



# Plasma chemistry as a tool for green chemistry, environmental analysis and waste management

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Received 7 April 2000; received in revised form 20 June 2000; accepted 20 June 2000

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## Abstract

The applications of plasma chemistry to environmental problems and to green chemistry are emerging fields that offer unique opportunities for advancement. There has been substantial progress in the application of plasmas to analytical diagnostics and to waste reduction and waste management. This review discusses the chemistry and physics necessary to a basic understanding of plasmas, something that has been missing from recent technical reviews. The current status of plasmas in environmental chemistry is summarized and emerging areas of application for plasmas are delineated. Plasmas are defined and discussed in terms of their properties that make them useful for environmental chemistry. Information is drawn from diverse fields to illustrate the potential applications of plasmas in analysis, materials modifications and hazardous waste treatments. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Plasma; Analysis; Waste treatment; Materials modification

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## 1. Introduction

Recent publications on the application of electrical plasmas to oxidation of solids [1], to treatment of nonhazardous and hazardous wastes [2], environmental protection [3], and

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green chemical applications [4,5], illustrate the broad interest in plasma chemistry and associated technologies. One of the major concerns before the world today is to maintain a cleaner environment. The natural ecosystems are under ever increasing threat due to greatly enhanced anthropogenic activities associated with growing industrialization. The multi-faceted environmental problems arising from the production, uses and improper disposal of man-made or altered materials pose enormous challenges to contemporary science. New and innovative technologies are being sought and existing ones are being manipulated in order to meet the primary demands of environmental chemistry, such as analysis and appropriate conversion of harmful substances to less hazardous ones. These efforts sometimes lead to the evolution of new techniques for better solutions to environmental problems. One such technology lies in the broad field of plasma chemistry [6]. In the present article we will describe physical and chemical properties of plasmas and their applications in green chemistry and waste management. Some suggestions for future applications will also be provided.

The importance of plasmas was recognized in 1879 when Crookes [7] investigated the electrical discharges in gases. However, it was not until the post-war years that plasma technology became of major economic importance. Today plasma processing has become a mainstay of the electronics industries [5] and has made enormous advances in materials preparation such as amorphous Si [8] and diamond synthesis [9–11] and materials modification as in polymer treatments [12]. However, the use of plasmas in environmental chemistry is still in its infancy, but substantial gains have been made in the last decade. The potential applications of plasma technology to environmental problems still remain a rather unexplored opportunity. There is beginning progress made in the fields of plasma mediated treatment, like disintegration, decontamination etc., of hazardous waste materials as well as green chemical efforts such as solvent replacement by plasma chemical cleaning [4]. The purpose of this article is to provide an introduction to the basic physical principles, which determine the chemical behavior of materials in electrical plasmas. Their understanding is crucial to develop novel applications to environmental problems.

Tonks and Langmuir [13] used the word plasma ‘to designate the portion of an arc-type discharge in which densities of ions and electrons are high but substantially equal’. The authors implied two basic requirements for the plasma state: quasi-neutral and a high concentration of free charge carriers. In a plasma state of matter the free electrons occur at reasonably high concentrations and the charges of the electrons are balanced by positive ions. The densities of charge carriers vary within a wide range from  $10^6 \text{ cm}^{-3}$  in the ionosphere of the earth to  $10^{22} \text{ cm}^{-3}$  in lightning. The plasma state is often called ‘the fourth state of matter’. The characteristics that make plasmas useful in environmental chemistry are summarized in Table 1.

## 2. Basic plasma properties

The nature of low-pressure plasmas and atmospheric plasmas are quite different. The interrelationships between basic plasma properties, which can be used in environmental chemistry, are shown in Fig. 1a and b. These properties are discussed separately in the following sections.

