Atomic Absorption Spectroscopy with High Temperature Flames

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An account is given of the history of the development of high temperature flames for the atomic absorption measurement of metals forming refractory oxides. The principles governing the design of premix burners for such flames, and the relative merits of different types of nebulizer burner systems are described. After a brief account of the structure and emission characteristics of the premixed oxygen–acetylene and nitrous oxide–acetylene flames, the scope and limitations of the latter flame in chemical analysis are discussed.

I. Introduction

In his original paper drawing attention to the potentialities of the atomic absorption technique in chemical analysis, Walsh[1] discussed the principles of the method without making any presuppositions about the means used to produce the atomic vapor. It is clear from his paper, however, that he appreciated the simplicity and convenience of using a flame to atomize* a solution of the analytical sample, and, in the first published description of an atomic absorption spectrophotometer,[2] the sample solution was introduced into the air supply of a Meker burner operating on air and coal gas, with the help of a nebulizer similar to that used in early types of Perkin-Elmer flame photometers. Even at this early stage of development of the subject it was realized that the problem of atomization was central to the whole atomic absorption technique, and since that time considerable effort has been expended in attempts to devise methods of effectively atomizing the widest possible range of elements. Although several other techniques have been tried, such as cathodic sputtering,[3–8] the arc heated graphite crucible,[9] the induction coupled plasma,[10] and gas stabilized arc discharges,[11] use of a suitable flame still remains the method of atomization favored by the overwhelming majority of workers in the field. This is hardly surprising since convenient and efficient nebulizers and burners have been developed for flame photometry and are commercially available. While the flame has certain disadvantages, the equipment required is simple, inexpensive, easy to use, and well adapted to rapid measurement of a series of different solutions, so that it is unlikely that any other method of atomization will replace it for the great bulk of analytical work.

II. Equipment

As the development of high temperature flames for use in atomic absorption spectroscopy has required close attention to the design of nebulizers and burners, it is necessary to discuss briefly the types of equipment currently used to introduce the sample solution into the flame; a more detailed account may be found elsewhere.[12] Nebulizer burner equipment can be divided into two types which appear in the literature under several different names.

A. Turbulent Flow Burners

The characteristic feature of this type of burner is that the fuel gas and the combustion supporting gas are not mixed until the point at which they enter the flame, and the solution to be nebulized is also introduced at this point. Thus, the burner is a combination nebulizer burner; it is also known as a *direct injection* or *total consumption* burner, since all the liquid aspirated enters the flame and is converted to a spray at the point of entry. This type of burner is used in many emission flame photometers, since it is particularly well suited to safe operation with gas combinations having high burning velocities, such as oxygen–hydrogen or oxygen–acetylene. It has been used to some extent in atomic absorption following the early work of Robinson.[13,14]

B. Laminar Flow Burners

In this type of system the combustion supporting gas aspirates the liquid sample and produces an aerosol which passes into a spray chamber where the larger droplets (usually 80–90% by weight of the total) settle out. The fuel gas may be added either before or after the spray chamber, and the mixture of fuel gas, support

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* The word *atomization* is used in its exact sense to mean production of atoms rather than in its colloquial sense meaning production of a fine spray. The device used for spraying a solution into a flame is referred to as a *nebulizer*.

gas, and fine droplets proceeds to a burner where it is burned. This system, also known as a *premix burner* or *indirect nebulizer burner*, was popularized by Lundegårdh for emission measurements using the air–acetylene flame,[15] and was introduced into atomic absorption work by Allan[16] and David[17]; it is favored by most workers in the field. The design and performance of a typical nebulizer spray chamber system have been discussed recently by the author.[18]

A typical burner for a premixed system consists of a block[19,20] or tube[21] of stainless steel or other chemically resistant material containing either an array of holes or a slot at which the flame burns. An array of holes serves well for low burning velocity, low temperature flames, such as air–propane,[22] but the rapid encrustation of the very small holes required for high burning velocity, high temperature flames has led to almost universal use of slot burners for high temperature premixed flames. Water cooling is not necessary except with the very hottest (oxygen–acetylene) flames.[23–25]

C. Relative Merits of Turbulent Flow and Laminar Flow Burners

Both types of burner have been extensively used and their relative merits widely discussed.

