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**ATOMIC ABSORPTION SPECTROMETRY WITH
SAMPLE ATOMIZATION BY CATHODIC
SPUTTERING IN A GLOW DISCHARGE**

by

Kurt Lee Headrick, B. Sc.

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfilment of
the requirements for the degree of

Doctor of Philosophy

Department of Chemistry

Carleton University

Ottawa, Ontario

September 3, 1991

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CATHODIC SPUTTERING IN A GLOW DISCHARGE

submitted by

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ABSTRACT

The introduction of a commercial cathodic sputtering atomizer designed for atomic absorption spectrometry has stimulated interest in its application, mainly to the analysis of conducting solids. This work details the assessment of the analytical potential of the commercial atomizer in atomic absorption spectrometry in general, and particularly for the analysis of solution residues. Limitations in the application of cathodic sputtering atomizers to atomic absorption spectrometry are examined. Ways to remove these limitations are examined, as is the design, construction and evaluation of a laboratory-built cathodic sputtering atomizer which does not have the above limitations. Kinetic modelling of analyte atom transport inside the atomizer has shown that the transient mode of atomization and especially the pulsed mode of atomization are much more sensitive than the traditional steady-state mode of atomization used in the analysis of bulk solids; the sensitivity of the pulsed mode of atomization is similar to or better than that of graphite furnace atomic absorption spectrometry. Matrix interferences are examined and radiofrequency sputtering is shown to be a promising approach to their possible removal.

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CHAPTER ONE - TRANSIENT ATOMIZATION

INTRODUCTION

The glow discharge has been studied for a long time by workers in various fields of chemistry, engineering and physics. The phenomenon of cathodic sputtering in a glow discharge was first reported in 1852 [1]. Cathodic sputtering was considered a nuisance since it caused erosion of the cathode and made observation of the glow discharge more difficult because of the deposition of sputtered material on the observation windows. Since that time the glow discharge has been recognized as a valuable tool for studying plasmas, atomic spectra, thin films and as an atom/ion source for atomic spectroscopy. This last area of application of the glow discharge is receiving more and more attention as analytical atomic spectroscopists recognize both the fundamental limitations of the various thermal methods of atomization currently used in atomic spectrometry, and the great and largely unexplored potential of cathodic sputtering in a glow discharge as a means of non-thermal atomization for analytical atomic spectrometry.

The glow discharge is one type of gas discharge, the particular type of gas discharge is dependent on the current, as shown in Figure 1 [2]. A glow discharge results from the application of a potential to two separate electrodes, usually in the presence of a noble gas at a reduced pressure. The applied potential ionizes the noble gas atoms present which are then accelerated towards the cathode. These ions may be backscattered (estimated probability 0.1 %) [3], but most penetrate the cathode where they dissipate their energy. Dissipation of potential energy produces secondary electron

Figure 1 - Schematic representation of characteristics of a gas discharge [2].

emission through Auger-type transitions; electrons are accelerated away from the cathode and into the glow discharge where they can excite and ionize various gaseous species present. This sustains the discharge and produces the glow characteristic of these discharges. Kinetic energy is dissipated through collisions with cathode atoms at and near the surface. Most of this energy is dissipated as heat [4], a large number of atoms being displaced for each collision [5]. Atoms at or near the surface that acquire sufficient energy to overcome the binding energy of the atom with its neighbours in the crystal lattice, as well as a favourable velocity vector, can escape from the cathode and enter the vapour phase, as shown in Figure 2. This is the process of physical cathodic sputtering, in which cathode atoms are physically ejected from the cathode by momentum transfer from collisions with accelerated gaseous discharge gas ions. Chemical or reactive sputtering occurs when the incident ion and the target ion form a volatile compound, which is then volatilized into the glow discharge [7]. This thesis is concerned only with physical sputtering, and chemical sputtering will not be discussed any further.

Figure 3 shows that the glow discharge can consist of up to eight distinct regions, depending on the exact configuration of the discharge used [8]. The regions of interest to the analytical chemist are the cathode dark space and the negative glow. Glow discharges can exist without a negative glow or any of the other regions farther from the cathode, but they can never exist without a cathode dark space [10]. As electrons are accelerated away from the cathode and into the cathode dark space, they lose energy through collisions with the discharge gas and through ionization of the discharge gas. This ionization creates a large number of positive ions, producing electron multiplication

Figure 2 - Representation of ion bombardment of a solid leading to sputtering [6].

Figure 3 - Discharge zones of a conventional dc glow discharge [9]; D. S. stands for dark space.

and a large potential gradient which takes up almost all of the discharge voltage. This potential gradient is called the cathode fall potential'. As the electrons are slowed to near thermal energies they are better able to excite the gaseous species present. The point where large numbers of these thermal electrons are first encountered marks the beginning of the negative glow. The negative glow is a region of continuing ionization and intense emission, the intensity of which is greatest just after the start of the negative glow. It is the negative glow which is of interest for atomic emission spectrometry (AES) and for glow discharge mass spectrometry (GDMS). For AES, the hollow-cathode effect is usually employed to produce very intense radiation [11,12]. For GDMS, positive ions are sampled from the negative glow. Positive ions are sputtered from the cathode surface but are not detectable since they are either quickly neutralized or re-deposited on the cathode because of the large cathode fall potential near the cathode [13]. Atoms sputtered from the cathode diffuse away from the cathode because of concentration diffusion. A large proportion of the sputtered atoms are redeposited on the cathode surface or are deposited on the walls of the sputtering chamber. Thus, only a small fraction of the atoms sputtered are available for producing analysis signals.

Most of the studies that have provided information about the fundamental processes that influence cathodic sputtering in a glow discharge have been done using secondary-ion mass spectrometry (SIMS), in which the target cathode is bombarded by a collimated ion beam in a high vacuum. The physical aspects of the ion-surface interactions are similar to those of cathodic sputtering in a glow discharge [14], but the results must be extrapolated to the much higher pressures normally used for the glow

discharge. The use of an ion gun in a high vacuum allows independent control of experimental parameters such as the incident ion energy, flux and angle of incidence that are impossible to achieve using a glow discharge. For example, in a glow discharge the incident ions are not monoenergetic, but have an energy distribution because of collision and symmetric charge transfer with discharge gas atoms. The fraction of ions reaching the target cathode with the full cathode fall potential has been found to be proportional to $N_0 \exp(-L / \lambda)$, where N_0 is the number of ions starting from the negative glow, L is the length of the cathode fall region (the cathode dark space) and λ is the mean free path for charge transfer [15]; both L and λ are reported to be inversely proportional to the pressure [16]. For similar reasons there is no one angle of incidence in a glow discharge since at the pressures normally used the sputtered atoms will have mean free paths such that they will undergo numerous gas-phase collisions before colliding with the target cathode. As a result, the glow discharge is not suitable for studying the fundamental processes that affect cathodic sputtering, with the consequence that the phenomenon is poorly understood.

From Figure 1 it can be seen that there are two types of glow discharge - the normal and the abnormal glow discharge. In a normal glow discharge, the discharge covers only a portion of the cathode surface. Increasing the discharge current increases the area of the cathode surface covered by the discharge, while the discharge voltage remains constant. Once the entire cathode surface is covered by the discharge, an increase in the discharge current causes the discharge voltage to increase as well, producing what is known as an abnormal glow discharge. It is the abnormal glow

discharge that is analytically useful (and hence, used in this thesis) since only here is the entire cathode surface being sampled. The proportionality between the discharge current and the discharge voltage continues until thermionic emission begins. Still further increase in the discharge current results in the formation of an arc discharge. The arc discharge is a high current, low voltage discharge in which cathode atoms are volatilized by the high temperature of the arc. Since the arc discharge is a thermal means of atomization and we are interested in non-thermal atomization by cathodic sputtering in a glow discharge, the arc discharge will not be considered further.

In the glow discharge the discharge current determines the bombarding ion flux and the discharge voltage determines the bombarding ion kinetic energy. In order for sputtering to occur the bombarding ions must have an energy greater than the threshold energy of the target cathode. For sputtering under normal incidence with Ne, Ar, Kr or Xe the threshold energy is approximately 4 times the heat of sublimation of the target, and is characteristic for a given combination of discharge gas and target, the heat of sublimation being used to provide a measure of the average binding energy of the target cathode.

A term that is used to characterize the phenomenon of cathodic sputtering is the sputtering yield. The sputtering yield is defined as the number of atoms sputtered per primary ion colliding with the solid (cathode) surface [17]. Figure 4 shows the variation in sputtering yield with ion energy for the bombardment of a copper cathode with argon. Above the threshold energy the sputtering yield exponentially increases at first, and then linearly with increasing energy of the bombarding ion. The sputtering yield vs.

Figure 4 - Variation of sputtering yield with energy of Ar^+ ions bombarding copper [20].

bombarding ion energy curve eventually levels off and reaches a maximum (at approximately 30 keV for $\text{Ar}^+ - \text{Cu}$) [4] after which it decreases with increasing bombarding ion energy, since very energetic ions will penetrate the crystal lattice of the target cathode so deeply that most of their energy is dissipated far from the surface of the cathode, resulting in a reduction in the sputtering yield.

The discharge gas pressure affects the energy distribution and the angle of incidence of the bombarding discharge gas ions. Higher pressures increase redeposition of the sputtered atoms on the cathode. Redeposition is reported to account for 90% of the sputtered atoms in a discharge of 0.1 Torr gas pressure [18]. Decreasing the pressure does not necessarily increase the number of sputtered atoms in the glow discharge. In a low pressure glow discharge the bombarding ions will have a smaller energy distribution because of the longer mean free path; however, the bombarding ion flux will also be less. Thus, the pressure that gives the maximum number of sputtered atoms in the glow discharge must be determined experimentally. At pressures $< 10^{-3}$ Torr, where the mean free path of the sputtered atoms is greater than the dimensions typical of sputtering cells, the sputtering yield has been found to be independent of the product of the pressure and the discharge gap [19]. Lorentz broadening of atomic spectral lines is reported to be unimportant for the glow discharge [9].

The sputtering yield depends on the mass and the electronic configuration of both the bombarding ion and the target. Cathodic sputtering occurs by a mechanism of momentum transfer, the sputtering yield having been found to be proportional to $m \cdot M / (m + M)^2$ where m and M are the respective atomic weights of the bombarding ion and

the target cathode element [4]. Sputtering yields for H^+ and He^+ are very low, and sputtering with electrons is negligible unless they have energies in the MeV range. For moderate ion energies and atomic weight targets Ar usually provides the largest sputtering yield, whereas Kr and Xe sputtering yields become more favourable with increasing ion energy and target cathode atomic weight. Atoms with filled outer electron shells have the largest sputtering yields since their collisions are more elastic than those of atoms with unfilled outer electron shells, providing for more efficient momentum transfer. The sputtering yield increases across a given period [20] and has been found to be roughly inversely proportional to the binding energy of the target [21]. These trends can be seen in Figure 5 which shows the variation in sputtering yield with atomic number of the bombarding ion for 45 keV bombardment of copper, silver and tantalum targets. The above accounts for why the noble gases (He, Ne, Ar, Kr and Xe) and the noble metals Cu, Ag and Au are commonly employed in sputtering studies. From Figure 5 it can be seen that the sputtering yields for Zn, Cd and Hg are higher than for Cu, Ag and Au, respectively, but their large vapour pressures limit their use at low pressures. It should be pointed out that it is the electronic configuration of the bombarding atom, rather than the ion, that is important as the incoming ions are neutralized by electrons emitted from the cathode immediately before impact.

Less is known about the sputtering of compounds and alloys. In the case of alloys or pure substances contaminated with dirt particles or impurities, components of high sputtering yield are preferentially sputtered; low sputtering yield components shield the underlying material so that the overall sputtering yield is determined by that of the most

Figure 5 - Variation of sputtering yield with atomic number of the bombarding ion for 45 keV bombardment of copper, silver and tantalum targets [20].

difficult-to-sputter component. This leads to the development of cones and a variety of surface topographical features [22, 23]. The surface becomes enriched in the low-sputtering-yield component until the product of the sputtering yield and the surface concentration becomes constant for each component present, after which the components are sputtered in proportion to their bulk concentration. Chemical analysis using cathodic sputtering in a glow discharge usually involves measurement of the sputtered atom/ion population during this equilibrium period. There is little sputtering yield data available for compounds. Kelly and Lam [21] have found that for many metals the sputtering yield of the metal oxide is greater than the sputtering yield of the metal itself. They also found that for some metal oxides oxygen is preferentially sputtered.

The surface topography and preparation affect the sputtering yield. Topography and roughness affect the sputtering yield because for sputtering to occur, the target atom must acquire not only sufficient energy to overcome its binding energy with its neighbours in the crystal lattice, but also acquire a velocity vector which will carry it away from the cathode and into the glow discharge. Redeposition is more likely when the surface is rough or has a well developed topography. Surface preparation determines the roughness of the surface and can also introduce dirt and other impurities which affect the sputtering yield. A real surface prepared for irradiation will always include local variations of binding energy over the surface and this will lead to a change in the sputtering yield [22]. Ion bombardment, especially at high energies and low temperatures, tends to break-up the surface and make it amorphous. This can be understood by analogy to the surface of the moon, which is covered by a dusty layer of

"lunar soil" several meters thick, largely because of the breaking-up of the surface rocks caused by the continual bombardment of the surface by micrometeorites and cosmic rays [24]. Thus, the most reproducible surface will be the one which has been presputtered, or sputter-cleaned.

The velocity vector acquired by the target atom (and therefore, the sputtering yield) depends on the angle of incidence of the bombarding ion. The velocity vector of a target atom acquired from a normally incident ion will likely knock the target atom farther into the cathode, rather than into the glow discharge; this effect is known as "knock-in". The failure to observe the 10 Å periodicity of K in a depth profile of a mica crystal [25] has been attributed to knock-in. Atoms sputtered from incident ions nearly parallel to the cathode surface will very likely be redeposited. The optimum angle of incidence is usually about 70° to 80° from the normal, the exact angle depending on a number of parameters [22]. Single crystal targets show a complex dependence of the sputtering yield on the angle of incidence for ions incident on different crystal faces [20].

Cathodic sputtering in a glow discharge is a non-thermal means of atomization; however, certain temperature related effects must be taken into account. The large amount of energy dissipated in the cathode as heat can raise the temperature considerably unless the cathode is efficiently cooled. The sputtering yield is reported to be virtually independent of the temperature to within ~ 250 °C of the melting point [4, 26] as can be seen in Figure 6. At higher temperatures there is an apparent increase in the sputtering yield which is due to vaporization. High temperatures will reduce the adsorption of low sputtering yield gaseous contaminants on the surface, will increase

Figure 6 - Variation of sputtering yield with target temperature for 3 keV N_2^+ ions on copper [20].

solid-state diffusion in the cathode and will anneal sputter-induced damage. Exposed atoms are annealed to positions of greater binding energy, making them more difficult to sputter. For the glow discharge, Doppler broadening is considered to be the major determinant of atomic spectral line width [27]. Line widths of uncooled cathodes are reported to be $\sim 10^{-3}$ nm [8, 28]; line widths of cooled cathodes will be correspondingly less.

The majority of sputtered particles are neutral ground-state atoms. Dimers [29-31], clusters [32-34] and molecular species [3, 35-40] have also been reported. As mentioned previously, electrons are also emitted from the cathode. Excited-state atoms constitute about 1 % of the sputtered flux [41]. Sputtered ground-state neutral atoms can be excited and ionized in the glow discharge (usually in the negative glow) - up to 1 % can be ionized by electron impact ionization and $\sim 1-10$ % can be ionized by the Penning ionization (ionization by collision with a metastable noble gas atom). Some of the molecular species sputtered may dissociate in the glow discharge [29]. The sputtered flux therefore consists almost entirely of neutral ground state atoms. This is ideal for atomic absorption spectrometry since this is exactly what the technique measures. Atomization by cathodic sputtering in a glow discharge has been successfully used in combination with atomic emission spectrometry [42-87], mass spectrometry [88-103] and with atomic fluorescence spectrometry [104-112] despite the fact that only a fraction of the sputtered flux gives the analytical signal for these techniques. Until the introduction of a commercial cathodic sputtering atomizer designed for atomic absorption spectrometry [113-115] little continuing work had been done with atomic absorption

spectrometry using cathodic sputtering atomization [116-120] except for the work of Walsh and co-workers [121-131], the reason for the lack of interest in cathodic sputtering atomization for atomic absorption spectrometry undoubtedly being the poor sensitivity reported [127].

The success of any atomic spectrometric analysis is critically dependent on the common first step of sample atomization. Whatever means of sample atomization is employed, the resulting composition of the gas phase being sampled (by whatever measuring technique) must be representative of the composition of the condensed phase being analyzed. The commonly employed means of sample atomization at present include the flame, the electric arc, various furnaces (usually graphite furnaces), laser ablation and the inductively-coupled plasma (ICP). Each of these atomizers has its own advantages and applications, but they all have one thing in common - each is a type of thermal atomizer and relies on the application of a high temperature to atomize the sample. This means that the production of atoms is a function of vapour pressures, which can vary by many orders of magnitude for different components in a sample.

L'vov in his classic book [132] says the following: "With any thermal means of atomization, the rate at which sample components are atomized is proportional not only to the composition of the sample, but also to the vapour pressure of the sample components, there can therefore be no conformity between the composition of the sample and of the vapour being analyzed." There is no question that the various thermal atomizers mentioned above have proved and will continue to prove to be very useful; however, there is no way to remove the fundamental limitation common to all thermal

means of atomization, mainly the dependence of atom production on vapour pressures and bond-dissociation energies. Graphite furnace atomic absorption spectrometry (GFAAS), arguably the most sensitive trace element technique currently available [107], has been developed to the point where it is unlikely that future developments will significantly improve its sensitivity [130, 133]. To quote Sir Alan Walsh, "If AA methods are to be substantially improved it seems inescapable that the advances can only result from improved methods of atomization" [130].

The comments of L'vov [132] on thermal atomizers can be extended to non-thermal atomization by cathodic sputtering in a glow discharge. For thermal atomizers it was stated that the composition of the vapour being analyzed is proportional to the composition of the sample as well as the vapour pressure of the different sample components. For atomization by cathodic sputtering in a glow discharge, the composition of the vapour being analyzed will be proportional to the composition of the sample as well as the sputtering yield of the different sample components. However, sputtering yields for different elements or their compounds rarely differ by more than a factor of 10. For instance, the sputtering yield for W (under Ar^+ - ion bombardment) is only a factor of 2 or 3 lower than for Al, whereas the evaporation rate for these two metals differs by more than 9 orders of magnitude (at 2000 °C) [4]. Thus, sample components are atomized much more uniformly by cathodic sputtering atomization than by thermal atomization. Cathodic sputtering atomization is thus a potential solution to the outstanding problem of all atomic spectrometry, the problem of sample atomization by thermal atomizers [125].

A major attraction of cathodic sputtering atomization is its ability to atomize solid samples without dissolution. Virtually all work that has been done in any field of atomic spectrometry using cathodic sputtering atomization has involved direct atomization and determination of solid samples. The inspiration for the present work came from Walsh [130] and L'vov [132], the following being taken from Walsh [130].

"While flame methods have remained basically unchanged since 1965, there has been an ever-increasing development and application of electro-thermal methods of atomization, originated by B. V. L'vov in 1959. The essence of his idea is to completely vaporize a small sample and to measure the transient absorption signal. In retrospect this ingenious idea may appear simple and almost obvious. But I am sure that many other spectroscopists had considered, as I had, the possibilities of furnace atomization and failed to see how it could be used because we thought only in terms of steady-state systems. ... If atomic absorption methods are to be substantially improved it seems inescapable that the advances can only result from improved methods of atomization. For this reason I believe cathodic sputtering merits further study, since it is a method of atomization which is different in principle to the thermal processes occurring in flames and furnaces. To date all sputtering work has been concerned with steady-state systems. Would it not be worthwhile considering the use of cathodic sputtering in association with the 'total vaporization' method evolved by L'vov?"

The impetus for the present work came from the introduction by Analyte Corporation of the first (and to date, the only) commercial cathodic sputtering atomizer

designed for use with atomic absorption spectrometry, called the Atomsources [113-115]. A schematic diagram of the Atomsources is shown in Figure 7 [134]. The main features of interest in the design of the Atomsources are the T-shaped geometry of the atomizer, and the pneumatic accelerator, which is shown in Figure 8 [135]. The idea of the T-shaped geometry is to allow atomic absorption measurements to be made without interference from the negative glow of the glow discharge which is, as mentioned, an intense emission source. McCamey and Niemczyk [120] reported that the precision of their hollow-cathode glow discharge atomizer for atomic absorption spectrometry was limited by the background emission noise. Spatial separation of the analytical volume (as defined by the geometry of the beam of radiation from the hollow-cathode lamp) from the cathode surface and the most intense portion of the negative glow removes this limitation. The location of the vacuum ports down the long axis of the T serves to pull the atoms along this axis, thus lengthening the absorption path length and therefore, increasing the sensitivity. The pneumatic accelerator is an expansion of the gas jet employed by Gough [127], and considered by Walsh [130] to be essential. The six concentric channels serve to introduce the argon discharge gas as high velocity, highly directed gas jets aimed at the cathode surface. These gas jets produce a characteristic 6-bladed leaf pattern on the cathode surface within the sputtering cavity, showing that sputtering is most intense where these gas jets impact the cathode surface. Kim and Piepmeier [136] found that the use of gas jets increased the rate of weight loss for the sputtering of a copper cathode. The gas jets formed by the accelerator also sweep the sputtered atoms away from the cathode surface (thus preventing their redeposition on the

Figure 7 - Schematic diagram of the Atomsource showing (a) emission sensor; (b) window; (c) atom wedge; (d) vacuum port; (e) atom filter; (f) quartz window; (g) atomizer body; (h) anode; (i) silpad insulator; (j) sample cathode; (k) cathode plate; (l) water cooling for cathode plate; (m) temperature sensor; (n) accelerator; (o) sample clamp; (p) turn screw [134].

Figure 8 - Drawing of the Atomsources six-jet accelerator and arrester, and of the internal shape of the Atomsources (arrows indicate discharge gas flow) [135].

cathode surface) and into and along the observation volume, with the effects as noted above.

The introduction of gas jets in the Atomsources has stimulated other workers to examine their application to atomic emission spectrometry [44, 45] and to mass spectrometry [94, 98]. Introduction of the Atomsources has led to a renewed interest in the use of cathodic sputtering in a glow discharge, particularly for atomic absorption spectrometry [137]. However, most of the work that has been done in this field is still concerned with the steady-state atomization of bulk solids [138-140]. The objective of this thesis is to examine the analytical potential of cathodic sputtering in a glow discharge for atomic absorption spectrometry, in general, and in particular with respect to the analysis of solutions to generate transient signals, as suggested by Walsh [130].

For the initial investigations of the application of the Atomsources to atomic absorption spectrometry it was decided to use the atomizer strictly as a replacement for the flame or graphite furnace on a commercial atomic absorption spectrophotometer, which is how the Atomsources were intended to be used by the manufacturer. It was felt that this was the best approach to begin with since it was the easiest and would be of most interest to the analytical community. Kinetic analysis of the absorbance signals generated with the Atomsources was done in order to investigate the mechanism of atom introduction into and removal from the analysis volume of the atomizer, similar to the kinetic analysis of the transient signals generated by graphite furnace atomic absorption spectrometry which had aided greatly in understanding mechanisms of atom formation and loss in a graphite furnace, and therefore, in improving its performance. This chapter

presents the analytical figures of merit for and the results of the application of kinetic analysis to the atomic absorption signals generated using the Atomsource in conjunction with a commercial atomic absorption spectrophotometer.

THEORY

The kinetic analysis is confined to the introduction of atoms into and their loss from the analysis volume of the atomizer, as defined by the geometry of the beam of radiation from the hollow-cathode lamp. Assuming that consecutive, first-order reactions occur during atom introduction into and loss from the analysis volume, the following model has been shown to be valid for graphite furnace atomic absorption spectrometry [139-141]:

where A represents the analyte atoms entering the analysis volume, B the analyte atoms within the analysis volume, C the analyte atoms that have been lost from the analysis volume; k_1 and k_2 are first-order rate constants for the introduction of atoms into and their loss from the analysis volume, respectively. The results of experimental studies presented in this thesis show that the above assumption of consecutive, first-order reactions is valid. It should be noted that the geometry of this atomizer, with its spatial separation of the cathode surface (where atoms are formed by cathodic sputtering in a glow discharge) and the analysis volume (defined by the geometry of the incident beam of radiation from the hollow-cathode lamp inside the atomizer as shown in Figure 7) may

result in a difference between the rates of atom formation and loss at the cathode surface (which cannot be measured with the present apparatus) and the rates of introduction of atoms into and their loss from the analysis volume (which have been measured in this thesis). This is in contrast to the situation in a graphite furnace, in which the rate of introduction of atoms into the analysis volume is identical to the rate of atom formation, since the site for atom formation is spatially the same as the analysis volume.