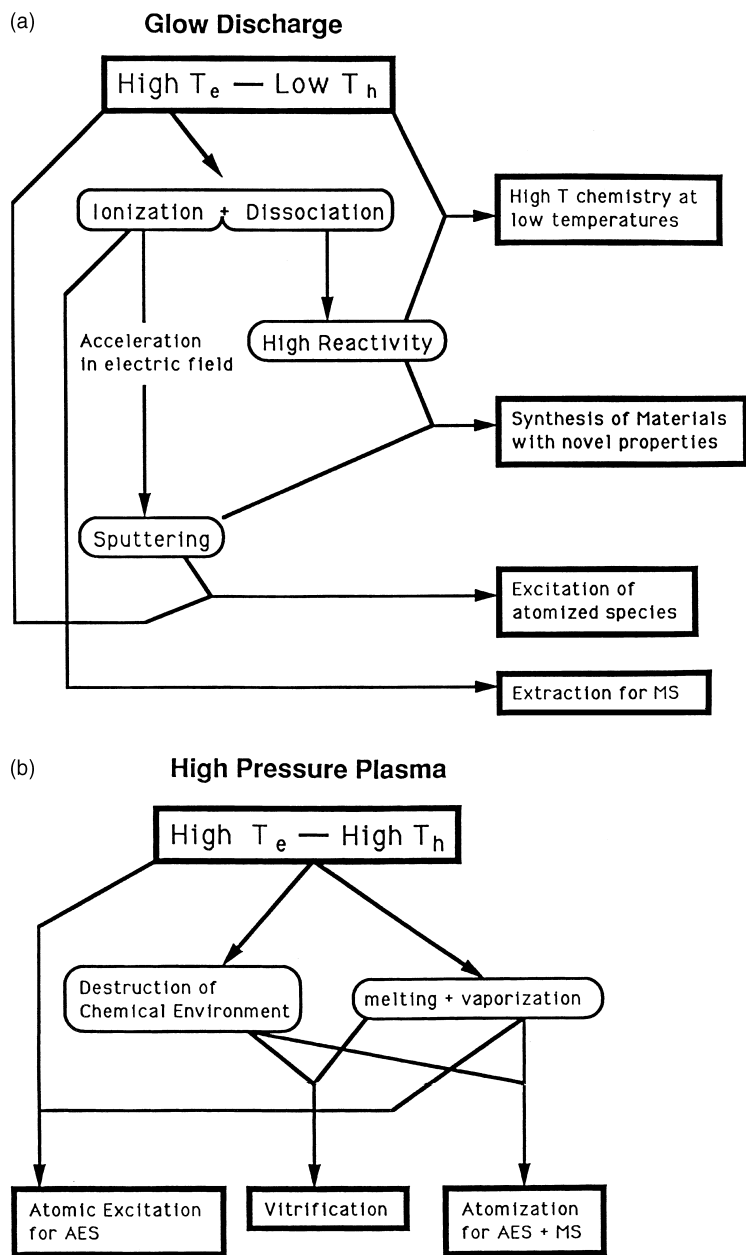


Fig. 1. Basic plasma properties that are useful in environmental chemistry: (a) glow discharge; (b) high-pressure plasma.

Table 1  
Characteristics of plasmas applicable to environmental chemistry

Plasma property	Effect	Environmental chemical application	References
High electron energy	Electronic excitation, ionization, bond destruction	Emission spectroscopy, mass spectrometry, chemical detoxification, ashing	[14–21]
Variable thermal energies	Material phase change	Melting/vaporization	[21–23]
High chemical reactivity	Low activation barriers	High-temperature chemistry at low temperatures	[24–26]
	Fast reactions		[24]
	Radical reactions	Mineralization Ozonation	[27]
Energetic ions	Sputtering	Surface cleaning	[26]
		Analysis	[28–31]

### 2.1. Low-pressure plasmas

One of the fundamental properties of both types of plasmas is their high electron temperature, which causes excitation, ionization and dissociation of gaseous species. In low-pressure plasmas, homolytic dissociation of gases produces radicals, which readily react at much lower temperatures than molecular species. As a result, the relatively low temperature of the ions, atoms or molecules present in low-pressure plasmas allows the performance of high-temperature chemistry at low temperatures. The electrical fields occurring in the marginal zones of plasma strongly accelerate ions present in the electrical discharge towards the wall or electrodes. At certain conditions, the electric fields can cause sputtering of these materials or materials placed on them. Sputtered atoms can be further excited by electron impact and their relaxation can be monitored by atomic emission spectroscopy. The ions generated during discharge can be extracted to perform mass spectroscopy. The high reactivity of radicals can be combined with the variable impact energy of ions to synthesize environmentally friendly materials at low temperatures (typically 200–500°C). Such materials may exhibit unique surface properties (e.g. wettability) which may not be achieved by classical chemical methods. For example, they may exist in certain defined states of stress and show special mechanical (e.g. wear protection) or electrical (e.g. conductivity) properties. These may be used for monitoring chemical and/or physical parameters for analytical purposes.

### 2.2. Atmospheric plasmas

At higher pressure the plasma state can be initiated at very high temperatures, which results in the destruction of chemical bonds and thus destroys the chemical environments of virtually all materials. These plasmas are therefore powerful tools for use in converting harmful organic or inorganic substances to less noxious oxidized species. The high temperatures lead to vaporization, atomization, excitation and ionization of materials introduced into the plasma system and therefore can be used for spectroscopic purposes, such

as atomic emission spectroscopy (AES) and/or mass spectroscopy (MS). In addition, atmospheric plasmas are used for vitrification of materials which otherwise could be mobile metal ions from chemical wastes.

### 2.3. Electron energies

It is customary to describe the energy content of a system of known chemical identity by its temperature. However, the description of temperature in plasma is more complicated than in conventional chemical systems. Temperature, in the usual sense, implies a situation in which all particles under consideration are in thermodynamic equilibrium exhibiting a Maxwell–Boltzmann distribution. In a plasma discharge, there is a continuous loss of charge due to recombination, especially on the walls confining the discharge. In order to maintain the discharge in a steady state, these losses are compensated by an external feed of energy, in form of electric current through the conducting gas. A plasma consists of free electrons, ions, radicals and neutral species (atoms or molecules). The mobility of these various species, their excitation cross-section and recombination processes differ by orders of magnitude, especially between electrons and heavy particles. The mean energy gains for various species arise from different processes, e.g. collisional energy transfer, electron impact dissociation and ionization as well as acceleration in an electric field. As a consequence of the high mass differences ( $m_1/m_e = 5000\text{--}50,000$ ) between ions ( $m_1$ ) and electrons ( $m_e$ ), the energy transfer in elastic binary collisions is very inefficient and consequently equilibrium is not established between the species. This leads to thermal isolation of the electrons from the atoms and the molecules. However, the electrons accumulate sufficient kinetic energies through acceleration in an electric field to sustain gas ionization, while the heavier particles remain at low temperature. Nevertheless there are usually equilibrium energy distributions for the different particle subsystems, which can be described by equilibrium statistics [24]. Therefore, it is necessary to describe the temperature for each species separately (e.g. ‘electron temperature’  $T_e$ , ‘ion temperature’  $T_i$ , ‘vibrational temperature’  $T_v$ , and heavy particle or neutral gas temperature  $T_h$ ) to characterize the chemical reactivity of the plasma state. Generally, the temperatures relate roughly as  $T_e \gg T_v > T_h$ . These discharges are often called nonisothermal plasmas, because of the existence of different temperatures. Since electron–molecule reactions are responsible for plasma chemistry, the reaction rate depends on the average electron energy and the overlap of the electron energy distribution function (EEDF) with the cross-section of the reaction under consideration. The EEDF can be described by a Maxwellian velocity distribution function, which can be specified by the electron temperature,  $T_e$ , in a manner similar to ordinary gas systems. The EEDF peaks usually around several electron volts, which corresponds to the strength of almost all chemical bonds ( $N_2$ : 9.6 eV). However, in many cases deviations from the Maxwell–Boltzmann behavior in these subsystems are observed.