The turbulent flow burner gives a flame which is tall and narrow; while suitable for emission work it provides a much shorter light path and hence poorer sensitivity in absorption than does a laminar flow burner. The path length can be increased by using several burners in series or by passing the light beam several times through the flame.[26]

The uptake of solution by the turbulent flow burner is usually less than by the laminar flow one, and, since all the aspirated solution enters the flame, the production of atoms should be more efficient. However, there is evidence that some of the liquid aspirated in the total consumption type of burner passes through the flame without being vaporized.[27,28]

No quantitative comparison of the stabilities of atomic concentrations in the flame at the two types of burner under similar conditions seems to have been made, but one would expect the fluctuation level to be worse for the turbulent flow burner, if only because of the presence of large drops in the flame. Even the addition of a small premixing chamber above the turbulent flow burner improves the signal-to-fluctuation ratio in both emission and absorption.[29] Changes in the temperature of the flame brought about by the introduction of the liquid sample are very much smaller in the laminar flow burner.[30]

Chemical interferences, which arise at least in part from incomplete vaporization of the solid particles formed from the larger drops entering the flame, are known to be worse with the turbulent flow than with the laminar flow burner.[31]

There is no doubt that the turbulent flow burner is inherently safer than the laminar flow type, since the fuel and support gases do not mix until the actual point of entry into the flame, and thus flashback is impossible. One drawback of the turbulent flow burner, however, is the unpleasantly loud audible noise which it emits while running; the laminar flow burner on the other hand is almost completely silent in operation.

The author feels that for atomic absorption work, at least, the laminar flow burner is superior, and it is significant that almost all the commercial instruments currently produced use this type.

D. Design of Laminar Flow Burners

It is not possible to go into detail here about the theory of flame propagation, on which the whole subject of burner design depends, and reference must be made to specialized books on the subject.[32,33] An excellent analysis of the factors involved in designing a premix burner for high temperature flames has been given recently by Fiorino *et al.*[25]

The production of a stationary flame requires that the stream velocity of the fuel–oxidant mixture through the burner port be at least equal to the burning velocity. If this condition is not met, the flame is liable to flash back down the burner port and cause an explosion in the spray chamber. In practice, both to ensure a margin of safety and achieve a reasonably stiff flame, i.e., one which is not unduly disturbed by air currents in its neighborhood, the burner is designed so that the stream velocity is several times the burning velocity. The flame is prevented from flashing back at the walls of the burner port, where the stream velocity is zero, by the *quenching* effect of the walls, and since the quenching effect extends some distance out from the walls, there is a limiting size of burner port below which the flame of a given gas mixture will not flash back. Unfortunately, however, this size is usually so small for high temperature flames that it is not practicable to rely on the quenching effect alone to avoid flashback.

The burning velocity of a fuel–oxidant mixture is a function of its composition, and usually, though not always, reaches its maximum value near the stoichiometric ratio. Thus, it can be seen why a moderately fuel rich flame may burn satisfactorily at a burner but flash back when it is extinguished by the usual procedure of cutting off the fuel supply. During this process the flame will pass momentarily through the stoichiometric condition, where, if the gas stream velocity is too low, flashback will occur. If the fuel gas comprises an appreciable part by volume of the total gas mixture, the reduction in stream velocity when the fuel is shut off may be sufficient to cause flashback.

The problems of designing burners for high temperature flames arise principally from the fact that gas mixtures having high flame temperatures usually have high burning velocities. This requires limitation of the size of the burner port, with the attendant disadvantage of easier blockage by deposits of salt or carbon. If a large burner port is desired, it is necessary to use large flow rates of gas mixture and either design a nebulizer to operate on the whole of the oxidant or else introduce part of the oxidant as an auxiliary supply direct to the spray chamber. It may be noted also that for some gas mixtures the burning velocity increases with the temperature of preheating,[33] so that the burner top should be kept sufficiently cool; it must in any case be kept well below the ignition temperature of the gas mixture.

E. Optical and Electronic Instrumentation

The use of high temperature flames imposes somewhat more stringent requirements on the optical and electronic components of the atomic absorption spectrometer than does most work with conventional low temperature flames.

Many of the metals for which a high temperature flame is necessary, such as the rare earths and the members of groups IVB, VB, and VIB, have complicated spectra, and effective isolation of the resonance line often calls for a monochromator with a resolution of 1 Å or better. Furthermore, the heat generated by high temperature flames is such that suitable shielding may be necessary to prevent thermal effects causing drift in the wavelength setting of the monochromator.

Since emission of light by high temperature flames is considerable even in the uv, it is essential to use a modulated light source and an ac amplifying system; in many cases it is highly desirable that the amplifier be tuned fairly closely to the modulation frequency of the source. Fortunately, hollow cathode lamps of most of the metals requiring use of a high temperature flame do not show appreciable self-absorption, so that frequently it is possible to maintain an adequate signal-to-noise ratio merely by running the lamp at a sufficiently high current. For some elements, such as silicon, use of a high intensity lamp[34] may be beneficial.

The signal-to-noise level of the system determines the limit of detection, which is usually defined as the concentration of element in solution required to produce an absorption signal equivalent to twice the rms background fluctuation in the zero absorption signal. It does not, however, affect the sensitivity, which is conventionally defined as the concentration of element in solution required to produce 1% absorption with a particular nebulizer and burner system.