At all times the following equality prevails:

$$A_t + B_t + C_t = A_o \quad (2)$$

where the subscripts t and o represent the number (or the number density since the analysis volume is constant) of the analyte atoms at any time, and the initial number of the analyte atoms (which is equal to the total number of the analyte atoms) at time $t = 0$, respectively. The above model (Equation 1) yields the differential equation

$$\frac{dA}{dt} = -k_1 A \quad (3)$$

By solving Equation 3 one obtains

$$\ln \frac{A_o}{A} = k_1 t \quad (4)$$

Also,

$$\frac{dB}{dt} = k_1 A - k_2 B \quad (5)$$

In the limit, A tends to zero, which is identified with the exhaustion of the supply of the analyte species entering the analysis volume. At this point, Equation 5 simplifies to

$$\frac{dB}{dt} = -k_2 t \quad (6)$$

or

$$\ln B = -k_2 t \quad (7)$$

As absorbance is proportional to the number of the absorbing atoms, B, the rate constant k_2 for atom loss can be determined from the falling edge of a plot of $\ln B$ (or $\ln$ absorbance due to B) as a function of time. This plot should be linear, yielding the rate constant k_2 from the slope.

Extrapolation of this straight line plot to zero time (i.e., $t=0$) will give the amount of B (resulting from the complete conversion of A_0 into B) necessary to produce the decay of the signal by the diffusion process alone. However, Equation 5 shows that the rate of formation of B is equal to the difference between the rate of conversion of species A into species B and the rate of loss of species B by concentration diffusion. The difference between the extrapolated absorbance and the experimental absorbance at any time t is equal to the number of the analyte species entering the analysis volume. Equation 4 suggests that a plot of the natural logarithm of this difference vs. time should be linear, with a slope equal to the rate constant k_1 for the entry of atoms into the analysis volume.

If the kinetic parameters are evaluated, the shape of the absorbance profile can then be determined by solving Equation 5. The use of the solution of Equation 3 with the initial amount (i.e., at $t=0$) of the species A as A_0 and with no B present initially gives the following solution to Equation 5:

$$B_t = \frac{k_1}{k_1 - k_2} A_o (e^{-k_2 t} - e^{-k_1 t}) \quad (8)$$

The number of atoms in the analysis volume B_t , which is initially zero, at first increases and then reaches a maximum when dB/dt is zero, and the system is then said to have reached a stationary state. Absorbance by analyte atoms will be used as a measure of B , recognizing that the absorbance is proportional to the analyte atom number density and the latter is proportional to B (since the analysis volume does not change).

The following two cases are of special interest [144] and are shown below without derivation, the equations involved and their derivation being in the reference cited.

Case 1. If $k_2 \gg k_1$, $dB/dt = 0$, and the system is said to have reached a steady state, and,

$$B = A_o \frac{k_1}{k_2} \quad (9)$$

which is much less than A_o ; hence, the steady-state vapour system gives poor relative sensitivity. This mode of atomization requires that the total number of analyte atoms which enter the analysis volume, A_o , greatly exceeds the rate of atomization multiplied by the total duration of atomization. This mode will be called the "steady-state atomization". Steady-state vapour systems are useful for the purpose of quantitative determination when the total number of analyte atoms entering the analysis volume A_o is relatively high, so that even with $k_1/k_2 \ll 1$, $A_o k_1/k_2$ gives a measurable analyte signal. Note that for a constant rate of introduction of atoms, and therefore a steady-state signal is obtained regardless of the relative values of k_1 and

$$B = A_0 \frac{k_1}{k_2} \quad (9)$$

k_2 , provided that the total number of atoms which enter the analysis volume, A_0 , greatly exceeds the rate of atomization multiplied by the total duration of atomization, and the ratio of k_1/k_2 remains constant. This is true for the direct atomization of solid samples by cathodic sputtering in a glow discharge.

Case 2. If $k_1 \gg k_2$, $B \cong A_0$ and B reaches its maximum possible value, giving the maximum possible peak-height absorbance. This mode of atomization requires that the total number of analyte atoms entering the analysis volume A_0 is small enough for them to enter the analysis volume in a relatively short time. The absorbance signal rises extremely rapidly (compared with the "steady-state signal") to attain a peak value and then decays exponentially; the result is a transient signal, which is in sharp contrast to the steady-state signal. This mode will therefore be called "transient atomization".

This initial portion of the work on transient atomization (Chapter one) attempts to differentiate between the steady-state atomization mode (case 1) and the transient atomization mode (case 2) on the basis of the difference in the kinetics of these modes of atomization. The results of a study of the kinetics of both modes of atomization are presented, followed by the figures of merit and other studies on the analytical performance of only the transient atomization mode in cathodic sputtering in a glow discharge.

EXPERIMENTAL

Apparatus

The experiments were carried out using the Atomsource atomizer, manufactured by Analyte Corp., Grants Pass, OR, U.S.A. and supplied with its power supply and usual accessories. It was mounted in the usual position of the burner assembly in a Perkin-Elmer Zeeman 5000 atomic absorption spectrophotometer and was operated as part of the atomic absorption spectrophotometer. Two L-brackets were attached to the outer surface of the cathode plate. These L-brackets are positioned perpendicular to each other so that one corner of the square, removable cathode can be placed at their intersection, making the position of the cathode reproducible. Absorbance vs. time plots were recorded with a Perkin-Elmer PE 7500 professional computer and hard copies were obtained with a Prism 132 printer, manufactured by Integral Data Systems, Milford, NH, U.S.A. The discharge voltage was recorded with a Nicolet Model 2090-III two-channel digital oscilloscope. The following hollow-cathode lamps were used: Co, Cu, Fe, Mo, Mn and V, by Perkin-Elmer; Cd, by Cathodeon; Al, by Instrumentation Laboratory; and Ni, by Westinghouse. The lamps were operated using lamp currents which were below the maximum currents prescribed by the manufacturers.

Test solutions and reagents

Chemically pure metals or their salts were used to prepare standard solutions. Stock solutions containing 1000 $\mu\text{g/mL}$ were prepared as follows. For Al, the metal was dissolved in 20% (v/v) HCl (ULTREX) and the solution was diluted with ultrapure water. For Mo and V, the stock solution of each metal was prepared separately by

dissolving MoO_3 or V_2O_5 in concentrated ammonium hydroxide (ACS reagent grade) and the solution was diluted with ultrapure water. For Cd, CdO was dissolved in 50% (v/v) nitric acid (ULTREX) by heating and the solution diluted with ultrapure water. For Co and Ni, each metal was separately dissolved in concentrated nitric acid (ULTREX) by heating and the solution diluted with ultrapure water. For Cu, Fe and Mn, each metal was separately dissolved in 50% (v/v) nitric acid (ULTREX) and the solution diluted with ultrapure water. All stock solutions were made to contain 1% (v/v) of the acids or the ammonium hydroxide used to dissolve the metals or their salts. The ULTREX brand acids were manufactured by Baker Chemical Co. Ultrapure water of resistivity 18.3 megohm-cm was obtained direct from a Milli-Q 2 Water Purification System (Millipore Corp.). All test solutions were prepared by serial dilution of the above stock solutions immediately prior to determination.

Atomizer Gas

Argon (99.997% pure) was used as the atomizer gas.

Procedure

Cathodes of steel or pure anisotropic pyrolytic graphite, copper and tantalum, as described below, were used. Excluding tantalum (which was supplied by the manufacturer as a polished sheet of metal), the working surface was polished with sandpaper using an electric polishing machine, final surfacing was with 400 grit emery paper. The cathodes were then cleaned with pure ethanol and air dried. The dry, clean cathode was then clamped to the atomizer. Prior to every atomization cycle, the cathodes were sputter-cleaned to ensure a reproducible atomization surface.

The selected cathode was subjected to a glow discharge of 100 mA at an argon gas pressure of 12 Torr (1 Torr = 133 Pa) in order to produce a circular depression (diameter ca. 5 mm) into which the test solution was later deposited. The sputtering times for the formation of the circular depression were 60 s for the graphite cathode and 120 s for the metal cathodes. Although the atomizer was in the six-jet configuration (as supplied by the manufacturer and used as such in this study, except as noted) the effect of the sputtering action was to produce one circular depression containing six cavities made by the six individual jets.

The cathode was then detached from the atomizer and laid flat with the prepared surface facing up. A 1 μ L volume of the test solution was then deposited in the centre of the circular depression with a Hamilton microsyringe, fitted with a Chaney Model 7105 NCH adaptor, Part No. H88004 (Chromatographic Specialties). The test solution was then air-dried, the cathode was then re-clamped to the atomizer and the following gas flushing sequence was used. The atomizer pressure was maintained at 10 Torr of argon for 10 s, the atomizer was evacuated to 300 mTorr, then repressurized to the pre-selected operating pressure, which was optimized individually for each element and matrix combination. When the atomizer had reached the operating pressure, the glow discharge was initiated. Positive pressure was maintained between runs to prevent contamination of the atomizer. The argon gas flow was regulated with a 0-1 SLPM mass flow controller (supplied with the Atomsource). The Perkin-Elmer atomic absorption spectrophotometer and the Nicolet digital oscilloscope were triggered manually just prior to the initiation of the discharge. The discharge current was optimized and the

corresponding voltage was monitored using the digital oscilloscope, and the discharge current and voltage for each element and matrix combination were noted.

Experimental Conditions

Tables 1 and 2 show the experimental conditions used for the steady-state and transient modes of atomization, respectively. The experimental conditions were optimized for each element individually for determination by the particular mode of atomization. The optimum experimental conditions were taken as those giving the greatest absorbance with an acceptable noise level.

RESULTS AND DISCUSSION

For all the studies presented in this thesis the Atomsources atomizer was used without any modification except for an initial study to examine the effect of varying number and geometry of the gas jets in the accelerator. The normal Atomsources accelerator has six gas jets of 0.016" width. These gas jets are symmetrically arranged about the cathode surface as shown in Figure 8 and impact the cathode surface at an angle of 58° from normal, which is the presumed angle of incidence for the argon ions bombarding the cathode surface. The following modified accelerator gas jet arrangements were examined: six, eight and twelve gas jets of 0.005" width; twelve gas jets of 0.016" width; six gas jets of 0.016" width with the gas jets each offset from the centre of the cathode surface by 30° instead of the gas jets all intersecting at the centre of the cathode surface as for all the other accelerators; and six gas jets of 0.016" width intersecting at the centre of the cathode surface but with the angle of incidence of the

Table 1 - Experimental conditions for steady-state atomization of solid Standard Reference Materials (SRMs). The SRMs themselves were also used as the cathodes.

Element	Concentration in SRM %	Wavelength nm	Hollow- cathode lamp current mA	Ar gas pressure Torr	Instrumental setting of discharge current mA	Measured voltage V‡
Co*	0.15	240.7	8	8	150	567±2
Cu†	0.0058	324.8	6	15	150	466±13
Mn*	0.25	279.5	10	8	100	569±11
Mo†	0.0050	313.3	7	8	150	684±10
Ni†	0.041	232.0	8	10	170	530±11
V*	0.10	318.4	20	15	200	624±26

*NBS SRM 1264a, Low-Alloy Steel.

†NBS SRM 1265a, Electrolytic Iron.

‡The values shown after the ± represent one standard deviation of four replicate determinations made in a single run.

Table 2 - Experimental conditions for transient atomization of solution residues. Aqueous solutions of pure salts of the elements prepared as described under Test Solutions and Reagents were used.

Element	Wavelength nm	Cathode	Hollow- cathode lamp current mA	Ar gas pressure Torr	Instrumental setting of discharge current mA	Measured voltage V*
Al	309.3	Copper	10	15	200	481 ± 17
Cd	228.9	Graphite	4	15	150	556 ± 4
Co	240.7	Copper	10	20	270	715 ± 38
Cu	324.8	Tantalum	15	15	200	494 ± 30
Fe	248.3	Copper	10	20	250	489 ± 7
Mn	279.5	Copper	8	10	250	866 ± 45
Mo	313.3	Copper	10	8	200	1004 ± 14
Ni	232.0	Copper	10	10	215	758 ± 32
V	318.4	Copper	8	20	200	503 ± 3

*The values shown after $\pm$ represent the uncertainty, in volts, of a single measurement of the voltage.

bombarding argon ions changed to 61° instead of the usual angle of 58° from the normal (note that this last arrangement required the use of a modified arrester as well). The best gas jet arrangement was found to be that supplied with the Atomsource by Analyte Corp., namely six gas jets of 0.016" width intersecting at the centre of the cathode surface with an angle of incidence 58° from the normal. The accelerator and arrester arrangement was therefore used as supplied with the Atomsource in all other experiments.

Figure 9 shows absorption profiles for Mo atomized from the National Bureau of Standards (NBS) Standard Reference Material (SRM) 1264a, Low-Alloy Steel. The figure was obtained by the steady-state mode of atomization of the solid SRM's. It can be readily seen from Figure 9a that the absorbance increased slowly and it took a few seconds to reach the steady-state value, whereas at the end of the steady-state signal the absorbance decreased rapidly.

Table 3 shows the rate constants for the steady-state atomization of solid SRMs 1264a, Low-Alloy Steel, and 1265a, Electrolytic Iron. For the steady-state atomization of the above solid SRMs, the rate constant k_1 was obtained as follows:

$$\ln \left(\frac{m_o - m_t}{m_o} \right) = -k_1 t \quad (10)$$

where m_o = the initial mass of the SRM and m_t = the mass of the SRM at time t . The mass loss of the SRM, $(m_o - m_t)$ was multiplied by the percentage composition of the SRM.

It should be noted that a zero-order rate constant for the process, normalized to

Figure 9 - Absorption profile of Mo obtained using the steady-state mode of atomization of Mo from a solid sample of NBS SRM 1264a Low-Alloy Steel, containing 0.49% Mo; from an unspattered surface. (a) unspattered surface; and (b) after the surface in (a) had been sputter-opened.

Table 3 - Rate constants for steady-state atomization of solid Standard Reference Materials (SRMs). The values shown after $\pm$ represent one standard deviation of four replicate determinations made in a single run.

Element	Element con- centra- tion mg	Rate Constant			N/M ratio
		Zero-order k_1 g/s	First-order k_1 s ⁻¹ (=M)	k_2 s ⁻¹ (=N)	
Co*	110±80	$(1.1±0.8) \times 10^{-7}$	$(2.6±0.6) \times 10^{-6}$	39±1	1.5×10^7
Cu†	4±2	$(4±2) \times 10^{-9}$	$(3±1) \times 10^{-6}$	26±9	8.7×10^6
Mn*	180±80	$(1.7±0.8) \times 10^{-7}$	$(4±2) \times 10^{-6}$	37±3	9.3×10^6
Mo†	1.1±0.4	$(1.1±0.2) \times 10^{-9}$	$(1.1±0.4) \times 10^{-6}$	36±5	3.3×10^7
Ni†	24±2	$(2.3±0.2) \times 10^{-8}$	$(3.1±0.3) \times 10^{-6}$	33±8	1.1×10^7
V*	110±30	$(1.1±0.1) \times 10^{-7}$	$(4.7±0.2) \times 10^{-6}$	24±4	5.1×10^6

*NBS SRM 1264a, Low-Alloy Steel.

†NBS SRM 1265a, Electrolytic Iron.

the mass of the SRM, gave the same value of k_1 ; in other words, zero-order and first-order processes are indistinguishable for low conversions. The rate constant for atom loss, k_2 , was determined experimentally using Equation 7 and the values are given in Table 3. The values for k_1 and k_2 show that $k_2 \approx k_1$ and fulfil the conditions for the steady-state atomization mode (case 1).

The difference between Figure 9a and 9b was in the leading edge of the signal; Figure 9b had a faster rise than Figure 9a, the falling edges of both figures having identical features. Although the same SRM and the same experimental conditions were used for both parts of the figure, there was a significant difference between the atomization surface used to obtain them. Figure 9a was obtained with an unspattered surface (the solid SRM itself served as the cathode in both Figure 9a and 9b). Figure 9b was obtained by sputtering from the sputtered surface left after Figure 9a was obtained. The observed difference in the rate of rise of the absorbance signals between Figure 9a and 9b points to a significant feature of the sputtering of solid metals and alloys, which has also been observed by other workers, [4] viz., that the sputtering rate and the sputtering yield depend on many factors including the physical conditions of the sputtering surface of the solid sample. As explained by G. K. Wehner [4], a sputtered atom has to receive an energy which is sufficient to overcome its surface binding energy. The heat of sublimation provides a measure of the average binding energy. After stripping of the surface by cathodic sputtering, many atoms may be found at sites with lower numbers of nearest neighbours, such as at grain boundaries or dislocations, or an atom may be sitting on top of a filled plane. Such exposed atoms have a lower binding

energy and are more readily sputtered than those from filled planes.

Figures 10 - 18 show the absorption profiles of nine elements obtained by the transient mode of atomization of solution residues; each figure is for a single analyte present as an inorganic salt. These absorption profiles were obtained using the experimental conditions shown in Table 2. These figures have the following common features. The absorbance signal rises rapidly to its peak value and then decreases slowly. Figures 19 - 27 show the kinetic profiles drawn with the data taken from Figures 10 - 18. These figures were drawn as described by Chakrabarti et al. [142, 143]. Table 4 shows the values of the rate constants k_1 , k_2 and k_3 , and also show that $k_1 \gg k_2$ and especially $k_3 \gg k_2$, which fulfils the condition required to produce a transient atom concentration, $B \approx A_0$, described earlier as case 2, and justifies the use of the term transient atomization mode.

Although the consecutive, first-order reactions postulated in the Theory do not show the rate constant k_3 , the kinetic profiles (Figures 19 - 27) show that at earlier times the straight- line plot (the slope of which is equal to $-k_1$), after passing through a transition period, becomes at later times another straight line plot of much steeper slope, which will be called $-k_3$. In other words, the first-order rate constant for atom introduction into the analysis volume appears to have a lower value (k_1) at earlier times, and a much higher value (k_3) at later times. The values of k_1 and k_3 have been obtained as a difference between the extrapolated line of B and the experimental values of B , and the difference was small, especially at later times which gave the values of k_3 . It was therefore necessary to estimate the uncertainties in k_1 and k_3 values and their possible

Figure 10 - Absorption profile for 1000 ng of Al (taken as an aqueous solution of the chloride) obtained using the transient atomization mode. For other details see Table 2.

Figure 11 - Absorption profile for 25 ng of Cd (taken as an aqueous solution of the nitrate) obtained using the transient atomization mode. For other details see Table 2.

Figure 12 - Absorption profile for 50 ng of Co (taken as an aqueous solution of the nitrate) obtained using the transient atomization mode. For other details see Table 2.

Figure 13 - Absorption profile for 250 ng of Cu (taken as an aqueous solution of the nitrate) obtained using the transient atomization mode. For other details see Table 2.

Figure 14 - Absorption profile for 50 ng of Fe (taken as an aqueous solution of the nitrate) obtained using the transient atomization mode. For other details see Table 2.

Figure 15 - Absorption profile for 50 ng of Mn (taken as an aqueous solution of the nitrate) obtained using the transient atomization mode. For other details see Table 2.

Figure 16 - Absorption profile for 500 ng of Mo (taken as an aqueous solution of ammonium molybdate) obtained using the transient atomization mode. For other details see Table 2.

Figure 17 - Absorption profile for 100 ng of Ni (taken as an aqueous solution of the nitrate) obtained using the transient atomization mode. For other details see Table 2.

Figure 18 - Absorption profile for 200 ng of V (taken as an aqueous solution of ammonium vanadate) obtained using the transient atomization mode. For other details see Table 2.

Figure 19 - Kinetic plots for Al drawn using the data from Fig. 10.

Figure 20 - Kinetic plots for Cd drawn using the data from Fig. 4.

Figure 21 - Kinetic plots for Co drawn using the data from Fig. 12.

Figure 22 - Kinetic plots for Cu drawn using the data from Fig. 13.

Figure 23 - Kinetic plots for Fe drawn using the data from Fig. 14.

Figure 24 - Kinetic plots for Mn drawn using the data from Fig. 15.

Figure 25 - Kinetic plots for Mo drawn using the data from Fig. 16.

Figure 26 - Kinetic plots for Ni drawn using the data from Fig. 17.

Figure 27 - Kinetic plots for V drawn using the data from Fig. 18.

Table 4 - Rate constants for transient atomization of solution residues. Aqueous solutions of pure salts of the elements prepared as described under Test Solutions and Reagents were used. The rate constants k_1 , k_2 and k_3 were evaluated using data from Figs. 10 - 18.

Element	Element atomized ng	k_1 s^{-1} *	k_3 s^{-1} *	k_2 s^{-1} *	k_3/k_2 ratio
Al	1000	26.4 ± 0.5	110 ± 10	0.7 ± 0.1	157
Cd	25	74 ± 4	370 ± 50	29 ± 1	13
Co	50	21 ± 1	190 ± 20	9.0 ± 0.6	21
Cu	250	30 ± 1	136 ± 9	6.3 ± 0.1	22
Fe	50	27 ± 3	91 ± 3	4.2 ± 0.2	22
Mn	50	69 ± 8	130 ± 6	5.2 ± 0.2	25
Mo	500	68 ± 3	118 ± 3	5.9 ± 0.4	20
Ni	100	40 ± 5	420 ± 20	2.06 ± 0.08	204
V	200	13.1 ± 0.7	74 ± 4	2.8 ± 0.2	26

*The values shown after $\pm$ represent one standard deviation obtained by least squares analysis.

effect on the kinetic profiles (Figures 19 - 27), especially the intersecting straight lines with slopes = $-k_1$ and $-k_3$. The experimental procedure used to obtain the rate constants made the value of k_2 (and that of the extrapolated B line) by far the least uncertain of the three rate constants. In calculating the above mentioned difference, it was therefore assumed that all the uncertainty resided in the experimental values of B. By assigning uncertainties of $\pm 1\sigma$ (σ is the standard deviation) in the experimental values of B, the k_1 and k_3 values were re-calculated and found to be within $\pm 25\%$ of the values plotted in Figures 19 - 27. The re-calculated values still gave two intersecting straight lines with $k_1 < k_3$. Hence, it was concluded that the experimental results were consistent with the mechanism that atom entry into the analysis volume proceeds by two processes - a slower process at earlier times and a faster process at later times.

Although subsequent results (presented in Chapter two) show otherwise, these experimental results were interpreted to suggest that two sets of consecutive, first-order reactions may occur at the cathode surface from which the analyte is ejected by cathodic sputtering as follows:

where A and A' are the same chemical species but have different atomization energies. In the early stages of the reaction the atoms were removed at a rate controlled by k_1 , but in later stages of the reaction a faster rate was observed, as indicated by the rate constant

k_3 . It was concluded that during the process of atomization, the sample undergoes a significant change in the properties of its atomization surface (the unopened surface initially present being replaced by a sputter-opened surface) that determines the rate at which atoms are released. One possibility for this difference between the bonding of A with its neighbours in the crystal lattice (when the solution residue forms a three-dimensional structure on the substrate), and the bonding of A' with the substrate when successive stripping of the surface layers of the crystal lattice finally leaves a two-dimensional structure (monolayer or submonolayer) of the analyte on the substrate. The above hypothesis is made by analogy with electrothermal atomization of a sample from a pulse-heated graphite furnace, in which, as vaporization of the sample proceeds, three-dimensional structures of analytes or their decomposition products eventually give way to two-dimensional structures (monolayers, submonolayers or "islands") of analytes, which ultimately become isolated adatoms. [145, 146] The bonding of the analyte atom (A) with its greater number of neighbours in the three-dimensional structures is stronger than that between the analyte atom (A') with its smaller number of neighbours in the two-dimensional structures. If the above mechanism correctly represents the actual mechanism, then one should expect two different rates of atom entry into the analysis volume - the slower one at earlier times and the faster one at later times.

An analysis of Figures 19 - 27 shows that k_1 and k_3 were obtained by using data points from the leading edge of the absorption profiles (Figures 10 - 18), k_1 by using the lower part (the earlier times) and k_3 by using the higher part (the later times). As k_3 (and k_2) determine the peak-height absorbance, the ratio k_3/k_2 (not k_1/k_2) should be used

for predicting the peak-height absorbance by the transient atomization mode. Table 4 gives the k_1 , k_2 and k_3 values and the k_3/k_2 ratios, which fulfil the criterion $k_3 \gg k_2$ for enhancement of the sensitivity of the transient atomization mode. Generally, metal cathodes give better sensitivity and limits of detection than graphite cathodes.