The relation between the neutral gas (or heavy particle) temperature and electron temperature is strongly influenced by the total gas pressure as shown in Fig. 2. The collision frequency between electrons and atoms increases with increase in pressure, and as a result the rate of their interactions increases. Therefore, the temperature of both species converge as the pressure increases and the plasma adopts a quasi-equilibrium nature, where the elec-

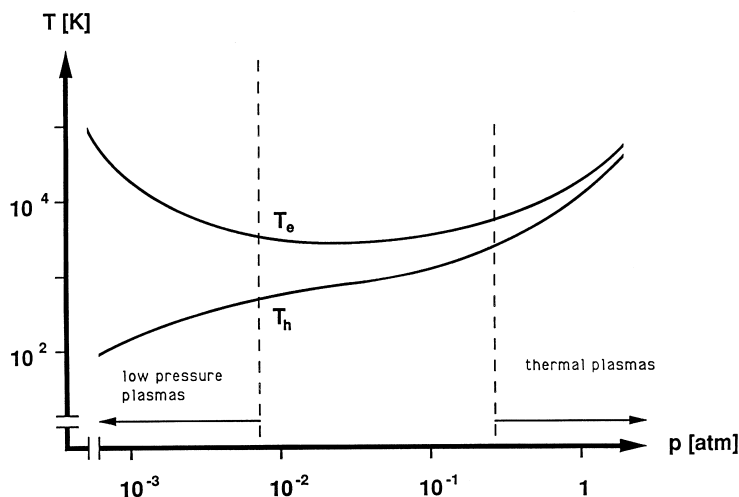


Fig. 2. Typical values for 'electron temperature'  $T_e$  and 'heavy particle temperature'  $T_h$  vs. total pressure.

tron temperature comes close to that of the neutral gas. This localized thermal equilibrium is usually reached for electron densities above  $\approx 10^{16} \text{ cm}^{-3}$ . Higher gas pressure means a higher concentration of particles, which can be ionized. This leads to the high currents (100 to several 10,000 A) at which atmospheric plasmas are operated.

Chemical behaviors of these two plasmas are quite different, and they arise due to the relative differences in electron and neutral gas temperatures at low pressures (0.1–10 mbar) and at high pressures ( $\geq 1$  atm). It is, therefore, essential to distinguish between low-pressure plasmas and high-pressure or thermal plasmas for a meaningful understanding of the chemistry of the two states.

#### 2.4. High reactivity

The high reactivities of low-pressure plasmas are due to high electron temperatures (30,000–80,000 K) and comparably low neutral gas temperatures (100–1000 K). The concentration of radicals in such discharges is typically  $10^2$ – $10^3$  times higher than that of the ions. The high degree of dissociation (up to 30%) greatly reduces activation energy barriers that chemical reactions have to overcome. In this way, the plasma exhibits a kinetic 'factor effect'. The predominant radicals add a strong exothermic term to the adduct side of the chemical equation. Thus, the effect of a glow discharge can also be thermodynamically feasible [25]. The glow discharges can thus be used as powerful tools in materials science where it is necessary to process materials at relatively low temperatures.

The high temperatures of thermal plasmas (atmospheric or high-pressure plasma) on the other hand lead to a complete destruction of the chemical environment of any atomic species in the gas phase leaving matter atomized and usually in highly excited states. Therefore, thermal plasmas are excellent excitation sources for various spectroscopic techniques and are good for destroying hazardous wastes.

## 2.5. Energetic ions

The ionization energies of many atoms and molecules lie in the range between 10 and 20 eV. The EEDF has low values outside this range since it continuously decreases from its maximum value (typically several electron volts). The overlap of the ionization cross-section with EEDF is thus fairly low and therefore the concentration of ions (and electrons) in glow discharges is very low. However, they can play a decisive role in the chemistry going on during discharges. Depending on different experimental setups, strong electrical fields may arise near confining walls and/or electrodes of the discharge tubes which allows ions to gain kinetic energies. This may be used to perform sputtering and reactive cleaning (i.e. to atomically bombard surfaces to remove contaminants which are then transported away via the gas phase).

## 3. Experimental arrangements

Typical setups of different plasma configurations are shown in Fig. 3a–e. The energy necessary to maintain an electric discharge can be transferred to a system in several differ-

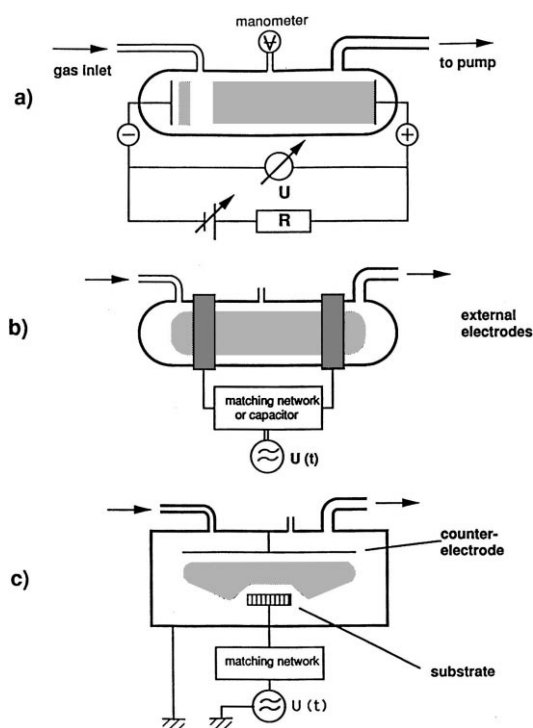


Fig. 3. Typical experimental plasma arrangements. (a) Low-pressure dc- or rf-discharge; (b) low-pressure rf-discharge with external electrodes; (c) low-pressure asymmetric rf sputtering arrangement; (d) high-pressure ICP torch; (e) high-pressure dc arc plasma (adapted from [19]).