III. Development of High Temperature Flames

A. Low Temperature Flames

Air–coal gas and air–propane flames satisfactorily atomize the metals of groups IA, IB, IIB, together with gallium, indium, thallium, lead, tellurium, manganese, nickel, and palladium, but several important metals such as magnesium, calcium, iron, and cobalt are incompletely atomized and are subject to chemical interferences, while most of the remaining metals are scarcely atomized at all.

The introduction of the air–acetylene flame around 1958 brought the list of metals showing useful sensitivity in absorption to about thirty-five,[20,35] but a number of these metals were still subject to chemical interferences; calcium absorption, for instance, was depressed in the presence of phosphorus, and both calcium and magnesium absorption were depressed in the presence of aluminum. That degree of atomization is not merely a function of flame temperature was demonstrated by Gatehouse and Willis[20] and by David,[36] who found that some metals, such as molybdenum and tin, showed higher absorption in a fuel rich air–acetylene flame than in a hotter, more nearly stoichiometric one. Later it was discovered[24,37,33] that use of an air–hydrogen mixture, though giving a cooler flame than air–acetylene, led to improved atomization for tin, arsenic, and selenium. However, even with flame conditions chosen to give the highest sensitivity chemical interferences may still be serious.

The burning velocities of oxygen–hydrogen mixtures are so high that premixed flames using these gases have seldom been employed in flame spectroscopy, while a turbulent oxygen–hydrogen flame, of the type widely used in emission flame photometry, may have an effective temperature of less than 2300°C when aspirating aqueous solutions.[39] For this reason, the oxygen–hydrogen flame used by some workers in atomic absorption spectroscopy must be regarded as a low temperature flame, and this view is substantiated by the results published on its range of usefulness[14] and tendency to show chemical interferences.[31,40] In emission, however, the use of this flame with force fed organic solutions has recently shown promising results in the detection of a number of metals forming refractory oxides.[41]

Table I shows the burning velocities and calculated and measured flame temperatures for a number of gas mixtures which have been used or considered for use in atomic absorption work.

B. The Oxygen–Cyanogen Flame

The first published attempt to use a high temperature flame in atomic absorption spectroscopy was made by Robinson,[14] who used a total consumption burner in which the sample was aspirated by premixed oxygen–cyanogen. For several metals he achieved sensitivities slightly better than those obtained with a turbulent flow, oxygen–hydrogen flame, but he was unable to detect any absorption for tin, tantalum, tungsten, and aluminum, while vanadium was only detectable with poor sensitivity. Since Robinson had observed emission signals from these metals at the same wavelengths in the oxygen–cyanogen flame, it is surprising that he failed to detect absorption; this failure may be explained in several ways; e.g., (1) the atoms of metals forming refractory oxides probably exist only in highly localized regions of this flame, and it is possible that too small a portion of the light beam was intercepted by the optimum part of the flame; (2) the excited atoms detected in emission may be formed by some chemiluminescent process rather than by thermal excitation, so that they are not in equilibrium with a ground state population of atoms which can absorb radiation.

Although the oxygen–cyanogen flame, with its low burning velocity and high temperature, looks promising for the atomization of metals forming refractory oxides it has several drawbacks: (1) cyanogen is a highly toxic and explosive material, so that it is difficult to envisage

Table I. Characteristics of Premixed Flames of Interest in Atomic Absorption Spectroscopy

Gas mixture	Maximum flame speed (cm sec^{-1})	Reference[a]	Maximum temperature, °C			
			Calculated	Reference[a]	Measured by reversal	Reference[a]
Air–coal gas	ca. 55	30			1918	42
Air–propane	43	33			1925	30
Air–hydrogen	440	30	2047	44	2045	44
	320	43	2100	33		
Air–acetylene	266	30	2250	33	2325	44
	170	43	2290	45	2275[b]	45
50% oxgyen–50% nitrogen–acetylene	640	43	2815	43		
Oxygen–coal gas					2720	46
Oxygen–propane	390	43	2835	43		
Oxygen–hydrogen	1190	43	2815	43		
	1120	47	2810	33		
			2680	46	2660	46
Oxygen–acetylene	2480	30	3257	46	3140	46
	1130	43	3060	43		
			3110	48	3100	48
Oxygen–cyanogen (1:1 molar ratio)	140	30	4600	49	ca. 4500[c]	49
	270	50	4540	51	4370	51
Nitrous oxide–propane–butane	ca. 250	52			ca. 2550	52
Nitrous oxide–hydrogen	390	53	ca. 2660	53	ca. 2550	55
	380	54	ca. 2640	54		
Nitrous oxide–acetylene	160	53	ca. 2950[d]	53	ca. 2700	55
Nitric oxide–hydrogen (1:1 molar ratio)	30	53	2840	53	2820	53
Nitric oxide–acetylene	87	53	3090	53	3095	53
Nitrogen dioxide–hydrogen	150	53	2660	53	1550[e]	53
Nitrogen dioxide–acetylene	135	53				

[a] Reference 30 contains figures from the older literature.