Assuming that the number of atoms produced by cathodic sputtering in either mode of atomization is proportional to the mass of the sample lost during the initial period of cathodic sputtering, it would be informative to compare the rates of atomization observed for each element for both the steady-state and transient atomization modes. In each instance, the initial rates should be compared. This is particularly important for the solid SRM sample used for the steady-state atomization mode, where the rate of atomization increased considerably once the sputtering action had stripped away the outer surface. The study of initial rates of the solid SRM by the steady-state atomization mode necessarily produced such a small mass loss that the rate data for the initial period fitted both zero-order and first-order kinetics. Therefore, the rate of mass loss of the element is given simply by the mass loss of the SRM divided by the time period over which the loss occurred. Figure 28 shows that the rate of mass loss (Table 3, column 4) of a particular element in the steady-state mode of atomization depends (correlation coefficient = 0.98) on the concentration of the element (expressed as a percentage) present in the SRM because the whole target area receives bombardment of Ar^+ ions. To compare the rate of loss in the steady-state mode with the rate of mass loss in the transient mode, the same initial mass of the element should be considered in both instances. The rate of mass loss for each element in the steady-state atomization mode was therefore calculated

Figure 28 - Correlation of the rate of mass loss of an element in the steady-state atomization mode with the concentration (expressed as a percentage) of the element present in the SRM. Data from Tables 1 and 3 were used.

on the basis of the mass used for the transient atomization mode (as shown in Table 4) using the zero-order rate constants. This normalized rate is given in Table 5, column 2.

The mass loss in the transient mode was found to proceed by a first-order rate, and a first-order rate constant k_1 was obtained (Table 4). The initial rate of mass loss was obtained from the sample mass and the rate constant k_1 (Table 4) and is given in the last column of Table 5, which shows that the initial rate of mass loss in the transient mode of atomization is much greater than the initial rate of mass loss in the steady-state mode of atomization. This should result in an enhancement of the sensitivity and of the limit of detection in the transient mode of atomization over those in the steady-state mode of atomization.

Tables 6 and 7 present the sensitivities and the limits of detection of the two modes of atomization. In presenting Table 6 showing the sensitivity in terms of characteristic mass for the transient atomization mode, and in terms of characteristic concentration for the steady-state atomization mode, the accepted convention has been followed of reporting the sensitivity in terms of characteristic mass for the transient atomization, as in atomic absorption spectrometry using a graphite furnace, and in terms of concentration for the steady-state atomization, as in atomic absorption spectrometry using a flame atomizer-burner. In Table 7, the real improvement in the limit of detection for transient atomization would be greater than what was shown as the limit of detection for the steady-state atomization (reported by Analyte Corp.), which was based on twice the standard deviation of the background signal, whereas that of the transient atomization

Table 5 - Comparison of rates of mass loss by elements in the steady-state and the transient modes of atomization.

Element	X steady-state atomization, normalized initial rate of mass loss g/s	Y transient atomization,* initial rate of mass loss of solution residues g/s	Y/X ratio
Co	3.9×10^{-8}	1.1×10^{-6}	27
Cu	1.2×10^{-7}	7.5×10^{-6}	63
Mn	3.5×10^{-7}	3.5×10^{-6}	10
Mo	2.5×10^{-7}	3.4×10^{-5}	136
Ni	4.8×10^{-8}	4.0×10^{-6}	83
V	1.0×10^{-7}	1.0×10^{-6}	26

*These results were obtained using the data in Table 4.

Table 6 - Characteristic masses and characteristic concentrations.

Element	Characteristic mass for transient atomization* pg	C h a r a c t e r i s t i c concentration for steady- state atomization† ppm
Al	1140	-
Cd	31	-
Co	525	13.6
Cu	183	6.3
Fe	524	-
Mn	724	30
Mo	63	2.2
Ni	2100	14.2
V	723	84

*Mass/0.0044 absorbance. Aqueous solutions of pure salts of elements prepared as described under Test Solutions and Reagents and the experimental conditions shown in Table 2 were used.

†Concentration/0.0044 absorbance. Experimental conditions as shown in Table 1 were used with NBS SRMs 1264a and 1265a. The SRMs themselves were also used as the cathodes.

Table 7 - Limits of detection.

Element	Transient atomization* pg	Steady-state atomization† ppm
Al	1340	-
Cd	40	-
Co	716	-
Cu	740	9
Fe	1670	12
Mn	650	15
Mo	164	14
Ni	3700	21
V	723	17

*Mass giving a signal = 3σ /slope of the analytical calibration curve (σ = 1 standard deviation). Aqueous solutions of pure salts of elements prepared as described under Test Solutions and Reagents and the experimental conditions shown in Table 2 were used.

†Concentration giving a signal = 2σ (reported by Analyte Corp.).

was calculated by using the more rigorous criterion of three times the standard deviation divided by the slope of the analytical calibration curve.

Figures 29 and 30 show the peak-height absorbance of Co vs. discharge current and power, respectively. The peak-height absorbance increased linearly with increasing discharge current and power. As the Atomsources uses an abnormal glow discharge in which the discharge voltage increases rapidly with discharge current, the discharge power is a more meaningful experimental parameter than either the discharge voltage or current. These figures indicate that the peak-height absorbance can be increased by using higher discharge power.

Figures 31 and 32 show the analytical calibration curves for Co obtained using the transient atomization mode. The analytical calibration curves were linear over the range 0-200 ng of Co but was non-linear (but still usable) when higher masses (up to 1000 ng) of Co were atomized. The peak-area absorbance was not used in this study as the peak areas provided lower sensitivity than the peak heights.

CONCLUSIONS

The transient mode of atomization offers characteristic masses and limits of detection which are generally in the sub-nanogram range, and should be amenable to improvement by applying greater discharge power. The kinetics of atom entry into and loss from the analysis volume are consistent with a mechanism of consecutive, first-order reactions, indicating that the analyte atom binding energy changes with time as the surface is sputter-opened.

Figure 29 - Peak-height absorbance for 250 ng of Co (taken as an aqueous solution of the nitrate) as a function of the discharge current. Graphite cathode, Ar pressure 15 Torr, hollow-cathode lamp current 10 mA.

Figure 30 - Peak-height absorbance for 250 ng of Co (taken as an aqueous solution of the nitrate) as a function of the applied discharge power. Graphite cathode, Ar pressure 15 Torr, hollow-cathode lamp current 10 mA.

Figure 31 - Analytical calibration curve for Co (taken as an aqueous solution of the nitrate). Ar pressure 15 Torr, discharge current 200 mA, hollow-cathode lamp current 15 mA.

Figure 32 - Analytical calibration curve for Co (taken as an aqueous solution of the nitrate). Ar pressure 15 Torr, discharge current 200 mA, hollow-cathode lamp current 15 mA.

CHAPTER TWO

KINETIC MODELLING OF TRANSIENT ATOMIZATION

INTRODUCTION

This chapter presents the results of further investigation into the kinetics of atom entry into and loss from the analysis volume of the Atomsources atomizer for atomic absorption spectrometry using the transient mode of atomization. If the kinetic model is valid then it should be possible to calculate the absorbance of the analyte atom as a function of time using the calculated rate constants. Comparison of the calculated and experimental absorbance as a function of time will enable the validity of the kinetic model and the calculated rate constants to be tested.

THEORY

As previously, the kinetic analysis is confined to the introduction of atoms into and their loss from the analysis volume of the atomizer, as defined by the geometry of the beam of radiation from the hollow-cathode lamp. It is also assumed that consecutive, first-order reactions which occur during the introduction of atoms into and their loss from the analysis volume can be described by the following model:

where A represents the analyte atoms entering the analysis volume, B the analyte atoms

within the analysis volume, C the analyte atoms that have been lost from the analysis volume; k_1 and k_2 are first-order rate constants for the introduction of atoms into and their loss from the analysis volume, respectively.

When no B is present initially, this mechanism yields the following equation for the instantaneous number of atoms within the analysis volume at time t

$$B_t = \frac{k_1}{k_1 - k_2} A_o (e^{-k_2 t} - e^{-k_1 t}) \quad (8)$$

where the subscripts t and o represent the number of the analyte atoms at any time, and the initial number of atoms, respectively. From Equation 8 it can be seen that B_t , which is initially zero, increases to a maximum and then decays exponentially at a rate controlled by the smaller of the two rate constants. Absorbance by analyte atoms is used as a measure of B_t , recognizing that the absorbance is proportional to the analyte atom density, and the latter is proportional to B_t .

When one of the two rate constants is greater than the other, for example $k_1 > k_2$, Equation 8 simplifies as follows

$$\ln B'_t = (-k_2 t) + \ln \left(A_o \frac{k_1}{k_1 - k_2} \right) \quad (12)$$

where B'_t is the absorbance due to B in the falling edge of the absorbance profile. Therefore, a plot of $\ln B'_t$ vs. t at longer times will give the value of k_2 . The difference between Equations 8 and 12 gives

$$\ln \Delta B = (-k_1 t) + \ln \left(A_o \frac{k_1}{k_1 - k_2} \right) \quad (13)$$

where $\Delta B = B'_t - B_t$.

A plot of the natural logarithm of the difference between the measured absorbance in the leading edge of the profile and the extrapolated values from Equation 12 will give the value for k_1 .

A similar treatment for the case where $k_2 > k_1$ gives

$$\ln B'_t = (-k_1 t) + \ln \left(A_o \frac{k_1}{k_2 - k_1} \right) \quad (14)$$

and

$$\ln \Delta B = (-k_2 t) + \ln \left(A_o \frac{k_1}{k_2 - k_1} \right) \quad (15)$$

From the above, it can be seen that a plot of $\ln B'_t$ vs. t always gives the smaller rate constant and that a plot of $\ln \Delta B$ vs. t always gives the larger rate constant. It is impossible to decide from the shape of the absorbance profile which of the rate constants, k_1 and k_2 , is larger. Therefore, the rate constant obtained from the leading edge of the signal (the larger rate constant) will be denoted by k_a and the rate constant obtained from the falling edge of the signal (the smaller rate constant) will be denoted by k_b . It is important to note that the intercept when $\ln \Delta B$ is plotted vs. t for Equation 12 is

approximately $\ln A_0$, whereas for Equation 14 it is approximately $\ln\left(A_0 \frac{k_1}{k_2}\right)$, which is

less than A_0 since $k_2 > k_1$. Equation 12 describes a transient mode of atomization, whereas Equation 14 describes a steady-state mode of atomization. However, this difference will not allow the two cases to be distinguished since the absolute relationship between B_t and the absorbance due to B_t is not known.

The validity of the kinetic model will be tested by examining experimental atomic absorption profiles in order to obtain the rate constants k_a and k_b . These rate constants are then used to calculate the absorbance of analyte atoms in the analysis volume as a function of time using Equation 8 to produce a theoretical absorbance profile. Comparison of the theoretical with the experimental absorbance profile will allow the validity of the kinetic model to be tested, thereby providing insight into the sequence of reactions involved in atom formation and loss from the Atomsources.

EXPERIMENTAL

Apparatus

The experiments were performed as described in Chapter one using an Atomsources manufactured by Analyte Corp., Grants Pass, OR, U.S.A. and supplied with its power supply and usual accessories. Software version 3.12 was used for all elements except for Ag, Au, Fe, Pb and V, for which software version 3.14 was used. The least-squares and kinetic calculations were done using a Honeywell CP-6 mainframe computer. Hard copies of the results of these calculations were obtained using a Laser Printer,

model IP/III (Imagen Corp., Santa Clara, CA, U.S.A.). All programs were written in Fortran 77. The following hollow-cathode lamps were used: Ag, Co, Cu, Fe, Mo, Mn and V, manufactured by the Perkin-Elmer Corp., Au and Cd by Cathodeon; Al by Instrumentation Laboratory, and Ni and Pb by Westinghouse. The lamps were operated using lamp currents which were below the maximum currents prescribed by the manufacturers.

Test solutions and reagents

Chemically pure metals or their salts were used to prepare standard solutions. Stock solutions containing 1000 $\mu\text{g/mL}$ were prepared as follows. For Al, Cd, Co, Cu, Fe, Mn, Mo, Ni and V the stock solutions were prepared as described under Test Solutions and Reagents in Chapter one. For Au, the stock solution was supplied by Harleco (Philadelphia, PA, U.S.A.) and was prepared by dissolving the metal in dilute aqua regia. For Pb, $\text{Pb}(\text{NO}_3)_2$ was dissolved in 2% (v/v) nitric acid (ULTREX) and the solution diluted with ultrapure water. For Ag, the metal was dissolved in 50% (v/v) nitric acid (ULTREX) and the solution diluted with ultrapure water. All stock solutions were made to contain 1% (v/v) of the acids or the ammonium hydroxide used to dissolve the metals or their salts. The ULTREX brand acids were manufactured by Baker Chemical Co. Ultrapure water of resistivity 18.3 megohm-cm was obtained direct from a Milli-Q 2 Water Purification System (Millipore Corp.). All test solutions were prepared by serial dilution of the above stock solutions immediately prior to determination.

Atomizer Gas

Argon (99.997% pure) was used as the atomizer gas.

Procedure

The procedure followed is given in Chapter one.

Experimental conditions

The experimental conditions are given in Table 8. The discharge parameters are given in Table 9. It should be noted that these experimental conditions are not necessarily those providing the greatest sensitivity. For this study, larger masses of analyte and higher hollow-cathode lamp currents were often used since these provided relatively low-noise signals. The difficulty of obtaining reliable values for the rate constants increased with increasing signal noise, making it desirable to work with signals that were as noise-free as possible.

RESULTS AND DISCUSSION

Figures 33 - 37 present experimental atomic absorption profiles for Ag, Au, Fe, Pb and V; the experimental absorbance profiles for Al, Cd, Co and Cu are given in Figures 10 - 13, respectively, and the experimental absorbance profiles for Mn, Mo and Ni are given in Figures 15 - 17, respectively. The corresponding kinetic plots of $\ln$ absorbance ($\ln B$) vs. time and for $\ln \Delta B$ vs. time for the experimental absorbance profiles are shown in Figures 38 - 49. Table 10 shows the values of the rate constants k_a and k_b that were obtained for all the elements studied. Since the values obtained for the rate constant k_a depends on an extrapolation of the line with slope k_b , the k_b values are more reliable than the k_a values. Assuming that all the uncertainty in k_a was due to

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Table 8 - Experimental conditions for the atomic absorption determination of solution residues* by the transient mode of atomization.

Element	Wavelength nm	Cathode	Sample sputtered ng	Hollow-cathode lamp current mA
Ag	328.1	Copper	50	13
Al	309.3	Copper	1000	10
Au	242.8	Copper	50	12
Cd	228.9	Graphite	25	4
Co	240.7	Copper	50	10
Cu	324.8	Graphite	250	15
Fe	248.3	Copper	50	10
Mn	279.5	Copper	50	8
Mo	313.3	Copper	500	10
Ni	232.0	Copper	100	10
Pb	283.4	Copper	150	6
V	318.4	Copper	200	8

*Used aqueous solutions of pure salts of the elements.

Table 9 - Discharge parameters for the glow discharge atomization of solution residues* by the transient mode of atomization.

Element	Ar gas pressure Torr	Instrumental setting of discharge current mA	Corresponding Voltage V
Ag	6	150	903 ± 5
Al	15	200	481 ± 17
Au	6	150	923 ± 21
Cd	15	150	556 ± 4
Co	20	270	715 ± 38
Cu	15	200	494 ± 30
Fe	20	250	489 ± 7
Mn	10	250	866 ± 45
Mo	8	200	1004 ± 14
Ni	10	215	758 ± 32
Pb	6	200	573 ± 31
V	8	200	503 ± 3

*Used aqueous solutions of pure salts of the elements.

The values shown after ± represent the arithmetic mean of the peak - to - peak noise of the measurement.

Figure 33 - Absorption profile for 50 ng of Ag taken as an aqueous solution of the nitrate. For other details see Tables 8 and 9.

Figure 34 - Absorption profile for 50 ng of Au taken as an aqueous solution of the chloride. For other details see Tables 8 and 9.

Figure 35 - Absorption profile for 50 ng of Fe taken as an aqueous solution of the nitrate. For other details see Tables 8 and 9.

Figure 36 - Absorption profile for 150 ng of Pb taken as an aqueous solution of the nitrate. For other details see Tables 8 and 9.

Figure 37 - Absorption profile for 200 ng of V taken as an aqueous solution of ammonium vanadate. For other details see Tables 8 and 9.

Figure 38 - Kinetic plots for Ag drawn using the data from Fig. 33.

Figure 39 - Kinetic plots for Al drawn using the data from Fig. 10.

Figure 40 - Kinetic plots for Au drawn using the data from Fig. 34.

Figure 41 - Kinetic plots for Cd drawn using the data from Fig. 11.

Figure 42 - Kinetic plots for Co drawn using the data from Fig. 12.

Figure 43 - Kinetic plots for Cu drawn using the data from Fig. 13.

Figure 44 - Kinetic plots for Fe drawn using the data from Fig. 35.

Figure 45 - Kinetic plots for Mn drawn using the data from Fig. 15.

Figure 46 - Kinetic plots for Mo drawn using the data from Fig. 16.

Figure 47 - Kinetic plots for Ni drawn using the data from Fig. 17.

Figure 48 - Kinetic plots for Pb drawn using the data from Fig. 36.

Figure 49 - Kinetic plots for V drawn using the data from Fig. 37.

Table 10 - Rate constants for transient mode of atomization of solution residues*.

Element	Wavelength nm	k_a s^{-1}	k_b s^{-1}	k_a/k_b ratio
Ag	328.1	255 ± 20	5.4 ± 0.3	47
Al	309.3	24 ± 1	0.7 ± 0.1	34
Au	242.8	100 ± 10	21.7 ± 0.4	5
Cd	228.9	127 ± 13	29 ± 1	4
Co	240.7	235 ± 24	9.0 ± 0.6	26
Cu	324.8	132 ± 10	6.3 ± 0.1	21
Fe	248.3	44 ± 8	4.6 ± 0.5	10
Mn	279.5	110 ± 5	5.2 ± 0.2	21
Mo	313.3	106 ± 11	5.9 ± 0.4	18
Ni	232.0	51.8 ± 0.4	2.06 ± 0.08	25
Pb	283.4	393 ± 39	40.2 ± 0.3	10
V	318.4	28.6 ± 0.6	3.2 ± 0.3	9

*Used aqueous solutions of pure salts.

The values after $\pm$ represent one standard deviation obtained by least-squares analysis excepting k_a for Au, Cd, Co, Mo and Pb where it represents an uncertainty corresponding to 10% relative standard deviation.

the uncertainty in k_b , k_a was recalculated for the cases $k_b = k_b \pm \sigma$, where σ represents one standard deviation of the slope and intercept of the line having slope k_b , as calculated by least-squares analysis. Al was chosen for this calculation since Al had the largest relative uncertainty of k_b of all the elements studied. In both cases, a straight line for k_a was still obtained, the slope of which was within 21% of the previously calculated value of k_a ; therefore, the individual k_a values should be accurate to within 21%. Besides having the largest relative uncertainty in k_b , Al also has a k_b which is much lower than that of all the other elements. Also, the k_b values for Au, Cd and Pb are much higher than those for all the other elements. Except as noted, values of k_b are similar to the k_2 values found previously whereas there is now no rate constant which corresponds to the previously reported k_3 [147]. The reason for these changes are that with the new data obtained and the realization of the importance of the time constant of the spectrophotometer for accurately interpreting the kinetic data (explained later), understanding of the mechanism of atom formation and loss in the Atomsources atomizer has greatly improved. Whereas it was previously thought that atom formation and loss in the Atomsources occurred via two sets of consecutive, first-order reactions (Equations 1 and 11), it is now thought that atom formation and loss in the Atomsources proceeds by a single set of consecutive, first-order reactions, shown by Equation 1.

Figures 50 - 61 compare the theoretical absorbance profiles (calculated from Equation 8 using the rate constants given in Table 10) with the experimental absorbance profiles for all the elements studied. If $k_1 > k_2$, the theoretical absorbance profile for Ag (Figure 50) is given by the rate constants $k_1 = 255 \text{ s}^{-1}$ and $k_2 = 5.4 \text{ s}^{-1}$, with $A_0 =$

Figure 50 - Comparison of the theoretical and the experimental absorbance profile for A_g .

Figure 51 - Comparison of the theoretical and the experimental absorbance profile for Al.

Figure 52 - Comparison of the theoretical and the experimental absorbance profile for Au.

Figure 53 - Comparison of the theoretical and the experimental absorbance profile for Cd.

Figure 54 - Comparison of the theoretical and the experimental absorbance profile for Co.

Figure 55 - Comparison of the theoretical and the experimental absorbance profile for Cu.

Figure 56 - Comparison of the theoretical and the experimental absorbance profile for Fe.

Figure 57 - Comparison of the theoretical and the experimental absorbance profile for Mn.

Figure 58 - Comparison of the theoretical and the experimental absorbance profile for Mo.

Figure 59 - Comparison of the theoretical and the experimental absorbance profile for Ni.

Figure 60 - Comparison of the theoretical and the experimental absorbance profile for Pb.

Figure 61 - Comparison of the theoretical and the experimental absorbance profile for V.

0.5007. If $k_2 > k_1$, the same theoretical absorbance profile can be obtained with $k_1 = 5.4 \text{ s}^{-1}$ and $k_2 = 255 \text{ s}^{-1}$, but now the value of $A_0 = 23.6$. Since when these studies were done there was as yet no independent information which would allow the identification of k_1 and k_2 unambiguously (this has been presented in Chapter three), the rate constant for the leading edge of the signal is simply referred to as k_a and the rate constant for the falling edge of the signal is referred to as k_b , without identifying which of these corresponds to k_1 and which to k_2 .

For the experimental absorbance profiles, the last point on the baseline was taken as the time at which the absorbance profile began. This is not necessarily correct, however. The spectrophotometer is modulated at 60 Hz and therefore takes a reading every 17 ms (to be exact, every $16 \frac{2}{3}$ ms). The absorbance profile could actually begin anytime within the first 17 ms and it would not be immediately observed with the present spectrophotometer, so that the actual start of the absorbance profile could not be located more accurately than within the first 17 ms. Therefore t_0 (the time at which $t=0$ for the theoretical absorbance profile) was made a variable. The effect of taking a larger value of t_0 was to decrease A_0 (and hence, the maximum absorbance) and to shift the leading edge and the peak of the theoretical absorbance profile to longer times; the falling edge of the theoretical absorbance profile was practically unchanged, especially at longer times. A_0 was calculated from the least-squares equation for the k_b line at the selected time, and the value of A_0 was then used with the rate constants obtained previously to generate theoretical absorbance profiles using Equation 8. Although this procedure is not very complicated, it is more complicated than was previously found necessary when

determining rate constants for absorbance profiles generated by a constant-temperature graphite furnace [141]. The reason for this is that the ratio of k_a/k_b is at least one order of magnitude greater for the transient mode of atomization for the Atomsources atomizer than the ratio of k_1/k_2 for graphite furnace atomic absorption spectrometry (GFAAS) [142, 143], whereas values of k_b for the transient mode of atomization for the Atomsources are generally similar to values of k_2 for GFAAS.

The larger values of k_a mean that the absorbance profiles rise much more rapidly for transient atomization by cathodic sputtering in a glow discharge than for GFAAS. This raises the question of whether the absorbance profiles obtained by the transient mode of atomization by cathodic sputtering in a glow discharge are distorted by the present spectrophotometer, which was designed to record the relatively slowly changing absorbance profiles generated by GFAAS. To check for possible signal distortions, the Atomsources was used with a fast detection system [148]. Atomic absorption profiles for Mn, generated under identical experimental conditions for the two detection systems, were compared. The time constant of the fast detection system was 4 ms. No signal distortion was observed, i.e., the profiles recorded by the two detection systems had the same shape. Figures 50 - 61 (especially Figure 60) suggest, however, that there may be a reduction in the measured peak-height absorbance due to the inability of the spectrophotometer to measure rapidly enough to determine accurately the exact peak of the absorption profile. When analyzing solution residues by the transient mode of atomization it would, therefore, be advantageous to work with a faster detection system than is normally available in commercial atomic absorption spectrophotometers.

