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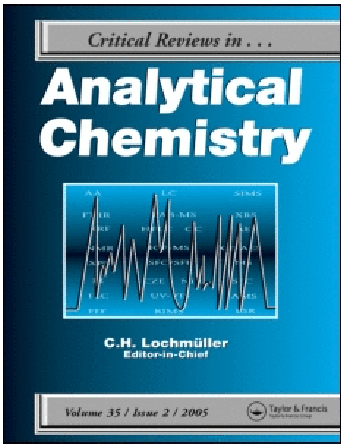

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High-Temperature Atomic and Molecular Spectroscopy

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HIGH-TEMPERATURE ATOMIC AND MOLECULAR SPECTROSCOPY

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I. INTRODUCTION

High-temperature spectroscopy found its real beginning in 1860 when Michael Faraday demonstrated the uniqueness of the candle as a chemical system in his six Christmas lectures. Since that time, no area of analytical chemistry has received greater or more extended attention; and it is becoming more and more evident as increased research is carried out in this field that its potential uses, not only for analytical purposes, but also for studies of the fundamental processes of atoms in the gaseous state, have only begun to be recognized. Presently, high-temperature spectrometric analytical techniques have been developed for most of the elements in the periodic table in various sample types. Methods are also under investigation which will extend this list to include many of the group VA, VIA, and VIIA elements.

Several excellent reviews are available covering various aspects of high-temperature spectroscopy. Garton[1] has assembled a review of articles dealing with spectral information obtained in the vacuum UV region, and Hilton[2] has published a discussion of the equipment, applications, and operating procedures involved in vacuum UV spectrometric methods. An exhaustive compilation of references containing spectral data on various radicals occuring in high-temperature sources has been presented by Milligan and Jacox.[3] A similar review of spectroscopic studies of the electronic structures of molecules and free radicals is presented by Herzberg.[4] Gilmore et al.[5] have presented a review of atomic and molecular excitation mechanisms in nonequilibrium gases up to 20,000°K including mechanisms which result in the production or depletion of rotationally or vibrationally excited species as well as a classification of these mechanisms. Many reviews of a general nature are available, including those on emission spectroscopy with flame, arc, and spark sources;[6] emission, absorption, and fluorescence flame techniques;[7] and high-temperature plasma chemistry.[8]

Fundamental research in high-temperature spectroscopy has found application in the space industry in the areas of rocket propulsion studies,[9-11] astrological data analysis,[11,12] energy conversion devices,[13] in the internal combustion engine industry, the pollution control industry, and many others,[14] thus providing a wealth of information concerning numerous chemical systems of great practical importance to our lives today. Applications are also being found using high-temperature environments such as flames and plasmas for synthetic processes.[11]

In all high-temperature atomic and molecular spectrophotometric methods, the process involved is essentially the same. The analyte is heated to a temperature sufficient to produce the element of interest in either the atomic or molecular gaseous state. The species is either thermally excited, as in the case of emission studies, or is excited with an external source such as a hollow cathode, as in the case of absorption or fluorescence studies. In the case of emission and fluorescence, the excited atom or molecule emits characteristic radiation which is then monitored; while in the case of absorption, the amount of radiation absorbed by the atom or molecule is monitored. The purpose of this review is to provide an overview of the published research dealing with individual techniques which have application to the process just described. This review is not intended to be a complete, comprehensive compilation of data, as the volume of published information makes this prohibitive; but rather, it is an overview of the state of the art and the direction it is following with special emphasis on analytical applications. It is divided into sections, each dealing with a specific source or atom reservoir. Each section is subsequently divided into areas of standard analysis, special applications, unique developments, and future work with the technique.

II. FLAMES

A. General

The major areas of interest in high-temperature spectroscopy as well as the areas providing the most analytical applications have concerned flame emission spectroscopy (FES), flame atomic absorption spectroscopy (AAS), and, to a lesser extent, flame atomic fluorescence spectroscopy (AFS). A great many reviews and bibliographies have already been published dealing with these flame techniques in general, the principles governing them, and comparisons among them.[7,15-26] There have also been a number of reviews dealing with the chemical processes occurring in flames, including flame equilibria, kinetics and reaction mechanism, thermodynamics, temperature calculations, etc.[27-33] The greatest volume of published research has dealt with the compilation of data concerning present standard methods of analysis (including usable AAS, FES, and AFS lines[34]) sample matrix effects,[35] sensitivities, detection limits, precision and accuracy,[36] instruments and instrument parameters,[37,38] and variations in standard methods allowing for specialized determinations.[39-42] But by far the most interesting literature to the analytical chemist deals with new methods and modifications to existing instruments and flame sources.

B. Instrumentation

Mavrodineanu[43] has presented a compilation of numerous unconventional burner designs which are not commercially available. These designs utilize unusual systems for sample nebulization and different burner configurations for premixed and diffusion flames. He also points out the recent interest in, and the utility of the split flame. By separating the blue cone and the outer cone of a premixed flame, one is able to examine (under better conditions) the radiation from them and, therefore, the reactions occurring in these two distinctly different zones.[44] He also describes the advantages of using preflame sample nebulization by employing an ultrasonic generator rather than the more conventional pneumatic nebulizer. This method of sample nebulization increases the sensitivity of the determination by increasing the nebulization efficiency, while the memory effects, the relative fragility of the apparatus, and the large minimum sample size required decrease its utility.[45] If these problems were alleviated, the ultrasonic aerosol generator would find a more prominent place in conventional analyses. Stupar and Dawson[46] have devised an ultrasonic nebulizer which utilizes a glass capillary for sample introduction into an ultrasonically vibrated chamber. This allows for a much smaller minimum sample size and faster sample change. However, the fragility of the system and its memory effect still present problems.

One method of sample introduction for solid samples which had been investigated in the past[47] and which has faded into the background since the advent of carbon rod techniques is the method of heating the sample to a high temperature in an external chamber, vaporizing the element of interest, and then sweeping its vapor into a standard flame for analysis. With this method, larger sample sizes are required and the sensitivity is slightly less than with carbon rod techniques. However, for quantitative determinations, the precision and accuracy greatly surpass those of carbon rod; also, with this technique, excitation up to 8.5 eV has been attained,[47] thus greatly increasing the range of species which may be detected. If the heated chamber could be modified to make rapid sample change possible, the potential applications of this technique would be considerably enhanced.

C. Multi-element Spectrometry

Instrumental arrangements have been constructed which are capable of simultaneously determining as many as six elements at one time.[48] For routine industrial determinations, it would seem that spatial and alignment difficulties have been the only limiting factor to the number of elements which may be monitored at one time, since, until recently, this was done by merely increasing the number of detectors used (and sources for AAS) to correspond to the number of elements sought. These spatial devices monitor, both simultaneously and independently, the signal from the excitation source. This is accomplished by a number of different systems, including photographic, direct reading, and electronic imaging methods of detection. The photographic detection system, which is best suited to emission analysis, involves placing a photographic plate behind the dispersive optics and recording a portion of the total spectrum. While having the advantage of being simple in both principle and operation, this method requires additional time-consuming processes such as development, calibration, and emulsion quantization, which limit the utility of this type of detection device. In direct reading devices, the emission signal passes through standard dispersive optics and then into a multiple slit-photomultiplier arrangement. The individual signals from each photomultiplier are then amplified and recorded separately. This system of detection suffers from cost factors, spatial limitations, and difficulty in alignment. One way to overcome the last two of these limitations has been suggested by Margoshes[49] who used a television camera tube to collect the signal with subsequent electronic scanning to record the information. Since then, other electronic imaging devices have been investigated, including the vidicon tube,[50] the orthicon tube,[51] and photodiode devices.[52] However, the limited spectral response, resolution, and dynamic range of these types of devices have placed severe restrictions on their use.

Two spatial devices which do not make use of dispersive optics have been investigated by Walsh.[53] The multichannel device described uses resonance detectors to simultaneously determine six elements via AAS. It has the advantage that it is not severely affected by fluctuations in room temperature and pressure or by mechanical vibration. This is because detection is accomplished by employing a series of resonance detectors. Walsh[53] has also developed a nondispersive apparatus for the determination of up to seven elements in a flame via AFS. This device makes use of a separate hollow cathode for each element, each of which is sequentially activated. The fluoresence signal is collected on a concave mirror and passed to a single detector fitted with a synchronous demodulating amplifier. Perhaps an adaptation of multiplex methodology to this system will greatly reduce the time factor involved in the sequential activation format.

Multiplex systems, which make use of a unique means of transmitting information, have been proposed for use in multi-element emission spectrometric analysis.[54] These systems simultaneously receive a number of separate spectral components and encode them in a way which enables them to be transmitted and recorded with a single detector using a single channel. The recorded message may then be decoded to provide the separated spectral information. The techniques involving multiplex systems, including Fourier transform spectroscopy, Hadamard transform spectroscopy, and autocorrelation spectroscopy, are outlined in a review on the subject of multi-element spectroscopy by Winefordner et al.[55]

Extension of the application of many of these multi-element devices to include sources other than flames has also been suggested. Two of the sources which have received the most attention are the inductively coupled radiofrequency plasma and the microwave-induced plasma. The inductively coupled radiofrequency plasma produces strong emission from many elements, however, it suffers greatly from ionization interferences; the microwave-induced plasma has essentially the same emission intensities and detection limits as does the inductively coupled radiofrequency plasma, but is limited in its ability to detect those elements which form stable monoxides.[55] Therefore, both the inductively coupled radiofrequency plasma and the microwave-induced plasma are more limited in their general utility as sources for multi-element analysis than are flames.

Busch and Morrison[56] have compiled a review of multi-element spectrometric analyses and have included excellent tables listing the advantages and disadvantages of various flame characteristics, detection systems, and light sources for both AAS and AFS. However, they have dealt only with flames as atom reservoirs, and have neglected multiplex techniques. Winefordner et al.[55] have included these topics in their review and have also presented an excellent critical discussion on the various methods.

Multi-element spectrometric methods of analysis have the advantage of being rapid and relatively simple. Therefore, the development of new multicomponent light sources and simple instrumentation for multichannel detectors should greatly increase the potential for inexpensive industrial, clinical, and environmental analyses. However, many intrinsic problems encountered in the development of multi-element instrumentation will remain as major stumbling blocks to the method. These difficulties include:

1. Only one set of working conditions is available at any one time for a large number of elements. Therefore, for one specific sample, the various pathlengths and dilutions which may be desirable for each different element sought must be compromised.

2. The location of the atom reservoir which provides optium results varies with the element and varies with the atom reservoir parameters.

3. The optimum type of fuel and oxidant, or their mixture, varies from element to element.

4. Correct wavelength adjustments must be maintained, so that extensive alignment procedures and stringent control of room temperatures are often necessary.

D. Distribution of Ions, Free-atom Fraction, and Chemiluminescence

Any atomic absorption or emission signal measured by flame spectrometric techniques is a direct function of the free-atom fraction of the analyte present in the flame. Therefore, the degree of sensitivity and the amount of interference can be greatly altered by changing any parameter which affects the magnitude of the free-atom fraction. Free-atom fractions in various types of flames have been the subject of several investigations. Smyly[57] has presented a selective review on the subject in the introduction to a paper on the relative absorption technique as used to determine the free-atom formation of various elements in a hydrogen/oxygen/argon flame. Studies of free-atom fractions[58,59] have produced the following two generalities: 1. elements which form refractory oxides have highly localized free-atom populations; and 2. flame stoichiometry plays an important role in monoxide formation. As a result of these generalities, it can be seen that any reported free-atom fraction is only meaningful if both the flame position and stoichiometry are given. Koirtyohann and Pickett[60] have described a simple, novel method of measuring the free-atom fractions of elements which form monoxides that produce measurable emission. The emission of the monoxide and the absorbance of the atom are measured in both rich and lean acetylene/nitrous oxide flames which are maintained at the same temperature by dilution with nitrogen. Using the following equations:

$$B_1 + C_1 = 1 \qquad (1)$$

$$B_2 + C_2 = 1 \qquad (2)$$

$$(A_1/A_2)B_2 + (E_1/E_2)C_2 = 1 \qquad (3)$$

where B = fraction as atoms, C = fraction as monoxide, A = absorption of the metal, E = emission of the monoxide, and the subscripts indicate the two flames. The free-atom fraction, B, may be calculated. If the ratio A_1/A_2 is set equal to B_1/B_2 and $E_1/E_2 = C_1/C_2$, then Equation 1 can be replaced by Equation 3 and the result inserted into Equation 2. The only requirements for the success of this method are the validity of the assumption that all of the metal exists in either the atomic or the monoxide form and, of course, that the monoxide produces measurable emission. However, while the validity of the former requirement may, in some cases, prove to be a reasonable assumption, in most cases the presence of ions and higher order oxides alters the free-atom fraction significantly, thereby making the assumption invalid.

Some discrepancies which have been encountered using direct methods for the determination of free-atom fractions have been described by Willis.[61] To avoid some of these discrepancies, Zeegers et al.[62] have proposed comparing the absorbance of the element of interest to that of copper. By taking into account the necessary parameters, they were able to determine the free-atom fraction of four elements and also determine the dissociation energy of their monoxides to ± 0.1 eV.

The presence of ions or free electrons in the flame also alters the free-atom fraction. One means to measure the behavior of species which act as electron acceptors involves the use of cyclotron resonance techniques. This method involves measuring the amount of microwave power that is absorbed by a flame containing the species being investigated when a magnetic field is applied. Bulewicz and Padley[63] have used this technique to investigate the behavior of bromine and chlorine atoms and CN, NH_n, and various sulphur compounds as electron acceptors in low-pressure acetylene/oxygen flames. Also, Calcote and Miller[64] have reviewed the interpretation of reactions involving the production and depletion of ions. In pure flames, it has been found[65] that the maximum ion concentration due to chemi-ionization is observed at the border of the luminous reaction zone and envelopes the flame cone for all flames except those which are very fuel rich. Nesterko and Taran[66] have investigated the degree and mechanism of ionization of the alkali metals when chlorine (in the form of CCl_4, $CHCl_3$, and HCl) is added. In light of their investigation and that of Hayhurst and Sugden,[67] who suggested the following mechanism in the presence of halogen:

$$M + X = M^+ + X^-$$

where M = alkali metal and X = halogen, it may be possible to use this effect to produce an indirect method for halogen determination.

One way in which the "effective" free-atom fraction can be altered is through overexcitation, or chemiluminescent reactions. While failing to actually alter the free-atom fraction, these reactions cause significantly greater emission from the free atoms which are present. Alder et al.[68] have investigated the chemiluminescent reactions of 14 elements in acetylene/oxygen and acetylene/oxygen/argon flames and have attempted to catagorize these mechanisms into four general groups.