[b] The flame was sheathed and the burner top was made of silver and insulated to minimize heat losses.

[c] Temperature measurements made on the vibrational structure of the violet CN band system.

[d] This temperature was read by interpolation from a graph in Ref. 53. It was probably calculated.[93]

[e] Combustion does not go to completion.

its routine use by unskilled operators; (2) owing to the poor diffusivity of cyanogen into oxygen it is difficult to maintain a steady flame with this combination of gases; (3) the oxygen–cyanogen flame is cooled by as much as 2000°C when aspirating even small volumes of liquid.[56]

C. The Oxygen-Acetylene Flame

In 1963, several workers published accounts of atomic absorption measurements with fuel rich turbulent oxygen–acetylene flames. Fassel and Mossotti,[26] using multiple passages of light from a xenon arc through the flame, obtained useful absorption at a number of wavelengths for vanadium, titanium, niobium, scandium, yttrium, and rhenium, while Slavin and Manning,[57] using hollow cathode lamps as sources, demonstrated strong absorption for aluminum, vanadium, titanium, and beryllium. They, too, used ethanolic or isopropanolic solutions sprayed into a turbulent flame. Fassel and Mossotti's work was later extended to demonstrate the feasibility of spectral continua as primary sources in the determination of a large number of metals, including many of the rare earths.[58]

Dowling *et al.*[59] extracted aluminum from aqueous solutions into 2-methyl-4-pentanone and sprayed this extract into a turbulent oxygen–acetylene flame. They showed that use of a fuel rich flame was necessary to obtain the highest concentration of aluminum atoms, that the atoms were highly localized in the flame, and that replacement of the organic solvent by water reduced the absorption almost to zero.

The first published atomic absorption measurements on the lanthanide metals were made by Skogerboe and Woodriff,[60] who used an oxygen–hydrogen flame fed with a solution of the lanthanide salt as a line source, with an oxygen–acetylene flame as the absorbing medium. Absorption was demonstrated in this way for organic solutions of europium, thulium, and ytterbium, but the limits of detection were poor on account of the low intensity and lack of stability of the light emitted by the source flame.

The improvement in a signal-to-fluctuation ratio in emission achieved by the addition of a small spray chamber to the turbulent flow oxygen–acetylene burner[29] led to the use of this type of burner by Cowley *et al.*[61] in a study of the absorption profiles of scandium, chromium, and lanthanum in oxygen–acetylene flames of different stoichiometry, and pointed the way to the development of fully premixed oxygen–acetylene flames.

Amos and Willis[24] carried out a few experiments with a premixed oxygen–acetylene flame burning at a single row of twenty-five holes of 0.6-mm diam, but abandoned the use of this flame in favor of the nitrous oxide–acetylene one. Fiorino *et al.*[25] have described a burner with an 8-cm slot of adjustable width designed for use with both premixed oxygen–acetylene and nitrous oxide–acetylene flames, and have shown that for a range of metals forming refractory oxides, fairly similar limits of detection are observed with the two flames. However, even with this carefully designed burner, when using oxygen–acetylene mixtures, care must be taken to avoid flashback by using a narrow slot (0.25 mm), by keeping a total gas flow through the burner of at least 25 liters/min, by always keeping the mixture fuel rich, and by turning off the oxygen first when extinguishing the flame.

D. The Oxygen–Nitrogen–Acetylene Flame

Amos and Thomas[23] investigated the absorption of aluminum in premixed, air–acetylene flames in which the air was enriched with oxygen up to a maximum of 85%, using a burner consisting of a row of fourteen holes of 1-mm diam in a steel plate 3 mm thick. Explosion hazards forced these workers to turn to mixtures containing not more than about 50% oxygen burning at a burner consisting of a stainless steel block 1.25 cm thick with a 3-cm × 0.45-mm slot. Later work showed that the same technique could be applied to many other metals forming refractory oxides.[24]

However, the oxygen–nitrogen–acetylene flame has some disadvantages in routine work since it requires the provision of either commercial oxygen–nitrogen mixtures or fairly complex gas mixing equipment in order to prevent the inadvertent use of mixtures too rich in oxygen. Furthermore, the length of the burner slot seems limited to about 3 cm because of the high burning velocities of gas mixtures sufficiently rich in oxygen to give adequate atomization of metals forming refractory oxides.