From Figures 38 - 49 it can be seen that values of the rate constants can be found such that there is good agreement between the experimental and the theoretical absorbance profile, despite the fact that the rate constants cannot as yet be unambiguously distinguished. This indicates that the rate constants and the kinetic model used to obtain the rate constants are valid, and that the entry of atoms into and their loss from the analysis volume is adequately described by Equations 1 and 8. Although the rate of formation of atoms by cathodic sputtering in a glow discharge at the cathode surface cannot be measured, the rate of entry of atoms into the analysis volume must depend on the rate of formation of atoms at the cathode surface. The rate of entry of atoms into the analysis volume can therefore be assumed to give some insight into the process of atom formation at the cathode surface. The results of this study are consistent with a mechanism whereby atoms are sputtered direct into the vapour phase from the solution residue on the cathode surface without significant formation of an intermediate. This is in agreement with the findings of other workers, that almost all of the sputtered particles are unexcited neutrals that have been sputtered direct into the vapour phase, mostly as atomic rather than molecular species, and excited atoms or ions constitute only a small fraction of the flux of sputtered species [16].

CONCLUSIONS

Entry of atoms into and loss of atoms from the analysis volume for solution residues atomized by the transient mode of atomization by cathodic sputtering in a glow discharge can be described by consecutive, first-order reactions. Atomization appears

to occur by direct sputtering of analyte atoms from the solution residue present on the cathode surface.

CHAPTER THREE

THE PULSED MODE OF ATOMIZATION

INTRODUCTION

Up to now analytical applications of cathodic sputtering in a glow discharge have almost wholly involved production of a steady-state atomic vapour from a bulk solid sample. Kinetic limitations result in relatively poor sensitivity and limit of detection for the steady-state mode of atomization. A method which overcomes these limitations, using rapid production of analyte atoms to produce a greater transient concentration of atoms in the analysis volume than is possible for the steady-state mode of atomization, is described in this chapter. Two new modes of atomization are presented. The transient mode of atomization uses a high-power discharge for the rapid production of analyte atoms, whereas the pulsed mode of atomization uses a discharge of much shorter duration and higher power to achieve even faster atomization than is possible with the transient mode of atomization. An important factor leading to faster production of analyte atoms is the difference in bonding between the solution residues and the solid, bulk samples as the source of atoms. The faster kinetics of atom formation for the pulsed and the transient mode of atomization result in better (sometimes, much better) sensitivity for these modes of atomization compared to the steady-state mode of atomization. Since both the pulsed and the transient modes of atomization are based on faster production of analyte atoms and differ in that in the former a short (milliseconds) duration discharge

is used, whereas in the latter a long (seconds) duration discharge is used, they are treated together as a single new analytical technique. This new analytical technique and the conventional steady-state vapour technique have been evaluated using a commercially available cathodic sputtering atomizer, the Atomsources.

These techniques have been characterized by kinetic modelling, and the superiority of the new analytical technique in sensitivity and limit of detection over the conventional technique based on the steady-state atomic vapour is shown. The sensitivity of the new analytical technique is, in some cases, similar to or greater than that of graphite furnace atomic absorption spectrometry. Factors affecting the sensitivity and areas for future improvement are discussed. The performance of the new analytical technique is also discussed in terms of the linear dynamic range of analytical calibration curves.

THEORY

Cathodic Sputtering

The Atomsources produces a Grimm-type glow discharge [11]. In previous work [147] using the Atomsources and a pyrolytic graphite cathode it was reported that for the transient atomization of Co (taken as an aqueous solution of the nitrate), the peak-height absorbance shows a linear relationship to both discharge power and discharge current. Fang and Marcus [149], using preliminary factor analysis of their experimental results, found that for oxygen-free hard copper the weight loss was directly proportional to the applied power. Both the above studies [147, 149] suggest that power is the key to

increasing the analytical sensitivity when using cathodic sputtering atomization. It was therefore decided to use the highest power which the power supplies are capable of giving to provide a stable glow discharge using the pulsed and the transient mode of atomization.

Kinetic Modelling

As previously, the kinetic analysis is confined to the introduction of atoms into and the removal of atoms from the analysis volume. If the atoms are sputtered direct from the surface of the cathode without the formation of any condensed-phase or gas-phase intermediates, and the convection/diffusion of the atoms out of the analysis volume is a first-order process [150], then atom introduction and atom loss can be represented by the following consecutive, first-order reactions:

where A represents the analyte atoms entering the analysis volume, B the analyte atoms within the analysis volume, C the analyte atoms that have been lost from the analysis volume by diffusion/convection, and k_1 and k_2 are first-order rate constants for introduction of atoms into and their subsequent loss from the analysis volume, respectively.

When there is no analyte initially present in the analysis volume, this mechanism gives the following equation for the number of analyte atoms within the analysis volume as a function of time

$$B_t = A_o \frac{k_1}{k_1 - k_2} (e^{-k_2 t} - e^{-k_1 t}) \quad (8)$$

The form of this equation requires that B_t , which is initially zero, increases to a maximum and then decays at a rate which is controlled by the smaller of the two rate constants.

When one of the rate constants is smaller than the other the tail of the absorbance profile decays exponentially at a rate controlled by the smaller of the two rate constants as follows:

$$B'_t = C A_o (e^{-k_a t}) \quad (16)$$

where B'_t is the number of absorbing atoms at later times, C is a constant dependent upon which of the two rate constants is smaller, and k_a is the smaller of the two rate constants. Therefore a plot of $\ln(B'_t)$ vs. t has a slope $= -k_a$ and an intercept $= C A_o$. The value of the intercept, and therefore also of the peak-height absorbance, depends on C , the value of which depends on which of the rate constants is larger than the other. From Equation 8, if $k_1 > k_2$, then $C = 1$, whereas if $k_2 > k_1$, then $C = k_1/k_2$ which is less than 1 since $k_2 > k_1$. The maximum sensitivity can therefore be expected when $k_1 > k_2$, i.e. when atomization is rapid, as it is for the pulsed and the transient mode of atomization, as opposed to the slow atomization which occurs when a solid, bulk sample is sputtered to give a steady-state atom population.

To get the larger of the two rate constants the difference between Equations 8 and 16 is taken,

$$B'_t - B_t = \Delta B = C A_0 (e^{-k_b t}) \quad (17)$$

where ΔB is the difference between the measured absorbance due to B and the extrapolation of Equation 8, C is as previously defined, and k_b is the larger of the two rate constants. It can be seen that a plot of $\ln(\Delta B)$ vs. t has a slope $= -k_b$ and an intercept $= C A_0$. These two kinetic plots are used to determine the magnitude of the two rate constants.

The above method (to be called the "kinetic plot" method) requires fairly lengthy data treatment and is used only to check that the plots generated are indeed linear. In practice, k_a is determined from the half-life of the signal decay (i.e. $k_a = \ln 2/t_{1/2}$). This value for k_a and the time required for the signal to reach its maximum value, $t_{\max}$, are then used to determine k_b by using the following equation;

$$t_{\max} = \frac{(\ln k_b - \ln k_a)}{(k_b - k_a)} \quad (18)$$

The values obtained in this manner can be easily checked against those obtained by using the "kinetic plot" method, and this was done frequently.

It is impossible to say from the shape of the absorbance profile which of the two rate constants, k_1 or k_2 , is larger. Other information is required to make this determination possible. The following two experiments can make this determination: 1) the rate constant for atom loss, k_2 , can be identified by cutting off the discharge power (and thus stopping the formation of analyte atoms) while there is still a measurable analyte atomic vapour in the analysis volume; 2) the rate of atom formation should increase with an increase in the applied power at a given pressure, while the rate of atom

loss should stay the same, thus allowing k_1 , the rate constant for atom formation to be identified. If the discharge power is cut off during the falling portion of a transient signal, the resulting decay of the signal will indicate the loss of the analyte atoms from the analysis volume. If there is no change in the slope of the plot for the decay corresponding to Equation 16 when the voltage is switched off, then k_2 corresponds to k_a , the smaller of the two rate constants. On the other hand, if the slope of the plot becomes more negative when the voltage is switched off and the new slope is equal to $-k_b$ (Equation 17), then k_2 is the larger of the two rate constants.

The validity of the above model can be tested by determining the rate constants from an experimental absorbance profile and then using these values to calculate a theoretical absorbance profile using Equation 8. Agreement of the experimental absorbance profile with the theoretical profile will indicate the validity of the model.

EXPERIMENTAL

Apparatus

The experiments were performed using an Atomsources cathodic sputtering atomizer for atomic absorption spectrometry, manufactured by Analyte Corporation, Grants Pass, OR, U.S.A. Software versions 3.14 and 3.15 were used for all experiments. The Atomsources consisted of a sputtering cell with a power supply, gas regulation equipment, operator interface and supporting software, and was designed to replace the flame or graphite furnace of an existing atomic absorption spectrophotometer (it was also available with an atomic absorption spectrophotometer designed for rapid,

sequential multi-element analysis [151]. The Atomsources were used with two different spectrophotometers and power supplies to suit the needs of the particular experiment being performed. A summary of the four different experimental arrangements is given in Table 11; the details of the different equipment are given below. The experiments on the analytical performance included studies of the linear dynamic range and were done using the transient mode of atomization.

For experiments not requiring a fast detection system or where background correction was desired (the analytical determinations and the steady-state measurements) the Atomsources were mounted in the usual place of the burner assembly in a Perkin-Elmer atomic absorption spectrophotometer, Model Zeeman 5000 equipped with a deuterium-arc background corrector, and was operated as a part of the spectrophotometer. The time constant of the above spectrophotometer is ~ 17 ms (60 Hz). The experimental absorbance profiles were recorded with a Perkin-Elmer professional computer, Model 7500, and hard copies of the plots were obtained with a Printer, Model Prism 132 (Integral Data Systems, Milford, NH, U.S.A.). The discharge voltage was recorded using a Nicolet model 2090-III, two-channel digital oscilloscope. For experiments where a fast detection system was required or where background correction was not required (the pulsed and transient mode of atomization experiments) the Atomsources were used in conjunction with another apparatus having a fast detection system [148]. This apparatus consisted of a Varian-Techtron atomic absorption spectrophotometer, Model AA-5, with a laboratory-built power supply for the hollow-cathode lamp modulated at 843 Hz and a synchronous detection system with a laboratory-built lock-in amplifier having a time

Table 11 - List of apparatus used.

Experiment	Spectrophotometer	Power supply
Determination of the characteristic mass and calibration curves using the transient mode of atomization	Perkin-Elmer Z 5000	Atomsource
Transient mode of atomization	Varian-Techtron AA-5	Atomsource
Pulsed mode of atomization	Varian-Techtron AA-5	MDX
Steady-state mode of atomization	Perkin-Elmer Z 5000 or Varian-Techtron AA-5	MDX

constant variable from 2-104 ms. A time constant of 2 ms was used unless otherwise specified. The absorbance and the discharge voltage were recorded simultaneously with the Nicolet digital oscilloscope. Hard copies were obtained with a plotter, Model 7470A (Hewlett Packard, Palo Alto, CA, U.S.A.).

The Atomsorce power supply was used for analytical determinations and for the transient atomization experiments. The Atomsorce power supply is capable of either direct current or voltage regulation. The power supply has a maximum output of 300 mA at 1500 V, giving a maximum output of 450 W. The microprocessor controlling the power supply allows for discharges of 1 s and multiples thereof. For the other experiments, a different power supply was used to achieve fine control of the discharge duration and to investigate the use of higher powers than the Atomsorce power supply is capable of. Fine control of the discharge duration was required for the steady-state atomization and also for the verification of the rate constants for the pulsed mode of atomization, whereas for the pulsed mode of atomization experiments discharges of high power and short duration were required. For these experiments the Atomsorce power supply was disconnected from the atomizer. The power supply used for these experiments was a 1 kW High Z DC Magnetron, Model MDX-1K, manufactured by Advanced Energy Industries Inc., Fort Collins, CO, U.S.A.. The MDX power supply has a rated output of 1 A at 1000 V for a maximum power output of 1000 W. This power supply was used in conjunction with a function generator, Model No. 164, manufactured by WAVETEK, San Diego, CA, U.S.A. This combination allows for single or multiple, positive-going square-wave pulses of variable duration (frequency) and

amplitude. Typical discharge durations with this power supply were of the order of 50 ms. The power supply permits current, voltage or power regulation. Power regulation was generally used for these studies as it was found to give more reproducible results than current or voltage regulation.

For the steady-state atomization the Atomsources was used with the Perkin-Elmer Zeeman atomic absorption spectrophotometer, model No. 5000 for Mo, and the Varian-Techtron atomic absorption spectrophotometer, model No. AA-5 was used with a time constant of 16 ms for all other elements. A Mettler microbalance, Model M5 (Mettler, Zurich, Switzerland) was used for the measurements of mass.

The following hollow-cathode lamps were used: Ag, Au, Cd, Fe, Mg, Mn, Mo, Ni and Pb, manufactured by Westinghouse, Al, Co, Cr and Cu by Varian, Ag, Cd, Mo and V by Perkin-Elmer, Au and Cd by Cathodeon, Mn by EEL and Mo by Analyte Corporation.

Test Solutions and Reagents

Chemically pure metals or their salts were used to prepare standard solutions. Stock solutions containing 1000 $\mu\text{g/mL}$ were prepared as follows. For Al, Cd, Co, Cu, Fe, Mn, Mo, Ni and V the stock solutions were prepared as described under Test Solutions and Reagents in Chapter one. For Ag, Au and Pb the stock solutions were prepared as described under Test Solutions and Reagents in Chapter two. For Mg, MgO was dissolved in 10% (v/v) nitric acid (ULTREX) and diluted with ultrapure water. For Cr, $\text{K}_2\text{Cr}_2\text{O}_7$ was dissolved in 1% (v/v) nitric acid (ULTREX). All stock solutions were made to contain 1% (v/v) of the acids or the ammonium hydroxide used to dissolve the

metals or their salts except for Al, which contained 2% (v/v) HCl. The ULTREX brand acids were manufactured by Baker Chemical Co. Ultrapure water of resistivity 18.3 megohm-cm was obtained direct from a Milli-Q2 Water Purification System (Millipore Corporation). All test solutions were prepared by serial dilution of the above stock solutions immediately prior to determination.

Gas

Argon gas (99.997% pure) was used as the discharge gas. A molecular seive trap (Chromatographic Specialties Model No. MT120-4) was used to remove water vapour from the discharge gas.

Procedure

Cathodes of copper (99% pure), steel, anisotropic pyrolytic graphite, or tantalum (99.99% pure), as described below, were used. Excepting tantalum (which was supplied by the manufacturer as a polished sheet of metal), the cathodes were polished (working surface only) to 400 grit with an electric polishing machine, then cleaned with ethanol and air-dried. The clean, dry cathode was then clamped to the atomizer. The following procedure was used for all the experiments except for the steady-state atomization experiments, where the analyte was present in the bulk, solid steel (cathode). This was in contrast with the other experiments where the analyte was present as a discrete (solution) residue on the surface of the cathode. The procedure for the steady-state atomization experiments is given later. Prior to every atomization cycle, the cathodes were sputter-cleaned to ensure a reproducible atomization surface and to prepare a depression (cavity) into which the sample solution was deposited. The depth of the

cavity was found to have no effect on the results; however, the cavity must be of sufficient depth to contain the sample solution. For copper and tantalum, about 5-10 s sputtering at the optimum operating conditions (Tables 13 and 14) for the particular experiment was found to be sufficient. For graphite, the cathode was sputtered for 240 s at 12 Torr argon gas pressure and a current of 100 mA.

The cathode was then detached from the atomizer and laid flat with the prepared surface facing up. A 1 μ L volume of the test solution was then deposited in the centre of the cavity with a Hamilton microsyringe, fitted with a Chaney adaptor, Model 7105 NCH adaptor, part No. H88004 (Chromatographic Specialties). The test solution was then air-dried outside the atomizer and the cathode was reclamped to the atomizer. When the Atomsource power supply was used, the following gas flushing sequence was used as a part of the run mode. The atomizer pressure was maintained at 10 Torr of argon for 10 s; the atomizer was evacuated to 0.3 Torr, then repressurized to the preselected operating pressure. When the atomizer reached the operating pressure, the glow discharge was automatically initiated. The Nicolet oscilloscope (and the Perkin-Elmer spectrophotometer, if used) were triggered manually just prior to the initiation of the discharge. When the MDX power supply was used, the atomizer standby flush pressure mode was used to flush the atomizer at the desired operating pressure. Once the operating pressure was attained, the discharge could be initiated whenever desired. The oscilloscope (and spectrophotometer, if necessary) were triggered as before. For low concentrations of the aqueous standard solutions used for most of the experiments, a discharge of 25 ms duration was found to be sufficient to ensure complete atomization

of the sample. Longer sputtering times were occasionally needed, particularly for determining the peak-area absorbance for high analyte concentrations. In all cases, blanks were run to ensure that there was no sample carryover from run to run and to determine blanks and background absorbance. The blanks were subtracted from the absorbances of the samples, and the net absorbances were noted.

The procedure for the steady-state experiments was as follows. The cathode for all elements was the National Bureau of Standards, Standard Reference Material # 1264a, High Carbon Steel. A preliminary test was done on the cathode to determine the minimum pulse duration required to reach the first point on the plateau of the steady-state peak-height absorbance. The cathode was sputtered for a period of time sufficiently long to establish the steady-state peak-height absorbance. The pulse duration was then reduced until a transient signal (i.e., a peak-shaped signal) was obtained. Another sample of the same cathode was used for the remaining portions of the steady-state atomization experiments. The clean, dry cathode was weighed on the microbalance and then clamped to the atomizer. By use of the predetermined pulse duration, the cathode was then subjected to 10-15 pulses to cleave the surface. The cathode was then subjected to a further 16 single pulses and the absorbance and the discharge voltage were recorded. The discharge was then continuously pulsed and the total number of pulses was determined. Several hundred pulses were accumulated in order to obtain a reasonable weight loss. The cathode was then reweighed. The mass of analyte sputtered in one pulse was then calculated, from which the characteristic mass for the steady-state atomization was calculated after subtraction of the blank, which consisted simply of the

noise from the hollow-cathode lamp (since that was the only blank). For Co and Mo, a total of four determinations were made consisting of 16 absorbance values for each determination. For each of the other elements, a total of 64 atomization cycles were completed and absorbance measurements made but only one mass determination was made for the cumulative loss of mass over the 64 atomization cycles. The number of pulses used for the determination of the weight loss was made large in order to reduce the relative error in the measurement of mass.

Experimental Conditions

The hollow-cathode lamp and monochromator settings normally used for all the experiments are given in Table 12. The discharge parameters used for the analytical studies and the transient atomization experiments are given in Table 13. The discharge parameters used for the pulsed and the steady-state mode of atomization are given in Tables 14 and 15, respectively. The discharge parameters for each element were optimized individually for each mode of atomization. The optimum experimental conditions were taken as those giving the greatest absorbance with an acceptable noise level.

RESULTS AND DISCUSSION

The experimental conditions shown in Tables 12 -15 were those found to give the maximum analytical sensitivity and were used to determine the characteristic masses and limits of detection. The characteristic masses and limits of detection are given in Table 16 for the transient mode of atomization. The characteristic masses for graphite furnace

Table 12 - Hollow-cathode lamp (HCL) and monochromator settings

Element	Wavelength nm	HCL manufacturer	HCL current mA	Spectral bandpass nm
Ag	328.1	Westinghouse	5	0.08
Al	309.3	Varian	4	0.2
Au	242.8	Westinghouse	6	1.0
Cd	228.8	Cathodeon	6	0.1
Co	240.7	Varian	11	0.08
Cr	357.9	Varian	2	1.0
Cu	324.8	Varian	4	0.3
Fe	248.3	Westinghouse	6	0.5
Mg	285.2	Westinghouse	1	1.0
Mn	279.5	Westinghouse	3	1.0
Mo	313.3	Westinghouse	3	1.0
Ni	232.0	Westinghouse	11	0.1
Pb	283.3	Westinghouse	3	0.5
V	318.5	Perkin-Elmer	4	0.8

Table 13 - Discharge parameters for the transient mode of atomization.

Element	Instrumental setting of pressure Torr	Instrumental setting of current mA	Measured voltage V	Calculated power W
Ag	8	230	1000	230
Al	8	260	1300	338
Au	8	220	750	165
Cd	10	260	1270	330
Co	8	250	1290	323
Cr	12	260	940	244
Cu	10	250	1180	295
Fe	8	150	613	92
Mg	8	280	560	157
Mn	12	250	723	157
Mo	8	250	640	181
Ni	8	260	1240	322
Pb	8	250	1100	275
V	8	250	1144	286

Table 14 - Discharge parameters for the pulsed mode of atomization.

Element	Instrumental setting of pressure Torr	Instrumental setting of power W	Measured current mA	Measured voltage V
Ag	8	400	287	1400
Al	8	229	250	920
Au	8	410	284	1410
Cd	10	250	305	820
Co	8	200	227	880
Cr	8	301	251	1200
Cu	10	149	198	750
Fe	8	200	240	830
Mg	8	299	262	1140
Mn	10	300	310	970
Mo	8	203	285	810
Ni	10	200	227	880
Pb	10	249	312	800
V	8	250	250	1000

Table 15 - Discharge parameters for the steady-state mode of atomization.

Element	Concentration in SRM %	Instrumental setting of pressure Torr	Instrumental setting of current mA	Measured power W	Measured voltage V	Duration of sputtering ms
Co	0.15	8	152	97	710	50
Cu	0.25	15	151	70	460	50
Mn	0.25	8	99	53	540	100
Mo	0.49	8	152	97	710	50
Ni	0.14	10	169	95	560	50
V	0.10	15	200	95	480	100

Table 16 - Characteristic mass and limits of detection for the transient mode of atomization.

Element	Limit of Detection* pg	Characteristic mass Transient atomization pg	Characteristic mass GFAAS pg
Ag	140	26	1.2
Al	7.0	2.9	11.8
Au	550	47	7.3
Cd	27	4.9	0.39
Co	3000	130	5.4
Cr	0.50	0.25	1.8
Cu	43	8.0	3.0
Fe	210	30	2.8
Mg	0.50	0.11	0.30
Mn	68	25	1.7
Mo	0.34	0.041	5.4
Ni	1500	210	0.50
Pb	1600	210	7.7
V	185	68	69

*Mass giving a signal = 3σ /slope of the analytical calibration curve (σ = 1 standard deviation).

atomic absorption spectrometry (GFAAS) are those reported by L'vov et al. [152]. Of the 14 elements in the Table, six have sensitivities within an order of magnitude of GFAAS, whereas 4 elements have sensitivities better than GFAAS. The pulsed and the transient mode of atomization is a new technique which is still in its infancy, and it is felt that there is still a lot of room for improvement in these values, as will be discussed later. It should be noted that thus far attention has been confined to elements which are commonly determined by GFAAS. As Ohls [139] has demonstrated, it is possible to determine using cathodic sputtering atomization elements such as Zr which are not suitable for determination in a graphite furnace because of the formation of refractory carbides.

The values presented in Table 16 are at least an order of magnitude more sensitive than the previous values [147] for the characteristic mass for the transient mode of atomization. There are a number of reasons for the increase in sensitivity. These reasons are discussed in detail below, and include the time constant of the detection system, the hollow-cathode lamp current, the design of the hollow-cathode lamp, the method of modulation, and the discharge power. The differences in sensitivity are also partly due to the different optics of the two different spectrophotometers used. However, these differences have not been quantified and will therefore not be discussed further.

One reason for the above-mentioned improvement in the characteristic mass is that the previous values were obtained using the Perkin-Elmer spectrophotometer, the time constant of which was ~ 17 ms, which was too large to define accurately the peak of the rapidly changing transients [150]. The values in Table 16 were all obtained using the

fast detection system described in the Experimental Section. A time constant of 2 ms was used. However, even a time constant of 2 ms is too large for some elements which have faster signals. For some elements, the absorbance peak near the limit of detection has a duration of only about 5 ms. There is therefore a need for a detection system whose time constant is even smaller than the 2 ms used in this work. The effect of the time constant of the detection system on the characteristic mass can be seen from the characteristic mass of the transient mode of atomization for Mo in Table 17. The hollow-cathode lamp used was the "new" lamp (Westinghouse); the meaning of the "new" lamp is given later.

Hollow-Cathode Lamps

Piepmeyer [153] has reported on the influence of the spectral profile of the source lamp on the analytical results for low pressure, cathodic sputtering cells for atomic absorption spectrometry. One of the assumptions of the Walsh method for atomic absorption spectrometry is that the emission line from the hollow-cathode lamp is much narrower than the absorption line. One would expect that this condition would be more or less fulfilled for a flame or a graphite furnace, since the atomizer is at atmospheric pressure and at a high temperature, whereas the hollow-cathode lamp is at a low pressure and at a low temperature. Hence, the absorption line is much more broadened by Lorentz and Doppler broadening than is the emission line from the hollow-cathode lamp. For a cathodic sputtering atomizer, however, this is not the case. The atomizer pressure is only slightly greater than that of the hollow-cathode lamp, whereas the temperature of the atomizer is less than that of the hollow-cathode lamp because of the fact that the

Table 17 - Effect of time constant on the characteristic mass of Mo.