1. $C_2H_2 + O_2 + M \rightleftharpoons Q + R + M^*$

2a. $C_2H_2 + O_2 + S \rightleftharpoons Q + R + S^*$

2b. $S^* + M \rightleftharpoons M^* + S$

3. $H + H + M \rightleftharpoons H_2 + M^*$

4. $H + OH + M \rightleftharpoons H_2O + M^*$

where Q, R, and S are flame gas molecules and M is the metal of interest. A similar paper includes two more reaction mechanisms for chemiluminescence which predominate when the metal of interest is zinc.[69] They are

5a. $CH + O \rightleftharpoons CHO^*$

5b. $CHO^* + M \rightleftharpoons CHO + M^*$

6a. $M + O \rightleftharpoons MO^*$

6b. $MO^* + CH \rightleftharpoons M^* + CHO$

These authors concluded that Reactions 3 and 4 predominate when the excitation energy of the metal is below about 5.2 eV. However, in the cases where the excitation energy is in excess of 5.2 eV, as is the case for zinc (which has an excitation energy of 9.0 eV), Reactions 5 and 6 predominate. A similar conclusion was also reached by Vickers et al.[70] who observed the emission from tin in both a hydrogen/air flame using water as the solvent and in the same flame using 2-propanol as the solvent. In the former case, only slight enhancement over the calculated emission intensity, attributed to Reactions 3 and 4 above, was noted. However, in the latter case, strong enhancement was noted. The chemiluminescent reactions responsible for this enhancement, according to these authors, are Reactions 5 and 6 above plus the following reaction, which they indicate should predominate:

7. $CH + OH + Sn \rightleftharpoons CO + H_2 + Sn^*$

Halstead and Jenkins[71] have calculated the rates of chemiluminescent reactions of the type:

$$H + A + B \overset{k}{\rightleftharpoons} HA + B^*$$

and have found them to be between 1.8 and 8 X 10^{15} ml^2 mol^{-2} sec^{-1}.

E. Flame Temperature

A complete understanding of the methods of calculation of flame temperatures and the accuracy and utility of each type of measurement is a prerequisite to the comprehension of fundamental flame characteristics, including nebulization, excitation, and disposition of in-flame equilibria. A rigorous theoretical calculation of the effect of flame temperature on the excitation process in FES and the resulting effect on the emission signal has been presented by de Galan and Winefordner.[72] Reif et al.[73] have compiled a review of the theoretical concepts and physical significance of spectrometric methods of temperature measurements. This is based on the fact that expressions for rate constants, populations of excited states, etc., are usually an exponential function of temperature, T, and are of the form:

$$P = C \exp[-E/kT]$$

where P = some chemical or physical parameter, C = a constant, E = energy, and k = Boltzmann's Constant. The relative error in the calculation of P, dP/P, is related to the error in the temperature by the expression:

$$dP/P = E/kT_2\ dT$$

Some relative errors associated with P as a result of small errors in T are presented in Table 1.[73] Kirkbright et al.[74] and Willis et al.[75] have also published reviews of flame temperature measurement methods from a slightly different viewpoint. They present discussions in which the relative merits, difficulties, and errors associated with the "two line" and "line reversal" techniques are considered.

TABLE 1

Percent Errors Introduced by Small Errors in Measured Temperatures

	$\Delta T(°K)^a$				
Energy (cm^{-1})	10	20	30	40	50
1,000	0.2	0.3	0.5	0.6	0.8
5,000	0.8	1.6	2.4	3.2	4.0
10,000	1.6	3.2	4.8	6.4	8.0
20,000	3.2	6.4	9.6	12.8	16.0
30,000	4.8	9.6	14.4	19.2	24.0
40,000	6.4	12.8	19.2	25.6	32.0

^{a}([dP/P] X 100) at T = 3000°K

From Reif, I., Fassel, V. A., and Kniseley, R. N., *Spectrochim. Acta Part B*, 28(3), 105, 1973. (With permission.)

Numerous methods have been proposed for the calculation of flame temperatures. Omenetto et al.[76] have proposed a system which makes use of the flame atomic fluorescence of thallium to determine flame temperatures and have found remarkably close agreement with results obtained for the same flame using "line reversal" and "two line" methods. Bulewicz et al.[77,78] have proposed a method to calculate the temperature of metal oxide particles containing up to 10^9 molecular units based on Wien's Law. It is stated in their studies that these particles in hydrogen/oxygen/nitrogen flames undergo the following overexcitation reactions which result in temperatures as much as 500°K greater than that of the ambient flame gases:

$$H + H + S \rightleftharpoons H_2 + S^*$$

$$H + OH + S \rightleftharpoons H_2O + S^*$$

where S is a particle which emerges at a higher temperature.

In light of the fact that temperature measurements generally vary widely depending upon the method used and the fact that the accuracy of many calculations depends upon this measurement, much effort still needs to be devoted to this area.

F. Flame Emission

1. General

Considerable interest has developed within the last few years in the application and routine use of FES as opposed to the use of standard AAS techniques for the analytical determination of numerous elements. This interest has been generated in part by the fact that FES has considerably more versatility than AAS. It is quite simple to determine a large number of elements using FES without a great loss in sensitivity and, more importantly, without a separate light source for each element. Also, since the hotter acetylene/nitrous oxide flame has come into use with FES, a decrease in the chemical interferences is noted over those interferences which are normally encountered when using a cooler flame.[79]

Many discussions on the general aspects of FES, including optimum instrument parameters, detection limits, wavelengths, etc., are available,[80-88] as well as discussions of the basic principles behind electronic spectra.[89] Christian and Feldman[90] have compared FES and AAS techniques for 68 elements and have found that 15 elements have lower detection limits using FES. Of these 15 elements, gadolinium, iridium, lanthanum, terbium, yttrium, boron, and uranium all show markedly greater sensitivity when molecular band emission is used.

In AAS, the use of modulated sources has greatly increased the sensitivity of analysis; and until recently, FES has been unable to benefit from these modulation techniques. However, it has been shown[91] that an increase in sensitivity of a factor of 10 can be achieved through sample flow modulation. To effectively modulate the sample flow, the net solvent flow must remain constant to insure the absence of temperature fluctuations. Bojović and Antic-Jovoanović[92] have suggested a technique to satisfy this requirement which makes use of a chopper which alternates between solvent and sample-plus-solvent flow. By perfecting this technique, they report that it should be possible to realize an increase in sensitivity of more than the 10% they observed. One method to sidestep the problems associated with sample modulation might be to use twin flames, one nebulizing the sample-plus-solvent and the other nebulizing just the solvent. By using the appropriate optics, the emission from each of the two flames could be alternately monitored. This would produce a d-c background signal with an a-c analyte signal. This technique was demonstrated by Rogge et al.[93] when they used two acetylene/oxygen flames, both with approximately the same H_2O concentration, but one with a much higher OH concentration to study OH radiation in the 1.5 M region. By using a-c electronics, they were able to greatly reduce the H_2O interference. Kirkbright and Wilson[94] used an interesting system involving two flames, which is somewhat more straightforward and considerably more simple from the standpoint of optical arrangement than alternate flame monitoring. They used two flames which were identical, except that one flame contained the analyte while the other contained the major interferent. The emission from the first flame (containing the analyte) was collimated and passed through the second flame. By defocusing the second flame, it was found that the interference could be eliminated or at least greatly reduced. Therefore, one may use this system to reduce background or spectral interference from a specific, known metal. While this technique might have inherent difficulties (producing two identical flames, for instance), it does allow for rapid sample changeover – the major problem which has plagued the method of sample modulation.

Sheathed premixed flames have also been investigated extensively,[95-97] and it has been generally found that argon or nitrogen sheathing increases the emission of numerous bimolecular species and has allowed for an extension of the detection limits of numerous elements in AAS, FES, and AFS. The basic theory behind this enhancement is discussed quite well by Kirkbright and West.[98] These investigators place special emphasis on the application of sheathed flames to AFS.

Instrumentation has progressed rapidly and many recent developments are worthy of consideration. Snelleman et al.[99] have developed a flame-emission spectrometer which makes use of a quartz plate vibrating at 145 Hz which is placed behind the entrance slit of the monochromator to repetitively scan a narrow wavelength region. When the amplifier, which is syncronized with the vibrations of the quartz plate, is turned to twice the frequency of vibration, the second derivative of the spectrum is obtained. This minimized the interferences from band systems, continua, and flame background emission (the measurement of barium emission in the presence of calcium is used as an example). An analysis can be performed with as little as 50 μl of sample solution by dripping it on a tungsten wire loop and placing it in the flame, thus making the instrumentation applicable to biochemical and air pollution analyses. Maines et al.[100] discussed the advantages and disadvantages of using repetitive scanning of the emission signal from seven elements in an acetylene/nitrous oxide flame. They have listed the detection limits in table form and have concluded from their results that repetitive scanning is best suited to qualitative or semiquantitative analyses as the improvement in quantitative analyses is indeed small in most cases.

The possibility of using the band emission arising from triatomic or even larger molecules has been the subject of a number of articles. Belcher[101] has presented a review which deals with many new methods for determination of trace quantities of elements, one of which is molecular emission spectroscopy. Kallend[102] has attempted to use V_2O_3 or V_2O_4 emission in the 5600 Å region to determine vanadium. Vanadium is very difficult to determine under normal conditions due to the formation of the very weakly emitting VO molecule. However, in a hydrogen/oxygen/nitrogen flame, it was found that the emission from one of the two mentioned oxides may be usable. A mechanism involving chemiluminescence or overexcitation via one or both of the following reactions, which are identical to those discussed by Alder et al.[68] has been proposed:

$$H + H + M \rightleftharpoons H_2 + M^*$$

$$H + OH + M \rightleftharpoons H_2O + M^*$$

where M is the oxide of vanadium. To further substantiate this mechanism, a hydrogen atom scavenger was added (SO_2) and a marked decrease in emission was noted.

The emission from BO_2 (5476 and 5182 Å) has been used to determine boron by FES with great success.[103] However, the determination suffers from numerous interferences, most notably from fluorine which forms the fluoroborate and from AlO (5180 Å) and sodium continuum overlap.[104] Extraction techniques using 2-ethyl-1,3 hexanediol have been used to reduce many of these interferences.[105] After extraction, the reported detection limits in a hydrogen/nitrous oxide flame are as low as 50 ppb,[106,107] which is much lower than the detection limits using AAS.[108] An extensive compilation of kinetic and thermodynamic data concerning the combustion of boron-containing compounds in a hydrogen/oxygen/nitrogen flame has been assembled by Jensen.[109]

The spectra of the oxides and hydroxides of the alkaline earths have been used for many fundamental studies.[110-113] A method is described by Vander Hurk et al.[114] by which the identity of the species (monoxide or hydroxide) responsible for molecular emission can be determined in acetylene/air, hydrogen/air, carbon monoxide/oxygen/nitrogen, and carbon monoxide/nitrous oxide flames when an alkaline earth is nebulized. The method is based on a measurement of the ratio of band to atomic line intensity for a given element in two different flames at the same temperature. By knowing the mechanism of M, MO, MOH, and $M(OH)_2$ formation, the above data may be inserted into an expression which is capable of identifying the species most probably responsible for the emission.

A listing of molecular species which have been studied, and the type of study undertaken is given in Table 2 (in this table, emphasis has been placed on variety rather than duplication).

2. *Effects of Fuels*

For most standard FES determinations, hydrogen or acetylene is used as the fuel and air or oxygen is used as the oxidant; however, in recent years, many new combinations of gases have been investigated to determine their utility in analytical determinations,[336] including discussions of background emission and advantages and disadvantages of using various flame-solvent combinations with ammonia and methane flames,[190,337,338] propane/air flames,[194] and cyanogen/oxygen flames.[148,337,339] Sugden[340] has presented a rather exhaustive listing of excited species occuring in various flames and has used their presence as a means of performing thermodynamic calculations of flame characteristics. Where insufficient thermodynamic data is available to predict the concentration of gaseous species from normal equilibrium equations, computer calculations have proven useful. Such computer-predicted data is available for acetylene/air, oxygen, nitrous oxide, and nitric oxide; hydrogen/air, oxygen, and nitrous oxide; propane/air and nitrous oxide; and cyanogen/oxygen flames.[341-343] Table 3 is a listing of some of the flame types which have been investigated; their applicability to AAS, FES, and AFS; and the work that has been done with them.

The standard acetylene/air or oxygen flame has come under close scrutiny,[150] with much data being generated involving the mechanism, kinetics, and population distributions of radicals such as OH, CH, C_2, C_3, CO, and CH_3[149,154,181,370] and the changes in their formation upon the admittance of various addends to the flame.[371] Time-resolved emissions from explosions of mixtures of acetylene and oxygen have also provided useful kinetic data on this type of flame.[372] Stephens and West[373] investigated the use of low-pressure acetylene/oxygen or nitrous oxide flames in the determination of six metals using small amounts of sample. By introducing the sample via a tungsten wire loop upon which the sample is dripped, they report absolute measurements of 10^{-9} - 10^{-12} g of analyte. This increased sensitivity for the six metals tested (strontium,

TABLE 2

Observed Molecular Species

Species	Type of study[a]	Source	Ref.
AlBr	Calc, mech	Discharge	115
AlCl	Calc, mech	Discharge	115
AlI	Calc, mech	Discharge	115
AlO	Obs	Discharge	116
	Data	Shock tube	117
	Calc	Flame	118
	Calc, mech	Flame	119, 120
	Calc	Hollow cathode	121
AsF	Data	Discharge	122
AuAs	Obs	Hot tube	123
BBr	Data, calc	Discharge	124
BCl	Obs	Discharge	116
	Calc	Plasma	125
BF	Calc	Discharge	126
	GC	Flame	127
BF$_2$	Calc	Discharge	128
BO	Data, mech	Plasma	129
	Anal	Flame	105, 108
	GC	Flame	130
BOF$_2$	Obs	Discharge	116
BO$_2$	Obs	Discharge	116
	Data, mech	Flame	103
	Calc	Discharge	128
	Anal	Flame	104, 106
BS	Calc	Discharge	131, 132
BS$_2$	Obs	Discharge	116
BaCl	Data, calc	Flame	133
BaCl$_2$	Data, calc	Flame	133
BaD	Calc	Furnace	134
BaF	Obs	Furnace	135
	Anal	Flame	136
BaH	Calc	Furnace	134
BaI	Data, calc	Discharge	137
BaO	Calc	Flame	110, 111, 113
	Mech	Flame	112
	Data, mech	Flame	138
	Calc, mech	Flame	114
BaOH	Obs	Flame	139
	Calc	Flame	110
BeF	Calc	Discharge	140
BeF$_2$	Anal	Arc	141
BrCl	Obs	Hot tube	142
C$_2$	Obs	Plasma	143, 144
		Shock tube	145, 146
	Obs, data	Shock tube	147
	Data	Flame	148
	Data, calc	Flame	149, 150

[a] Obs, reference cited reports observation only; data, reference cited lists spectral data; calc, reference cited presents calculations of bond energies, rotational and/or vibrational analysis, etc., from the spectral data obtained; anal, reference cited describes an analytical method; mech, reference cited deals with kinetic or mechanistic investigations; GC, reference cited deals with a gas chromatographic detection system.