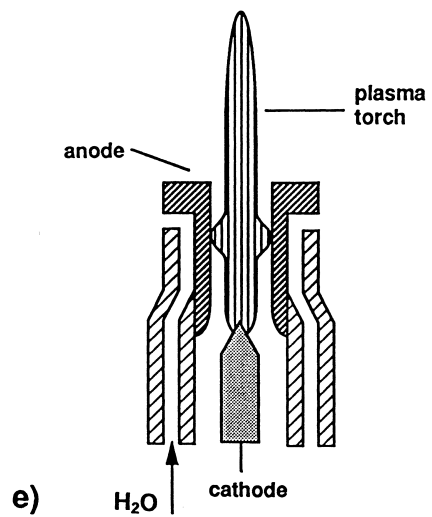
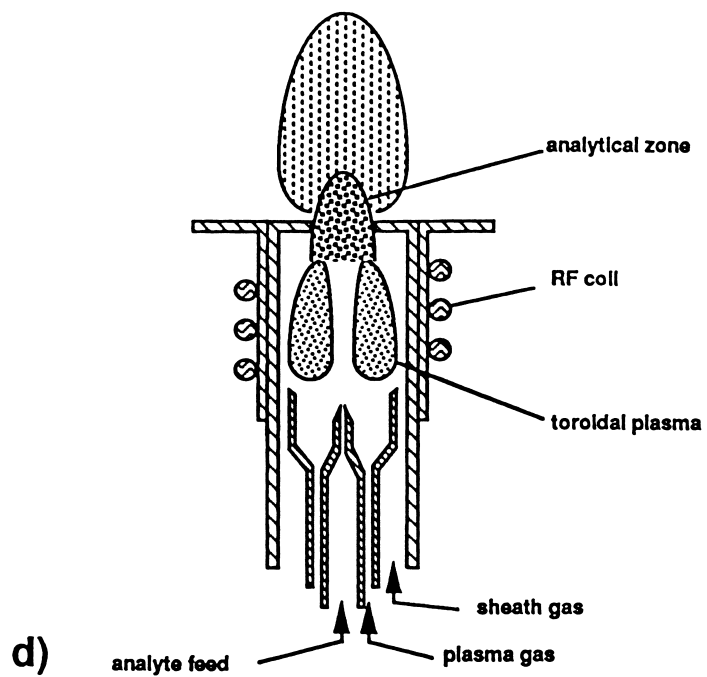


Fig. 3. (Continued).



ent ways. The excitation of the discharge can be achieved by direct current (dc) (Fig. 3a) or by high frequency current (either radio frequency (rf) or microwave (MW)) (Fig. 3b). Both forms find their applications in low-pressure plasmas (Fig. 3a–c) as well as in thermal plasmas (Fig. 3d and e). Since rf-current and MW can be transferred through insulators (e.g. through a glass wall reactor), the use of external electrodes is possible when a discharge is rf-excited (Fig. 3b) and a microwave cavity for MW excitation exists. In this way, the electrodes or exciting entities are not exposed to the severe conditions of thermal plasmas and therefore do not contaminate the reactor with sputtered electrode material.

Low-pressure plasma equipment requires a vacuum system to maintain a stable low pressure in the range between 0.1 and 5.0 mbar. Rotary pumps are commonly used for small volumes (<100 l). Furthermore a gas dosage system and electrical power supply unit are necessary. The balance between the gas flow and the pumping speed determines the pressure under which the discharge is maintained. A steady flow of gas (i.e. constant gas pressure) is necessary for desired results. A dc-system is provided with internal electrodes, whereas in rf-discharges different types of electrode arrangements can be used. Since atmospheric plasmas generate very high temperatures they usually extend into an open space (Fig. 3d and e).

#### 4. Low-pressure plasmas and their applications

Due to large differences in mobility between ions and electrons, electrons essentially carry the total current flowing through a plasma. Radio frequency glow discharges exhibit a different behavior in terms of the space charge, field distribution and ion energies relative to dc-glow discharges.

##### 4.1. Radio frequency glow discharges

A high frequency discharge occurs at frequencies where the ions are no longer capable of following the oscillations of the electric field due to their size, but the motion of the electrons can interact with the field changes. The frequencies, at which the ions produced in such a discharge are no longer able to respond rapidly enough to cross the boundary of the plasma ('sheath') in one half cycle, typically lie in the order of 1 MHz. The walls of the discharge as well as objects immersed in the plasma will be at a negative potential with respect to the unperturbed plasma. The 'floating potential', which is basically the difference between wall potential and the potential of the bulk plasma, is dependent on the excitation frequency [32]. These potentials are dependent on the nature and the pressure of the gas and may range from several hundred volts (~1 MHz) to a few millivolts (GHz range). The voltage distribution can furthermore be influenced by changing the ratio of the areas of the two electrode surfaces to properly match the energy of the impinging ions [26]. The possibility to control the potential difference between the bulk plasma and the walls in a wider range is a valuable tool to properly set up the desired ion energy for applications such as sputter cleaning or materials modification (Fig. 3c).

#### 4.2. Direct current glow discharges

The structure of the dc-glow discharge (Fig. 3a) is fundamentally different from rf-plasmas, since the electric field distribution in a dc-glow discharge does not change with time. This leads to the development of different regions in the glow discharge (Fig. 3a). The region near to the cathode is called 'the cathode dark space' or 'the cathode fall'. Most of the charge carriers in this region are generated by electron impact ionization. The ions generated in the cathode dark space are accelerated to the cathode causing emissions of secondary electrons from the cathode due to ion bombardment, which increases the total current density. A region adjacent to the cathode dark space has maximum light intensity, which is called the negative, or the cathodic glow. The space between the negative glow and a zone (very close to the anode) of constant luminosity is known as the Faraday dark space. The Faraday dark space is characterized by a zero electric field. The zone of constant luminosity is called the positive column. Only the dark space is necessary to maintain a glow discharge [33]. If the electrodes are moved close enough so that the development of the Faraday dark space and of the positive column is suppressed, the voltage drop across the electrodes is the sum of the difference across the dark space and the anode fall. As the voltage across the electrodes is a monotonic function of the current density (as long as the cathode is fully covered with negative glow), the cathode fall potential drop and hence the energy of the ions impinging on the surface can be influenced directly by the discharge current density. It is thus possible to influence the chemistry while carrying out deposition of thin films in terms of ion bombardment [33,34]. Similarly, sputtering can be carried out in a controlled way at significantly higher acceleration voltages than achievable in rf-glow discharges.