Time constant ms	Characteristic mass pg
2	0.11
8	0.50

cathode is water-cooled and that very short sputtering times were generally used, thereby preventing any temperature change for the cathode. The absorption and emission line widths are therefore probably not much different. It has been found that the highest sensitivity is obtained when the lowest possible lamp current is used, in agreement with the findings of Bernhard [114] and Keliher and Wohlers [154]. A low current for the hollow-cathode lamp means a lower lamp temperature and, therefore, a narrower emission line. Of course, using a low current for the hollow-cathode lamp means a decrease in the intensity of incident radiation and a resulting increase in the signal noise. The experimental conditions that have been employed are those which have been found to give the highest sensitivity (lowest characteristic mass) but not necessarily the lowest limit of detection. The effect of the hollow-cathode lamp current on the characteristic mass is shown for Mo in Table 18; the Mo hollow-cathode lamp used was the Perkin-Elmer lamp. It is important to use electronic, rather than mechanical modulation of the radiation from the hollow-cathode lamp (as is the case with the Perkin-Elmer spectrophotometer), since for electronic modulation the average power dissipated in the cathode is less than that when the current is dc and the radiation is mechanically modulated. The former results in a lower temperature for the hollow-cathode lamp, a narrower width for the emission line, and, therefore, a lower characteristic mass than if the radiation from the hollow-cathode lamp were mechanically chopped. Another advantage of electronic modulation is, of course, an increase in the useful life of the hollow-cathode lamp.

The age and the type of hollow-cathode lamp used were found to have a large

Table 18 - Effect of hollow-cathode lamp current on the characteristic mass of Mo.

Hollow-cathode lamp current mA	Characteristic mass pg
3	4.8
10	11

effect on the characteristic mass. This is shown in Table 19 for Cd, Mn and Mo. In previous work [147, 150] Perkin-Elmer hollow-cathode lamps were generally used. When an old Westinghouse Mo lamp was used, the sensitivity was enhanced by two orders of magnitude over that given by the Perkin-Elmer lamp. Both of the hollow-cathode lamps were tested and were found to be in good, working condition. The Westinghouse lamp was purchased in 1973 and even though it was still usable, it was near the end of its useful life, as was soon discovered. This hollow-cathode lamp will be referred to as the "old" Westinghouse Mo lamp, as opposed to the "new" Westinghouse lamp which was purchased in late 1988 to replace it. As can be seen from Table 19, the new Westinghouse lamp was not as sensitive as the old Westinghouse lamp, but it was still much better in sensitivity than the Perkin-Elmer lamp. A hollow-cathode lamp marketed by Analyte Corporation, the manufacturer of the Atomsource, was also tried. As can be seen, it was the least sensitive of the Mo lamps tested. These results are confirmed by the results obtained for Cd (Table 19). As can be seen from Table 19, hollow-cathode lamps by Westinghouse and Cathodeon gave similar sensitivities, whereas the Westinghouse lamp was found to be an order of magnitude more sensitive than the Perkin-Elmer lamp. Although a direct comparison had not been made, it was suspected that Varian lamps also gave good sensitivity, as evidenced by the high sensitivity of Al and Cr. The only other lamps that have been directly compared are Mn lamps by EEL and by Westinghouse, which had similar sensitivities. Obviously, there is a need for a detailed study of the sensitivity given by various, commercial hollow-cathode lamps for use in atomic absorption spectrometry when using cathodic

Table 19 - Effect of hollow-cathode lamp on characteristic mass.

Element	Hollow-cathode lamp	Characteristic Mass pg
Mo	Westinghouse, old	0.041
Mo	Westinghouse, new	0.11
Mo	Perkin-Elmer	4.8
Mo	Analyte	17
Mn	Westinghouse	25
Mn	EEL	33
Cd*	Westinghouse	150
Cd*	Perkin-Elmer	1500
Cd	Westinghouse	6.4
Cd	Cathodeon	7.3

*Perkin-Elmer Zeeman 5000 atomic absorption spectrophotometer. Graphite cathode.

sputtering atomization. It should be kept in mind that these hollow-cathode lamps (and the rest of the apparatus for that matter) were not used as advised by the manufacturers. The Perkin-Elmer Mo lamp, for example, had a continuous current rating of 30-40 mA; the lamp current that was used was 3 mA. The maximum lamp currents recommended by the manufacturer are shown in Table 20, along with the currents at which the hollow-cathode lamps were actually used.

The above observations can be explained by taking into account the work of Wagenaar et al. [155], who studied the emission line profiles and intensities of various hollow-cathode lamps as a function of lamp current. They found that the 423 nm Ca line from a Perkin-Elmer lamp was strongly self-reversed at 15 mA lamp current, whereas the same line from a Varian lamp showed no self-reversal up to 25 mA lamp current. They found that the intensity of the line of the Perkin-Elmer lamp at 15 mA lamp current was equal to the intensity of the line of the Varian lamp at 25 mA lamp current, and that self-reversal for both hollow-cathode lamps began at the same intensity, although the current densities were different. Thus, for a given lamp current, Perkin-Elmer lamps produce broader, more intense lines than Varian lamps, because of differences in filler gas or cathode material [155], as well as in geometry and size. For atomic absorption spectrometry using flame or graphite furnace atomization, the width of the emission line usually does not have a large effect on the sensitivity. This is not the case for cathodic sputtering atomizers for atomic absorption spectrometry. The results indicate that the loss in sensitivity due to the decrease in the emission line intensity with decreasing lamp current is more than offset by the increase in sensitivity due to the better overlap between

Table 20 - Hollow-cathode lamp (HCL) currents.

Element	Manufacturer	HCL recommended maximum current mA	HCL current used mA
Ag	Perkin-Elmer	25	13
Ag	Westinghouse	20	5
Al	Varian	20	4
Au	Cathodeon	10	12
Au	Westinghouse	20	6
Cd	Cathodeon	6	6
Cd	Perkin-Elmer	6	6
Cd	Westinghouse	12	6
Co	Varian	25	11
Cr	Varian	?	2
Cu	Varian	15	4
Fe	Westinghouse	20	6
Mg	Westinghouse	20	1
Mn	EEL	20	3
Mn	Westinghouse	25	3
Mo	Analyte	30	3
Mo	Perkin-Elmer	40	3
Mo	Westinghouse	30	3
Ni	Westinghouse	20	11
Pb	Westinghouse	8	3
V	Perkin-Elmer	40	4

the emission and the absorption line as the emission line becomes narrower. At present, manufacturers of hollow-cathode lamps for atomic absorption spectrometry make their hollow-cathode lamps as intense as possible, as evidenced by a number of hollow-cathode lamps that bear labels stating "high spectral output" on the hollow-cathode lamp. The results indicate that for the cathodic sputtering atomizers the greatest sensitivity is obtained with hollow-cathode lamps that have the narrowest emission line and that the intensity of the hollow-cathode lamp is of secondary importance. This explains why the old Westinghouse lamp was more sensitive than the new lamp - the new Westinghouse lamp has a "high spectral output" sticker, whereas the old Westinghouse lamp does not. Probably, at a given lamp current the emission line from the new Westinghouse lamp is broader than the emission line from the old Westinghouse lamp.

Pulsed mode and Transient mode of atomization

It was realized early on that the sensitivity of the transient mode of atomization was limited by the power available from the Atomsources power supply [147]. It was decided that a higher effective power (and a higher sensitivity) could be obtained by concentrating a great deal of power into short pulses rather than using a dc discharge. A power supply was therefore constructed which will be referred to as the striking power supply. The Atomsources power supply was used to charge a bank of capacitors which was then discharged into the atomizer. The output could be modulated using a shunt resistor or the power supply could be operated in the strike mode, in which a high-power, short-duration (0.25 ms) pulse could be added on top of the modulated output. The frequency of the striking power supply modulated output was 60 Hz and was

synchronized with the 60 Hz modulation frequency of the Perkin-Elmer spectrophotometer, with which this power supply was used. The theoretical striking power supply voltage is shown in Figure 62. Some results obtained with this power supply are shown in Figure 63. All absorbance peaks are for 20 ng of Mn, taken as the nitrate in an aqueous solution. The dc pulse was obtained with the Atomsources power supply in the current regulation mode and produced a voltage of 460 V. The strike peak was obtained with a 300 V strike on top of the 460 V output, producing a strike voltage of 760 V. As can be seen, modulating the power supply output seemed to increase the sensitivity, whereas the addition of the 300 V strike almost doubled the sensitivity. Although these results were felt to demonstrate the potential of using using a modulated or striking power-supply output, the striking power supply itself was found to be impracticable. The reason for this was that the striking power supply was used in conjunction with the Atomsources. The problem was that the Atomsources was designed for careful regulation of the current, and it did this very well. The Atomsources therefore tried to compensate when the shunt resistor was connected by increasing the current to try to keep the current constant, and vice versa when the shunt resistor was disconnected. The result was an unstable discharge, short circuits and blown transistors in the striking power supply. Attempts to defeat the Atomsources feedback loops and software proved unsuccessful. It was therefore decided to abandon this approach.

The pulsed mode of operation uses constant power and a strike voltage (about 300 V) of microsecond duration superimposed on single or multiple, positive-going square-wave pulses of millisecond duration and of higher amplitude (compared to the transient

Figure 62 - Theoretical output of the striking power supply. (a) dc output (Atomsource power supply) (b) modulated output (c) strike output.

Figure 63 - Absorbance profiles for 20 ng of Mn taken as an aqueous solution of the nitrate for the striking power supply. Experimental conditions: argon gas pressure, 10 Torr; discharge current, 200 mA; Perkin-Elmer hollow-cathode lamp, hollow-cathode lamp current, 8 mA; spectral bandpass, 0.2 nm. (a) dc output (Atomsource power supply) (b) modulated (c) 300 V strike.

mode of atomization). The transient mode of atomization uses constant current and positive-going square-wave pulses of second duration and lower amplitude (compared to the pulsed mode of operation). The pulsed mode of operation offers the capability of high power (which is required for a fast rate of atomization and, therefore, for maximizing the sensitivity), whereas the transient mode of atomization uses limited current at a maximum voltage. It was also necessary to use the pulsed mode of atomization to compare the sensitivity of the pulsed and the transient mode of atomization with the sensitivity of the steady-state mode of atomization by variation of the pulse duration, as explained in the Theory. It should be emphasized that the difference between the pulsed and the transient modes of atomization is the much shorter duration of the discharge and the higher power capability of the pulsed power supply used for the pulsed mode of atomization compared with the Atomsource power supply used for the transient mode of atomization. The pulsed mode of atomization is similar to the transient mode of atomization and can be expected to give similar results for similar experimental conditions; it is, however, easier to achieve high-power discharges (and therefore, higher sensitivity) for the pulsed mode of atomization than for the transient mode of atomization.

The characteristic mass obtained for the pulsed mode of atomization is given in Table 21. Typically, a single pulse of 50 - 500 ms duration was used. Pulses under 25-ms duration were found to result in incomplete atomization of the sample, as shown in Table 22. After the 10 - ms pulse a second pulse of 500 - ms duration was applied in order to check for the completeness of atomization. When the peak-height absorbances

Table 21 - Limits of detection and characteristic masses for the pulsed mode of atomization.

Element	Limit of detection* pg	Characteristic mass pg
Ag	280	46
Al	7.0	2.6
Au	260	48
Cd	5.6	2.0
Co	260	38
Cr	0.23	0.17
Cu	31	7.5
Fe	140	53
Mg	6.5	1.1
Mn	71	27
Mo	0.32	0.08
Ni	410	100
Pb	560	1900
V	140	840

*Mass giving a signal = 3σ /slope of the analytical calibration curve (σ = 1 standard deviation).

Table 22 - Effect of pulse duration on Mo peak-height absorbance.

Pulse duration ms	Peak-height absorbance
500	0.579
50	0.555
25	0.568
10 + 500	$0.208 + 0.363 = 0.571$

for a 10 - ms pulse and a subsequent 500 - ms pulse were added, the combined absorbance was found to be the same as for a pulse of 25 - ms or greater duration. The characteristic mass for the pulsed mode of atomization is smaller than or equal to that of the transient mode of atomization for 9 of the 14 elements listed in Table 21. Of the other 5 elements, 4 are within a factor of about 2 of the characteristic mass obtained for the transient mode of atomization. The characteristic masses obtained for the pulsed mode of atomization are higher than expected. This is probably because of the low voltage rating of the MDX power supply. As can be seen from Tables 13 and 14, the discharge parameters for the pulsed mode of atomization are not very different from those used for the transient mode of atomization. The MDX power supply is rated at only 1000 V, and although it was possible to draw up to 1400 V, the performance degraded above ~ 900 V. Above ~ 900 V, the rise time of the power supply output increased and multiple bursts of variable power were often seen, usually producing a number of small absorbance peaks (as many as seven were observed) instead of just one large peak. The behaviour of the power supply is illustrated in Figure 64. Figure 64a is for 10 ng of Mo taken as an aqueous solution of ammonium molybdate atomized with a single pulse of 50 - ms duration; the discharge voltage was 720 V. Figure 64b is for 10 ng of Mn taken as an aqueous solution of the nitrate, atomized with a single pulse of 500 - ms duration; the discharge voltage was 920 V. Figure 64c is for 10 ng of Mn taken as an aqueous solution of the nitrate, atomized with a single pulse of 500 - ms duration; the discharge voltage was 1180 V.

Figure 65 presents the dynamic resistance of the Atomsource as a function of

Figure 64a - Absorbance profile and discharge voltage for the pulsed mode of atomization for 10 ng Mo taken as ammonium molybdate in an aqueous solution. Solid line is absorbance. Experimental conditions: argon pressure, 8 Torr; power, 155 W; discharge current, 205 mA; V, 720 V; for other details see Table 11.

Figure 64b - Absorbance profile and discharge voltage for the pulsed mode of atomization for 10 ng Mn taken as the nitrate in an aqueous solution. Solid line is absorbance. Experimental conditions: argon pressure, 10 Torr; power, 298 W; discharge current, 324 mA; V, 920 V; for other details see Table 11.

Figure 64c - Absorbance profile and discharge voltage for the pulsed mode of atomization for 10 ng Mn taken as the nitrate in an aqueous solution. Solid line is absorbance. Experimental conditions: argon pressure, 8 Torr; power, 298 W; discharge current, 252 mA; V, 1180 V; for other details see Table 11.

Figure 65 - Dynamic resistance as a function of pressure for the Atomsources. Numbers are pressures in Torr.

pressure. Figure 65 was obtained with the Atomsources power supply in the current regulation mode using a copper cathode with no sample. From this figure one finds that if one is limited to 900 V and wants to increase the power, the pressure must be increased. There is a problem in that an increase in pressure also means an increase in the flow rate of the argon gas (Table 23), with a consequent decrease in the residence time of the analyte atoms in the analysis volume, since the Atomsources is not capable of independent control of the pressure and the flow rate of the discharge gas. The flow rates of the discharge gas were measured with a Matheson model 603 flow meter on the atomizer gas inlet. Figure 65 shows that a power of 1000 W could be obtained if the pressure was high enough, but use of higher pressures was found to decrease the sensitivity, presumably because an increase in the gas pressure meant an increased flow rate of the gas (Table 23), resulting in an increased convectional loss, which more than compensated for any increase in the sputtering rate due to higher power. Another atomizer was therefore constructed that allows independent control of the pressure and the flow rate of the discharge gas, thus allowing the use of higher pressures and powers while still maintaining an optimum flow rate of argon; details of this atomizer and the results obtained with it will be discussed in the next chapter.

The MDX power supply was also used to determine the characteristic mass (sensitivity) of the steady-state mode of atomization. This was done in order to compare directly the sensitivity of the steady-state mode of atomization with that of the pulsed and the transient mode of atomization. This is normally not done since the sensitivity of the steady-state mode of atomization is expressed in terms of the concentration required to

Table 23 - Variation in argon gas flow rate with argon gas pressure in the Atomsource.

Pressure Torr	Measured flow rate L min⁻¹
10	0.9
15	1.9
20	2.6
30	3.5
40	4.1
50	>4.4
60	>4.4

give 1% absorption, whereas for the pulsed and the transient mode of atomization the sensitivity is expressed in terms of the absolute mass required to give 1% absorption. In order to make the comparison valid a pseudo-transient signal for the steady-state mode of atomization was created by varying the steady-state pulse duration. This is illustrated in Figure 66 for 0.49% Mo in the National Bureau of Standards, Standard Reference Material #1264a, High Carbon Steel. Figure 66a was for a pulse of 1.7 - s duration, whereas Figure 66b was for a pulse of 50 - ms duration. Figures 66a and 66b were obtained using the Perkin-Elmer spectrophotometer and the "new" Westinghouse hollow-cathode lamp operated at 10 mA current; all other the experimental conditions were as listed in Table 15. With a lamp current of 3 mA, the results were similar except that the peak-height absorbance was approximately 0.22. Similar results were obtained for the other elements using the Varian-Techtron spectrophotometer. From Figure 66, it can be seen that it is possible to turn a steady-state signal into a transient signal of the same peak-height simply by varying the pulse duration, thereby allowing the absolute mass required to give 1% absorption (the characteristic mass) to be determined so that the sensitivity of the steady-state mode of atomization can be compared directly with the pulsed and the transient mode of atomization.

The average mass of steel sputtered per second at the various experimental conditions is shown in Table 24. The sensitivity of the steady-state mode of atomization expressed as the characteristic mass is presented in Table 25. When this characteristic mass is compared with that of the pulsed and the transient mode of atomization, in most cases the characteristic mass of the pulsed mode and the transient mode of atomization

Figure 66a - Absorbance profile for a 1.7 - s pulse of Mo in steel by the steady-state mode of atomization. Hollow-cathode lamp current was 10 mA. For other details see Tables 11 and 15.

Figure 66b - Absorbance profile for a 50 - ms pulse of Mo in steel by the steady-state mode of atomization. Hollow-cathode lamp current was 10 mA. For other details see Tables 11 and 15.

Table 24 - Average mass of steel sputtered for the steady-state mode of atomization.

Instrumental setting of pressure Torr	Instrumental setting of current mA	Measured power W	Measured voltage V	Mass sputtered $\mu\text{g/s}$
8	99	53	540	3.4
8	152	97	710	11
10	169	95	560	12
15	151	70	460	3.5
15	200	95	480	9.0

Table 25 - Characteristic mass (CM) of the steady-state vs. the transient and the pulsed mode of atomization.

Element	Steady-state CM pg	Transient CM pg	Pulsed CM pg	CM ratio transient/ steady-state	CM ratio pulsed/steady- state
Co	60	130	38	0.46	1.6
Cu	27	8.0	7.5	3.4	3.6
Mn	230	25	27	9.3	8.6
Mo	52	0.11	0.08	473	650
Ni	72	210	100	0.36	0.72
V	990	68	140	15	7.1

is lower (in some cases, much lower) than that of the steady-state mode of atomization, the exceptions being Co and Ni. Both of these elements also show a significant improvement in sensitivity for the pulsed mode of atomization over the transient mode of atomization, which is important to note. The sensitivity of the steady-state mode of atomization is not likely to improve since the maximum sensitivity for the steady-state mode of atomization is obtained for relatively low power discharges; there is therefore no possibility for improving the sensitivity of the steady-state mode of atomization by changing the experimental conditions. This is in contrast with the pulsed and the transient mode of atomization, the sensitivity of which is at present limited by the usable power available from the present power supplies. The sensitivity of the pulsed and the transient mode of atomization, but not the steady-state mode of atomization, can also be expected to increase with the use of a faster detection system because a faster detection system will allow the quickly-rising peak-height absorbance to be recorded without any distortion caused by the relatively long time constant of the slower detection system. There is therefore a lot of room for improvement in the sensitivity of the transient mode and especially of the pulsed mode of atomization that is not possible for the steady-state mode of atomization. When the above factors are taken into account in light of the present sensitivity, it may reasonably be expected that the pulsed mode of atomization can be made at least as sensitive as GFAAS for most elements.

Kinetic Modelling

Chakrabarti et al. [150] concluded that the entry of atoms into and the loss of atoms from the analysis volume of the Atomsource could be described by Equation 1 and

the kinetic equations derived from it in the Theory. It was stated [150] that it was not known which of the rate constants corresponded to k_1 , the rate constant for atom entry into the analysis volume, and which to k_2 , the rate constant for atom loss from the analysis volume. Figures 67a and 67b present absorbance pulses obtained using the transient mode of atomization for 50 ng of Ag and Au, respectively, obtained with the Perkin-Elmer spectrophotometer for a discharge current of 150 mA at an argon pressure of 6 Torr. The two absorbance profiles have similar rise times but dissimilar fall times. Since they are both atomized at the same pressure (and therefore, the same argon gas flow rate), they should have similar values for k_2 , but not necessarily for k_1 . That this should be so can be seen from the results of Gough et al. [135], who found that the analyte atoms are efficiently entrained within the flow of the argon discharge gas. If this is so, the mechanism of atom loss would be by diffusion/convection of the analyte atoms out of the analysis volume, which should be roughly similar for all elements at a given pressure and flow rate if they are entrained in the argon discharge gas. This seems to indicate that for the low-sensitivity (low-power) experimental conditions deliberately used to obtain these absorbance peaks by the transient mode of atomization, atomization of the sample is the rate-limiting step. Since the smaller of the two rate constants corresponds to the rate-limiting step, k_2 must be greater than k_1 for Figures 67a and 67b.

Table 14 shows the high-sensitivity (high-power) experimental conditions used for the pulsed mode of atomization, as explained in the Theory. The rate constants for the pulsed mode of atomization are presented in Table 26. Figure 68 illustrates how the rate constants are determined and the subsequent curve-fitting to the experimental data using

Figure 67 - Absorbance profiles by the transient mode of atomization. (a) - 50 ng Ag taken as the nitrate in an aqueous solution. Experimental conditions: argon pressure, 6 Torr; discharge current, 150 mA; Perkin-Elmer hollow-cathode lamp, hollow-cathode lamp current, 13 mA; spectral bandpass, 0.7 nm; wavelength, 328.1 nm. (b) - 50 ng Au taken as the chloride in an aqueous solution. Experimental conditions: argon pressure, 6 Torr; discharge current, 150 mA; Cathodeon hollow-cathode lamp, hollow-cathode lamp current, 12 mA; spectral bandpass, 0.7 nm; wavelength, 242.8 nm.

Table 26 - Rate constants for the pulsed mode of atomization.

Element	Mass ng	A_o^*	k_1 s^{-1}	k_2 s^{-1}	k_1/k_2
Ag	1.0	0.25	100	52	1.9
Al	1.0	0.61	740	105	7.0
Au	10.	0.60	90	26	3.5
Cd	0.1	0.59	170	110	1.5
Co	10.	0.92	160	58	2.8
Cr	0.1	0.47	750	310	2.4
Cu	1.0	0.35	140	90	1.6
Fe	10.	0.94	115	87	1.3
Mg	0.1	0.37	500	140	3.6
Mn	1.0	0.18	160	80	2.0
Mo	10.	1.15	200	110	1.8
Ni	10.	0.50	185	45	4.1
Pb	10.	0.23	160	120	1.3
V	10.	0.31	190	40	4.8

* A_o is defined by Equation 8.

Figure 68 - Rate constant determination for 10 ng Ni taken as the nitrate in an aqueous solution. For other details see Tables 11 and 14.

Equation 8 and the parameters given in Table 26 for 10 ng of Ni. Preliminary assignments of the determined rate constants as k_1 or k_2 were made for each element as explained in the Theory. The absorbance profiles obtained with the high-sensitivity (high-power) experimental conditions for the pulsed mode of atomization gave profiles that had dissimilar rise times and similar fall times, which would indicate that now $k_1 > k_2$. A rough estimate of the theoretical residence time of the analyte atoms within the Atomsource at an argon pressure of about 8 Torr gave a value of about 12 ms, which corresponds to $k_2 = 80 \text{ s}^{-1}$. The effect of diffusion was neglected in this calculation, so these numbers are very approximate. Nevertheless, when the rate constants in Table 26 are averaged, they have average values of $k_1 = (150 \pm 40) \text{ s}^{-1}$ and $k_2 = (80 \pm 40) \text{ s}^{-1}$. Although not conclusive, these results do lend support to the rate constant assignments. The rate constants for Al, Cr and Mg are not very reliable. The reason for this is that their absorbance profiles had a rise time of only 2 ms, which was the time constant for the detection system, so there were no data points on the rising portion of their absorbance profiles, making it impossible to obtain reliable values for their rate constants.