TABLE 2 (continued)

Observed Molecular Species

Species	Type of study[a]	Source	Ref.
C_2 (continued)	Data mech	Flame	151, 152
		Plasma	129, 153
	Calc, mech	Flame	154–156
	Calc	Flame	157
		Shock tube	158
	Mech	Flame	159
		Discharge	160
		Shock tube	161
	Anal	Flame	162–166
		Plasma	167
		Arc	168
		Discharge	169, 170
	GC	Flame	171
		Discharge	172
C_2	Obs, data	Shock tube	147
	Calc	Discharge	173
C_3	Data, calc	Flame	149
CCl	Data	Flame	163
	GC	Discharge	174
CD	GC	Discharge	175
CF	GC	Discharge	170
CF_2	Data	Discharge	176
	Mech	Flash photolysis	177
CH	Obs	Plasma	144
	Obs	Shock tube	145, 146
	Calc, data	Flame	149, 150
	Calc	Flame	157
	Data, mech	Flame	151, 152
	Calc, mech	Flame	154–156
	Mech	Flame	159, 178
	Anal	Flame	162–166, 179, 180
		Discharge	169
	GC	Discharge	174, 175
	GC	Flame	171
CH_2	Obs	Flame	181
CN	Obs	Plasma	143, 144
	Obs	Shock tube	145, 182
	Data	Flame	148
	Data, mech	Flame	183
		Plasma	129, 153
	Mech	Flame	184
	Data, calc	Flame	185
		Discharge	185
	Calc	Flame	186
		Arc	187
		Plasma	188
		Shock tube	158
	Anal	Flame	162, 166, 189
		Plasma	167
		Discharge	169
HCN	Data	Flame	190
NCN	Data	Flame	148
C_2N_2	Data	Arc	191
CO	Obs	Flame	181
		Plasma	144
		Discharge	192, 193

TABLE 2 (continued)

Observed Molecular Species

Species	Type of study[a]	Source	Ref.
CO (continued)	Mech	Flame	178, 194
	Data	Arc	191
HCO	Data, calc	Flame	195
CO_2	Obs	Discharge	192, 193
	Data	Flame	196
		Discharge	197
	Calc	Shock tube	198
CO_2^+	Obs	Discharge	192, 193
COF_2	Obs	Shock tube	199
CS	Data	Flash photolysis	200
	Anal	Flame	163
	GC	Discharge	172, 174
		Plasma	201
CaBr	Calc	Plasma	202
CaCl	Data, calc	Flame	133
	Calc	Plasma	202
$CaCl_2$	Data, calc	Flame	133
CaF	Data, calc	Furnace	203
	Calc	–	204
		Plasma	202
		Arc	205
	Anal	Flame	136
		Arc	206–208
	GC	Flame	209
CaI	Obs, calc	Discharge	210
	Calc	Plasma	202
		Discharge	211
CaO	Data	Shock tube	212
	Mech	Flame	213, 214
	Calc	Flame	110
CaOH	Obs	Flame	139
	Data	Shock tube	212
	Calc	Flame	110, 215
	Calc, mech	Flame	114
CrO	Data	Flame	216
	Calc	Flame	62
CrO_2	Data	Flame	216
CrS	Obs, calc	Furnace	217
Cs_2	Data	Discharge	218
Cs_2^+	Obs	Discharge	219
CuF	Anal	Flame	136
CuH	Calc	Furnace	220
CuO	Data, mech	Flame	138
EuCl	Obs	Flame	221
FeO	Calc	Arc	222
		Flame	62
	Calc, mech	Flame	223
GaCl	Anal	Flame	224
GaBr	Anal	Flame	224
GaI	Anal	Flame	224
GeI	Data	Plasma	225
	Calc	–	226
GeO	Data	Combustion tube	227
HCl	Calc	Flame	228
HF	Calc	Flame	228
H_2O	Calc	Flame	228
I_2	Mech	Flame	229

TABLE 2 (continued)

Observed Molecular Species

Species	Type of study[a]	Source	Ref.
IBr	Data	Arc	230
ICl	Mech	Flame	229
IO	Data	Flame	196
InBr	Calc, mech	Discharge	115
	Anal	Flame	224, 231
	GC	Flame	232–235
InCl	Mech	Flame	236
	Calc	–	237
	Calc, mech	Discharge	115
	Anal	Flame	224, 238, 239
	GC	Flame	232–235, 240
InI	Calc, mech	Discharge	115
	Anal	Flame	224, 241, 242
	GC	Flame	233–235
InO	Obs, calc	Arc	243
K_2	Data	Discharge	218
KD	Data, calc	Hot tube	244
KH	Data	Shock tube	212
LaO	Data	Shock tube	212
LuCl	Obs	Flame	221
MgBr	Calc	–	245
MgF	Anal	Flame	136
MgO	Obs	Plasma	246
	Mech	Flame	247, 248
	Calc	Flame	62
		Arc	249, 250
MgS	Obs	Discharge	116
MnO	Calc	Flame	62
MnS	Obs, calc	Furnace	217
Mo_2	Data	Flame	251
MoO_2	Calc	Discharge	252, 253
N_2	Obs	Plasma	143, 144
		Discharge	192, 254
	Obs, calc	Shock tube	255
	Data	Flame	256
		Discharge	197, 257
	Mech	Discharge	258, 259
		Shock tube	260
	Anal	Spark	261
		Discharge	262
	GC	Plasma	263
N_2^+	Obs	Discharge	192
		Plasma	143
	Mech	Shock tube	264
NH	Obs	Plasma	144
		Shock tube	265
	Data	Flame	190
	Mech	Flame	63
		Arc	266
		Discharge	259
	Anal	Flame	162, 163, 166, 179, 189
	GC	Plasma	263
NH_2	Obs	Shock tube	265
	Data	Flame	190
	Mech	Flame	63, 266
		Discharge	259, 267

TABLE 2 (continued)

Observed Molecular Species

Species	Type of study[a]	Source	Ref.
N_2H_4	Mech	Discharge	259
NO	Obs	Discharge	192
	Mech	Flame	194
		Shock tube	268
	Calc	Plasma	188
		Shock tube	269, 270
	Anal	Flame	163
	GC	Plasma	263
NO_2	Data	Flame	196
	Mech	Flame	271
		Shock tube	271
HNO	Mech	Flame	266
	Data, GC	Flame	272
NSe	Obs, data	Discharge	273
	Data, calc, mech	Flame	274
NS	Obs	Plasma	275
	Data, calc, mech	Flame	274
Na_2	Data	Discharge	218
OH	Obs	Discharge	192, 276
		Plasma	144, 275
	Mech	Shock tube	277
	Data, calc	Flame	149, 150
	Calc	Flame	157
		Discharge	278
		Plasma	188
		Shock tube	279
	GC	Plasma	263
O_2^-	Mech	Discharge	280
PF	GC	Flame	127
PH	Calc	Discharge	281
PH_2	Data, calc	Flame	282
PO	Data, calc	Discharge	283
	Calc	–	284–287
	Anal	Flame	163, 167, 288, 289
HPO	Data, anal	Flame	290
	Anal	Flame	289, 291–294
	GC	Flame	240, 295
PbBr	Data, calc	Plasma	296
PbO	Data, calc	Flame	297
	Calc	Arc	298
PtO	Obs, data	Hollow cathode	299
Rb_2	Data	Discharge	218
ReF	GC	Flame	127
S compounds	General review	Flame	300, 301
S_2	Data	Flash photolysis	200
	Data, anal	Flame	290, 302, 303
	Data, GC	Flame	272
	Mech	Flame	266
		Shock tube	304
	Calc	Discharge	305
	Anal, mech	Flame	289
	Anal	Plasma	306
		Flame	306
	GC	Flame	240, 295, 307–312
SF	GC	Flame	127
SH	Mech	Flame	266

TABLE 2 (continued)

Observed Molecular Species

Species	Type of study[a]	Source	Ref.
H_2S	Mech	Flame	266
SO	Obs	Plasma	275
S_2O	Obs	Discharge	313
SO_2	Obs	Shock tube	146
	Mech	Shock tube	314
		Flame	266
ScD	Calc	Shock tube	315
ScH	Calc	Shock tube	315
Se_2	Data, calc	Flash photolysis	316
SeF	GC	Flame	127
HSe	Data, calc	Flash photolysis	316
SiBr	Calc	–	317
$SiBr^+$	Data, calc	Discharge	318
SiH^+	Data, calc	Hollow cathode	319
SiI	Obs	–	320
SiF	Data, mech	Plasma	129, 153
	GC	Flame	127
SiO	Obs	Bomb	321
	Data, mech	Plasma	129, 153
SiO^+	Calc	Discharge	322
SnBr	Obs	Discharge	323
	Calc, mech	Discharge	115
SnCl	Calc	Flame	324
	Calc, mech	Discharge	115
SnH	Data, calc, mech	Flame	325
SnI	Calc, mech	Discharge	115
SnO	Obs, mech	Flame	326
SnOH	Obs, mech	Flame	326
SrBr	Calc	Discharge	327
SrF	Anal	Flame	136
SrI	Calc	Discharge	328
SrO	Data	Shock tube	212
	Calc	Flame	110
SrOH	Calc	Flame	110, 215
	Calc, mech	Flame	114
TaO	Calc	Arc	329
HTe	Data, calc	Flash photolysis	316
H_2Te	Data, calc	Flash photolysis	316
TiBr	Obs	Discharge	330
	Calc	Discharge	331, 332
TiCl	Obs	Discharge	330
TiF	Obs, data	Discharge	333
TiO	Data, mech	Flame	334
VD	Calc	Shock tube	315
VH	Calc	Shock tube	315
VO	Data, calc	–	335
V_2O_3 (?)	Anal	Flame	102
WBr	Calc, mech	Discharge	115
WCl	Calc, mech	Discharge	115
WF	GC	Flame	127
WI	Calc, mech	Discharge	115
YO	Data	Shock tube	212

TABLE 3

Flame Types and their Applicability to AAS, FES, and AFS

Fuel	Support (diluent)	Work[a]	Ref.
CO	O_2 (N_2)	Data, gen, mech	196
	N_2O	Data, gen, mech, temp	344
CH_4	–	Data, gen	190
	O_2	Data, gen	337
		Data, mass spec	338
	O_2 (N_2)	Data, mass spec	338
	F_2	Data, temp	345
CCl_2F_2	F_2	Data, gen, mech	346
C_2H_2	–	Data, gen	339
	N_2O	Data, gen	341, 343, 347
		Data, ion	348
		Appl AAS	56, 247, 349, 350
		Appl FES	81, 83–85, 347, 351
		Appl AAS, FES, AFS	352
		Sep appl FES, AFS	56
		Sep(inert gas) appl AAS	353
		Sep(inert gas) appl AAS, FES, AFS	98
		Sep(Ar, N_2) data, gen, appl FES	95
		Sep(Ar) appl FES, AFS	354
		Shield appl FES	355
		Shield appl FES, AFS	356
	O_2	Data, gen	341, 342, 345, 357
		Data, gen, mech	58
		Data, gen, temp	149, 150, 344
		Appl FES	56, 82, 347
		Appl AAS	349, 358
	Air	Data, gen	341, 343, 359
		Data, ion	348
		Appl AAS	349, 350, 360
		Sep appl AFS	56
		Sep(N_2) appl FES	361
		Sep(N_2) appl AAS	362
		Sep(N_2) appl FES, AFS	96
		Sep(inert gas) appl AAS, FES, AFS	98
	NO	Data, gen	342
C_2N_2	–	Data, gen	148, 339
	O_2	Data, gen	342, 363
	O_2 (Ar)	Data, gen	363
	O_2	Appl AAS, FES	337
	NO	Data, gen	363
		Data, temp	364
C_3H_8	Air	Data, gen	342
		Data, ion	348
		Data, kin, mech	194
		Appl AAS	349
	N_2O	Data, gen	342
C_4N_2	–	Data, gen	339

[a] Data, reference cited presents information on the flame itself, including data on temperature (temp), kinetics (kin), mechanisms (mech), ionization (ion), and general (gen); appl, reference cited presents information on the applicability of the flame for atomic absorption spectroscopy (AAS), flame emission spectroscopy (FES), or atomic fluorescence spectroscopy (AFS); sep (G), indicates that the flame is separated with the gas, G; shield, indicates that the flame is shielded with a mechanical shield.

TABLE 3 (continued)

Flame Types and their Applicability to AAS, FES, and AFS

Fuel	Support (diluent)	Work[a]	Ref.
H_2	–	Data, gen	339
	O_2	Data, gen	339, 341
		Data, gen, mech	365
		Appl AAS	349
	Air	Data, gen	339, 341
		Data, gen, mech	365
		Appl AAS	349
	N_2O	Data, gen	341, 342
		Appl AAS, FES	366
	OF_2	Data, gen	367
HS	F_2	Data, temp	368
NH_3	–	Data, gen	190
	O_2	Data, gen	337, 369
N_2H_4	–	Data, gen	369

aluminum, copper, chromium, titanium, and vanadium) is due to the fact that the atomization efficiencies increase greatly as the pressure of the flame decreases – an effect which is attributed to the high reducing power of the low-pressure flame.

Many other less common flames have also been investigated. Chain branching and recombination reactions and effects of metal additives in hydrogen and hydrocarbon flames have been studied by Jenkins and Sugden.[365] Cros and Bouvier[364] have determined the maximum temperature of the cyanogen/nitric oxide flame, using the rotational temperature of the CN radical, as 4850°K (calculated) and 4770°K (measured) and have presented flame profiles. A characterization of carbon monoxide/nitrous oxide flames, including hydrogen atom concentrations, burning velocities, electron concentrations, background emission, and temperatures, (2750 to 2900°K) has been done by Kalff and Alkemade.[344]

One very powerful type of oxidizing flame which has been extensively investigated has been the fluorine-supported flame. The dichloro difluoro methane/fluorine flame,[346] the methane/fluorine flame,[345] and many other similar flames which make use of the large negative change in enthalpy (-105 kcal/mol) involved in the formation of the C-F bond have been investigated as to their general characteristics. The kinetics of the stepwise replacement of the substituents on the carbon with fluorine have also been examined. These types of flames, along with those using hydrogen sulphide/fluorine[368] and hydrogen/oxygen difluoride,[367] produce very hot chemical environments with calculated maximum temperatures ranging between 3000 and 4000°K. These flames have excellent potential for analytical applications since they have relatively low background radiation below 4000 Å and the reaction conditions are vigorous enough to excite many species which are impossible to excite with more conventional flames. The obvious difficulty in handling the combustants and the combustion products will probably exclude this type of flame from use in routine analysis; however, the advantages of using the extreme chemical environment of fluorine-supported flames for the purpose of fundamental studies are sufficient to ensure their continued use in the research laboratory.

