions up to +4, polymerization up to the trimer, formation of oxide up to the trioxide and carbide to the tricarbide, and charge-exchange species with initial charges of +4 or less.

Major elements have more extensive coverage: singly-and-multiply charged ion up to +6, polymerization up to four atoms, formation of tetra-oxide and tetra-carbide, charge-exchange species with initial charge of 7 or less, and some complex species having two atoms of the major species and one to three atoms of carbon or oxygen. Polymer formers such as carbon, aluminum, and silicon are considered to form even more complex species and some combinations of these elements with other major elements are included. Appropriate higher degrees of polymerization and carbide and oxide formation are listed for these three elements.

Only the lower-charged species of rare gases are considered.

Hydrocarbons up to mass 100 are included.

The first hydrides (MH) of all elements from lithium to molybdenum plus barium, lanthanum, and cerium are also listed.

The mass range covered is from 1 to 270 with reductions in the number of entries from mass 210 to 270 where only two elements, thorium and uranium, are of interest.

REFERENCES

1. E.B. Owens and A.M. Sherman, Mass Spectrographic Lines of the Elements, MIT Tech. Rep. No. 265, 1962
2. J.W. Guthrie and F.L. Heath, Table of Atomic Masses, Sandia Corporation Monograph SCR-245, 16th Ed., 1961
3. H.C. Hill, Introduction to Mass Spectrometry, Heydon and Son, London, 1966