E. The Nitrous Oxide–Acetylene Flame

A more generally useful flame is that of acetylene burning in nitrous oxide.[62] Here the burning velocity is relatively low, and the high temperature of the flame is due in part to the energy liberated by the decomposition of the nitrous oxide. This flame can be safely burned at a slot as long as 10 cm, though a 5-cm slot is found to be optimum for most metals. Amos and Willis[24] demonstrated that this flame could be safely used with standard commercial instruments providing a sufficiently solid burner top was fitted and found good sensitivities for almost all the metals which form refractory oxides and had proved difficult or impossible to atomize with low temperature flames. This flame has been adopted by the manufacturers of commercial atomic absorption spectrophotometers as the standard method of atomizing metals which are not satisfactorily atomized in the air–acetylene flame, and detailed accounts of the performance of such instruments are available.[63–66] Its usefulness in emission work has also been demonstrated.[94–96]

F. The Nitric Oxide–Acetylene and Nitrogen Dioxide–Acetylene Flames

The lower burning velocities and higher flame temperatures attainable by burning acetylene with nitric oxide or nitrogen dioxide suggest that such flames might be valuable,[62] but the expense and corrosive nature of these oxides of nitrogen militate against their use. Slavin and co-workers[64] have found that the sensitivity for several metals is slightly greater in the nitric oxide–acetylene than in the nitrous oxide–acetylene flame, but the stability of the flame is so poor that the detection limits are usually worse than in the latter.

G. The Nitrous Oxide–Propane–Butane Flame

Though this flame is not sufficiently hot to atomize all the metals forming refractory oxides, Butler *et al.*[52] have shown that in the determination of the alkaline earth metals it eliminates phosphorus and aluminum interference almost as well as does the nitrous oxide–acetylene one.

H. The Nitrous Oxide–Hydrogen Flame

The author has found[55] that for the alkaline earth metals this flame gives useful sensitivities and limits of detection, which, however, are distinctly poorer than those obtained with the nitrous oxide–acetylene flame; molybdenum and aluminum are not atomized to any appreciable extent. Ionization of calcium, strontium, and barium appears negligible in this flame.

IV. Structure and Emission Characteristics of Oxygen–Acetylene and Nitrous Oxide–Acetylene Flames

A. The Oxygen–Acetylene Flame

The fuel rich, premixed oxygen–acetylene flame burning at a slot burner shows three distinct regions: (1) the primary reaction zone, which is usually only 1–2 mm high and intensely bright; (2) the interconal zone, which is also intensely bright and difficult to distinguish by eye without the use of dark glasses; and (3) the blue outer mantle.

The interconal zone is relatively rich in carbon containing species, particularly C_2, and it seems largely these species that determine the ability of the oxygen–acetylene flame to reduce refractory oxides to free metal atoms. In conventional, near-stoichiometric flames, metals such as scandium and lanthanum are not detectable in either emission or absorption, while in the fuel rich flame their atomic species appear only in the interconal zone and not in the outer mantle.[25,61]

B. The Nitrous Oxide–Acetylene Flame

The premixed, nitrous oxide–acetylene flame burning at a slot burner is also characterized by three regions: (1) the primary reaction zone, which is usually 1–3 mm high and white-blue in color; (2) the characteristic red interconal zone, sometimes referred to as the red

Table II. Sensitivities and Limits of Detection for Metals Determined in the Nitrous Oxide–Acetylene Flame

Metal	Line, Å	Approximate sensitivity[a] μg/ml	Approximate limit of detection[b] μg/ml	Notes	Applications
Aluminum	3092.7	1	0.1	c	Alloys,[23] bauxites,[68] organo–aluminums,[69] titanium alloys,[77] cements,[82] wool,[92] rocks,[97,98] polymers[99]
Barium	5535.5	0.4	0.1	d	Rocks[68]
Beryllium	2348.6	0.02	0.003	c	Process liquors,[70] environmental materials[100]
Boron	2497.7	50	6	e,f	Biological materials[101]
Cerium	5200	83		g	
Dysprosium	4211.7	0.7	0.4	c,d	Phosphate rock,[71] yttria[84]
Erbium	4008.0	0.9	0.1	c,d	Phosphate rock,[71] yttria[84]
Europium	4594.0	0.8	0.2	d	Phosphate rock,[71] yttria[84]
Gadolinium	4078.7	17	4 (at 3684 Å)	c,d	Phosphate rock[71]
Germanium	2651.6	1.5	1	f	
Hafnium	3072.9	14	15	e,f,h	
Holmium	4103.8	1.5	0.3	d,f	Phosphate rock[71]
Lanthanum	5501.3	42	8	d	Phosphate rock[71]
Lutetium	3359.6	12		c	
Molybdenum	3132.6	0.4			Steels,[72] niobium and tantalum,[73] indirect determination of silicon[80] and phosphorus[81]
Neodymium	4634.2	10	2	d,f	Phosphate rock,[71] yttria[84]
Niobium	3349.1	24	5 (at 3343.7 Å)	h	
Osmium	2909.1	1			
Praseodymium	4951.4	13	10	d,f	Phosphate rock[71]
Rhenium	3460.5	12	1.5	f	
Samarium	4296.7	9	5	d	Phosphate rock[71]
Scandium	3911.8	0.6	0.2	c,d	
Silicon	2516.1	2.5	0.1	e,f,i	Bauxite,[68] steels,[74] cement,[82] rocks[97]
Strontium	4607.3	0.06		d	Rocks,[68] cement[82]
Tantalum	2714.0	11	6	f,h	
Terbium	4326.5	7.5	2	d	Phosphate rock,[71] yttria[84]
Thorium	3245.8	850		g	
Thulium	3717.9	0.5		d	
Titanium	3642.7	3.5	0.2	f,h,i	Steels,[68,75] nickel-base alloys,[76] bauxite,[68] cement,[82] polymers[99]
Tungsten	2551.4	5	3 (at 4008 Å)	f	
Uranium	3584.9	120	30 (at 3514 Å)	c,j	
Vanadium	3184.0	1.5	0.02	f,i	Oils,[68,78] steels,[78] titanium alloys[77]
Yttrium	4102.4	1.5	0.3 (at 4077 Å)	c,d	Phosphate rock[71]
Ytterbium	3988.0	0.2	0.04	c,d	Phosphate rock[71]
Zirconium	3601.2	15	5	h	Thorium oxide samples,[79] indirect determination of fluoride[89] and ammonia,[90] aluminum alloys[102]