3. The Halides

The molecular emission of various metal salts has proven useful in the determination of the halides. For the determination of fluorine, it has been found that the barium, calcium, copper, magnesium, and strontium salts are useful, with SrF (5850 Å) providing the best results in the absence of chloride and with CaF (6064 Å) providing the best results when chloride is present.[136] For the remaining halides, the indium salts have proven to be quite useful,[238,239,241,374] especially in clinical analyses.[231,242] Some success has also been attained using the gallium salts.[224] The method for halide determination which has proven to be the most successful utilizes a standard hydrogen/air or hydrogen/oxygen/nitrogen turbulent flame which is confined in a chimney, packed or lined with an inert metal coated with indium. The atomic halide in the flame reacts at the surface to produce InX which vaporizes almost immediately. The emission from the resulting InX molecule is then monitored. This method, however, suffers from two problems: the limits of the determination are on the order of 1 to 2 ppm; and it has been found that sulphate, phosphate, and hydrogen ions in the sample solution produce serious interferences.[224] One possible reason for the high limits of detection may be the fact that once vaporized, the indium halide is in equilibrium with its dissociated atoms.[236] By using a glass chimney, this equilibrium becomes slightly less important,[239] but its presence is still a problem.

The possibility of using the Beilstein Effect to determine the halides has also been investigated.[375,376] This method involves the use of the same arrangement mentioned above except that the indium-coated tubing is replaced with copper. When the halide (notably chloride) strikes the hot copper surface, the copper halide is formed. Upon vaporization, the molecule dissociates to produce free copper atoms in a concentration dependent upon the number of chlorine atoms striking the copper surface. Therefore, by monitoring the copper emission, the analysis is accomplished. However, besides suffering from numerous interferences, especially from other halides, the chlorine atom is the only halide which can be effectively determined by this method.

Another method which is presently under investigation[377] uses an arrangement similar to that used in the indium and Beilstein techniques except that, in this case, the tubing is coated with silver. When the halide atom in the flame strikes the silver surface, the silver halide is formed. Once vaporized, it dissociates to form atomic silver and atomic halogen. However, during nebulization of the aqueous sample solution containing the halide, the rate of formation of the silver halide exceeds its rate of vaporization; therefore, it accumulates on the silver surface. Then, if the sample solution is replaced with 95% ethanol, the carbon in the flame causes a sensitization of the silver present from the vaporization of the accumulated silver halide. If the silver emission (3382.9 Å) is plotted as a function of time, the resulting curve rises rapidly to a maximum and then decays exponentially, with the maximum in the emission intensity being proportional to the concentration of the halide in the sample solution. The intensity of the silver emission is contingent upon the rate of vaporization of the silver halide, which is itself dependent upon its vapor pressure. Also, the slope of a plot of the log of the silver emission intensity as a function of time is independent of the concentration of the halide in the sample solution and remains constant from run to run. Since the rate of decay is proportional to the vapor pressure of the specific silver halide, it is different for iodide and bromide. Therefore, it is possible to determine both iodide and bromide simultaneously. Since the maximum silver emission intensity is dependent upon the amount of silver halide formed on the surface, the time of sample nebulization may be varied to accomodate solutions with very low iodide or bromide concentrations.

The type of gas-solid phase in-flame interactions mentioned above show great potential for the analysis of many of the Group VI A and VII A elements and perhaps continued efforts in this area will provide analytical methods for molecular entities. Weltner[378] has used matrix isolation techniques to investigate some of these in-flame surface interactions. Species such as LiO, Li_2O, LiF, AlF, AlF_3, and many others have been trapped in an inert gas matrix on a cold window, and then the nature of the matrix and the species contained in it have been investigated by means of UV spectroscopy, IR spectroscopy, etc. This technique may produce other avenues through which to investigate similar flame methods of analysis as well as aid in the determination of mechanisms in existing techniques.

4. *Interference Effects*

The presence of interferences in standard flame methods of analysis has long been recognized as one of the major stumbling blocks to using flame techniques. But, the categorization and investigation of the nature and origin of these interferences has provided for variations in methodology capable of eliminating or at least reducing many of them, and in some cases has produced ways of effectively using these interferences for indirect determinations of the interferent. Condensed phase interferences, which have been somewhat neglected in the past, have lately been extensively investigated. Alkemade[379] has presented a general, verbal, qualitative treatment of the interferences due to solute vaporization in flame photometry. He has categorized these interferences into four major areas:

1. Depression due to the formation of compounds which are less volatile than the analyte alone
2. Enhancement due to the formation of compounds which are more volatile than the analyte alone
3. Depression due to the occlusion of the analyte in a less volatile matrix of concomitant
4. Enhancement due to the occlusion of the analyte in a more volatile matrix of concomitant

Similar conclusions were also reached experimentally by Wendt[380] who characterized numerous interferences in the determination of nickel using acetylene/oxygen and hydrogen/oxygen flames, and by Sastri et al.,[381,382] who investigated the interference in the determination of polynuclear oxygen-bonded metal atoms in solution. While the conclusions of these investigations were not as systematically presented as those of Alkemade,[379] they concluded that almost all interferences noted were due to changes in the structure of the solid particles formed after solvent evaporization, and that these structural changes resulted in a change in the vaporization and decomposition rates. In addition, the role of physical-chemical reactions in the condensed phase and its influence on the speed of vaporization of the analyte in acetylene/nitrous oxide flames has been discussed by Rubeska.[383] Calcium emission (4227 and 5541 Å) has been investigated more extensively, it seems, with regard to interferences of this nature, and therefore has provided an excellent example.[384-387] Shatkay[388] has used the calcium system to illustrate the invalidity of the assumption that condensed phase matrix interferences are a linear function of matrix concentration, thereby invalidating the use of the simple two-solution standard addition method of analysis for calcium determination. Smith and Winefordner[389] and Pleskach and Beremzhanov[390] studied the interferences from phosphate in hydrogen/oxygen, hydrogen/air/argon, and acetylene/air flames and determined that the mechanism of the depressive effect is due to the formation of the slowly vaporizing $Ca_3(PO_4)_2$ particle, while the same depressive effect of the calcium signal in the presence of aluminum has been attributed to the formation of the slowly vaporizing $CaAl_2O_4$ particle.[390] In other work, Mohay[214] has investigated the role played by solvent evaporization and dissociation of calcium-containing species in the mechanism of anion interferences. Also, Rains[391] has discussed the reduction and/or the elimination of condensed phase interferences through strict control of flame parameters such as flame temperature, fuel/oxidant systems, nebulizer and burner systems, the region of the flame which is monitored, and the role of organic solvents. Hambly and Rann[392] have discussed practical mathematical treatment of the distribution of atomic analyte concentration in the flame as a function of the type of flame, the fuel composition, the rate of nebulization, the solvent composition, and reaction rates for the production and removal of atoms. This discussion also lends support to the work done by Rains.[391] However, the formation of complex species incorporating the analyte may also be used to eliminate some interferences. In the case of citrate interference in the determination of iron, it has been found[393] that the addition of sodium chloride or phosphoric acid results in the preferential formation of Na_3 $FeCl_6$ and $FePO_4$ respectively. These compounds form ferric oxide, which volatilizes more rapidly upon solvent evaporization than does the citrate complex. Therefore, the depressive effect of the citrate ion is eliminated.

Chemical interferences due to equilibria in solution and to aqueous and organic solvent reaction in the sample solution have also come under scrutiny.[394-396] Unfortunately, these types of interferences do not lend themselves well to logical classification at the present time.[397] Perhaps future work in this area will produce a pattern of interference effects which can be categorized.

Recent investigations involving in-flame interactions that are responsible for interferences in many determinations have provided a wealth of valuable information which has been used both for fundamental research as well as analytical methods development.[213,398-400] Dagnall and Taylor[401] have presented an interesting discussion on the use of scavengers to decrease the interference caused by oxide formation in metal determinations. By preferentially forming the oxide, these scavengers reduce the rate of formation of the analyte oxide and thus increase the formation of free metal atoms. Roos[360] has used the distribution pattern of metal and metal oxide species in an acetylene/air flame as a basis for a qualitative discussion of this type of interference phenomena. Ionization interferences are a major factor leading to inaccuracies in determinations via FES. A kinetic determination of the rate of ionization of alkali metal atoms in flames[402] according to the reaction has produced the following rate expression:

$$M + X \overset{k}{=} M^{+} + e^{-} + X$$

$$k = (9.9 \pm 2.7) \times 10^{-9}\ T^{1/2} \exp\,[-V/RT]$$

$$\text{ml molecule}^{-1}\ \text{sec}^{-1}$$

where T = temperature and V = ionization potential of the individual metal. It was also found that the value of K does not depend upon the specific conditions of the flame and is essentially the same, within the stated error, for each metal. From the information which can be derived from this expression, the degree of interference from preferential ionization of an alkali metal can be estimated if the rate constant for the ionization of the analyte is known. Since the advent of the use of ionization suppressors, such as lanthanum,[403] and the recognition of their potential, the use of data of this nature should increase in the future.

5. Indirect Methods

Indirect methods of analysis are providing reasonably rapid means to analyze samples for many elements and ions which have previously been impossible to determine by FES. Sulphate concentrations have been determined by a simple indirect method where excess barium is added to the sample to precipitate the sulphate as barium sulphate which is subsequently removed by filtration. The excess barium is then determined at 4930 Å using standard flame methods.[404,405] An interesting method to determine phosphate has been suggested by Ratner and Scheiner.[406] Using this technique, the calcium (either added or present naturally) emission intensity from the sample is measured in an acetylene/oxygen/air flame. Since the interference from phosphate is eliminated at the temperature of this flame, the concentration of calcium may be calculated. Then the intensity of the calcium emission is measured in a propane/air flame (the temperature of which is not sufficiently high to eliminate interference from phosphate). By measuring the depression of the calcium emission intensity due to the phosphate in this flame, the phosphate concentration can be determined. While it must be assumed that phosphate is the only interferent, and while it is doubtful that this method is as sensitive as using HPO emission, the idea is interesting indeed.

Gilbert[407] has determined iodide by a method which involves the addition of a known excess amount of dichromate to the sample solution. A portion of the dichromate is reduced by the iodide, and the remaining dichromate is extracted. The amount of dichromate is then determined using standard flame methods for chromium analysis.

This combination of standard wet chemical analytical procedures with flame methods of analysis has extended the utility of the flame as an analytical tool, and perhaps with a little imagination, it may be possible to adapt other wet chemical techniques to flame methods. Pleskach[408] has evaluated the accuracies of three indirect methods of analysis using flame methods and compared them to the accuracy of existing methods. The three indirect methods investigated are

1. The ion of interest is precipitated and removed by filtration. The solid is redissolved and the analyte determined by standard flame methods.
2. The ion of interest is precipitated with excess metal ion and the remaining metal is determined by standard flame methods.
3. The change in the absorbance of an alkaline earth in the presence of the ion to be detected (for instance, using the supression of the calcium signal to determine aluminum or phosphate) is measured.

The interesting conclusion that Pleskach reached in this study is that the accuracies encountered are, with some variation in individual determinations, quite comparable to those realized using standard flame methods.

G. Shielded and Sheathed Flames

Shielded flames, which are used to produce a more controlled chemical environment in the flame, have been used to assist in the exclusion of atmospheric oxygen from flames used to determine metals such as aluminum and vanadium[355] which readily form refractory oxides. Hingle et al.[409] used a separated acetylene/nitrous oxide flame to determine the rare earths and found virtually no interference from fifteen other elements which were tested. It has also been found that these mechanical shields, which are usually made of silica, quartz, borosilicate glass, or pyrex, produce excellent results in the determination of phosphorus in specialized samples such as detergents,[292,294] in oil[291] with reported detection limits on the order of 9 ppm phosphorus, and in air samples with detection limits as low as 9.5 ppb phosphorus being reported.[410,411] Shielded flames also provide the means of determination of sulfur and phosphorus in numerous flame photometric detectors for gas chromatographic analyses.[412] A comparison has been made by Hollowell et al.[306] between using S_2 emission in flame methods of analysis and twelve other methods. These authors have concluded that the flame method provides results comparable to the other twelve techniques, and that the cost and maintenance factors make use of the flame technique the most desirable. The determination of sulfur and phosphorus involving mechanical shields are based on the Salet Effect,[413,414] which uses a cool surface (the composition of which matters little) to enhance the emission from S_2 (3840 Å) or HPO (5265 Å) molecules. A more detailed description of the experimental arrangement is presented by Veillon and Park.[290] It has been found that in the absence of a shield, little or no S_2 or HPO emission is noted, and that for sulfur, the emission intensity varies as the square of the sulfur concentration in the sample.[290] The potential for use of the S_2 emission for specialized analyses is great. Hollowell et al.[306] have used a system which is capable of monitoring SO_2 in a gaseous sample by monitoring the S_2 emission intensity of a flame into which the gas is pumped. However, the use of the emission from S_2 and HPO has several disadvantages. While the detection limits have been reported to be as low as 0.1 ppm,[293] it has been found that a large depressive effect is produced when any organic solvent is used in the case of S_2 emission; however, a threefold enhancement in HPO emission intensity has been reported when an organic solvent is used.[289] Matrix interferences and the fact that different compounds produce different emission intensities[289] make it necessary, in the case of sulfur, to use special sample preparation techniques to convert all of the sulfur-containing species present to a common form (usually sulfate).[302] A list of these interference effects in phosphorus determinations via this method is presented by Dagnall et al.[293]

The Salet Effect has also been observed when a sample is placed in a hole at the end of a metal rod, and the rod is placed in the flame.[415] This last technique has been commercially exploited as Molecular Emission Cavity Analysis (MECA). However, the mechanism of the Salet enhancement has yet to be determined; there are several theories, but none is yet capable of providing a reasonable explanation. The technique of matrix isolation might prove useful here. Paramount to any investigation concerning this mechanism is a knowledge of the kinetics and distribution of sulfur-containing species in a flame. This has been discussed by Kallen.[300] Also, an excellent general review of the subject of the kinetics of combustion of sulfur compounds has been presented by Cullis and Mulcahy.[301] Once the mechanism responsible for the Salet enhancement has been determined, it is possible that systems may be developed to utilize this effect to produce better sensitivities and lower limits of detection for many similar species.