One of the most important applications of glow discharges is the plasma-enhanced and plasma-induced deposition of thin films. The broad variety of techniques involving plasma-physical vapor deposition (PVD) as well as plasma-chemical vapor deposition (CVD) allows the deposition of materials at temperatures and conditions which cannot be otherwise achieved by classical chemical or physical methods [25]. Moreover, the ion bombardment achievable in glow discharges is another parameter to optimize material processing ranging from building up controlled strains and controlling stoichiometry in wear abrasive layers [33,34] to achieving complete dehydrogenation in silicon layers [25,35].

Another common application of plasma chemistry is plasma etching. In this case, the discharge is operated in such a manner that either no deposition is possible or that the ion impact erosion of the surface overrides any deposition. Sputtering provides highly controllable anisotropic etching of various materials. This field of plasma chemistry is frequently used in the semiconductor industry where precision control and anisotropic removal of thin films are required [36].

Modification of surfaces by ion implantation from the glow discharge is also used to increase the surface hardness of nitride steels in order to improve corrosion resistance, change the wettability of polymer surfaces and to alter the adsorption properties of solids [37].

### 5. High-pressure plasmas and their applications

High-pressure plasmas are operated at about atmospheric pressures. The temperatures of the individual species present in the high-pressure plasmas are much closer to each other

than in low-pressure plasmas. Therefore, these types of discharges have often been described as ‘thermal plasmas’. The classical arc discharge known from arc lamps is an example of a thermal plasma. The differences between dc- and rf-plasmas are much less pronounced in high-pressure plasmas and therefore a distinction as for glow discharges is not necessary. The ac-driven plasmas are usually operated at radio frequency. Both types of excitation (ac and dc) provide intense plasmas in which temperatures can be as high as 12,000–20,000 K depending on the operating conditions [19,23] and the nature of discharge [38]. In this temperature range, almost all matter is ionized as opposed to the low-pressure plasmas where the degree of ionization is of the order of 1% or less. Because the surrounding solid containment (such as electrodes, tubes and gas-leads) immediately disintegrate upon exposure to this high temperature, the high-pressure plasmas are generated in a fast-flowing gas stream which normally emerges into an open space (Fig. 3d and e). Under such conditions, no interaction of the plasma with solid material is possible. Therefore, such discharges are called plasma jets or plasma torches. If thermal plasma is to be confined within a tube, extensive cooling of the tube walls is necessary to avoid melting.

However, these high temperatures occur only in the core of the plasma. In the marginal zones where the temperature decreases rapidly, matter is present in the gaseous or liquid state. These properties of thermal plasmas are utilized for coating applications of high melting materials such as  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and other refractory materials [23]. Due to the high speed of the gas, this technique is also called ‘plasma spraying’. Oxides are melted in an oxygen plasma jet, while for uses in an inert atmosphere, discharges are carried out in argon or helium gases. The use of plasmas for melting and processing steels has become a widely used technique in the steel industry [38]. The thermal plasma systems are now being considered for treatment of hazardous substances. Thermal plasmas have the following advantages for material melting and consolidation which are potentially important for processing hazardous substances: (a) bulk gas temperature is much higher than attainable by combustion, (b) can be operated in a controlled atmosphere and (c) high throughput rates of materials in a variety of forms is possible.

## 6. Applications of plasmas for analytical purposes

Both high-pressure and low-pressure plasmas are now widely used in different kinds of analytical spectroscopy tools that are important to detect and to monitor hazardous substances in the environment.

### 6.1. High-pressure plasmas

One of the early applications of high-pressure plasma for analytical purposes was the use of an electric spark as the ionization source in secondary ion mass spectrometry (SIMS). This method utilizes a repetitive series of high voltage spark discharges between two electrodes one of which is the sample. A very high efficiency of ion production is realized in this method, and in fact the ionization is almost 100% for most elements. SIMS is now an established technique for chemical analysis of trace and inorganic constituents in a variety of materials [17]. It has high sensitivity ( $\approx 10$  ppb) and can detect virtually all elements

in a sample. Disadvantages are slow sample throughput (1 sample per day), complexity of operations and difficulties in quantification.

There are several requirements with regard to the plasma source that must be met for optimal performance for spectral analysis. The residence time of the analyte species in the plasma must be long enough to ensure satisfactory vaporization, atomization, excitation, and/or ionization. There should not be any elemental interactions during the processes. This can be largely achieved by complexing the metal atoms [39]. A further demand is the capability to analyze liquids, gases and solids with minimal sample preparation. The plasma source that meets these requirements, to a reasonable degree, is an inductively coupled plasma torch, which is discussed in some detail in the following section.

The excitation of the analyte is usually effected by a radio frequency discharge, which is inductively coupled to a fast flowing gas stream. Radio frequency allows the use of an external electrode, which will not be consumed by the plasma. The arrangement consists of a cooled tube, through which the carrier gas (argon or helium) flows, and a coil surrounding the tube, through which the radio frequency travels (Fig. 3d). Such a discharge is commonly referred to as inductively coupled plasma (ICP). The oscillating magnetic field generated by the coil induces an eddy current of toroidal form in the gas stream in the tube, which causes a helical motion of charged particles and thereby more frequent collisions between all streaming species. The highest temperature is reached in the center of this torus. Fassel [40] gives a theoretical description of an ICP. For more details and the modeling of such discharges the reader is referred to the works of Boulos [22] and Thompson and Walsh [14].