As explained in the Theory, there are two experiments which would allow the unambiguous assignment of the rate constants. The first experiment was performed for Al, Au, Mn and Mo. Figure 69 shows the results for Mn; the results for the other elements are similar. Figure 69a shows the experimental absorbance and discharge voltage of a low-power discharge and 10 ng of Mn as an aqueous solution of the nitrate. Figure 69b shows the absorbance of Mn (on a logarithmic scale) as a function of time,

a

b

Figure 69 - Low-power atomization of 10 ng Mn taken as the nitrate in an aqueous solution. (a) Experimental absorbance and discharge voltage. Solid line is absorbance. Experimental conditions: argon pressure, 10 Torr; power, 120 W; discharge current, 195 mA; V , 620 V; for other details see Table 11. (b) Absorbance (plotted on a logarithmic scale) vs. time for Figure 69a. The arrow indicates the time at which the discharge voltage was switched off. A - Line corresponding to B_1 (Equation 17); B - Line corresponding to ΔB (Equation 18); C - Line with slope = $-k_2$.

where the arrow indicates the point at which the voltage was terminated. Using the data up to this point the curve was analyzed in the usual way to obtain values of k_a and k_b . The slope of line A represents $-k_a$ (Equation 16) and the slope of line B represents $-k_b$ (Equation 17). At the point where the voltage is cut off the only process occurring is the loss of analyte atoms, as explained earlier, which is the process represented by k_2 . Figure 69b shows that the slope of the plot after the voltage is cut off is equal to the slope of line B, or $-k_b$. Therefore, in this experiment using low power (Figure 69), k_2 is the larger of the two rate constants. The value of $k_2 = 95 \text{ s}^{-1}$ obtained from these figures is in agreement with the theoretical estimate of $k_2 = 80 \text{ s}^{-1}$, whereas the value of k_1 was found to be 19 s^{-1} .

The second experimental approach was used with only Mn using the high-sensitivity (high-power) experimental conditions given in Table 14. The rate constants were: $k_1 = 160 \text{ s}^{-1}$ and $k_2 = 80 \text{ s}^{-1}$. The value of k_1 has now increased for the more vigorous (high-power) discharge, whereas the value of k_2 has remained constant, as predicted by the Theory. These experiments have shown that for the low-power experimental conditions, $k_1 < k_2$, whereas for the high-power experimental conditions used for the pulsed mode of atomization, $k_1 > k_2$. Since the maximum sensitivity is obtained when $k_1 \gg k_2$, it can be seen from Table 26 that there is still room for improvement in the sensitivity of the pulsed mode of atomization.

Analytical Calibration Curves

Thus far the characteristic mass has only been discussed with respect to peak height and not peak-area absorbance. This is because it has been found that, for the

Atomsource equipment (with the limitations imposed by its power supply and gas regulation), the characteristic mass for peak-height absorbance (the mass of analyte required to give a peak-height absorbance of 0.0044) is lower (more sensitive) than the characteristic mass for peak-area absorbance (the mass of analyte required to give an peak-area absorbance of 0.0044 absorbance · s). The characteristic mass for peak-area absorbance was determined for Au and Mo and compared with the characteristic mass for peak-height absorbance in Table 27. The absorbance profiles obtained with the Atomsource by the pulsed and the transient mode of atomization are of very short duration and therefore have a very small peak-area absorbance, whereas the peak-height absorbance can be considerable. This is because the Atomsource, as mentioned previously, does not allow independent control of the pressure and the flow rate of the argon discharge gas. Another reason for the high peak-area characteristic masses in Table 27 is that the units of absorbance-seconds (this definition is taken from GFAAS) for the characteristic mass do not accurately reflect the true sensitivity of the much faster peaks generated by the pulsed and the transient mode of atomization for cathodic sputtering. In GFAAS, absorbance peaks have similar peak-height and peak-area absorbances and so a peak area of 0.0044 absorbance · s would normally be below the detection limit. For the pulsed and the transient mode of atomization, peak-area absorbances of 0.00044 are still above the detection limit, so a peak-area characteristic mass of 0.00044 absorbance · s may be more appropriate than 0.0044 absorbance · s for peaks generated by the pulsed and the transient mode of atomization for cathodic sputtering. If this reasoning is applied to the peak-area characteristic mass, the values

Table 27 - Peak height vs. peak area characteristic mass.

Element	Hollow-cathode lamp type	Hollow-cathode lamp current mA	Peak height characteristic mass pg	Peak area characteristic mass pg
Au	Westinghouse	6	47	30
Mo	Perkin-Elmer	10	11	134
Mo	Perkin-Elmer	3	4.8	115
Mo	Westinghouse (old)	3	0.041	27

in Table 27 would be one order of magnitude smaller, the peak-area characteristic mass would therefore be similar to the peak-height characteristic mass.

Analytical calibration curves for aqueous solutions of Ag, Au, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and V have been determined for both peak-height and peak-area absorbance using the transient mode of atomization. Table 28 gives the linear dynamic ranges that have been found for peak-height absorbance and for peak-area absorbance for the elements. The values for the peak-area linear dynamic range for Ni and V in Table 28 are in brackets to denote that these were the largest masses examined for these elements, whereas masses of analyte up to 1000 ng were examined for all the other elements except for Co, the results being taken from Chakrabarti et al. [147], and Ag and Co, for which the peak-area linear dynamic range has not been determined. The peak-area analytical calibration curve for Fe gave two linear ranges of 0 - 50 ng and 50 - 1000 ng, as shown in Table 28. Peak-area absorbance has been found to give linear analytical calibration curves, usually extending over a range of mass up to 10^3 ng, whereas peak-height absorbance was found to give linear analytical calibration curves of greater sensitivity (defined as 0.0044 absorbance or absorbance $\cdot$ s divided by the slope of the analytical calibration curve), but over a smaller range of analyte mass. An example is Mg atomized from a copper cathode, the analytical calibration curves for which are shown in Figure 70. The characteristic mass of Mg from Figure 70 is 26 pg for peak-height absorbance and 700 pg for peak-area absorbance, whereas the linear dynamic ranges for the analytical calibration curves from Table 28 are up to 5 ng and 1000 ng, respectively.

Table 28 - Linear dynamic ranges for analytical calibration curves of elements.

Element	Cathode	Peak-height linear range ng	Peak-area linear range ng
Ag	copper	0 - 10	-
Au	copper	0 - 5	0 - 1000
Cd	graphite	0 - 15	0 - 800
Co	copper	0 - 200	-
Cr	graphite	0 - 600	0 - 1000
Cu	graphite	0 - 50	0 - 1000
Fe	copper	0 - 5	0 - 50
			50 - 1000
Fe	graphite	0 - 200	0 - 1000
Mg	copper	0 - 5	0 - 1000
Mg	graphite	0 - 8	0 - 800
Mn	copper	0 - 200	0 - 1000
Ni	copper	0 - 5	(0 - 100)
Pb	copper	0 - 150	0 - 1000
V	copper	0 - 10	(0 - 10)

Figure 70a - Peak-height analytical calibration curve for Mg taken as the nitrate in an aqueous solution. Hollow-cathode lamp current, 2 mA; for other details see Tables 11 and 13.

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Figure 70b - Peak area analytical calibration curve for Mg taken as the nitrate in an aqueous solution. Hollow-cathode lamp current, 2 mA; for other details see Tables 11 and 13.

Table 29 gives the effect of sputtering a solution residue consisting of 5 ng of Mn taken as the nitrate in an aqueous solution from the C - plane (which is perpendicular to the AB - plane) of anisotropic pyrolytic graphite instead of the AB - plane normally used. As can be seen, both the peak-height absorbance and the peak-area absorbance were substantially reduced, while the absolute uncertainty remained about the same. Use of the C - plane of anisotropic pyrolytic graphite would be difficult even if the sensitivity improved since the graphite is only weakly bonded in this plane and tends to cleave along this plane when clamped to the atomizer, whereas the AB - plane has much greater mechanical strength and does not have this problem.

Gough et al. [135] and Larkins [156] have examined the effect of water vapour on the production and maintenance of atoms in the gas phase for Atomsource-type atomizers and have shown that the presence of as little as 10 ppm water vapour can cause interferences. 8 ng of Mg was sputtered from a graphite cathode (transient mode of atomization, Perkin-Elmer spectrophotometer) with and without the water trap on the argon gas inlet to the atomizer. When the water trap was added it was found that the peak-height absorbance, the peak-area absorbance and the relative standard deviation for both peak height and for peak area decreased by 36 %.

Table 30 shows the effect of the test volume of the analyte sample solution for 25 ng Ni taken as the nitrate in an aqueous solution using a copper cathode and the Varian-Techtron AA-5 atomic absorption spectrophotometer. As can be seen, both the peak-height absorbance and the relative standard deviation are considerably better for a 1 μ L sample volume than for a 5 μ L sample volume. There are two reasons for this.

Table 29 - Determination of 5 ng Mn taken as the nitrate in an aqueous solution. The solution was sputtered off the C - plane of anisotropic pyrolytic graphite instead of the AB - plane normally used.

Plane of anisotropic pyrolytic graphite from which the sample was sputtered	Peak-height absorbance	Peak-area absorbance
AB - plane	0.237 ± 0.026	0.087 ± 0.005
C - plane	0.139 ± 0.028	0.063 ± 0.003

Table 30 - Effect of the test volume (dried on the cathode surface) on the peak-height absorbance and the relative standard deviation for 25 ng Ni taken as the nitrate in an aqueous solution using the Varian-Techtron AA-5 spectrophotometer and a copper cathode.

Test volume μL	Peak-height absorbance	Relative standard deviation %
1	0.483 ± 0.001	0.2
5	0.274 ± 0.038	14

One reason is that a smaller volume of sample solution is more easily contained in the cavity and less likely to spread outside of the cavity. A smaller volume sample solution can also be deposited and concentrated where the sputtering action is most vigorous, which is where the gas jets strike the cathode surface. For a large sample volume much of the solution dries on portions of the cathode surface which are not vigorously sputtered, thus decreasing the sensitivity.

CONCLUSIONS

As predicted by the Theory (kinetic modelling), greater (sometimes, much greater) sensitivities are given by the pulsed and the transient mode of atomization compared with the steady-state mode of atomization, and this advantage in sensitivities is expected to increase in favour of the pulsed and the transient mode of atomization with better instrumentation, whereas for the steady-state mode of atomization, with its kinetic limitations, no such increase in sensitivities is possible.

CHAPTER FOUR

PERFORMANCE OF A NEW LABORATORY - CONSTRUCTED CATHODIC - SPUTTERING ATOMIZER

INTRODUCTION

Previous results obtained with the commercial Atomsources cathodic sputtering atomizer for the analysis of solution residues by atomic absorption spectrometry [147, 150, 157, 158] have shown that better sensitivities than those of GFAAS can be obtained for some elements. These high sensitivity values were obtained using the Atomsources with a fast detection system and a power supply capable of delivering greater power than the Atomsources. It was at this time that the need for an atomizer with independent control of the argon flow rate and the pressure was realized. The commercially available Atomsources [114] controls the pressure by varying the argon flow rate; the result is a high and variable argon flow rate over which the operator has no control. Since the residence time of the analyte atoms in the atomizer is inversely proportional to the argon flow rate, it stands to reason that the argon flow rate is an important experimental parameter which needs to be optimized along with other experimental parameters, such as argon pressure and discharge power.

Kim and Piepmeier [136] added a massflow meter with a micrometer valve to the gas inlet of an Atomsources to achieve independent control of argon flow rate and pressure. Banks and Blades [44] have built an atomizer for atomic emission spectrometry

that uses an auxiliary gas inlet to maintain a constant pressure inside the atomizer as the argon flow rate is varied. The laboratory-constructed atomizer uses a needle valve and a massflow meter on the gas inlet to control the argon flow rate, while the pressure is controlled by valves on the vacuum line.

THEORY

The analytical performance of the Atomsources has been previously characterized as a function of discharge power, the time constant of the spectrophotometer, the type of hollow-cathode lamp used (identified by its manufacture) and the hollow-cathode lamp current; it has been shown how each of these factors affects the peak-height sensitivity. With the availability of an atomizer with independent control of the argon flow rate and the pressure, a parametric study has been conducted of the effect of power, argon flow rate and pressure on the peak height and the peak-area absorbance, and on the rate constants for the supply of atoms to and their removal from the analysis volume. The model has been shown to be valid in this case [158].

where A is the analyte atoms that have not yet entered the analysis volume of the atomizer, B is the analyte atoms that are in the analysis volume and C is the analyte atoms that are removed from the analysis volume; k_1 and k_2 are the first order rate constants for atom supply to and removal from the analysis volume, respectively. The effect of the above factors on the sensitivity of the new atomizer has been examined, with

the rate constants k_1 and k_2 being determined as in Chapter three [158].

Solution of the differential equations associated with the above mechanism yields the following equation which describes the time dependent behaviour of the absorbance signal.

$$B_t = \frac{k_1}{k_1 - k_2} A_o (e^{-k_2 t} - e^{-k_1 t}) \quad (8)$$

B_t is the time-dependent number of analyte atoms in the analysis volume which are giving the absorbance signal and A_o is the total number of atoms which enter the analysis volume. If all the analyte atoms that absorb (A_o) were in the analysis volume at one time then A_o would give the maximum possible absorbance. Integration of the above equation yields the following equation which represents the theoretical peak area absorbance.

$$\int_{t=0}^{t=\infty} B_t dt = \frac{A_o}{k_2} \quad (19)$$

Differentiating Equation 8 and setting the result equal to zero yields the following equation for the theoretical peak height absorbance.

$$A_{peak} = A_o \frac{k_1}{k_2} \exp \left[\frac{k_1}{k_1 - k_2} \ln \left(\frac{k_2}{k_1} \right) \right] \quad (20)$$

From Equations 8 and 19 it is possible to predict the effect of a change in the first order rate constants upon the analytical signals. It can be seen that in order to maximize the peak area absorbance signal it is necessary to make k_2 as small as possible. In order to maximize the peak height absorbance it is necessary to make $k_1 \gg k_2$. If $k_1 \gg k_2$ then $A_{peak} = A_o$.

Other factors that will have an effect upon the analytical signals are the transport efficiency and the sputtering efficiency. The transport efficiency is defined as the fraction of the total number of atoms sputtered from the cathode surface that reaches the analysis volume. The sputtering efficiency is defined as the fraction of the total number of analyte atoms that are sputtered from the cathode surface and are not redeposited. For the cathodic sputtering atomizer used in this work there is a spatial separation between the cathode surface (where sputtering occurs) and the analysis volume (defined by the geometry of the beam of radiation from the hollow-cathode lamp). Therefore the rate of atom formation at the cathode surface cannot be directly measured; only the rate of supply can be measured, i.e. the rate at which the atoms are transported from the cathode surface to the analysis volume. Thus, the absorbance arising from the total number of atoms which enter the analysis volume A_0 may not be due to all the analyte atoms present in the original sample. If either the sputtering or the transport efficiency is less than one, the absorbance arising from A_0 will represent less than the total possible absorbance. It should be made clear that k_1 , the rate constant for the supply of analyte atoms to the analysis volume, is a measure of the rate of transport of the gas-phase analyte atoms to the analysis volume and not of the rate of sputtering, even though k_1 will also reflect changes in the rate of sputtering. The rate constant k_2 is for the removal of analyte atoms from the analysis volume by whatever means, including diffusion of analyte atoms to and adsorption of the analyte atoms onto the cathode surface and the walls of the analysis cell and convection of analyte atoms out of the analysis volume.

INSTRUMENTATION

Figure 71 shows the schematic diagram of the apparatus [159]. The apparatus is composed of four basic systems: the cathodic sputtering atomizer, the gas control system, the power supply, and the measurement system. These systems are described below.

Cathodic sputtering atomizer

The new atomizer has been modelled after the Atomsources [114]. Figure 72 is a schematic diagram of the atomizer which shows the important dimensions [159]. A six gas-jet configuration similar to that in the Atomsources has been employed but all the components have been manufactured in-house. The body of the atomizer is constructed from Delrin. The atomizer is designed so that the optical path is parallel to the cathode surface as in the Atomsources. The interior of the atomizer is lined with pyrex glass to protect the body of the atomizer from the glow discharge. The new atomizer does not have the atom wedge, emission sensor or atom filters present in early model Atomsources atomizers (see Figure 7), it having been found that the atom wedge does not appear to enhance analyte atom transport. It has been found that atom filters are not required if there is no atom wedge, although the windows must periodically be cleaned to prevent any build-up of sputtered material on the windows. The windows of an Atomsources atomizer with an atom wedge but no atom filters were found to be covered very quickly (a few seconds) with sputtered material, whereas the windows of a later model Atomsources atomizer without an atom wedge (and with the atom filters removed) needed only to be cleaned every few days, depending on use. Atomsources atomizers were compared, one having an atom wedge and atom filters and the other having neither. It

Figure 71 - Modular diagram of the new, laboratory-constructed atomizer. A: Digital recording oscilloscope; B: monochromator and detection system; C: atomizer (1: anode; 2: cathode); D: light source; E: gas solenoid; F: Pirani gauge; G: flow transducer; H: ball valve; I: regulating valve for fine control of gas pressure; J: fine needle valve for control of gas flow rate; K: foreline trap; L: two-stage vacuum pump; M: power supply; N: argon gas tank and regulator; O: particulate filter and moisture trap.

Figure 72 - Schematic diagram of the new, laboratory-constructed atomizer.

was found that the peak-area absorbance for Mg sputtered from a graphite cathode (transient mode of atomization) was unchanged, whereas the peak-height absorbance improved without the atom wedge and atom filters.

Both the anode and the cathode plate are fabricated from copper. The cathode plate is water-cooled and is maintained at ground potential. Two L-brackets have been attached to the outer surface of the cathode plate. These L-brackets are positioned perpendicular to each other so that one corner of the square, removable cathode can be placed at their intersection, making the position of the cathode reproducible. The atomizer is rigidly mounted on an XYZ Φ adjustable stage on the optical rail of an atomic absorption spectrophotometer (Varian-Techtron, model AA5). All gas connections to the atomizer are made using Cajon Ultra-Torr fittings.

Gas control system

The sputtering gas used in this study was 99.997%-pure argon. A moisture trap (Chromatographic Specialties, model No. MT120-4) was used to remove water vapour from the sputtering gas as water vapour had been shown to have a detrimental effect when present in the discharge [135, 156]. The sputtering gas was then passed through a particulate filter (Matheson Gas Products). The flow rate of the argon was regulated using a Nupro fine-regulating needle valve and was measured using the flow rate transducer of a mass flow controller (Sierra Instruments, model No. 740-05-2). This transducer was capable of measuring up to 5 standard litres per minute (SLPM) argon gas. The argon gas was then admitted into the atomizer through the six gas jets. The pressure was monitored on the outlet side using a Pirani gauge (Granville-Phillips

Convectron Gauge, model No. 275). The gauge was calibrated for both nitrogen and argon gas. The pressure was controlled by throttling the vacuum line using a Whitey ball valve and a Whitey regulating valve in a parallel configuration. The ball valve was used for coarse control of the gas pressure while the regulating valve gave fine control. A two stage vacuum pump (Edwards High Vacuum, model 5) fitted with an oil mist filter (Edwards High Vacuum, model EMF10) and a foreline trap provided the vacuum for all studies. The foreline trap eliminated the back diffusion of pump-oil vapour into the sputtering cell.

Power supply

The power supply used for the sputtering studies was an Advanced Energy MDX 1K, which is capable of independent regulation of current, voltage, or power. The power supply is capable of supplying up to one kW with up to 1400 V at low currents. The maximum available current is 1 A at 1000 V. The power supply is controlled with a function generator that was constructed by the departmental electronics workshop. The function generator has the capability of delivering single or multiple positive-going square waves of variable amplitude and duration. A voltage divider is situated between the power supply and the sputtering cell. The discharge voltage signal is sampled from this voltage divider and is recorded on one channel of a dual-channel digital recording oscilloscope (Nicolet Instrument Corporation, model 201).

Atomic absorption measurement system

A laboratory-constructed power supply for hollow-cathode lamps that employed variable-frequency electronic modulation (from 400 Hz to 20 kHz) was used. This

power supply for hollow-cathode lamps enables the employment of a low time constant and also provides a fine control of the hollow cathode-lamp current. This fine control is necessary as it has been found that the best sensitivities can be achieved at the lowest usable lamp currents [158]. The light beam is focused to a minimum diameter of 7 mm as it passes through the middle (horizontal axis) of the atomizer. The atomizer, the hollow-cathode lamps, the two bi-convex lenses and the monochromator were all mounted on the same optical rail. The rail, the mounts and the lenses were cannibalized from an atomic absorption spectrophotometer (Varian-Techtron, model AA5). The monochromator used was from a Techtron atomic absorption spectrophotometer, model AA4. The photomultiplier was a Hamamatsu R1527, powered by a Kepco ABC 1500 V regulated dc power supply. The signal from the photomultiplier tube was passed to a dual-channel lock-in amplifier (Stanford Research, model SR530) having a variable time constant down to 1 ms. The output from the lock-in amplifier was passed through a log converter and the absorbance data were collected on one channel of the digital oscilloscope.

EXPERIMENTAL

Using the steady-state mode of atomization the atomic absorption of copper atoms was measured by sputtering a bulk solid, the National Bureau of Standards SRM # 1263a, Cr - V Steel, which contained 0.098% copper by weight. The atomic absorption of nickel and chromium atoms from bulk solids using the steady-state mode of atomization were measured by sputtering blocks of brass and steel, respectively. The

actual concentrations of nickel in the brass sample and chromium in the steel sample were not critical as only the effects that different experimental conditions had upon the magnitude of the atomic absorbance signals were of concern. For the pulsed atomization measurements, copper blocks (99% - pure) which had been polished to a smooth surface with 400 grit emery paper on an electric sander and then cleaned with ethanol were used as the cathode. All of the metals were taken as nitrates in an aqueous solution except Au which was taken as the chloride (from aqua regia) in an aqueous solution. The stock solutions were prepared as described in the previous chapters. The prepared cathode surface was sputtered for 1-2 s at conditions that were sufficient to produce a cavity into which the sample solution could be pipetted, it having been found previously [158] that the depth of the cavity had no effect upon the analytical signal as long as there was a distinct cavity.

For the pulsed atomization measurements the prepared cathode was removed from the atomizer (after the atomizer had attained atmospheric pressure) and 1 μL of the sample solution was pipetted into the cavity using a Hamilton microsyringe fitted with a Chaney adaptor, model 7105NCH, part No. H88004 (Chromatographic Specialties). The solution was air-dried and the cathode was then resealed to the atomizer. For all the measurements the following procedure was used. The cathode was clamped to the cathode plate of the atomizer and the gas solenoid on the vacuum line was opened, evacuating the cell to approximately 300 mTorr. When this pressure was attained the gas solenoid on the argon inlet line was opened and the fine-regulating needle valve was adjusted to give the desired argon gas flow rate. When the desired flow rate was attained

the valves on the vacuum line were adjusted to give the desired pressure. The oscilloscope and the function generator that controlled the power supply were then triggered simultaneously and plots of the signal intensity versus time were obtained together with the corresponding voltages.

Experimental conditions

The hollow-cathode lamps and the monochromator settings used are given in Table 31. The hollow-cathode lamp power supply was modulated at 1 kHz unless otherwise stated, and a time constant of 1 ms was used on the lock-in amplifier. The discharge parameters and the analyte masses that were used to determine the characteristic mass and limit of detection for each element are given in Table 32.

RESULTS AND DISCUSSION

Steady-state mode of atomization

Figure 73 shows the change in the normalized absorbance signals of copper, chromium and nickel, at a constant power of 300 W (and constant pressure of 10 Torr), with variations in the argon gas flow rate. These curves show an initial increase with increasing argon gas flow rate up to a flow rate of approximately 0.5 SLPM, after which all curves level off. At flow rates larger than 1.0 SLPM a decrease in the atomic absorption signals for all these elements was observed, probably because of a decreased residence time for atoms within the analysis volume. From Figure 73 it is reasonable to conclude that the transport efficiency of atoms is at a maximum at a flow rate of 0.5 SLPM for a pressure of 10 Torr. The optimum flow rate is pressure dependent and must

Table 31 - Hollow-cathode lamp and monochromator settings.

Element	Wavelength nm	Hollow-cathode lamp		Spectral bandpass nm
		Manufacturer	Current mA	
Ag	328.1	Westinghouse	3.0	0.08
Au	242.8	Westinghouse	4.0	0.20
Co	240.7	Varian	11.0	0.08
Cr	357.9	Varian	2.0	1.0
Cu	324.8	Varian	4.0	0.30
Fe	248.3	Westinghouse	5.0	0.30
Mg	285.2	Westinghouse	0.5	0.60
Ni	232.0	Westinghouse	8.0	0.20

Table 32 - Experimental parameters.