H. Organic Compound Observations

Molecular emission spectroscopy has been used extensively for fundamental studies to determine thermodynamic properties of various entities, and it is finding increasing success in the determination of elements such as sulfur, phosphorus, and the halides. Attempts have been made to obtain structural information on organic compounds from the molecular emission from such species as CH, CN, NH, HCO, and C_2.[162,180,416] As early as 1958, Spokes[417] used multiple reflection techniques to determine the absorption spectra of OH and NH when organic compounds were nebulized into the flame. More recently, Smith has done exhaustive studies on the UV emission and absorption of CH and NH to determine ethanol and pyridine.[179] Kroeten et al.[166] have found that a linear relation exists when the emission intensity of CH (4315 Å) is plotted as a function of the C_2 (5160 Å) or CN (4216 Å) emission intensities for a homologous series of alcohols and amines when a hydrogen/air flame is used. Dagnall et al.[163] have noted that in using C_2 and CH emission intensities in a hydrogen/nitrogen or hydrogen/air flame, a qualitative identification of organic compounds is possible; McCrea and Light[418] have used CH and C_2 emission in a hydrogen/oxygen flame to determine hydrocarbons in methanol solvent. However, this qualitative identification is made increasingly more difficult as the number of different compounds in the sample solution is increased and becomes almost impossible if more than two are present. The possibility of differentiating between two geometric isomers has been suggested by Parsons,[165] who has demonstrated this by plotting CH (4200 Å) emission intensity as a function of C_2 (5170 Å) emission intensity to differentiate between 16 different alcohols, some of which were geometric isomers. The fact that the emission caused by nebulizing these 16 different alcohols varies enough to differentiate between them lends support to the prospect of using a fingerprint spectrum in the region of 2000 Å to 7000 Å to confirm the identification of organic molecules, as proposed by Robinson and Smith.[419] These authors present the possibility that the emission in this spectral region is due to fragments of the organic molecule which are formed during its combustion. However, they have made no attempt to assign any of the emission bands or lines noted.

It is indeed feasible that the breakdown pattern in the combustion of large organic molecules should depend specifically upon the structure of the original molecule – something similar to the cracking pattern observed in mass spectrometry – and since C_2^*, CH*, and similar carbon-containing radicals are generated by chemical reactions and are not generated thermally,[151,152,470] it should indeed be possible to produce a fingerprint spectrum which could be used for identification purposes. However, if this is to become a usable tool of the organic chemist, a tremendous volume of data must be generated as reference material. To warrant this massive compilation of data, it must be possible to derive more information from these spectra than merely fingerprint information. At the present state of development, it appears that the presence of nitrogen and possibly the presence of an alchoholic structural group are determinable, but it is pointed out by Dagnall et al.[163] that the emission from the species which would indicate their presence is greatly affected by the instrument and the operating parameters. Bulewicz[421] has also made studies of the influence of flame parameters on chemiluminesence and chemi-ionization of carbon-containing species in flames and has arrived at the same conclusion. Since this is the case, the utility of the large volumes of reference spectra required to carry out an analysis would be minimal. Therefore, it is doubtful that this method of qualitative analysis will enjoy widespread use as is the case of other techniques from which one may derive similar information – infrared and mass spectroscopy for example.

I. Atomic and Molecular Absorption

1. General

Atomic absorption spectroscopy (AAS) has developed rapidly in the past 20 years into the most widely used standard technique for metal determinations. At the present time, methods are available for the direct determination of 68 elements,[349] and methods and instrumentation are being developed to both increase the sensitivity and accuracy with which these elements can be determined as well as to extend the list to include many new elements.[422] Of these 68 elements, determinations with sensitivities and detection limits comparable to those obtained with FES can be accomplished for 27 of them, while determinations with greater sensitivities and lower detection limits can be accomplished for 26 of them.[90] Molecular absorption spectroscopy (MAS) has also come into limited use and, with the development of better continuous sources, promises considerable utility. Many reviews on the subject of AAS and MAS have been published with emphasis on the physical basis of AAS,[423] indirect methods of analysis via AAS,[422] the precision of MAS,[424] and application of these techniques to trace metal determinations.[425] In a review by Christian,[425] commercial instrumentation, sample preparation, and standardization techniques are covered for trace metal determination. Tables in the review present lists of concentrations of 32 of the heavy metals found in the human body, the wavelengths and flame types used, and sensitivities for the determination of 16 of these metals.

2. Instrumentation, Burners, and Flames

The flames most commonly used for AAS are produced with either acetylene, propane, or hydrogen as the fuel, and air or nitrous oxide as the oxidant. Flames using these gas combinations can be produced using a long path slot burner thus providing a longer absorption cross-section. This burner arrangement is the most desirable for AAS. Table 3 lists many of the fuel/oxidant mixtures which have been investigated for use with AAS. There are a number of often competing characteristics which are of concern when selecting a combustant mixture for a specific determination. These include high-transparency, low-background radiation in the spectral region of interest, low-chemical interference, high-atomization efficiency, and low ionization. The acetylene/nitrous oxide flame, which has been extensively investigated for this purpose,[56,343,347,352] has proven to be especially effective in reducing the amount of monoxide formation because of its low-oxygen concentration and its higher operating temperature; however, the probability of interference due to ionization of elements with low-ionization potentials is higher than with the more conventional acetylene/air flame. Dagnall et al.[351] have characterized the use of the acetylene/nitrous oxide flame for the determination of aluminum (3962 Å), zinc (2139 Å), cadmium (2288 Å), lead (4057 Å), and calcium (3934 Å and 3968 Å), and have noted the following advantages over other conventional fuel/oxidant mixtures: (1) refractory oxides like A1O are much less prominent than in other commonly used flames, (2) the high temperature of the flame reduces or eliminates many matrix effects, and (3) the flame has a low level of background. Kirkbright et al.[353] have designed a triple-pass optical system which uses an acetylene/nitrous oxide flame sheathed with an inert gas to determine arsenic (1937 Å) and selenium (1960 Å) and have noted an increase in sensitivity and lower detection limits when compared to a single-pass system using an unsheathed flame. A unique burner system which uses a nitrogen separated acetylene/air flame has also been used by Kirkbright et al.[362] to determine the same two elements. When compared to the inert gas sheathed flame mentioned above, a decrease in the detection limits by a factor of two for arsenic and a factor of three for selenium was noted. The authors attributed these decreases in detection limits solely to the lower background in the nitrogen sheathed flame.

Instrumental alterations and advancements have also extended the utility of AAS as an analytical technique. Harrison and Berry[426] have described a system whereby the readout in an AAS determination is integrated, thus improving the signal-to-noise ratio (numerous applications of the system are also described). A rather unique apparatus which makes use of both flame and flameless principles, utilizing the advantages of each, has been suggested by Rubeska and Moldan.[427] They used a 45-cm hollow ceramic tube as the absorption volume and a hydrogen/air flame as the sample introduction mechanism to characterize long absorption tubes for use with AAS. A standard Beckman hydrogen/air burner was placed at one end of a ceramic tube which was heated with a furnace. The sample was introduced by the burner nebulizer, through the flame, and into the tube. Ten elements were investigated, and the general trend seemed to be a noted increase in sensitivity and lower limits of detection; however, a definite decrease in precision was also noted. A similar system was also used by Delves[428] to determine nine metals which exist at trace levels in biological samples. Twenty μl of a solution containing the analyte was placed on a platinum wire loop which was then inserted into the flame. The flame was situated beneath the center of a horizontal nickel tube. A small hole in the tube just above the flame allowed the sample to be swept into the tube which was situated in the light path of the cathode.

3. Indirect Methods

There are a considerable number of elements which are not presently determinable with conventional AAS instrumentation or which may be determined only with low sensitivity. These fall into three groups:

1. Those which have resonance lines in the vacuum UV region and thus require special instrumentation, including the halogens, nitrogen, oxygen, phosphorus, and sulphur
2. Those elements with which it is impossible to maintain a significantly high atom population in a flame or nonflame cell; these include many elements in the sixth row, and the lanthanide and actinide series
3. Those elements which for various other reasons may not be easily determined directly at trace levels; these include germanium, arsenic, selenium, and tellurium

In an attempt to extend the list of elements for which AAS will provide an adequate method of determination, numerous indirect methods have been developed. Parsons et al.[429] and Bache and Lisk[430] have determined phosphorus by using phosphomolybdic acid to form a complex with the phosphorus, extracting the complex, and then determining the molybdenum concentration (3133 Å). Molybdenum has also been used to achieve an indirect determination of niobium.[431] By adding molybdophosphoric acid, molydoniobophosphoric acid is formed. The excess molybdophosphoric acid is removed with isobutyl acetate and the molybdenum remaining is determined in an acetylene/nitrous oxide flame. The detection limit for this method is 15 ppb niobium. One reason for the low detection limit is that there are 11 molybdinum atoms per niobium atom in the molybdoniobophosphoric acid molecule, thus affecting a factor of 11 increase. Other elements which may be determined indirectly by using a similar method involving the formation of a molybdenum complex are germanium,[432] thallium,[433] thorium,[434] titanium,[435] vanadium,[436,437] arsenic,[438] phosphorus,[439-442] and silicon.[441,442] For samples in which gross interferences are present, the analysis of silver (3281 Å) has been successfully accomplished by first extracting the silver with di-*n*-butylammonium salicylate into methylisobutyl ketone. This extract is then nebulized directly into the flame. A detection limit of 0.01 ppm silver has been reported.[443]

Enhancement or depression of the absorbance of an addend by the analyte has also provided numerous indirect AAS methods, for example: iron enhancement (3441 Å) for the determination of aluminum[444] or titanium,[445] zirconium enhancement (3601 Å) for the determination of fluorine[446] or ammonia,[447] and magnesium depression (2852 Å) for the determination of fluorine.[446] However, while the use of enhancement or depressive effects to achieve an indirect method of analysis may prove useful in specialized instances for singular samples, the general use of the technique is not generally reliable. For instance, the enhancement of zirconium absorbance by fluorine has been found to be nonquantitative.[448] Also, the assumption must be made that there is no other interferent present in a sufficient quantity to alter the determination.

For those elements which form insoluble metal salts, successful indirect determinations may be achieved by adding a known amount of metal to the sample solution, allowing the precipitate to settle, and then determining the remaining excess metal. Those two elements to which this method has been most often applied are chloride[377, 449-452] and sulfur[453,454] which are precipitated as silver chloride and barium sulphate, respectively. Kirkbright and Johnson[422] have compiled an excellent review of the application of indirect AAS methods of determination and have covered many of the methods mentioned here. They have also compared the sensitivities and ranges of these indirect methods to those which are attainable by direct methods.

4. Interferences

Interferences in AAS measurements may all be listed in one of four categories: interferences due to light scattering from particles in the flame, interferences due to chemical reactions with the analyte, interferences due to molecular absorption, and interferences due to ionization of the analyte. Several papers have appeared containing extensive lists of interferences for specific determinations which also contain general discussions on those interferences.[455-457] Rubeska[458] has reviewed the subject of radiation interferences and has described methods for their elimination; Firman[459] and Koirtyohann and Pickett[460] have published a list of interferences in the determination of the alkaline earths; and Harrison and Wadlin[247] and Terashima[461] have presented general discussions concerning numerous different interferences and their mechanisms.

Chemical interferences occur as a result of compound formation with the analyte either in the absorption volume or in solution before nebulization. Addition of an element or compound which preferentially binds with the interferent can produce a sizable reduction in this type of chemical interference. The addition of lanthanum to depress the interference from phosphate in a calcium determination is an excellent example of this.[462] Due to the diversity of this type of interference, the reader is advised to consult some very well presented reviews on the subject.[463-465] Two interesting investigations have been undertaken, however, which should be mentioned more specifically because of their general applicability. A well organized categorization of the effects of solvent and the presence of assorted complexing agents in AAS determinations has been presented by Chakrabarti and Singhal.[466] In their article, they have presented, in table form, the type and magnitude of the interferences noted, the complexing agent, and the metal studied, and have followed the table with explanations of the sources of these effects. Also, Ghodsi and Van Severen[467] have presented theoretical calculations of the oxygen partial pressures above which calcium, barium, aluminum, magnesium, and zinc preferentially form monoxide molecules in flames operating between 2000 and 2500°K and the effect of this formation on their determination via AAS.

Interference due to ionization occurs primarily in the determination of elements which have low ionization potentials, e.g., the alkali and alkaline earth metals. As a result of this ionization, the free-atom fraction may be greatly decreased, thus lowering the sensitivity of the determination. To decrease these interferences, an ionization supressor may be added such as cesium or rubidium (i.p. = 3.87 and 4.16 eV, respectively). Due to their low ionization potentials, the cesium or rubidium is preferentially ionized, which effectively increases the electron concentration in the flame, thereby shifting the ionization equilibrium of the analyte to the unionized form. It should also be noted that the degree of ionization of an element varies greatly with the type of flame used.[348] Generally, the less energetic the combustion, the less ionization occurs. For instance, in a propane/air flame, cesium atoms are 28% ionized, while in an acetylene/nitrous oxide flame, they are 96% ionized.[348]

Interferences from light scattering are especially difficult to eliminate in routine determinations. Koirtyohann and Pickett[468] have studied how scattering of light affects a determination via AAS. They have calculated the percent of the absorption volume which is occupied by particles (generally between 2.3 and 5%) and have been able to calculate the amount of light which is lost. While such a calculation is useful for specific circumstances, the results are not generally applicable.

Interference due to molecular absorption is also especially difficult to estimate or eliminate in routine analyses. Molecular absorption may occur anywhere in the spectrum and may result from either the solvent or the sample matrix.[349] The only effective means of correcting both particulate light scattering and molecular absorption interferences is through use of a standard addition technique.

5. *Sources*

To effect an atomic absorption determination or a molecular absorption determination, a light source is required which provides radiation of a specific wavelength at which the analyte absorbs. There are essentially two ways to approach this requirement. Either one may use a source which emits principally that wavelength which is required, as is the case for a hollow cathode (HC), or one may choose to use a continuous source. In the former case, the requirements placed on the instrument are considerably less stringent than in the latter case. A HC source, the principles for which were first considered by Walsh,[469] emits only the line radiation from the element of interest superimposed on a line spectrum of the discharge gas. Using a HC source places only one requirement on the spectral apparatus – that of differentiating between the selected resonance line and any other lines emitted by the HC which are not absorbed. This advantage of the HC makes it possible to construct very small and compact instruments at a moderate price. However, there are several disadvantages to using HC:

1. A separate lamp must be used for each element (while multi-element lamps are available, the number of different combinations of elements is limited, and even in those cases where it is possible to construct such a lamp, the risk of spectral interference is greatly increased).
2. The quality of many HC lamps, for instance those for arsenic, selenium, and tellerium, is not satisfactory.
3. The use of HC lamps is limited to atomic absorbance determinations and those few molecular absorbance determinations where an atomic line of the lamp lies on top of a line in the molecular band system of interest.