The material to be analyzed is injected in the flow of the inert gas in which the plasma is maintained. The interaction of the analyte with the free electrons of the discharge and the excited noble gas atoms when passed through the annular zone of the torus causes atomization, excitation and ionization all within fractions of a millisecond. Upon leaving the heating zone, the excited species relax with the emission of light. The intensity and the energy (wavelength) of this emission can be recorded to provide information about the identity and elemental concentration of the analyte. The ionized species emerging from the discharge can be collected and analyzed in a mass spectrometer.

The most widely used spectroscopic techniques which use ICP as both the atomization and excitation source are atomic absorption spectroscopy (ICP-AAS), atomic emission spectroscopy (ICP-AES), atomic fluorescence spectroscopy (ICP-AFS) and mass spectroscopy (ICP-MS). Each of these techniques has its advantages, although (ICP-AFS) and (ICP-MS) have drawn the most attention. These spectroscopic techniques are among the most widely used methods for elemental analysis. The field of application is very broad as demonstrated by the large number of publications in this area of interest [14–16,18,39]. Both ICP-MS and ICP-AES provide excellent detection limits, which lie in the  $\text{ng l}^{-1}$  range for most elements. Furthermore, the range of linear signal response to the analyte concentration is very large, about  $10^6$ .

The main difference between ICP-MS and ICP-AES is that the emission technique probes photons, whereas in MS the ions are detected. This difference leads to the various advantages and disadvantages of the two techniques. Especially in high-atomic-weight elements, there are many energy levels and most of these are populated at the temperatures encountered in ICPs. As a result the line patterns detected in ICP-AES are usually complex. With an array of photodiodes it is possible to carry out simultaneous multi-elemental

analyses. In contrast, the ICP-MS exhibits comparably simple patterns as encountered in conventional mass spectrometry. Synchronous multi-elemental analysis by ICP-MS is not possible in many cases, because ion detection is usually done with a quadrupole mass analyzer. Some of the key features of the two methods are briefly discussed in the following sections.

### 6.2. ICP-mass spectrometry

The attractive features of ICP-MS are simpler spectra, wide linear dynamic range ( $10^4$ – $10^5$ ), flexibility, the ability to measure isotope ratios as well as elemental concentrations, and detection limits in solution in the range of 0.01–0.1 ng ml<sup>-1</sup> [28]. A detection limit up to the  $10^{-1}$ – $10^{-3}$  ng ml<sup>-1</sup> range can sometimes be achieved by preconcentration of the analyte [18,41,42].

A severe drawback of ICP-MS is the fact that sometimes the  $m/e$  (atomic mass/charge) ratio of doubly ionized atoms overlaps with the most intense lines of other elements, as in the case of Ba<sup>2+</sup> and Ga<sup>2+</sup>, for example [18]. The formation of polyatoms by interaction with the plasma gas (i.e. Ar or He), solvent (e.g. Cl from HCl-solutions, SO<sub>x</sub> from H<sub>2</sub>SO<sub>4</sub>, etc.), the surrounding atmosphere (O and N) and with the sample itself can cause problems in quantitative analyses due to overlapping with other peaks [43]. In order to minimize matrix interferences, the analyte concentrations should be kept at concentrations below 0.1%. At high concentration, problems arise with coulomb repulsion in the ion beam path, which leads to the depletion of the ion beam in lighter ions. Owing to the limitation of scanning devices such as a quadrupole mass spectrometer (QMS), the homogeneity of the sample signal has to persist considerably longer than the sweep time.

The rapid expansion of the extracted ion beam from the atmospheric plasma to about  $10^{-6}$  mbar in the mass spectrometer requires a multistage pressure reduction system. This often results in nucleation, cluster formation and condensation of the analyte atoms in the pressure reduction zone. In addition to these problems, especially when small sampling orifices are used, shifts of chemical equilibria are observed [44] and therefore problems in quantification arise. Another drawback of mass spectrometric detection manifests itself when analyzing radioactive samples since the ion lens system and the detector become contaminated.

### 6.3. ICP-atomic emission spectroscopy

ICP-AES has the advantage of a photon probing technique where no contamination of the spectrometer with the information-carrying species is encountered. In addition, problems arising upon ion extraction from plasmas in ICP-MS are not encountered in the emission spectroscopic technique. Due to its analytical performance (broad linear work range, detection limit) which typically compares to ICP-MS, and the lack of extraction problems in the MS technique, ICP-AES has become a widely used analytical tool for different applications. Examples include analyses of geological samples [45,46], wastewater analysis [47], analysis of radioactive samples [48], coal and fly ash [49]. These examples are only a few of the topics relevant to environmental scientists.

#### 6.4. Laser induced plasma spectroscopy (LIPS)

A more recent approach to plasma spectroscopy uses a high powered laser (several GW) light to form the plasma. The method uses a laser plume produced in or onto the analyzed sample. A laser pulse focused on the sample produces a high-pressure plasma for a few microseconds. After the laser pulse, the plasma cools down and the electrons recombine with ions resulting in optical emissions. While ICP is usually used with liquid samples, LIPS is more suitable for direct solid analysis. The absolute sensitivity of LIPS is better than that of ICP, but due to the small quantities sampled by the laser plasma, the detection limit is only in the ppm range. Further details of this versatile method can be found in a recent extensive LIPS review [50]. The possibility of using LIPS as an in situ system to measure aerosols [51] makes it a very important and useful tool for monitoring hazardous substances in aerosols.