Element	Analyte mass pg	Instrumental settings of			Measured	
		Flow rate SLPM	Pressure Torr	Power W	Voltage V	Current mA
Ag	1000	0.50	8.0	308	925	333
Au	2000	0.50	5.0	309	1380	224
Co	1000	0.70	8.0	221	705	313
Fe	500	0.70	10.0	496	945	525
Mg	10	0.50	5.0	309	1380	224
Ni	1000	0.70	8.0	571	1215	470

Figure 73 - Change in the normalized absorbance signal of Cu, Ni and Cr with variations in argon gas flow rate at constant power and pressure. Argon gas pressure, 10 Torr; power, 300 W.

be determined at a given pressure in order to achieve maximum sensitivity. This means that it is necessary to have the capability to control the argon gas flow rate independently of the argon gas pressure. Since the atomic absorption signal is based on the number of ground-state neutral atoms (present in the glow discharge) which make up the vast majority of the sputtered species [16, 41], it is reasonable to base any conclusions with respect to the transport and sputtering processes occurring in the atomizer on the atomic absorption signal. In order to maintain a constant power, while the argon gas flow rate is increased at a constant pressure, the discharge voltage must decrease. Figure 74 shows the decrease in discharge voltage, for a constant power (300 W), with the increasing argon gas flow rate at a constant pressure of 10 Torr.

Figure 75 shows the change in the absorbance signals, at a constant voltage of 1000 V, with variations in the argon gas flow rate at a constant pressure of 10 Torr. Once again, the curves for all the elements studied show similar features. These curves have two linear segments. In order to keep the voltage constant as the flow rate is increased at a constant pressure it is necessary for the discharge power to increase. Figure 76 shows the increase in the discharge power, at a constant voltage, with increasing argon gas flow rate. Since the power increases linearly, and the rate of sputtering increases linearly with power [149], it seems reasonable to conclude that in Figure 75 the initial, steeper segments of the curves are due to the combined effect of an increase in the atom transport (transport efficiency) with increasing gas flow rate and an increase in the rate of sputtering (sputtering efficiency) with increasing power; the final, lesser increase in the curves in Figure 75 would then be due to an increase in the

Figure 74 - Dependence of discharge voltage on the argon gas flow rate at constant power and pressure. Argon gas pressure, 10 Torr; power, 300 W.

Figure 75 - Change in the normalized absorbance signal of Cu, Ni and Cr with variations in argon gas flow rate at constant voltage and pressure. Argon gas pressure, 10 Torr; voltage, 1000 V.

Figure 76 - Dependence of power on the argon gas flow rate at constant voltage and constant pressure. Argon gas pressure, 10 Torr; voltage, 1000 V.

rate of sputtering (sputtering efficiency) with increasing power only. The fact that the intersection of the two linear segments of Figure 75 occurs around the previously determined optimum flow rate (defined as the flow rate giving the highest transport efficiency) of 0.5 SLPM supports this interpretation.

From the atomic absorbance measurements it can be seen that the transport efficiency increases with increasing argon gas flow rates up to the point where the maximum efficiency is attained at about 0.5 SLPM. It can be seen that for a given pressure there is an optimum flow rate that must be achieved in order to obtain the maximum sensitivity at a given gas pressure. The optimum flow rate is what gives the maximum transport efficiency. Therefore, it is necessary for the argon gas flow rate to be a controllable experimental parameter. The reduction in sensitivity at lower flow rates (and constant pressure) is due to lower transport efficiency caused by the deposition of material on the walls of the atomizer and the cathode surface before it reaches the analysis volume. At the optimum flow rate the amount of such deposition is minimal. At higher flow rates (at constant pressure) the decrease in the sensitivity is most likely due to a decreased residence time for analyte atoms within the analysis volume.

Parametric studies of the pulsed mode of atomization

For the parametric studies 10 ng of Ag taken as the nitrate in an aqueous solution was used in all cases. The hollow-cathode lamp and monochromator settings were as shown in Table 31 except that the hollow-cathode lamp current was 6 mA and the hollow-cathode lamp was modulated at 3.4 kHz instead of 1 kHz. The reason for the higher hollow-cathode lamp current is that low-noise signals were required for the

accurate determination of the rate constants, as explained previously in Chapter two [150].

Figure 77 shows the variation in the peak height and the peak area absorbance with the argon flow rate. Figure 78 shows the variation in the rate constants k_1 and k_2 with the argon flow rate. For these experiments the pressure and the power were held constant at 8 Torr and 200 W, respectively. Both the rate constants increase with increasing argon flow rate. The rate constant k_1 for atom supply to the analysis volume increases with increasing argon flow rate because the sputtered Ag atoms are efficiently entrained in the flowing argon gas [135], and an increase in the argon flow rate results in an increase in the rate at which the Ag atoms that have been sputtered are supplied to the analysis volume. The rate constant k_2 for atom removal from the analysis volume increases rapidly with increasing argon flow rate, starting at about 0.4 standard litres per minute (SLPM), which accounts for the maxima in Figures 77 and 78 at 0.4 SLPM. The increase in k_2 results from the increased convectional loss of analyte with increasing argon flow rate, as explained above. Figures 77 and 78 thus show the effect of forced convection on the supply of Ag atoms to and their removal from the analysis volume of the atomizer, and confirm that the argon flow rate is an important experimental parameter that must be controlled if maximum analyte transport efficiency and therefore, maximum sensitivity (peak height or peak-area absorbance) is to be obtained.

Figure 79 shows the variation in the peak height and the peak area absorbance with pressure. Figure 80 shows the variation in the rate constants k_1 and k_2 with pressure. For these experiments, the argon flow rate and the power were held constant

Figure 77 - Peak-height absorbance (●) and peak-area absorbance (■) vs. argon gas flow rate for 10 ng Ag (taken as the nitrate in an aqueous solution) at constant pressure and power. Pressure, 8 Torr; power, 200 W. For other details see Table 31.

Figure 78 - Rate constants k_1 (●) and k_2 (■) vs. argon gas flow rate for 10 ng Ag (taken as the nitrate in an aqueous solution) at constant pressure and power. Pressure, 8 Torr; power, 200 W. For other details see Table 31.

Figure 79 - Peak-height absorbance (●) and peak-area absorbance (■) vs. pressure for 10 ng Ag (taken as the nitrate in an aqueous solution) at constant argon gas flow rate and power. Argon flow rate, 0.6 SLPM; power, 200 W. For other details see Table 31.

Figure 80 - Rate constants k_1 (●) and k_2 (■) vs. pressure for 10 ng Ag (taken as the nitrate in an aqueous solution) at constant argon gas flow rate and power. Argon gas flow rate, 0.6 SLPM; power, 200 W. For other details see Table 31.

at 0.6 SLPM and 200 W, respectively. It can be seen that the rate constant k_1 for atom supply to the analysis volume increases with pressure. This can only be due to an increase in the sputtering rate since whatever is sputtered from the cathode surface is swept in to the analysis volume at a constant argon flow rate of 0.6 SLPM. That the sputtering rate increases with increasing pressure was observed earlier with the Atomsources, but it could not be determined if this was due to the increasing pressure, the increasing argon flow rate, or a combination of both, because the Atomsources does not allow for independent control of argon flow rate and pressure. With independent control of argon flow rate and pressure, it has been possible to examine the effect of argon flow rate and pressure separately and to confirm that increasing pressure results in an increased sputtering rate, at least for Ag, for the range of experimental conditions studied. The rate constant k_2 for atom removal is approximately constant at lower pressures and increases at higher pressures. Changes in the rate of removal of atoms from the analysis volume due to pressure reflect the relative importance of the diffusion and the forced convection for atom removal. Diffusion is more important at lower pressures and the rate of diffusion decreases with increasing pressure. Forced convection is more important at higher pressures and the rate of forced convection increases at higher pressures. With increasing pressure, as the increasing rate of atom removal due to forced convection more than offsets the decreasing rate of atom removal due to diffusion, k_2 increases (leading to a reduced absorbance), resulting in the maximums in Figure 80.

Figure 81 shows the variation in the peak height and the peak area absorbance

with power. Figure 82 shows the variation in the rate constants k_1 and k_2 with power. For these experiments the argon flow rate and pressure were held constant at 8 Torr and 0.6 SLPM, respectively. It can be seen that the peak height and the peak area absorbance increase with increasing power, as has been reported previously [147] for the determination of Co in solution residues. Not surprisingly, the rate constant k_1 for atom supply to the analysis volume also increases with power. With both argon flow rate and pressure held constant any changes in k_1 can only result from changes in the rate of sputtering. Again, it has been observed with the Atomsources that the sputtering rate increases with increasing power. The rate constant k_2 for atom removal should not show any dependence on power since variations in the power should not affect the rate of removal of analyte atoms from the analysis volume at constant argon flow rate and pressure, as was observed experimentally. It is also important to note that independent control of argon flow rate and pressure of the new atomizer has allowed use of higher powers than could be obtained using the power supply of the Atomsources [158]. At higher argon flow rates and pressures stable glow discharges have been obtained using a power of 1000 W, which is the limit of the new power supply; this high power cannot be obtained without independent control of argon flow rate and pressure.

The values of the rate constants k_1 and k_2 for 10 ng Ag at the "optimum" experimental conditions studied (8 Torr, 0.6 L min⁻¹, 200 W) are $k_1 = (650 \pm 40) \text{ s}^{-1}$, $k_2 = (4.6 \pm 0.6) \text{ s}^{-1}$, with $k_1/k_2 = 140$. This compares with the previous values for Ag of $k_1 = 100 \text{ s}^{-1}$, $k_2 = 52 \text{ s}^{-1}$, with $k_1/k_2 = 1.9$, obtained with the Atomsources [158]. The new atomizer thus enhances the k_1/k_2 ratio by a factor of 74 compared to the ratio

Figure 81 - Peak-height absorbance (●) and peak-area absorbance (■) vs. power for 10 ng Ag (taken as the nitrate in an aqueous solution) at constant argon gas flow rate and pressure. Argon gas flow rate, 0.6 SLPM; pressure, 8 Torr. For other details see Table 31.

Figure 82 - Rate constants k_1 (●) and k_2 (■) vs. power for 10 ng Ag (taken as the nitrate in an aqueous solution) at constant argon gas flow rate and pressure. Argon gas flow rate, 0.6 SLPM; pressure, 8 Torr. For other details see Table 31.

obtained with the Atomsource. Using Equation 20 and these values for the rate constants the enhancement in the k_1/k_2 ratio should result in twice the peak height sensitivity. The observed enhancement in peak height sensitivity is 3 times. The difference between the predicted and the observed enhancement in the peak height sensitivity is due to an increase in the transport efficiency with an increase in the argon flow rate [159], which increases the value of A_0 . The ability to optimize the argon flow rate allows maximization of the transport efficiency. Independent control of argon flow rate and pressure has allowed the rate constant for Ag atom removal, k_2 , to be decreased by an order of magnitude (which increases the Ag atom residence time by an order of magnitude), while increasing k_1 by a factor of 6.5. With $k_1 \gg k_2$, the maximum peak height sensitivity is obtained [132]. With the Atomsource, k_1 could be increased to the point where $k_1 > k_2$ [158]. That was as far as could be gone without independent control of argon flow rate and pressure required to decrease k_2 , and make $k_1 \gg k_2$. The new atomizer with independent control of argon flow rate and pressure allows control of k_2 and k_1 to the point where $k_1 \gg k_2$. From Equation 19

$$\int_{t=0}^{t=\infty} B_t dt = \frac{A_0}{k_2} \quad (19)$$

it can be seen that a large decrease in k_2 should result in a large increase in the peak area sensitivity, as was observed for the new atomizer compared to the Atomsource. From Equation 19, the fact that the rate constant k_2 decreases by an order of magnitude would lead one to expect an increase in the peak area sensitivity by an order of magnitude. This is not the case as the argon flow rate affects both the value of A_0 and k_2 . Since the

transport efficiency is increased and the atom residence time is decreased at higher argon flow rates, both A_0 and k_2 increase with increasing argon flow rate. Therefore, the maximum peak area sensitivity requires optimization of the argon flow rate to achieve the best compromise between these opposing trends. This is not to say that the sensitivity cannot be increased further; improvements are still possible in other areas, for example, by using light sources that have been designed for use with cathodic sputtering atomizers rather than thermal atomizers, and that provide a stable light beam at the lowest possible lamp current [158].

Sensitivity of the pulsed mode of atomization for the new atomizer

A comparison of the sensitivity of the new, laboratory-constructed atomizer and the sensitivity of the Atomsources (with the same power supply as the new atomizer) for Fe is given in Table 33. The peak height characteristic mass and the limit of detection for the Atomsources are taken from Chakrabarti et al. [158], in which a Westinghouse hollow-cathode lamp operated at 6 mA, spectral bandpass of 0.5 nm, time constant of the detection system of 2 ms, argon pressure of 8 Torr, discharge power 200 W, discharge current 240 mA and discharge voltage 830 V were used. To maintain a pressure of 8 Torr the argon flow rate in the Atomsources is at approximately 0.9 SLPM. The peak area sensitivity of the Atomsources for Fe was calculated from the same data, but was not previously reported. The new atomizer was used to determine the sensitivity of Fe with the same experimental conditions, which have been called the old experimental conditions in Table 33, except that the argon flow rate was set at 0.7 SLPM, and the resulting discharge current and voltage were 301 mA and 665 V,

Table 33 - Comparison of the sensitivity of the new and old atomizers for Fe.

	Peak height		Peak area	
	Characteristic mass pg/0.0044 A	Limit of detection* pg	Characteristic mass pg/0.0044 A · s	Limit of detection* pg
Old atomizer	30	140	3500	1500
New atomizer, old experimental conditions	30	83	1900	17
New atomizer, new experimental conditions	6.6	45	510	12

*Mass giving a signal = $3\sigma/\text{slope of the analytical calibration curve}$ (σ = 1 standard deviation)

respectively. An argon flow rate of 0.7 SLPM was used since this was about the maximum that could be used with the new atomizer that would still maintain a pressure of 8 Torr.

The values obtained under these experimental conditions thus show the effect that independent control of argon flow rate and pressure has on the sensitivity of Fe. Comparing these values with those obtained using the Atomsources, it has been found that the characteristic mass for peak height and for peak area is practically unchanged, there is some improvement in the limit of detection for peak height, whereas the limit of detection for peak area has improved by 2 orders of magnitude. The improvement in the peak height limit of detection and a part of the improvement in the peak area limit of detection can be attributed to the better lock-in amplifier used with the new atomizer (compared to the Atomsources), but most of the improvement in the peak area limit of detection has resulted from being able to optimize the argon flow rate, thus increasing the residence time of the analyte atoms in the atomizer.

Optimization of the experimental conditions for the new atomizer has allowed the use of lower hollow-cathode lamp currents, lower argon flow rates (for a given pressure) and higher powers than obtainable with the Atomsources. The new experimental conditions used for the new atomizer are those given in Tables 31 and 32. The use of lower hollow-cathode lamp current [114, 153, 158] and higher discharge power [147, 158] has resulted in increased peak height sensitivity, and this is reflected in the improved peak height characteristic mass observed for Fe with the new atomizer. The increase in peak height sensitivity is also accompanied by an increase in the peak area

sensitivity as expected, although again this is minor compared to the increase in the peak area sensitivity (limit of detection) resulting from the optimization of the argon flow rate. The overall effect observed for the new atomizer is a slight increase in the peak height sensitivity due to the lower hollow-cathode lamp current that can be used (because of the better lock-in amplifier used for the new atomizer compared to that used for the Atomsources) and the higher discharge power that is attainable (because of the optimization of the argon flow rate), whereas there is a large increase in the peak area limit of detection mainly because of the optimization of the argon flow rate. It can be seen that the argon flow rate is an important experimental parameter which must be controlled in order to achieve maximum sensitivity, especially for the peak area.

Table 34 presents the peak height sensitivity of Ag, Au, Co, Fe, Mg and Ni for the new atomizer compared to the Atomsources. Modest increases in the peak height characteristic mass are observed for all the elements except for Au, for which the peak height characteristic mass is about the same for the two atomizers. More substantial increases in the peak height limits of detection are the combined result of the improved peak height characteristic mass and better electronics. Table 35 presents the peak area sensitivity of the new atomizer compared to that of the Atomsources. As observed for the peak height, modest improvements in the characteristic mass are found for most elements, whereas the peak area limits of detection have improved by 1-2 orders of magnitude for all the elements.

For reference, the GFAAS peak area limits of detection reported by Slavin [160] are included. As has been previously discussed in Chapter three, the limit of detection

Table 34 - Peak height figures of merit.

Element	Characteristic mass, pg/0.0044 A		Limit of detection*, pg	
	new atomizer	old atomizer	new atomizer	old atomizer
Ag	15	46	63	280
Au	53	47	72	550
Co	14	38	72	260
Fe	6.6	30	45	140
Mg	0.079	0.11	0.86	6.5
Ni	20	100	220	410

*Mass giving a signal = 3σ /slope of the analytical calibration curve (σ = 1 standard deviation)

Table 35 - Peak area figures of merit.

Element	Characteristic mass, pg/0.0044 A · s		Limit of detection*, pg		
	new atomizer	old atomizer	GFAAS	new atomizer	old atomizer
Ag	710	1900	3.6	34	240
Au	1500	1400	22	13	1300
Co	1100	3100	15	19	7500
Fe	510	3500	11	12	1500
Mg	21	140	0.93	0.21	8.8
Ni	1900	4700	23	8.0	1900

*Mass giving a signal = 3σ /slope of the analytical calibration curve (σ = 1 standard deviation)

should be used when comparing the peak area sensitivity for different techniques and not the characteristic mass since the peak area characteristic mass is biased in favour of techniques with longer atomization time scales (such as GFAAS), whereas the limit of detection is not [158]. A significant improvement from the previous results obtained with the Atomsource [158] is that the peak area limit of detection of CSGD and GFAAS can now be compared, whereas previously only the peak height characteristic masses could be compared. This is an important advantage since it has been shown [158] that for the sputter atomization of solution residues, peak area is much less subject to matrix interferences than is peak height.

CONCLUSIONS

It has been shown that independent control of argon flow rate and pressure is critical for maximizing the sensitivity and for studying the sputtering and the transport efficiency of Ag in the cathodic sputtering atomizer designed for atomic absorption spectrometry. Pressure and power have been found to affect the sputtering rate (sputtering efficiency), whereas the argon flow rate seems to have a significant effect only on the rate of supply of analyte atoms to the analysis volume (transport efficiency), but not on the sputtering rate. Both argon flow rate and pressure can affect the rate of atom removal from the analysis volume. The combined effect of these parameters was shown for Fe for the new atomizer compared to the Atomsource. The peak height and peak area sensitivity of the new atomizer for the elements studied shows that the sensitivity of the new atomizer is equal to or better than that of GFAAS for the analysis of solution residues.

CHAPTER FIVE

MATRIX INTERFERENCES

INTRODUCTION

It has been shown [161] that the analysis of solution residues by atomic absorption spectrometry using cathodic sputtering atomization is a sensitive analytical technique, with the sensitivity obtained generally being similar to or better than those of graphite furnace atomic absorption spectrometry (GFAAS). Cathodic sputtering atomization can also be used to determine refractory elements such as La and Zr [139] which cannot be determined using a graphite furnace because of the low vapour-pressure of the element or its compounds in the furnace. The results (described in Chapter four) were obtained using the pulsed mode of atomization and a laboratory-constructed atomizer with independent control of argon gas pressure and flow rate for the analysis of solution residues of pure elements or their salts. The elements were prepared and sampled separately. In order for the technique to be analytically useful, the effect of various matrices on the analytical signal needs to be established and remedial measures sought out, if necessary.

The work of Gough et al. [135] and Larkins [156] on the effect of water vapour on the atomic absorption signal has already been discussed. McCamey and Niemczyk [120] reported on interferences in the sputter atomization of solution residues in atomic absorption spectrometry. They found evidence for redox reactions at the cathode surface

between the analyte element and the cathode element, and concluded that although interferences in GFAAS were reduced or eliminated when sputter atomization was used, the sputter-atomization of solution residues seemed to have its own interferences. It is also known that only conducting substances can be sputter-atomized using dc or low-frequency ac power. The results of various matrix interference studies with the Atomsource using the transient mode of atomization are presented in this study, as well as preliminary results of the application of radiofrequency (rf) sputtering as a possible solution to the problem of matrix interferences for atomic absorption spectrometric analysis using cathodic sputtering in a glow discharge.

EXPERIMENTAL

The experiments were performed with an Atomsource cathodic sputtering atomizer, manufactured by Analyte Corp., Grants Pass, OR, U.S.A. Software versions 3.14 and 3.15 were used for all experiments. For the rf experiments, the Atomsource was used with an insulating sample clamp, the atom wedge and the atom filters were removed, and the entire atomizer and sample clamp were enclosed in two separate pieces of solid aluminum sheet to prevent leakage of stray rf radiation and still allow quick sample access. Holes were drilled in the aluminum sheet to allow passage of the beam of radiation from the hollow-cathode lamp, the argon discharge gas line, the vacuum line and the cooling water lines for the cathode plate. The above modifications will be referred to as the rf atomizer.

For the matrix interference studies the Atomsource power supply was used in the

current regulation mode, whereas for the rf experiments the power supply used was a Plasma-Therm Inc., model No. HFS 1500D, equipped with an automatic impedance matching network, model No. AMNS 1500E. This power supply had a maximum output of 1600 W at a fixed frequency of 13.56 MHz. The rf atomizer was capacitively coupled to the rf power supply through a blocking capacitor which was a part of the matching network. The rf atomizer could be operated using either dc or rf sputtering. For the rf atomizer, power (dc or rf) was applied direct to the anode as in the Atomsources, while the cathode was left at ground potential.

For the matrix interference studies the Atomsources was mounted in the usual place of the burner-assembly in a Perkin-Elmer atomic absorption spectrophotometer, model Zeeman 5000, equipped with a deuterium-arc background corrector. The experimental absorbance profiles were recorded with a Perkin-Elmer professional computer, model 7500, and hard copies of the plots were obtained with a printer, model Prism 132 (Integral Data Systems, Milford, NH, U.S.A.). The discharge voltage was recorded with a Nicolet model 2020-III, two channel digital oscilloscope. Hard copies were obtained with a plotter, model 7470A (Hewlett-Packard, Palo Alto, CA, U.S.A.). For the rf experiments the atomizer was mounted on an xyz ϕ adjustable stage on the optical rail of a Varian-Techtron model AA-5 atomic absorption spectrophotometer. A laboratory-constructed lock-in amplifier [148] with a time constant variable from 2 - 104 ms was used. Absorbance and dc voltages were recorded simultaneously with a Nicolet digital oscilloscope, model No. 201, with hard copies being obtained with the Hewlett-Packard plotter. For the mass loss measurements a Mettler microbalance, model No. M5

(Mettler, Zurich, Switzerland) was used.

Test solutions and reagents

Chemically pure metals or their salts were used to prepare standard solutions. Stock solutions containing 1000 $\mu\text{g/mL}$ were prepared as follows. For Au, Pb, Ni, Ag, and Fe the stock solutions were prepared as described previously. All of the above solutions were all made to contain 1% (v/v) of the nitric acid used to dissolve the metals or their salts. Solutions of NaCl, CaCl_2 and MgCl_2 were prepared by dissolving each salt separately in ultrapure water. Solutions of HNO_3 (ULTREX), HCl (ULTREX), H_2SO_4 (ULTREX) and HF (AnalaR) were prepared by diluting the acid with ultrapure water. The ULTREX brand acids were manufactured by Baker Chemical Co. and the AnalaR brand acid was manufactured by BDH Co. Ultrapure water of resistivity 18.3 $\text{M}\Omega\text{ cm}$ was obtained direct from a Milli-Q2 Water Purification System (Millipore Corp.). All test solutions were prepared by serial dilution of the above solutions immediately prior to determination.

Gas

Argon gas (99.997% pure) was used as discharge gas after it had passed through a molecular sieve moisture trap to remove water vapour (Chromatographic Specialties model No. MT-120-4) and a particulate filter (Matheson Gas Products).