Electrodeless discharge lamps (EDLs) are presently available, or may be readily constructed, for a number of different elements. For elements for which HC lamps are unsatisfactory. EDLs provides much higher radiation densities.[470] But, as far as those elements for which good quality HC sources are available, there is no advantage in most cases to the use of EDL sources. This is due to the fact that it is very difficult to maintain the necessary high degree of constancy in radiation intensity with EDLs.

Another alternative to the HC is the continuous source. Rann[471] has compared the theoretical line profiles for HC and continuous sources and has determined that the sensitivity calculated on the basis of these line profiles should be twice as great for the HC sources. Therefore, for a standard AAS analysis, the HC is still the more desirable source. Experimental results have also indicated a decrease in sensitivity when a continuous source is used as compared to a HC source.[472,473] Also, the use of a continuous source places the added requirement on the spectral portion of the instrument that the line width of the instrument must be less than or equal to the absorption line width of the analyte. However, once this requirement has been met, there are certain applications where a continuous source does have definite advantages. Willis[474] has determined the atomization efficiencies of several elements in various flames using a continuous source and has noted considerable difference between his values for the free-atom fraction and those already in the literature. The reason for this is that there may be a difference in the absorption line in the flame relative to the emission line of the source. This is due to both neglect of hyperfine structure and an inadequate knowledge of the line profile in the flame. If this is indeed the case, the advantage in using a continuous source for this type of measurement is clear. This has also been discussed extensively in the article by Willis.[474]

Another application for which a continuous source is well suited is in the determination of the absorption spectra of molecular species, radicals, and ions. Jessen and Gaydon[164] used a continuous flashtube to make absorbance measurements of the C_2 (4050 Å) and the CH (4315 Å, 3900 Å, 3143 Å) radical band systems and have found that because radicals exist at very low concentration levels and are generally present only in a very small portion of the flame, it is difficult to obtain a satisfactory spectrum. To overcome these difficulties, the authors found it necessary to use a multipass system. However, by using the absorbance spectra of these radicals as opposed to the emission spectrum, it was found that the temperature and chemiluminescent reactions which altered the emission signal did not affect the absorbance signal, thus warranting the extra effort in obtaining it.

Tuneable dye lasers may also be used as sources for spectrochemical analyses.[475] Ba^+ (ca. 4550 Å) has been determined using such a laser[476] and provides an example of a species for which a HC source is not applicable. The dye laser, under ideal operating conditions, is capable of producing a decrease in detection limits of up to two orders of magnitude and its high pulse rate allows for a substantial decrease in interference. However, since the wavelength of the light produced by the dye laser is a critical function of the operating conditions, these conditions must be stringently controlled, and even then, prevention of wavelength deviation is difficult. Due to this fact, as well as the high initial purchase cost of a dye laser, their use outside of the research laboratory will probably remain limited in the near future.

J. Atomic and Molecular Fluorescence

The development of atomic and molecular fluorescence spectrophotometric methods of analysis has, in the past, been hindered greatly due to the fact that no suitable sources have been available. Until recently, only beryllium[356] and silicon[354] could be determined using standard sources, with comparable detection limits to those obtained when AAS or FES is used. However, with the advent of the tunable dye laser and other high-intensity sources, there has been a surge in the development of fluorescence methodology.

Much theoretical work has been done concerning the resonance fluorescence spectra of numerous entities in flames.[477-480] Hendra et al.[481] have used a 1.5 W argon-ion laser to obtain a laser Raman spectrum and laser-excited resonance of the C_2 radical in an ethylene/oxygen flame. The usability of this technique to obtain reasonable vibrational spectra of the same radical is also discussed. Vear et al.[482] have also obtained the laser-excited Raman spectra of CO_2, N_2, CH_4, and H_2. The influence of flame composition is the subject of a discussion by Jenkins.[483] The two areas considered and characterized in the article by Jenkins are the in-flame quenching and depopulation of free metal atoms. Omenetto and Rossi[484] have presented a theoretical discussion and experimental application of the mechanisms of population of upper states and have derived an equation which points out the role of thermal energy and its assistance with the upper state population.

There are three practical limitations to detectabilities via AFS and MFS. These are: 1. noise from the medium (usually due to scattering of the source emission from particulate matter in the flame); 2. collisional depopulation; and 3. lack of suitable sources. Dagnall et al.[354] have used an argon-separated acetylene/nitrous oxide flame to determine silicon (2516 Å) by AFS and have noted that interferences due to scattering may be significantly reduced when such a separated flame is used. Hingle et al.[356] have used a shielded (silica tube) acetylene/nitrous oxide flame with a microwave-powered electrodeless discharge lamp operated in the a-c mode to determine beryllium (2348.6 Å) and have noted the same decrease in background scattering interference. It has also been found that proper selection of flame parameters can significantly reduce collisional depopulation. Perhaps the use of low-pressure flames such as those used by Bulewicz and Padley[63] can be of use here.

Resonance fluorescence of the halides has provided useful kinetic and mechanistic data on halide reactions and interactions. Clyne and Cruse[485] have used the decay of the resonance fluorescence of Cl (1380 Å), Br (1577 Å), and I (1830 Å) to determine the rate parameters of exchange reactions of the nature:

$$X + XX' = X_2\ X'$$

where X and X′ are each one of the three halogens mentioned. They have also used resonance fluorescence of the halides and oxygen to determine kinetic parameters of the following reactions:

$$O + NO_2 = NO + O_2$$

$$Cl + ClNO = NO + Cl_2$$

$$Br + ClNO = NO + BrCl$$

At the present time, only three sources for AFS are used routinely, and none of these is really adequate. Walsh[53] has used standard HC sources for multielement determinations (the apparatus has been discussed earlier) and has found them applicable for specialized analyses; however, the low spectral density of the standard lamp imposes the most severe limitation to their use. Lowe[486] has developed an improved high intensity HC source which makes use of a "booster cathode" with a common anode and reports that factors of between 10 and 100 (generally 50) increase in fluorescence intensity may be obtained over standard HC sources. A combination HC-microwave discharge lamp which is capable of producing up to 200 W has been developed by Human.[487] Besides producing a greater spectral density, this lamp also has the advantage of being kept relatively free from evaporated impurities by flushing them from the lamp with the use of a flow-through gas system. Detection limits using AFS with this source are listed as 0.5 and 3 ppb for copper and gold, respectively.

Microwave-powered electrodeless discharge lamps have also been extensively investigated for use as AFS sources. Thompson and Wildy[488] have characterized their use for eight elements. Multielement microwave-powered EDLs have been suggested by Marshall and West[489] who have constructed such lamps for three different combinations: bismuth, mercury, selenium; tellurium, cadmium, and zinc; and gallium and indium. Also, Fulton et al.[490] have characterized the arsenic-antimony combination. While the utility of multielement EDL is greater than single element EDL, there has been relatively no increase in sensitivity noted over conventional HC sources.

While these sources are useful for determinations via atomic fluorescence, their use for molecular fluorescence studies similar to those carried out by Hendra et al.[481] is indeed limited. Since the advent of the tunable dye laser, its application to AFS and MFS has been clear. Piepmeier[491] has presented a calculation whereby the laser power densities required to effectively saturate the excited atom population are calculated for ten elements (these range from 22 to 210 kW/cm^2). These results were then compared to the power density output capabilities of presently available lasers. While it is possible to reach these levels with a pulsed tunable laser, it should be pointed out that with increased radiation density, the fluorescent emission-to-scattering ratio decreases. As the saturation level is approached, the maximum fluorescent emission intensity levels off while the scattering continues to increase linearly. Therefore, where scattering is a major source of interference, as is the case in most flame methods, the power density requirements must indeed be compromised. Due to this requirement, it would seem that, for most flame AFS methods of analysis, the major area of concern is the reduction of in-flame particle concentrations.

III. ARCS AND SPARKS

A. General

A-c and d-c arcs and a-c sparks are invaluable tools for the routine qualitative and semiquantitative analysis of many sample types such as glass,[492] abrasive metals,[493] high purity salts,[494] and metals,[495] all of which would require extensive preparation procedures if any other method were used. Due to their high gas temperatures of between 4000 and 8000°K, most sample types are quickly vaporized and the spectra produced are relatively free from interferences due to compound formation with the analyte. Arcs have also been used in the commercial production of high purity compounds. Dunas and Thorpe[496] have described a system which is used in the commercial production of TiO_2 from $TiCl_4$. Several papers dealing with the general principles, theoretical aspects, and applications of arcs and sparks are available. Walters[497] has reviewed the principles and development of the spark discharge with respect to equipment design, processes occuring in the spark and related plasma physics, and excited state population; Rautschke[498] has characterized reactions which take place at the carbon electrodes in a d-c arc and their influence on spectral line intensity; Ganz et al.[499] have discussed the effects of gas flow rate and geometry of the electrodes; and Karyakin and Kaigorodov[500] have developed a technique whereby it is possible to obtain time resolved emission spectra of vapors during excitation and have proposed explanations for their results. Numerous papers dealing with more specific aspects of arc and spark techniques, including investigations of volatilization rates of elements and minerals,[501] rotating disc methods,[502] analyses in refractory matrices,[503] and thermodynamic aspects of analyte reactions in carbon matrices,[504] are also available.

Temperature measurement techniques in arcs and sparks have been given much less attention than similar techniques in flames, possibly due to the greater difficulty involved in making such measurements. Bradis et al.[505] have outlined a method for calculating molecular temperatures in an arc via line intensity calculations using mixtures of nitrogen, oxygen, carbon monoxide, carbon dioxide, and hydrogen in different proportions, and Pavlovic et al.[506] have made comparisons between calculated and experimentally measured temperatures in an arc.

B. Sheathed and Shielded Arcs

Several variations in standard methods of analysis have been employed which merit attention. A low-temperature arc which is sheathed with a static inert gas atmosphere to both decrease spectral interference due to cyanogen and to slow the rate of dispersion of the sample vapor has been used to improve the sensitivity for the analyses of numerous metals in ashed biological samples.[507] Similarly, inert gas-sheathed arcs and glass-shielded arcs have been described by Marinković and Dimittijević[508] who used an aerosol sampling device to determine twelve metals in solution. Their method was proposed as an alternative to flame emission techniques and was shown to provide roughly comparable detection limits; however, the major advantages of the argon-sheathed or glass-shielded arc over the standard flame are its greater stability and a decrease in interference due to oxide formation in the case of those metals which form refractory oxides.

C. Methods of Sample Introduction

Several methods of sample introduction have been proposed for use with arcs and sparks. Herbst and Mannkopff[509] have developed a system whereby the sample is continuously added to the spark. The sample, which has been mixed with powdered carbon, is placed in the top electrode and is poured into the spark gap by means of the shock waves generated by the spark. The continuous addition of the sample allows for longer exposure times, thus lowering the detection limits. Seeley[510] has used the graphite electrodes as filters for particulate matter in an air sampling device before using them to strike an arc. This technique, which provides only 10 to 20% reproducibility, does have the advantages of simple and rapid sample collection and handling.

The addition of a carrier to the sample to increase the volatility or volatilization rate of the analyte has proven to be an effective method to increase the sensitivity and decrease the detection limits for many elements, including aluminum and silicon. It has been found that the addition of the chloride ion in the form of either the silver or copper chloride,[511,512] or the addition of fluoride in the form of either the silver or copper fluoride[513] to the sample causes the formation of the more volatile metal halide with the analyte. The salt, upon vaporization, dissociates to form the free metal which is then detected by standard methods.

D. Applications to Molecular Spectroscopy

The application of arc and spark sources to molecular spectroscopy is extremely limited due to the fact that very few molecular species of interest are stable at the high operation temperatures involved. In fact, most molecular species which are present in arcs and sparks, such as cyanogen, carbon monoxide, and some metal oxides, serve only to interfere with standard determinations.[191] However, limited application of these sources to molecular spectroscopy has been made; for example, a determination of fluoride has been accomplished by monitoring CaF emission (5291 Å).[205] Shoenfeld[206] has used the calcium already present in minerals to determine fluoride without any preliminary sample preparation procedures. However, theoretical and practical considerations of this procedure have indicated that the technique is very sensitive to conditions of sample handling and experimental procedure.[514] Petrov and Ognev[208] have suggested using a sample preparation procedure which involves mixing the sample 1:1 with a buffer mixture (60% graphite, 40% calcium oxide) before placing the sample in an electrode. But, even if this is done, spectral interference from chromium (5298.3 Å) and iron (5302.3 Å) emission still limits the determination. Ioffe and Leonova[141] have used the molecular emission of BeF_2 (3009 Å) to determine fluorine. By measuring the intensity of this line, they have been able to determine fluorine in an 80-mg sample of tungsten down to 1 ppm.

Mioc[168] has proposed using the Swan band emission of the C_2 molecule for the qualitative determination of organics in air samples. This researcher has monitored the C_2 emission (3747.1 Å) emitted when an arc is struck in atmospheres of air, acetylene, butane, carbon dioxide, argon, or argon-carbon dioxide mixtures and has found that the measured intensity in the last mixture is a linear function of the carbon dioxide partial pressure. While the application of this system suffers from the same problems as previously discussed for similar methods using flames, there are excellent possibilities for the use of this system in a portable air monitoring device.

Popovich et al.[261] have used the molecular emission of N_2 in a spark for the indirect determination of O_2 and O_3 in gaseous mixtures. It has been found that O_2 and O_3 quench the band emission of N_2 at 4344 Å and 4060 Å and that it is possible to use this datum to mathematically relate the measured depression of this emission to the concentrations of O_2 and O_3. In light of the present emphasis on environmental monitoring, the method may prove to be quite promising.

IV. PLASMA EMISSION AND ABSORPTION

A. General

Matter is believed to exist in one of four states: the solid, liquid, gaseous, or plasma state. Until recently, the existence of the fourth state has been regarded as inconsequential. However, it is now realized that the plasma state is the normal state for up to 99% of the matter in the universe and that the other three states are an exception which exist only in isolated locations such as the Earth and other similar celestial bodies.[515]

The plasma state is said to be established in a system when the number of ions and electrons present are sufficient in number to determine the behavior of the system. Early research concerning plasmas was done with little knowledge of the nature and temperature of the plasma. However, after World War II, the development of new techniques made it possible to produce plasmas in a controlled fashion and also made it possible to conduct investigations into the basic nature of the plasma state. Thus, the usefulness of plasmas for molecular and nuclear synthesis, for studying reaction kinetics, and for the development of analytical methodology has just begun to be recognized. Chemical reactions under plasma conditions for chemical or nuclear synthesis and for fundamental studies of matter or the nature of the plasma itself have been covered elsewhere and will not be discussed here.[516,517] If the reader is interested in fundamental research concerning plasmas and their operation, many articles are available which discuss the principles, evaluations, and applications of plasmas,[515,518-522] atomic and molecular processes occurring in plasmas,[515-517,523-533] background spectral intensities of various plasmas,[143,525,534-539] use of plasmas for chemical synthesis,[516,517,540,541] and methods of temperature determination in plasmas.[188,542,543] There are also some excellent bibliographies available on the subject of plasmas.[544-552] The attention herein given to plasmas will be directed solely to the use of plasmas for analytical purposes.