[a] Concentration giving 1% absorption when sprayed as an aqueous solution into a 5-cm premixed flame. Data from Ref. 12.

[b] Concentration which when sprayed as an aqueous solution into a 5-cm premixed flame in a Perkin-Elmer 303 instrument gives an absorption equal to twice the noise level of the background. Data from Refs. 63 and 65.

[c] Slightly fuel rich flame.

[d] Ionization suppressed with 1000-μg/ml potassium.

[e] Absorbance–concentration curve flattens markedly at high concentrations.

[f] Fuel rich flame.

[g] Heated spray chamber used.

[h] Measured in the presence of 2% hydrofluoric acid.

[i] High brightness, hollow cathode lamp used.

[j] Absorbance markedly dependent on spectral slit width.

feather, which varies in height from 0 mm to 20 mm or 30 mm depending on the acetylene/nitrous oxide ratio; and (3) the blue outer mantle.

Kirkbright *et al.*[67] have measured the radiation from various parts of the flame and have shown that the red interconal zone, which is generally used in atomic absorption work, is characterized by strong CN and NH emission. When enough acetylene is added, the red interconal zone tends to be masked by the yellow luminosity, extending throughout the flame, which arises from incandescent carbon particles. These authors suggest that the reactions occurring in this flame to produce metal atoms from refractory oxides are more complex than the simple reducing action of atomic carbon or incandescent carbon particles which has been invoked by various authors to explain the production of metal atoms in the oxygen–acetylene flame.

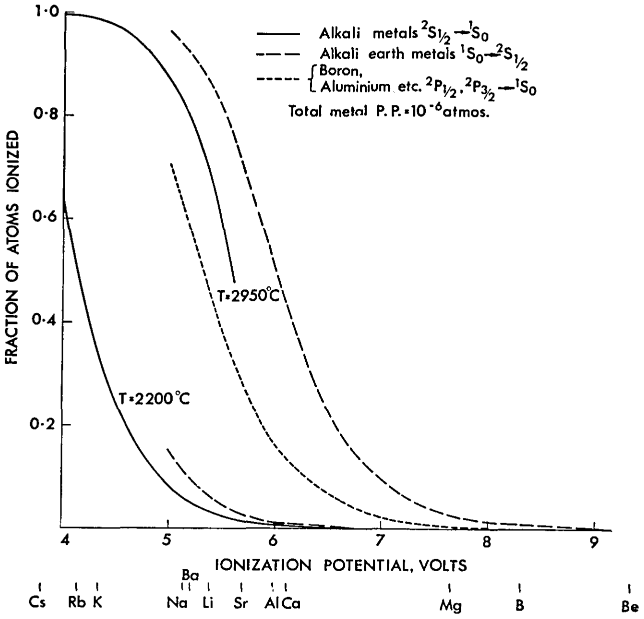

Fig. 1. Degree of ionization, calculated by the Saha equation, for various metals at temperatures of 2200°C and 2950°C, assuming a total metal partial pressure of 10^{-6} atm.

V. Use of High Temperature Flames in Chemical Analysis

A. Range of Application of High Temperature Flames

Of the high temperature flames mentioned above, the nitrous oxide–acetylene flame has been most widely studied and applied in practical analytical situations. Table II shows the approximate sensitivities and limits of detection for thirty-five metals for which the use of this flame is recommended. The table is based on the work of Amos and Willis[24] and of Manning,[63] to whose papers reference may be made for a detailed discussion of particular metals. The table also includes references to published applications of high temperature flames in practical analysis.