#### 6.5. Glow discharges (low-pressure plasmas)

Low-pressure plasmas have been used to erode surfaces by ion bombardment (sputtering). The high electron energies in glow discharge allow excitation of sputtered atoms. These excited atoms emit light upon relaxation, which can be used in AES. MS analysis of materials exposed to glow discharges has been carried out by using both, quadrupole [29] and magnetic sector mass analyzers [30]. These methods require that the sample to be analyzed be 'conducting' in order to maintain a glow discharge. If insulating samples such as ceramics, glass, cements, etc., are to be analyzed, it is necessary to press the material under consideration in a conducting matrix such as graphite or metal powders (Ag and/or Au) [29]. One solution to the problem of nonconductive samples is to use an rf-discharge at a frequency of about 1 MHz, where a considerably larger self-bias is observed [32] and where the sample is placed on the small electrode in an asymmetric arrangement [26]. Though it was reported that depth profiling with Ar sputtering and subsequent mass spectrometric analysis is viable within a few micrometers [33], it should be taken into account that the preferential sputtering and collisional mixing can lead to erroneous depth distributions.

The degree of ionization in glow discharges is typically very low ( $\leq 1\%$ ) [25] and therefore the efficiency for the mass spectrometric bulk analysis is considerably below the potential performance of this method although sensitivities in the order of ppb have been reported [33].

Plasma ashing is used to remove organic resins in semiconductor processing from device surfaces by oxygen plasma treatment. This technique has also been applied to remove organic matrices such as air filters and fly ash prior to their analysis [21]. Also application to biological tissues are reported. It is a procedure sensitive to the first few micrometers, which allows the controlled removal of near-surface material and its vaporization for analysis.

### 7. Treatment of harmful substances

The conversion of hazardous wastes into either environment-friendly or low-risk materials using plasmas is an attractive field of research. Examples of this are the precipitation of  $\text{SO}_x$  as sulfate or the oxidation of unsaturated organic compounds to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . This can be

achieved directly by a plasma treatment or indirectly by reaction with ozone [27], which is the product of a plasma gas-phase reaction. Today, the most important way to generate ozone is in a silent discharge. Photoassisted decontamination of water-soluble pollutants by ozone is a well-established method generally applied by many countries to purify water to meet the demands of millions of people.

### 7.1. Plasma disintegration

The high internal energies of plasmas provide the activation energies necessary for chemical detoxification even at low temperatures. The low pressures used in glow discharges mean that large volumes must be used to provide reasonable yields of product chemicals. The high degree of control and confinement in these systems may make them attractive for destruction or for surface decontamination of highly hazardous substances. High-pressure plasmas are also very attractive for chemical destruction through vaporization, but subsequent condensation of harmful gaseous products (e.g. radioactive) may cause some problems. The electrical energy driving high-pressure plasmas is transformed to a system reaching as high as 18,000 K at the center line of a reactor. The high temperatures of atmospheric plasmas are being used for the dissociation/disintegration of harmful substances. The wastes injected into such systems are instantaneously destroyed and changed into atoms, ionized species, and pyrolyzed species that do not reform into large hazardous molecular weight compounds. In addition, high-pressure plasmas can be used to vitrify solid materials for improved storage attributes. Such a device consists of an atmospheric air plasma torch, which melts chemically-contaminated solid materials. Organic contaminants are burnt at these temperatures and metals are trapped within the molten slag. However, first runs demonstrated a need for a secondary combustion system to control volatile organic compounds. Upon cooling, the slag solidifies to give a relatively unleachable matrix. The plant is equipped with an additional gas treatment system that neutralizes acids gases and cleans the exhaust. Contaminated soil as well as liquid and solid organic waste can be transformed in such a reactor [20]. This dual benefit of high-pressure plasmas has been tested using the system shown in Fig. 4 (RETECH Plasma Centrifugal Furnace).

Plasma arc systems, also known as the plasma arc technology, are used for the high-efficiency destruction of hazardous wastes [52]. As the activated compounds of the plasma decay, their energy is transferred to the waste materials exposed to the plasma. As a result, the waste materials are fragmented into atoms, ions or pyrolyzed species, and finally destroyed as they interact with the decaying plasma species. One of the advantages of the plasma arc technique is that the breakdown of the waste takes place almost instantaneously, and no large-volume intermediate compounds are formed.

### 7.2. Dielectric barrier discharge plasmas

Dielectric barrier discharge (DBD) plasmas have been used to remove NO [53], H<sub>2</sub>S and NH<sub>3</sub> [55] from gas streams. In this method NH<sub>3</sub> is injected into the DBD reactor along with the NO gas stream. The removal of NO is achieved by allowing it to react with NH<sub>2</sub> and NH radicals generated in the DBD reactor to produce N<sub>2</sub> and H<sub>2</sub>O. The removal efficiency of NH<sub>3</sub> is dependent on the applied voltage, residence time of the gas, and composition of

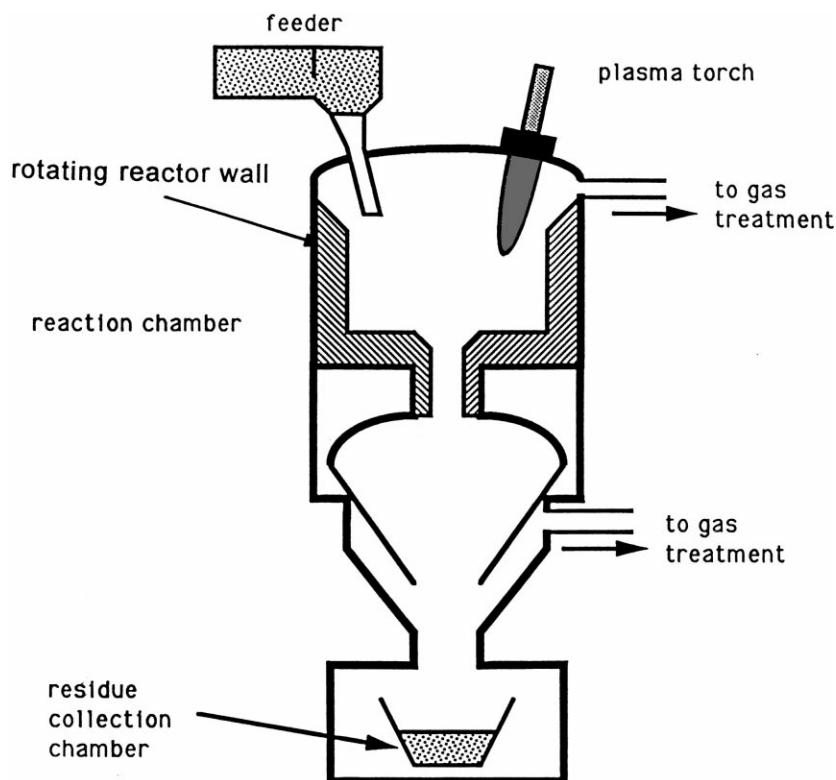


Fig. 4. Equipment for plasma combustion (adapted from [20]).