Several articles have appeared which are concerned with the analytical utility of plasmas for various general and specialized applications. Schirmer and Drost[553] have investigated, in theoretical terms, the elementary reactions which occur in plasmas and their influence on analytical methods. Kaiser et al.[554] have looked at the temperature fluctuations of a current carrying plasma and have compared them to a current free plasma when various samples were nebulized into the plasma. They found that the temperature in current carrying plasmas was a function of the concentration of elements with low-ionization energies; however, in a current free plasma, the temperature was shown to be a function only of the amount of air and water supplied by the aerosol. More recently, Lochte-Holtgreven[555] has presented a review of studies on both local and nonlocal thermal equilibrium conditions in plasmas and the effect of the existence of these conditions on the analytical utility of those plasmas studied. Also, general comparisons of various plasma sources for analytical purposes are presented by Pforr[556] and Schribner.[557] Several other papers dealing with excitation mechanisms, sample introduction, and visible properties of plasmas and their influence on the utility of these sources as analytical tools have also been published.

Most flames which are used for routine analysis are extremely inefficient for the production of elements in the atomic state and are also inefficient in atomic excitation processes. As a result, much work has been done since the early 1950's in an attempt to apply plasma sources to these analytical problems. Due to the high electron temperatures attainable in plasmas (10^4 - 10^7°K), they have been found to be extremely efficient in vaporization of solid particles and atomization of the element of interest. (It should be noted that electron temperatures in excess of 10^7°K are easily attainable; however, considerably less analytical work has been done with these high temperature plasmas as compared to those which operate at lower temperatures. Therefore, they will not be considered here.) Also, it has been found that if the carrier gas is argon or hydrogen, the neutral or strongly reducing characteristics, respectively, of the plasmas inhibit the formation of refractory compounds.[558] The results of research into the analytical utility of plasma sources indicate that such sources give excellent emission signals which can be used for determinations of several elements which are difficult to perform using other, more conventional sources. These include arsenic, selenium, silicon, mercury, tantalum, titanium, and some elements which readily form refractory oxides, and also for elements such as fluorine, which are not excitable using conventional sources. However, relatively poor detection limits are obtained for most transition, alkali, and alkaline earth metals when compared to the detection limits obtained when using flame AAS and FES. However, there are also three very practical disadvantages in the use of plasmas to replace more conventional sources: 1. the plasma condition results in the formation of ions of the analyte and thus significantly decreases the free-atom fraction; 2. the initial cost of the apparatus, especially the power source, is quite high; and 3. the sensitivity of the plasma discharge to water vapor makes it necessary to employ elaborate systems for sample introduction and sample changeover, thus making most systems inconvenient to use when the sample is in the liquid state.

This last problem has kept plasma sources from enjoying the popularity of other sources for routine analysis even though this difficulty can be circumvented by plasma flames to some extent. The ultrasonic nebulizer system discussed earlier[559] suffers from condensation problems; however, Kawaguchi et al.[560] have developed a rather elaborate ultrasonic nebulizer which reduces these problems. Nixon et al.[561] have described a system whereby the sample solution is carried into the plasma by way of a tantalum filament. The method uses 100 μl of solution and is capable of determining elements on the order of nanograms per milliliter. A sample nebulizer system described in 1962 by Yamamoto,[562] which has received little attention, involves an arc plasma jet that uses argon as the carrier gas. The sample is nebulized into the stream of argon downstream of the arc itself, thereby stopping electrode erosion and allowing for a more stable plasma.

B. Plasma Flames

A plasma torch or plasma jet which takes advantage of the efficient excitation capabilities of a plasma source and the efficient solvent evaporation capabilities of a flame source was first considered in the early 1960's by Karlovitz and Richardson.[563,564] The plasma flame involves a second-stage excitation, usually an a-c or d-c discharge, which takes place in the partially combusted flame gases and augments the excitation capabilities of the flame.[565,566] Kåpicka[567] used a plasma flame to obtain the spectra of barium, potassium, zinc, and iron and found that it was more efficient in its excitation of the analyte than was a flame alone. An excellent review which deals with the theoretical principles operative in plasma flames has been presented by Von Engel and Cozens.[568] The two main advantages of this system are 1. it is capable of nebulizing aqueous samples as is the case with a conventional flame, and 2. it is capable of producing sufficiently high temperatures to efficiently atomize the sample. It has been found that reaction processes which require between 25 and 30 eV predominate in the plasma flame.[153] Such a system was also used by Fells et al.[569] who have listed the operating parameters of this source and its characteristics, including voltage requirements, discharge diameters, etc. Kessler and Gebhardt[246] have discussed the systematic error limits and standard deviations obtained using a plasma flame and have compared them to those of other sources. Another advantage in using a plasma flame over a standard flame lies in its ability to minimize interferences due to oxide formation with the analyte. Suzuki[570] has demonstrated this in a determination of aluminum using a plasma flame. However, it was noted in the study that chemical interference from seven species, including iron and sodium, made it possible to realize only a small decrease in detection limits for real samples over those of standard flame methods.

The use of a radiofrequency (RF) coil has proven to be more effective than use of a discharge system to augument the excitation capabilities of the flame. Aldous et al.[571] used such a system to obtain increases in the emission signal of up to a factor of 250 for eight elements over conventional hydrogen/air or hydrogen/argon flames, while suffering less from chemical interferences. A similar RF plasma flame using a propane/air mixture has been investigated by Johnston and Lawton.[572]

C. Plasma Torches and Plasma Jets

The plasma torch and plasma jet are quite similar to the plasma flame. The predominant excitation and ionization processes which occur in the plasma jet and plasma torch require between 25 and 30 eV as is the case with the plasma flame.[129] The effect of temperature, solvent, charge, and flow rates on the analytical utility of the plasma jet have been investigated earlier.[573] Czakow et al.[574] report that reproducible results are attainable with samples ranging from 10 to 500 ppm when the samples are nebulized, and it was also reported that results for metal oxides pelleted with graphite varied less than 5% when the oxide was between 0.1 and 30% of the pellet weight. It has also been shown that very successful determinations may be accomplished using a plasma jet as the absorption volume for an AAS determination.[575] Greenfield and Smith[576] have described an apparatus in which the sample is passed into a high-frequency plasma and then is deviated 90° into a "T" shaped quartz tube, the horizontal portion of which is in the light path. While this arrangement allows for determinations with detection limits and sensitivities comparable to those obtained with standard flame AAS methods, this system may also be used as a light source for AAS determinations where a suitable HC source is unavailable.

D. Inductively Coupled Plasmas

Inductively coupled plasmas, the analytical utility of which have been reviewed in the past,[577] have an advantage over plasma flames in that there is more energy available for atomization and excitation. Inductively coupled plasmas are especially useful for the determination of elements such as aluminum[578] which readily form refractory oxides. However, they have the added disadvantage of making sample introduction much more difficult. An ultrasonic nebulizer may be used to partially overcome this difficulty;[559] but, the problem of rapid sample change is then introduced (the reader is referred to the introductory section on flames for a discussion of the ultrasonic nebulizer). Dikinson and Fassel[579] have investigated the problems of sample introduction into inductively coupled plasmas and have characterized and optimized other experimental parameters, including development of the plasma shape which allows for the most efficient sample introduction. They report better sensitivities for most of the 26 elements investigated than are achieved routinely with AAS or FES techniques (increase in sensitivity factors varied between 0.1 and 10^4). Unfortunately, inductively coupled plasmas suffer from numerous chemical interferences. Low-pressure plasmas have been employed in an attempt to reduce these interferences; however, the analytical utility of such plasmas is minimal due to the fact that they have poor reproducibility, they produce varying degrees of ionization throughout the plasma, and they are susceptible to interference due to compound formation.[580,581]

E. Molecular Emission from Plasma Sources

The opportunities for using molecular emission spectrometry with plasma sources are extremely limited due to the fact that few molecular species are stable enough to be detected in such extremely energetic environments. Marliere et al.[275] have constructed a microwave-induced plasma which operates in the 20 to 160 GHz range and was used to observe the SO, NS, and OH radicals. Kana'an et al.[129] have characterized bimolecular reaction products in a plasma jet with an emphasis on those species containing halogen atoms and have discussed the possible mechanisms for their production. A less energetic 25 Hz plasma has been employed to determine the relative intensities of a series of four calcium halide entities to determine halide concentration; the limits of detection are considerably higher in three of the cases than those obtained when the emission from the halide atom alone is used for the determination.

As is the case with nearly every source, attempts have been made to use molecular emission of carbon-containing species in plasmas to determine organic compounds. Those species most commonly used are the C_2, CH, CN, and CO entities.[144,159,167] Truitt[167] has used an inductively coupled radiofrequency plasma torch to determine the relationship between the electronic spectra of the PO, CN, and C_2 entities and the functional groups of the organic sample, the sample composition, the plasma gas composition, the radiofrequency power, and the height in the plasma of the recorded spectra by injecting the sample into four different regions of the plasma. Wendel[144] has also tabulated the effects of pressure on the emission from various bimolecular species when an organic sample is introduced into an inductively coupled plasma. In light of the problems involved in sample introduction, as well as those difficulties discussed earlier with respect to the determination of organic compounds via flame emission methods, it is unlikely that a qualitative analysis of organic compounds will be feasible using molecular emission from plasma sources. However, in the area of GC detectors, it is indeed possible that molecular emission could be used for both general and specific photometric detectors. The most notable reason is that the composition and flow rate of the carrier gas from the GC make it possible to easily adapt a plasma jet or plasma torch detector.

F. Discharge Plasmas

A source closely akin to those previously discussed is the discharge plasma. Several types of discharge plasmas have been investigated, including ultra high-frequency discharges for excitation of molecular spectra,[193] high-frequency discharges,[276] electrodeless discharge tubes (EDTs)[582] Grimm glow discharges.[583] and many more. Mavrodineanu and Hughes[584] have presented an interesting discussion and review of the radiofrequency discharge as a source with analytical applicability and have also presented many excellent spectra and color prints of some discharge sources. They have also included a short review of the history of research on the technique from 1891 through 1964. Also, Fite[585] has discussed the physical processes operative in gas discharges with respect to the active chemical species which they produce by using modulated beam mass spectrometry. Sealed tube discharges are used more for fundamental[586] or kinetic[160,258,280,588-590] rather than for analytical applications. Many of these studies which involve monitoring emission from molecular vapors are listed in Table 2.

One type of sealed tube discharge which is used considerably by the analytical chemist is the EDT. Considerable interest has been shown in use of EDT as sources for atomic absorption and fluorescence measurements for those elements for which suitable HC sources are not available or for absorption of fluorescence studies involving molecular species. This has been discussed previously. EDT as an emission source for analysis has one major advantage over most other sources, including flames and most plasmas, in that it is capable of almost completely excluding interference and background due to air and electrode material. Aldous et al.[592] have used this advantage to separate and store compounds which have been eluted from a gas chromatographic column for more extensive spectrometric investigation. Burkert et al.[582] have characterized a microwave EDT, with attention being given to high-frequency energy transmission mechanisms and tube configuration and their effect on background emission. Kleinmann and Svoboda[593] have constructed an EDT which vaporizes the sample from a heated graphite disc and have used it to determine 15 different elements (detection limits are listed). The advantage of this type of system is its capability to analyze liquid samples with good reproducibility, and the very low background produced assists greatly in reducing the detection limits.

The glow discharge has found considerable utility in the area of organic synthesis. Suhr[594] has presented a review of the subject in which the nature of synthesis to which this technique is applicable is discussed. The glow discharge has also been investigated as to its analytical utility. Dogan et al.[583] have done a general overall characterization of instrumental parameters, sample preparation procedures, and precision of the method. They have noted that the detection limits are essentially the same as those found using a spark source, however, the precision using a glow discharge is superior. The major disadvantages of using the glow discharge for analytical purposes include its low spectral intensity and restricted burning time, however, it has been found that neither of these problems pose severe restrictions on the method. Weisbeck and Voelkner[259] have monitored the emission from numerous nitrogen-containing molecular species, including N_2, NH, NH_2, and N_2H_4, to assess the effects of altering the glow discharge conditions. In doing so, they have arrived at a new chemiluminescent reaction mechanism for the production of the Schuster bands. Czakow[595] has extended the analytical utility of the Grimm Discharge Lamp (GDL) by using a graphite cathode mounted in a brass ring and an enlarged aluminum anode to produce a hot cathode. This arrangement makes it possible to successfully atomize solid samples; Dehrendorf and DeLaffolie[596] have constructed calibration curves for determinations of manganese, nickel, and sulfur in an effort to assess the applicability of a GDL to routine chemical analyses.

Determinations using conventional electrical discharge tubes have the major disadvantage of being subject to interferences due to reactions at the electrodes. Therefore, this type of discharge tube possesses relatively little analytical utility except for specialized applications; for example, they have been used as chromatographic detectors or for detection of impurities in gas samples. Some characterizations have been made of electrical discharge tubes including an investigation on the effect of varying the frequency of the discharge by monitoring the emission from molecular nitrogen[254] and an investigation of the distribution and electronic states of the tin, aluminum, indium, and tungsten halides. Use of conventional electrical discharge tubes for fundamental studies provides their greatest source of utility, however, these will not be covered here.

Organic compound identification using various discharges has received some attention and has proven at least in the case of gaseous samples, to be quite satisfactory. It has been found that it is possible to detect molecular emission from large organic molecules in discharge systems. Davidson et al.[597] have performed a vibrational analysis of the spectrum of tetrahydrofuran which was observed in a microwave discharge between 1850 and 2050 Å. Truitt and Robinson[598] have used a radiofrequency discharge source to record the spectrum resulting when an organic sample is placed in the discharge, and Taylor et al.[169] have been able to successfully determine trace amounts of organic impurities in 99.9995% pure argon by exciting the sample in a microwave discharge. The possibility of using a microwave discharge for the purpose of determining sulfur in organic compounds via atomic emission and atomic absorption techniques using the 2169 Å line has also been investigated by Taylor et al.[599] While this line is not the standard line used for atomic sulfur detection, it has been found by these researchers that detection limits comparable to other sources are attainable using the technique described.