B. Comparative Sensitivities of Nitrous Oxide–Acetylene and Oxygen–Acetylene Flames

Several workers[83–85] have compared sensitivities or limits of detection for various metals in these two flames, the usual procedure being to compare a premixed nitrous oxide–acetylene flame burning at a standard 5-cm × 0.5-mm slot burner with a turbulent flow oxygen-acetylene flame at a total consumption burner. In every case the longer light path achieved by use of the slot burner leads to the attainment of higher sensitivities with the nitrous oxide–acetylene flame, though in some instances it is possible to improve the sensitivity of the oxygen–acetylene flame to match that of the nitrous oxide–acetylene flame by using several burners in series and by replacing aqueous with organic solutions. In general, the fluctuation level of the turbulent flow burner is appreciably higher than that of the premixed system, so that limits of detection are likely to be worse for the former.[84]

The enhancement of absorption achieved by replacing aqueous solutions with solutions in organic solvents is usually greater in the turbulent flow than in the laminar flow flame, though close comparisons have seldom been made. Ramakrishna *et al.*[85] found a sixfold enhancement of beryllium absorption in a turbulent flow oxygen–acetylene flame, but only a 1.25-fold enhancement in a laminar flow nitrous oxide–acetylene flame on replacement of water with a 5–10% solution of diethyleneglycol diethyl ether. Such enhancements are not due to the greater rate of supply of the solution to the flame, as the rate of aspiration of the organic solution is actually less than of the aqueous one, at least in the case just cited, but must be due to the finer droplet size and improved atomization efficiency achieved by using solutions in organic solvents. The droplet size is more critically dependent on solvent properties with the total consumption than with the laminar flow burner, though even with the latter atomization efficiency is frequently very sensitive to changes in aspiration rate,[18,84] and use of an adjustable nebulizer is highly desirable.

Fiorino *et al.*[25] have made a more accurate comparison of the two flames, both of them premixed and burning at the same burner. The detection limits for most of the twelve refractory oxide forming metals studied by these authors were fairly similar in the two flames, though those for lanthanum and uranium were appreciably better with oxygen–acetylene.

C. Ionization Effects in High Temperature Flames

Even a low temperature flame such as air–propane possesses enough energy to ionize an appreciable fraction of the atoms of the alkali metals, and the degree of ionization rises rapidly with increase in flame temperature, so that in the oxygen–acetylene and nitrous oxide–acetylene flames, not only the alkali metals but many others may be ionized to a considerable extent. The degree of ionization, which is calculated by the Saha equation, depends among other things on the concentration of metal atoms in the flame, and is greatest at low concentrations, as discussed elsewhere.[12,86] Figure 1 shows the calculated degrees of ionization for different metals at two temperatures, assuming a partial pressure of metal of 10^{-6} atm.

The ionization of an atom M to its positive ion M^+ and a free electron e^- is assumed to behave as a simple dissociation process governed by the law of mass action, and it is found that the ionization of a metal in the flame can be suppressed by the presence of a sufficiently high concentration of electrons, which may be provided by the addition of a salt of a readily ionized metal such as cesium or potassium. From the change in absorbance of the neutral atomic species when this is done, the degree of ionization of the metal can often be approximately determined.

Table III shows calculated and measured degrees of ionization for a number of metals in the nitrous oxide–acetylene flame. The agreement between these two

Table III. Calculated and Measured Degrees of Ionization of *Metals in the Nitrous Oxide–Acetylene Flame*

		Degree of ionization		
Metal	Ionization potential, eV	Calculated for T = 2950°C $PP = 10^{-6}$ atm	Measured in nitrous-oxide-acetylene flame	Reference
Na	5.14	0.82		55
K	4.34	0.98		55
Be	9.32	0.00	0.00	24
Mg	7.64	0.03	0.06	24
Ca	6.11	0.43	0.43	24
			0.38	86
Sr	5.69	0.71	0.84	24
Ba	5.21	0.92	0.88	24
			0.92	86
Al	5.98	0.17	ca. 0.14	55
Eu	5.67	0.61	ca. 0.60	55
Yb	6.2	0.36	0.20	24

sets of values is surprisingly good, since neither the temperature of the flame nor the partial pressure of metal atoms in it is known with certainty; furthermore, the addition of potassium chloride may also affect the efficiency of vaporization of the metallic salts in the flame. The assumed flame temperature may well be too high by 200–300°C and the partial pressure of metal too high by a factor of 10–100, so that the happy agreement between calculation and experiment may arise merely through a compensation of opposing errors.

Ionization interference is overcome where necessary in atomic absorption work by the addition to the standards of the same concentration of interfering element as in the sample solution. Alternatively, a large excess of the interfering element may be added to each.[68]

D. Chemical Interferences in High Temperature Flames

Chemical interferences occur in atomic absorption, as in flame emission work, through the chemical combination of the element to be determined with other elements or compounds present in the flame. Well known examples occurring in low temperature flames are the combination of calcium with phosphorus and the combination of calcium and of magnesium with aluminum. The refractory compounds formed cannot be decomposed completely at the temperature of the flame and thus lead to partial or complete removal of metal atoms from the flame.