the gas stream. The DBD plasmas have also been used for the destruction of formaldehyde [54], volatile organic compounds (VOC), and odor-causing substances from a gas stream [54,55]. Enhanced removal of  $\text{NO}_x$  by a nonthermal plasma process with hydrocarbons as additives has been reported by Oda et al. [56].

Gas-phase plasma oxidation with electron beams has been investigated as an innovative technology to control  $\text{NO}_x$  emissions [54,57]. The method uses the oxidation of  $\text{NO}$  to  $\text{HNO}_3$  by gas-phase radicals such as  $\text{O}$ ,  $\text{OH}$  and  $\text{HO}_2$  generated by electron impact excitation and ionization. However, the generation of  $\text{HNO}_3$  as the end product may cause serious corrosion problems.

### 7.3. Plasma cleaning

Industrial cleaning with solvents often produces a large volume of waste tainted with various contaminants. Some of the waste solvents can be recycled, but a large portion of it must be disposed of either by incineration or by other means. A low-pressure plasma cleaning technique has been used as an alternative technique for cleaning surfaces, and particularly to remove surface contaminants [4]. If a material tainted with organic contam-



inants is immersed in a glow discharge plasma of a suitable gas (or mixture of gases), the surface of the material will be bombarded with high energetic ions and molecules, which remove the contaminants from the surface. The plasma in this case is achieved by reducing the pressure in the reactor to  $<1.0$  Torr and flowing a gas, such as oxygen or argon, through the system. The application of this method is industrially limited since it is a slow method. The performance of low-pressure plasmas can be significantly enhanced by changing many parameters, such as the geometry or the size of the reactor, electrode spacing and size, roughness of the electrodes or the reactor walls.

Plasma cleaning is widely used in the semiconductor industry to keep the vacuum systems for chemical vapor deposition clean. A major problem in the semiconductor industry is global warming gas emissions in the form of perfluoro compounds. Recently, a remote microwave plasma source (upstream from the process chamber) for cleaning chemical vapor deposition chambers was developed [58]. While conventional rf-plasma reactors that use perfluoro compounds release a large unreacted portion of the gas, the new remote microwave plasma source provides a 99.9% utilization removal efficiency. A major advantage of this system is that it can easily be introduced into existing production lines [58].

## 8. Green chemistry

Green chemistry is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products [59]. The core concept ingrained in 'green chemistry' is pollution prevention at a basic level. This new approach has received considerable attention. Others have coined similar terms: 'environmentally benign chemistry', 'clean chemistry', 'atom economy' and 'benign-by-design chemistry' [59].

Applications of plasma technology in waste remediation appear to meet the definition of 'green chemistry'. An example is the use of the plasma centrifugal furnace (PCF) for the stabilization and decomposition of toxic and radioactive wastes [60]. The PCF has been developed to stabilize solid-waste materials while decomposing the toxic substances contained therein into relatively innocuous and simple molecules. Heavy metals, organic wastes and hydrocarbons have been treated by this method. Hydrocarbons have been decomposed and reacted with  $O_2$  to produce  $CO_2$  and  $H_2O$  molecules. Complete oxidation can be attained with proper control of  $O_2$  and management of the feed materials.

Glow discharge mass spectrometry (GDMS) has the potential of analyzing contaminated soil or solid samples without actually disturbing the matrix [61]. The only necessary sample preparation is grinding, drying and mixing with a conducting host material to form an electrode. Therefore, the use of solvents that might be hazardous is avoided, making GDMS a 'green chemistry' tool. GDMS is a fast screening method for hazardous substances (mostly metals) in soils and rocks, as the need for sample preparation like in ICP-MS is avoided, but the advantages of MS as an analytical tool can be used [61].

Biosensors are useful tools in terms of green chemistry due to their compact size, real-time analysis capability, nearly reagentless operation and simplicity of use. A low-pressure rf-plasma is used for the interfacial design of biosensors [62]. Because the adhesion of enzymes, antibodies and other biological components to the sensor surface can only be

done at low temperatures to preserve the biochemical detectors, plasma-polymerized films have a large potential for interfacial design in biosensors [62].

## 9. Summary

Plasma chemistry is in the forefront of modern environmental analyses. Plasmas already play important roles in environmental chemistry. However, the unique characteristics of plasmas should result in much broader applications in environmental mitigation and in doing environmental analyses. Plasmas will increasingly become valuable environmental tools in future research of environmental areas. For example, existing plasma technologies currently applied in the steel industry may be adapted to solve environmental problems ranging from analyzing solid surfaces in glow discharges to analysis of wastewater in ICPs, operating large thermal plasma destruction units, utilizing microwave plasma cleaning in the semiconductor industry and applying onsite aerosol measurements with LIPS.

## Acknowledgements

The authors are grateful for the financial support of the Robert A. Welch Foundation (Houston, TX) under Grant no. V-1103 and the Gulf Coast Hazardous Substance Research Center under Grant no. EPA-118LUB. This material is based in part upon work supported by the Texas Advanced Research (Technology) Program under Grant no. 003581-004.

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