V. SHOCK TUBE OBSERVATIONS

While having relatively little actual analytical utility, shock tubes do provide a means of performing mechanistic and kinetic studies in high-temperature environments which are an integral part of any complete research in the area of high-temperature spectroscopy. The shock tube, as it applies to the study of plasmas, has been the subject of several reviews which deal with reaction processes under plasma conditions, including excitation mechanisms,[600] recombination and ionization mechanisms,[600,601] precision limitations,[602,603] and general utility.[601,604,605] Several reviews on the basic techniques involved in shock tube studies are also available, including considerations of shock wave front structure,[603,606,607] heat exchange,[607] optical properties,[603,607] relaxation processes,[606] and temperature considerations.[198] Also, Haluk[608] has discussed the use of mass spectrometric techniques for the study of shock tube decomposition products and has applied the method to kinetic investigations.

The greatest utility of shock tubes lies in their use for mechanistic studies. Numerous investigators have used shock tubes to elucidate excitation mechanisms of species such as C_2,[161] OH and Ha,[277] N_2,[260] N_2^+,[264] and SO_2[314] (a listing of those observations which involve molecular entities appears in Table 2). Ewing et al.[609] have used a shock tube arrangement with time resolved absorption techniques to determine the nature of the atoms produced upon dissociation of the alkali metal halides. It was found that CsX (where X = any halide) dissociates to form ions only, RbX and KX (where X = F, Cl, Br) dissociate to form ions only, LiX, NaI, and NaBr (where X = any halide) dissociate to form atoms only, and KI, RbI, NaCl, and NaF dissociate to form mixtures of both atoms and ions. Bott and Jacobs[304] have used a conventional shock tube arrangement to investigate the mechanism of S_2 emission. The fact that the emission intensity from the shock tube is proportional to the square of the sulfur concentration indicates that the mechanism involved might be the same as that responsible for the Salet Effect. These authors suggest that the mechanism involves a combination of two sulfur atoms in the ^3P state resulting in an excited S_2 molecule in the $B^3E_g^-$ state, this in turn produces radiation as it undergoes a transition to the ground state ($X^3E_g^-$). It is highly possible that, in a cooled flame, this recombination may occur at the wall of the burner.

VI. MASS SPECTROSCOPY

The use of mass spectrometric methods for the analysis of those species present in high-temperature sources has generated a great amount of data on the fundamental processes occurring in such sources. The instruments which have been used for this work include magnetic, radio frequency, time of flight, and quadrupole mass spectrometers. The general principle involved in mass spectrometric measurement of high-temperature environments is as follows: Species are extracted from the region of interest by means of a probe (usually quartz) and are then either led directly into the ionization chamber of the mass spectrometer or they may be led first through a series of chambers, each possessing a successively higher vacuum.[610] Hayhurst et al.[611] have presented the design and methods of construction of an apparatus for making measurements of both positive and negative ions in a flame burning as atmospheric pressure using a radiofrequency quadrupole mass spectrometer.

There are several general considerations which must be taken into account when working with a mass spectrometric sampling apparatus. When the hot gases in a high-temperature medium operating at atmospheric pressure enter into a region of high vacuum through a small orifice, a molecular beam is formed which reaches speeds approaching 350 m/sec at that orifice. The beam then continues to expand until its density is less than that of the surrounding gas, resulting in a phenomenon known as "barrel shock." Greene and Milne[612] have described these shocks and have proposed detailed methods for their compensation. Also, one must take into account the fact that inserting a probe, no matter how small, into a high-temperature source causes a perturbation of those processes occurring in the immediate vicinity of the probe. These perturbations have been shown to be both thermal and catalytic in nature. To exit through the orifice of a probe and enter into the low-pressure region inside of a probe, the gas molecules must pass through a layer of relatively cool gas (the thermal layer) along the tube surface, thus causing a severe distortion of the results. This problem is discussed extensively in a review by Wang.[613] Perhaps good use might be made of this perturbation by considering the fact that the probe could be employed as a cool body capable of catalyzing the Salet Effect (which has been discussed earlier), thereby resulting in direct sampling of reactants and products of the Salet process.

Several studies of the abundance of various species in assorted high temperature environments have been made and are listed in brief in Table 4.

Even if there is substantial distortion from perturbation due to insertion of a probe, it is still possible to obtain valuable information. For example, mass spectrometric analyses may be used to obtain relative concentration profiles of flames, to verify the existence of stable or metastable species in a source, or to determine reaction mechanisms. Another interesting application of this technique involves a kinetic treatment of the production of NO.[616] Using the mechanism:

$$O + N_2 \overset{k_1}{=} NO + N \tag{1}$$

$$N + O_2 \overset{k_2}{=} NO + O \tag{2}$$

where (1) is rate limiting, it has been shown that the oxygen atom concentration undergoes a "radical overshoot" early in the combustion process, thus increasing the amount of NO formed.

TABLE 4

Data Accumulation of Abundances of Species Existing in High Temperature Environments

Source	Original composition	Ref.
Flame	$H_2/N_2/O_2$	614–616
	K^+ in H_2/O_2	617
Microwave discharge	D_2O + coal	618
Radiofrequency discharge	CO_2	619
Electric discharge	COS	313
Glow discharge	CO_2, H_2/CO_2	620
Discharge tube	Air, N_2, O_2, Ar, C_2N_2/O_2	621
Corona discharge	Ether, H_2O, O_2/N_2	622

In this manner, the difference which had been noted earlier between the measured rate of production of NO and the calculated rate using the steady state concentration oxygen atoms in the following expression:

$$d[NO]/dt = 2k_1 [N_2] [O]$$

was accounted for.

Several other kinetic and mechanistic studies have been made using mass spectrometric techniques. An interesting method by which it is possible to study collision processes in decaying plasmas has been presented by Maerk and Oskam.[623] In other work, Jensen[624] has used mass spectral data from a hydrogen/oxygen/nitrogen flame seeded with tin to determine the mechanism and kinetic parameters of the formation of $SnOH^+$. Mass spectral data have also been applied to the standard aluminum and phosphorus depression of the calcium signal in flames. From their data on this system, Pleskach and Beremzhanov[387] have experimentally determined and verified an expression which characterizes this quenching. In addition, it has been shown that it is possible to generate thermodynamic data using mass spectrometric techniques, including electron affinity studies[625] and ionization potential determinations.[626]

VII. GAS CHROMATOGRAPHIC DETECTORS

Many high-temperature spectrophotometric sources are particularly well suited for use as detectors in gas chromatography, partially due to their specificity and high levels of sensitivity. Several general reviews have been published which discuss the cost, availability, adaptability, sensitivity, and overall utility of many high temperature sources, including plasmas,[627,628] flames,[628–631] and many others. Table 5 lists some specific studies which have used these sources as detectors for specialized determinations. In most of the studies listed, the detector was investigated for a specific application. The microwave and radiofrequency plasma detectors have received considerable attention recently because of their ready adaptability to gas flow systems, such as those encountered in a gas chromatograph, and their high excitation capabilities. Unlike flames, plasma detectors are capable of exciting atomic species such as sulfur, phosphorus, and the halides, thus making them more versatile than flame photometric detectors (FPD) which require a specially modified system to detect the halogens, sulfur and phosphorus, as well as carbon containing species. An excellent "down the line" comparison between radiofrequency (30 MHz) and microwave (2450 MHz) plasma detectors has been published by West.[627] This researcher found that the less expensive radiofrequency plasma detector was slightly more sensitive than the microwave plasma detector. The radiofrequency plasma detector has the additional advantage of being able to form a plasma with virtually any gas at atmospheric pressure. It is also simpler to adjust and operate than the microwave plasma detector and is less likely to foul the quartz plasma tube. On the other hand, more varieties of microwave plasma detectors are commercially available and are more readily adaptable to gas chromatographic systems. The microwave plasmas are also more easily thermostated and do not require extensive electrical shielding as do the radiofrequency plasma detectors.

Flames, as opposed to plasma sources, afford

TABLE 5

Studies Using High Temperature Sources as Gas Chromatographic Detectors

Source	Compounds determined	Species monitored	Description of study	Ref.
Arc	Organometallics	Cr, Be, Al, Ga, Cu, Fe, In	Characterization, used Ar saturated with trifluoroacetylacetone as carrier gas to form metal chelates	633
Discharge	General	–	Characterization	634
	S containing compounds	S	Analytical determination	635
Direct-current discharge	Halogen containing compounds	F, Cl, Br, I	Characterization	636
Radio frequency discharge	General	–	Characterization, parameter optimization	263
High-frequency discharge	General	CH, CCl, CS	Characterization	174
Microwave discharge tube	General	–	Used sealed tube to trap eluted sample for more extensive spectral analysis	592
Microwave discharge	General	S, C, N	Characterization	637
	Deuterated compounds	CD, CH	Determined degree of deuteration of sample	175
	C, P, Cd, F containing compounds	C_2, P, Cd, CF	Design and characterization	170
	S containing compounds	S, CS, C_2	Characterization, parameter optimization	172
	S, Cl containing pesticides	S, Cl	Characterization	638
	P containing compounds	P	Design and characterization	639
	P containing pesticide residues	P	Analytical determination	640, 641
Microwave EDT	General, P, S, halogen containing compounds	–	Design and characterization	642
Glow discharge	General	–	Design and characterization	643
Radio frequency plasma	General	–	Design for simple detector system	644
Microwave plasma	General	–	Design of circuitry and apparatus	645
	Hg containing compounds	Hg	Determine Hg in biological samples	646
	S, P, Cl, Br, I containing compounds	S, P, Cl, Br, I	Characterization	647–649
	S, P, halogen containing pesticide residues	S, P, Cl, Br, I	Analytical determination	650
	S containing compounds	CS	Technique modification	201
Flame	General	–	Design for combined FPD and FID	171, 651
		–	Characterization using fluoroalkanes	652
	General, metal halides	Metals, total	Selective/nonselective FPD which monitors both specific and total emission	653
	General, halogen containing compounds	InCl, InBr, InI	Design for combined FPD and FID	235
	Metal halides, metal chelates	Metals	Characterization	654
	Halogen containing compounds	InCl, InBr, InI	Design and characterization	233, 234
	Br, Cl containing compounds	InCl, InBr	Characterization	232
	Halogen containing compounds	Cu	Characterization, combust halogen containing compound in region of solid Cu	655

TABLE 5 (continued)

Studies Using High Temperature Sources as Gas Chromatographic Detectors

Source	Compounds determined	Species monitored	Description of study	Ref.
Flame (continued)				
		S	Determined halogenated compounds from enhancement or depression of the S signal	656
	Cl containing compounds	S	Enhancement or depression of S signal due to chlorinated hydrocarbons	657
	F containing compounds	CaF	Design for detector in which F and Ca react in the flame	209
	Halogen containing pesticides	Na	Increase of Na volatilization by halide	658
	S containing compounds	S_2	Characterization	659
	S, P, Cl containing compounds	S_2, HPO, InCl	3 Channel design and characterization for simultaneous determination	240
	S containing compounds	S_2	Determined S containing compounds at trace levels in air	311
		S_2	Determined S containing compounds in coal	309
		S_2	Determined S containing compounds in smoke	310
		S_2	Determined S containing compounds in pesticide residues	307
		S_2	Determined S containing fatty acids and oils	308
	S, P containing compounds	S_2, HPO	Determined S, P containing compounds in pesticide residues	632
	COS, H_2S	S_2 (?)	Design	312
	H_2S, SO_2	S_2	Characterization, parameter optimization	660
	S, N containing compounds	S_2, HNO	Characterization	272
	S, P containing compounds	S_2, HPO	Characterization	295, 661, 66
	P containing compounds	HPO	Analytical determination	663
	N containing compounds	–	Analytical determination	664
	C, Fe, Pb, Sn, S, P containing compounds	–	Design for FPD and conductivity detection	665
	C containing compounds, metals, metal halides	–	Characterization	666
	Organometallics	Fe, Sn, Pb, etc.	Characterization, parameter optimization	667
	W, Re, B, P, Se, S, Si, Te containing compounds	WF, ReF, BF, PF, SeF, SF, SiF, TeF	Determined metals by first reacting them with ClF_3	127
	Cr containing compounds	Cr	Chelate and detect Cr	668
	Si containing compounds	Si	Characterization	669
	Boron hydrides	BO	Characterization	130

much more sensitive measurements for sulfur- and phosphorus-containing compounds if the S_2 and HPO emission is used.[631] This is especially useful in pesticide residue analysis.[307,632] A unique FPD has been used by Dagnall et al.[127] for the determination of metals in samples not easily chromatographed. The sample is first passed through a specially designed reaction vessel containing ClF_3 in which the metals present react to form their fluorides (tungsten, rhenium, boron, phosphorus, selenium, sulfur, and silicon are used as examples), after which they are passed into the gas chromatographic column. After separation, the eluting metal fluorides are detected by monitoring the molecular emission from the metal monofluoride. Perhaps an adaptation of a multielement detector to this method will make it a viable substitute for other methods in the determination of metals in routine industrial analysis.

VIII. MISCELLANEOUS CONSIDERATIONS

Several new techniques or variations of old techniques have been used to extend the utility of high-temperature spectroscopy. Among these are microwave absorption spectroscopy, laser-induced plasma spectroscopy, nanosecond spectroscopy, and HC emission spectroscopy. Laurie[670] has presented a review of microwave absorption spectroscopy which includes both theoretical and experimental treatments as well as analytical applications. Microwave absorption spectroscopy has been used for isotope exchange studies,[671-673] analytical determinations of trace gas pollutants,[674] and alcohol impurities in gasoline.[675] Laser-induced emission has found increasing use in routine analyses when a rapid assay is required. However, due to the small area sampled, the technique has been found to suffer from surface variations when the sample is a solid, and it has been found that the limits of detection for most metals are considerably greater than those noted using other methods. Felske et al.[676] and Scott and Strosheim[677] have discussed these difficulties. They have also discussed the advantages of using laser-induced emission and the instrumentation involved. Recording spectra arising from laser-induced emission of short duration places stringent requirements upon the instrumentation. Luthjens and Schmidt[678] have described a system that is designed to be used for absorption methods and is capable of recording signals on the nanosecond time scale. However, the principles of the method are also applicable to other systems where recording must be done on a similar time scale.

The HC, which has enjoyed widespread use as a source for AAS and AFS measurements, has also been recently evaluated as an emission source for analytical purposes for both solid and liquid samples. Prakach[679] has constructed and characterized a demountable HC tube for the quantitative determination of metals in various sample types (lead, copper, boron, tin, and magnesium are used as examples) and has found that a precision of 3 to 5% is attainable. This type of HC may be used for liquid samples by evaporating the sample onto the cathode material (usually graphite),[680] for solid samples by placing them directly onto the cathode material (as is the case for biological samples), or using the sample in place of the cathode (as is the case for metal samples). While excellent precision and fairly low detection limits accompany determinations using HC sources, there are a number of time-consuming procedures which limit their utility. These include the sample preparation and mounting procedures and cleaning of the source before the next sample may be mounted.[681]

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