The mechanism of chemical interference is not fully understood in all cases, but interference is always least in hot flames and generally decreases in the upper parts of the flame.[18] It is also dependent on drop size, being least for the finest sprays, so that direct injection burners show higher levels of interference than do premix systems.[31]

One of the pleasing features of the premixed oxygen–acetylene and nitrous oxide–acetylene flames is their relative freedom from some of the chemical interferences found in flames of lower temperature. For instance, Amos and Willis[24] found that the presence of a relatively large concentration of phosphoric acid, which in the air–acetylene flame strongly suppresses calcium absorption, actually enhanced it slightly in the nitrous oxide–acetylene flame. They attributed much of this enhancement to reduction in the degree of ionization of calcium brought about by the presence of phosphorus, as when the ionization was suppressed by the addition of excess potassium chloride the enhancement effect all but disappeared. However, Manning and Capacho-Delgado demonstrated that the absorption at the wavelength of the calcium ion was unaffected by the addition of phosphoric acid, so that the enhancement of absorption of neutral calcium atoms must be attributed to increased efficiency in the dissociation of the calcium salt in the presence of phosphoric acid.[86] Becker and Fassel,[87] using the slot burner described by Fiorino *et al.*[25] have been unable to detect either an enhancing or a depressing effect of phosphorus on calcium, under the conditions of concentration used by Amos and Willis, in either the nitrous oxide–acetylene or oxygen–acetylene flame.

The almost complete suppression of magnesium absorption by low concentrations of aluminum in the air–acetylene flame is overcome by use of the nitrous oxide–acetylene flame; in fact, Fleming[88] has shown that this interference can be eliminated in a flame of acetylene burning with a 1:3 nitrous oxide–air mixture.

The absorption of calcium, strontium, and barium is completely suppressed by low concentrations of aluminum in the air–acetylene flame; this interference is not entirely removed, but is reduced to manageable levels, in the nitrous oxide–acetylene flame.[68]

E. Interelement Enhancement Effects in High Temperature Flames

Several interesting enhancement effects have been discovered recently when using the nitrous oxide–acetylene flame for chemical analysis, e.g., the appreciable enhancements found for aluminum and beryllium in the presence of acetic acid[85] and for vanadium[78] and titanium[68] in the presence of sulfuric acid. Probably the most striking is the marked enhancement of the absorption of titanium, tantalum, hafnium, and zirconium in the presence of small concentrations of hydrofluoric acid.[24] The magnitude of this effect is such that it is possible to determine fluoride ion down to a concentration of 10^{-3} M by making use of the enhancement with zirconium.[89] It is probable that the intermediate formation of volatile oxyfluorides such as $ZrOF_2$ increases the efficiency of conversion of the very refractory oxide to the metal in these cases. An even stranger effect is the enhancement of zirconium absorption caused by the presence of ammonia and of certain amines.[90]

A few examples of intermetal enhancement have been observed. Robinson, West, and co-workers[83,85] found that the absorption of vanadium in the nitrous oxide–acetylene flame was increased in the presence of aluminum, reaching a constant value at a molar ratio of about 1:1. Titanium was found to enhance the absorption of both vanadium and aluminum in much the same way. These authors suggested that the equilibrium: $V + O \leftrightarrows VO$, which exists in the flame, may be shifted to the left by aluminum or titanium competing with vanadium for combination with the available oxygen. Taken in conjunction with the observation that vanadium does not enhance the absorption of aluminum, these results suggested that the stabilities of the metal oxides are in the order $Ti > Al > V$. The fact that titanium absorption is enhanced in the presence of iron,[68] whose oxide is certainly less stable than that of titanium,[91] suggests that the full explanation of such enhancements is more complicated than the one given by Robinson, West, and their co-workers.

VI. Conclusions

The development of high temperature flames for use in atomic absorption and emission work has not only provided a powerful technique for the solution of problems in analytical chemistry but has also led to a more critical consideration of the factors determining the performance of flames as atomizing systems. This, in turn, has given rise to a number of fundamental studies on the structure and spectroscopy of flames and to the opening up of a fascinating field of research in high temperature chemistry.

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Cover

The illustration is taken from a book published in 1898 by John Tyndall, [*Six Lectures on Light* (D. Appleton Co., New York, 1898)]. The distinguished British physicist was describing the classical experiments by Kirchhoff in the 1860's leading to Kirchhoff's theory on the nature of solar energy. Light from the sun enters the laboratory through a window and is focused by lens *L* onto a screen *SS*. In passing through the prism *P*, the light is dispersed into the spectrum and the familiar Fraunhofer spectrum of the sun is observed. Introduction of a sodium salt in the Bunsen flame provides an atomic vapor of sodium and greatly intensifies the sodium absorption lines at *D*.