Procedure

Cathodes of steel, anisotropic pyrolytic graphite, copper (99% pure), and glass, as described below, were used. The cathodes were polished (working surface only) to 400 grit with an electric polishing machine (except for glass), then cleaned with ethanol,

and air-dried. The clean, dry cathode was then clamped to the atomizer. For the matrix interference studies, the following procedure was used. Prior to every atomization cycle, the cathodes were sputter-cleaned to ensure a reproducible atomization surface and to prepare a circular depression (cavity) into which the test solution was pipetted. The cathode was then detached from the atomizer and laid flat with the prepared surface facing up. A 1 μ L volume of the test solution was then pipetted in the centre of the cavity with a Hamilton microsyringe, fitted with a Chaney adaptor, model No. 7105 NCH, part No. H88004 (Chromatographic Specialties). The test solution was then air-dried outside the atomizer and the cathode was reclamped to the atomizer. For the matrix interference studies (using the Atomsources power supply), the following gas flushing sequence was used as a part of the run mode. The atomizer pressure was maintained at 10 Torr of argon for 10 s; the atomizer was evacuated to 0.3 Torr, then repressurized to the preselected operating pressure. When the atomizer reached the operating pressure, the glow discharge was automatically initiated. The Nicolet oscilloscope and the Perkin-Elmer spectrophotometer were triggered manually just prior to the initiation of the discharge. In all cases, blanks were run to ensure that there was no sample carryover from run to run and to subtract blanks and background absorbance from the gross absorbance to obtain the net absorbance.

For the rf experiments, the clean, dry cathode was clamped to the atomizer and the solid aluminum shielding was put in place. The atomizer standby flush pressure mode of the Atomsources was then used to flush the atomizer at the desired operating pressure. Once the operating pressure was obtained, the discharge could be initiated

whenever desired. The oscilloscope was triggered manually just prior to initiation of the discharge.

Experimental Conditions

The hollow-cathode lamp and monochromator settings used for the matrix interference studies are given in Table 36. The discharge parameters used for the matrix interference studies are given in Table 37. The analysis wavelengths and hollow-cathode lamp currents used for the rf experiments are given in Table 38. For the rf experiments a time constant for the detection system of 2 ms and a spectral bandpass of 1.0 nm were used in all cases.

RESULTS AND DISCUSSION

Matrix interferences

The first study of matrix interferences was the effect of alkali and alkali-earth chlorides on the atomic absorption of Ag, Au and Pb sputtered from solution residues deposited on copper cathodes. Figures 83 - 88 give the peak-height recovery for Au, Ag and Pb from NaCl matrix, and for Pb from CaCl_2 , MgCl_2 as well as NaCl matrices. Severe interferences were found for peak-height absorbance (the peak-area absorbance was not determined for these elements), an example of this interference being shown in Figure 89 [158]. Figure 89a is the absorbance profile for 50 ng of Au atomized from a copper cathode. Figure 89b is the absorbance profile for 50 ng of Au in the presence of a 400-fold mass excess (2 μg) of NaCl atomized from a copper cathode; the hollow-cathode lamp current for parts a and b of Figure 89 was 12 mA. Figure 89c gives the

Table 36 - Hollow-cathode lamp (HCL) and monochromator settings.

Element	Wavelength nm	HCL manufacturer	HCL current mA	Spectral bandpass nm
Ag	328.1	Perkin-Elmer	13	0.7
Au	242.8	Cathodeon	10	0.7
Fe	248.3	Westinghouse	6	0.2
Pb	283.3	Westinghouse	6	0.7

Table 37 - Discharge parameters.

Element	Analyte mass ng	Instrumental setting of pressure Torr	setting of current mA	Measured voltage V
Ag	10	6	150	940
Au	25	6	150	890
Fe	10	8	150	610
Pb	150	8	200	580

Table 38 - RF analysis wavelength and hollow-cathode lamp current.

Element	Wavelength nm	Hollow-cathode lamp	
		Manufacturer	Current mA
Al	309.3	Westinghouse	4
As	193.7	Cathodeon	7
Au	242.6	Westinghouse	6
B	249.6	Perkin-Elmer	4
Ba	553.8	Perkin-Elmer	4
Ca	422.7	Westinghouse	5
Cd	228.8	Westinghouse	4
Co	241.1	Varian	11
Cr	357.9	Varian	2
Cu	324.7	Varian	4
Fe	248.3	Varian	6
Li	671.1	IL	3
Mg	285.1	Westinghouse	1
Mn	279.5	EEL	3
Mo	313.3	Westinghouse	3
Na	589.0	Westinghouse	3
Ni	231.9	Westinghouse	11
Pb	283.2	Westinghouse	3
Si	251.6	Perkin-Elmer	4
Sn	224.5	Westinghouse	5
Sr	460.9	Perkin-Elmer	5
Ti	364.3	Perkin-Elmer	5
V	318.4	Perkin-Elmer	4
Zn	213.6	Westinghouse	5

Figure 83 - Recovery of 25 ng Au with NaCl sputtered from a copper cathode. For other details see Tables 36 and 37.

Figure 84 - Recovery of 10 ng Ag with NaCl sputtered from a copper cathode. For other details see Tables 36 and 37.

Figure 85 - Recovery of 150 ng Pb with NaCl sputtered from a copper cathode. For other details see Tables 36 and 37.

Figure 86 - Recovery of 150 ng Pb with CaCl_2 sputtered from a copper cathode. For other details see Tables 36 and 37.

Figure 87 - Recovery of 150 ng Pb with MgCl_2 sputtered from a copper cathode. For other details see Tables 36 and 37.

Figure 88 - Recovery of 150 ng Pb with separate matrices of NaCl (■), CaCl_2 (●) and MgCl_2 (▲) sputtered from a copper cathode. For other details see Tables 36 and 37.

Figure 89 - Interference of NaCl with Au taken as the chloride in an aqueous solution: (a) 50 ng of Au; (b) 50 ng of Au + 10 μ g of NaCl. Cathodeon hollow-cathode lamp; hollow-cathode lamp current, 12 mA; for other details see Tables 36 and 37. (c) Discharge voltage for parts a and b. The time scale of part c is not the same as that of a and b.

discharge voltages for Figure 89a and 89b. Since parts a and b of Figure 89 were obtained using the Perkin-Elmer spectrophotometer, it was not possible to obtain the simultaneous absorbance and voltage traces that were obtained by using the Varian-Techtron spectrophotometer, and therefore, the time scale of parts a and b of Figure 89 does not match that of Figure 89c.

Figure 89 is similar to the results obtained by Riby and Harnly [164] for the effect of the concentration of NaCl on the discharge voltage profile for hollow anode - furnace atomization nonthermal excitation spectrometry. In this technique a graphite furnace is used for sample atomization, while a glow discharge formed by a central coaxial graphite cathode is used for sample excitation. Riby and Harnly found that as the concentration of NaCl increased, the discharge voltage decreased until the discharge was entirely shorted, after which the discharge voltage returned to its original value as the NaCl disappeared and the discharge current was again carried by the inert gas ions (He^+ or Ar^+). The disappearance of the NaCl thus seemed to be connected to the presence of large numbers of electrons resulting in a low voltage arc instead of a stable glow discharge. From Figure 89, it seems that the interference being observed is a result of arcing to the NaCl matrix on the cathode surface. Once most of the NaCl has been removed the arcing stops and the discharge voltage increases to the point where cathodic sputtering by the argon ions begins. The appearance of the Au atomic absorption signal in Figure 89 coincides with the steep rise in the discharge voltage as the NaCl disappears and the discharge current is again carried by the Ar^+ ions instead of the electrons.

Figure 88 shows the peak-height recovery of Pb atomized from a copper cathode

in the presence of separate matrices of NaCl, CaCl₂ and MgCl₂. From this figure it seems that all the chlorides have a similar effect on the Pb peak-height absorbance, with the alkali earth chlorides giving a somewhat more severe interference than NaCl.

Figures 90 - 96 show the sequence of changes in the absorbance profile and the discharge voltage for 25 ng of Au atomized from a copper cathode with increasing mass of NaCl present; the hollow-cathode lamp current was 10 mA. Figure 90a is the absorbance profile for 25 ng Au without NaCl, Figure 90b is the corresponding discharge voltage profile. Figure 91 gives the absorbance and discharge voltage profiles for 25 ng Au in the presence of 0.5 μ g NaCl, Figure 92 is for 25 ng Au in the presence of 2 μ g NaCl, Figure 93 is for 25 ng Au in the presence of 3.325 μ g NaCl, Figure 94 is for 25 ng Au in the presence of 5 μ g NaCl, Figure 95 is for 25 ng Au in the presence of 10 μ g NaCl and Figure 96 gives the absorbance profile only for 25 ng Au in the presence of 25 μ g NaCl. From Figures 89 - 96 it can be seen that the discharge becomes more and more unstable with increasing mass of NaCl present on the cathode surface as a solution residue. From these figures it can also be seen that the peak-height absorbance (and the reduction in the peak-area absorbance) follows closely the discharge voltage. It thus seems that the discharge and the peak-height absorbance of gold atoms is very sensitive to the presence of NaCl, as the presence of even 0.5 μ g of NaCl on the cathode surface (Figure 91) causes a substantial reduction in the peak-height absorbance, despite the fact that the discharge voltage shows no obvious signs of instability at this point. Figure 91b does, however, show that there is a slight distortion of the rising portion of the discharge voltage profile compared to Figure 90b.

Figure 90a - Absorbance profile for 25 ng Au. For other details see Tables 36 and 37.

Figure 90b - Discharge voltage for 25 ng Au. For other details see tables 36 and 37.

Figure 91a - Absorbance profile for 25 ng Au + 0.5 μ g NaCl. For other details see Tables 36 and 37.

Figure 91b - Discharge voltage for 25 ng Au + 0.5 μ g NaCl. For other details see Tables 36 and 37.

Figure 92a - Absorbance profile for 25 ng Au + 2 μ g NaCl. For other details see Tables 36 and 37.

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Figure 92b - Discharge voltage for 25 ng Au + 2 μ g NaCl. For other details see Tables 36 and 37.

Figure 93a - Absorbance profile for 25 ng Au + 3.325 μ g NaCl. For other details see Tables 36 and 37.

Figure 93b - Discharge voltage for 25 ng Au + 3.325 μ g NaCl. For other details see Tables 36 and 37.

Figure 94a - Absorbance profile for 25 ng Au + 5 μ g NaCl. For other details see Tables 36 and 37.

Figure 94b - Discharge voltage for 25 ng Au + 5 μ g NaCl. For other details see Tables 36 and 37.

Figure 95a - Absorbance profile for 25 ng Au + 10 μ g NaCl. For other details see Tables 36 and 37.

Figure 95b - Discharge voltage for 25 ng Au + 10 μ g NaCl. For other details see Tables 36 and 37.

Figure 96 - Absorbance profile for 25 ng Au + 25 μ g NaCl. For other details see Tables 36 and 37.

Figure 97 shows the recovery (peak height and peak area) for Fe atomized from a copper cathode in the presence of $\text{Ni}(\text{NO}_3)_2$. In contrast to NaCl, no change was observed in the discharge voltage up to the maximum amount of $\text{Ni}(\text{NO}_3)_2$ matrix investigated, which was 1000 ng. Although no distortion of the discharge voltage profile was observed, the peak-height recovery was still unacceptable for all masses of $\text{Ni}(\text{NO}_3)_2$ matrix examined, whereas no interference was observed for peak-area absorbance for all masses of $\text{Ni}(\text{NO}_3)_2$ matrix examined. Figure 97 also shows the superiority of peak-area absorbance over peak-height absorbance for the analysis of real samples, since peak-area absorbance is not as subject to variations as a result of change in the kinetics of sample atomization/entry into the analysis volume as the peak-height absorbance is.

The superiority of peak-area absorbance over peak-height absorbance with respect to matrix interferences is confirmed by Figure 98. Figure 98 gives the recovery (peak height and peak area) for Fe atomized from a copper cathode in the presence of NaCl. Satisfactory recoveries are obtained for peak-area absorbance for all masses of the NaCl matrix examined (1000 ng maximum), whereas peak-height recoveries are all unsatisfactory. Figure 99 gives the recovery (peak height and peak area) for Fe atomized from a graphite cathode in the presence of NaCl. Recoveries were unsatisfactory for both peak height and for peak area for all masses of the NaCl matrix examined, with peak-area absorbance giving slightly better recoveries than peak-height absorbance. Thus, for the NaCl matrix, the use of a copper cathode and peak-area absorbance is preferred.

The last study of matrix interference was to examine the effect that various acids

Figure 97 - Recovery of 10 ng Fe with $\text{Ni}(\text{NO}_3)_2$ sputtered from a copper cathode. For other details see Tables 36 and 37. (■) Peak-height absorbance; (●) peak-area absorbance.

Figure 98 - Recovery of 10 ng Fe with NaCl sputtered from a copper cathode. For other details see Tables 36 and 37. (■) Peak-height absorbance; (●) peak-area absorbance.

Figure 99 - Recovery of 10 ng Fe with NaCl sputtered from a graphite cathode. For other details see Tables 36 and 37. (■) Peak-height absorbance; (●) peak-area absorbance.

have both on the cathode surface and on the atomic absorption of Fe deposited as a solution residue and sputtered from the cathode surface. It should be noted that although the stock solutions are prepared to contain 1 % (v/v) of the acid used to dissolve the metal or its salt, the test solutions are normally (in the absence of acid added for these matrix interference studies) merely diluted to the required volume with ultrapure water. Both peak height and peak-area absorbance were used, with copper and graphite being the cathodes used. The acids examined were HNO_3 , HCl , H_2SO_4 and HF as these are acids that are commonly used for sample dissolution.

Figure 100 gives the recovery (peak height and peak area) for Fe atomized from a copper cathode in the presence of nitric acid. Both peak height and peak area absorbance gave unsatisfactory recoveries at all concentrations of nitric acid examined, although peak area gave better recovery than peak height. That there is a severe interference should not be very surprising since even very dilute nitric acid reacts with metallic copper (especially freshly exposed copper), thus the surface would be changed and a large amount of $\text{Cu}(\text{NO}_3)_2$ would be present on the cathode surface along with the analyte. Even for 1 % HNO_3 , the sample solution was observed to react with the copper cathode and the solution turned blue (due to the formation of $\text{Cu}(\text{NO}_3)_2$). The discharge voltage was observed to be lower than in the absence of nitric acid but otherwise appeared normal. Sample atomization was incomplete, as evidenced by the visually identifiable residue of the sample solution left on the cathode surface after atomization. For 10 % nitric acid, there was much more $\text{Cu}(\text{NO}_3)_2$ formed on the cathode surface. The discharge voltage was initially unstable, then stable but higher than in the absence

Figure 100 - Recovery of 10 ng Fe with HNO₃ sputtered from a copper cathode. For other details see Tables 36 and 37. (■) Peak-height absorbance; (●) peak-area absorbance.

of nitric acid. Very little of the sample solution residue appeared to have been atomized. Figure 101 gives the recovery (peak height and peak area) for Fe atomized from a graphite cathode in the presence of nitric acid. Recoveries are again unsatisfactory for both peak height and for peak area with peak area giving better recovery than peak-height absorbance. The reason for the recoveries greater than 100 % (154 ± 16 % for peak height, 194 ± 3 % for peak area) for Fe atomized in the presence of 50 % (v/v) nitric acid is not known.

Figure 102 gives the recovery (peak height and peak area) for Fe atomized from a copper cathode in the presence of HCl. Both peak height and peak-area absorbance gave unsatisfactory recoveries, with peak area giving better recoveries than peak-height absorbance. Formation of some CuCl_2 on the cathode surface was observed, and the discharge voltage was unstable at higher concentrations of HCl. Figure 103 gives the recovery (peak height and peak area) for Fe atomized from a graphite cathode in the presence of HCl. In contrast to the results obtained with a copper cathode, both peak height and peak-area absorbance gave satisfactory recoveries for all concentrations of HCl examined when atomized from a graphite cathode, thus showing that the choice of cathode material can have a dramatic effect on matrix interferences. It is not known if this is strictly a chemical effect due to the differing reactivity of the cathode material to the matrix or if there is also an effect due to the different resistance of the different cathodes.

Figure 104 gives the recovery (peak height and peak area) for Fe atomized from a copper cathode in the presence of sulphuric acid. It can be seen from this figure that

Figure 101 - Recovery of 10 ng Fe with HNO₃ sputtered from a graphite cathode. For other details see Tables 36 and 37. (■) Peak-height absorbance; (●) peak-area absorbance.

Figure 102 - Recovery of 10 ng Fe with HCl sputtered from a copper cathode. For other details see Tables 36 and 37. (■) Peak-height absorbance; (●) peak-area absorbance.

Figure 103 - Recovery of 10 ng Fe with HCl sputtered from a graphite cathode. For other details see Tables 36 and 37. (■) Peak-height absorbance; (●) peak-area absorbance.

Figure 104 - Recovery of 10 ng Fe with H₂SO₄ sputtered from a copper cathode. For other details see Tables 36 and 37. (■) Peak-height absorbance; (●) peak-area absorbance.

both peak height and peak-area absorbance gave unsatisfactory recoveries for acid concentrations up to 10 % (v/v) of sulphuric acid, although again peak-area absorbance gave better recoveries than peak-height absorbance. Figure 105 gives the recovery (peak height and peak area) for Fe atomized from a graphite cathode in the presence of sulphuric acid. Peak-height absorbance gave unsatisfactory recoveries for all concentrations of sulphuric acid examined. Peak-area absorbance gave satisfactory recovery for up to 1 % (v/v) sulphuric acid, after which the recovery was unsatisfactory. For sulphuric acid, for both peak height and peak-area absorbance, the recoveries were better for graphite cathodes than for copper cathodes. The sample solutions took a long time to dry, especially the solutions containing 10 % (v/v) sulphuric acid. An infrared lamp could not be used to dry the sample with the copper cathode since the copper cathode was highly polished and reflected the radiation from the lamp. For the graphite cathode drying times for the 10 % (v/v) sulphuric acid solution were ~ 1 hour when air dried, and ~ 20 minutes when dried under the infrared lamp. Drying under the infrared lamp was found to cause the sample to spread outside the cavity, where it would not be subjected to sputtering, and would thus be lost.

Figure 106 gives the recovery (peak height and peak area) for Fe atomized from a copper cathode in the presence of HF. Peak-height absorbance gave unsatisfactory recovery for all concentrations of HF examined. Peak-area absorbance gave satisfactory recovery up to 1 % (v/v) HF, after which the recovery was unsatisfactory. Figure 107 gives the recovery (peak height and peak area) for Fe atomized from a graphite cathode in the presence of HF. The results are similar to those obtained for the copper cathode,

Figure 105 - Recovery of 10 ng Fe with H₂SO₄ sputtered from a graphite cathode. For other details see Tables 36 and 37. (■) Peak-height absorbance; (●) peak-area absorbance.

Figure 106 - Recovery of 10 ng Fe with HF sputtered from a copper cathode. For other details see Tables 36 and 37. (■) Peak-height absorbance; (●) peak-area absorbance.

Figure 107 - Recovery of 10 ng Fe with HF sputtered from a graphite cathode. For other details see Tables 36 and 37. (■) Peak-height absorbance; (●) peak-area absorbance.

with unsatisfactory peak-height recovery and satisfactory peak-area recovery up to 1 % (v/v) HF. The recoveries are better for both peak height and for peak-area absorbance using the graphite cathode as opposed to the copper cathode. For both cathodes, it was difficult to deposit the sample solution such that it did not spread outside of the cavity.

RF sputtering

Virtually all analytical work up to this time using cathodic sputtering atomization has been done using either conducting solid samples or solution residues from aqueous standard solutions of elements atomized from a conducting cathode. It is known that the direct analysis of solids using cathodic sputtering atomization is limited only to conducting samples. Thus, while W and Al *metal* may have similar sputtering yields, the sputtering yield for these elements (or any other element for that matter) in a non-conducting matrix is zero by conventional dc sputtering, since conventional dc sputtering is unable to sputter non-conductors. Thus, although the application of cathodic sputtering atomization to atomic spectrometry by dc sputtering is promising, it is limited to only conducting samples or samples that can be made conducting by mixing with conducting matrices.

So far, there have been two approaches to the analysis of non-conductors using cathodic sputtering atomization. One of these is to make the sample conducting by pelletizing it with a conducting matrix, usually copper or graphite powder [58, 64, 138, 165]. This procedure requires much more sample preparation than if the non-conducting solid could be directly determined, and is therefore more time consuming; this procedure also introduces the risk of sample contamination, which is a serious problem in trace

analysis. The sensitivity also suffers because the sample is diluted with the conducting matrix. A better solution to the problem is to use radiofrequency (rf) sputtering [67, 89, 90, 95, 96] instead of the dc sputtering normally used for cathodic sputtering. RF sputtering has been reported to be capable of directly atomizing various conducting and non-conducting substances, including various glasses [96, 166, 167], macor ceramic [166], shale, granite, paper, rubber and sodium chloride [167].

All of the experiments using the rf power supply reported in this thesis were performed with the rf atomizer, which is the modified Atomsources, as described in the Experimental section. All rf glow discharges in the atomizer were observed to be an orange-pink colour, regardless of the cathode and the experimental conditions employed. This is in contrast to our observations of dc glow discharges in the unmodified Atomsources atomizer, the colours of which have been found to vary with the cathode and the various experimental parameters, such as the pressure and the applied power. Unlike dc glow discharges, in rf sputtering, plasma was observed in the atomizer vacuum line, the length of which increased with increasing incident rf power up to a length of approximately 1 metre. Plasma was also observed in the atomizer gas line, but it did not extend beyond the sheet aluminum shielding at any time. It should be noted that the values of rf power quoted are those shown on the analog incident rf power meter on the power supply, the actual power delivered to the sample cathode is not known.

Results obtained by rf sputtering for Cu and Ni in the National Bureau of Standards (NBS), Standard Reference Material (SRM) # 1264a, High Carbon Steel showed an increase in absorbance with increasing rf power up to 400 W at 10 Torr Ar

discharge gas pressure. For both of these elements, the signal to noise ratio decreased with increasing rf power until the signal became almost indistinguishable from the noise. The absorbance of Ni in pure copper (known to be spectroscopically clean for Ni) produced results identical to that obtained for Ni in steel. It was therefore decided to see if the above results had been produced by leakage of stray rf radiation and its interference with the detection system electronics.

Current Canadian government guidelines [168] for exposure times and levels for microwave radiation workers in the frequency range 10 MHz-1 GHz limits the maximum emitted field strength (equivalent power density) of 1 mW/cm^2 for continuous exposure. Measuring with a field strength meter manufactured by Narda, model No. 8616, and electric and magnetic field strength probes, Narda models No. 8662B and 8623, respectively, it was found that the magnetic field strength of the rf atomizer was negligible for all conditions investigated; however, the plasma inside the atomizer vacuum line was found to radiate unacceptable electric field strengths. Wrapping the atomizer vacuum line with Al foil reduced the emitted field strength to near zero, but the Al foil rapidly heated up to the point where there was concern that the polyethylene vacuum tubing would melt. The Al foil was therefore replaced with steel wool. The steel wool did not heat up appreciably, and it was found to limit the emitted field strength to $< 2 \text{ mW/cm}^2$ at incident rf powers up to 600 W. This was deemed to be sufficient, considering that these measurements were taken approximately 3 cm from the atomizer vacuum line, whereas the operator is several tens of cm away. With the atomizer vacuum line shielded, the absorbance of Ni in pure copper was found to be zero with no

change in noise from baseline for incident rf powers up to 600 W. It would therefore seem that some component of the detection system had been earlier interfered with by the stray rf radiation and that adequate shielding of the atomizer vacuum line solved this problem.

Figure 108 shows the peak-height absorbance vs. incident rf power, with pressure as a parameter, for Al in NBS SRM # 1263a, Cr-V Steel. All absorbances shown and discussed are peak-height absorbances. The absorbance increases with increasing incident rf power up to 200 W at all pressures, the characteristic concentration decreasing with decreasing pressures. This is not entirely unexpected since rf discharges can be sustained and are normally operated at the lower end of their pressure range [168], from 1-40 mTorr, i.e. up to two orders of magnitude lower pressure than currently used. Figure 109 shows the absorbance vs. incident rf power, with pressure as a parameter for Al in NBS SRM # 1412, Multicomponent Glass. At higher pressures, the curves are similar to those shown in Fig. 108 for Al in steel. At lower pressures, a plateau develops when a further increase in the incident rf power does not result in a further increase in the absorbance. For Al in glass at 4 Torr the plateau starts at 100 W incident rf power, at 6 Torr the plateau starts at 150 W incident rf power, whereas no plateau is observed at higher pressures up to 500 W incident rf power. This suggests that the rf discharge is more stable at lower pressures than higher pressures for the rf atomizer.

The above results also suggest that the rf atomizer used for the rf sputtering was not very suitable - the result was that the rf sputtering was very inefficient and that most of the incident power was dissipated in the plasma rather than utilized in sputtering the

Figure 108 - Peak-height absorbance vs. rf power for Al in NBS SRM # 1263a, Cr-V Steel. ■ 4 Torr, ◆ 6 Torr, ▲ 8 Torr, + 10 Torr, × 12 Torr.

Figure 109 - Peak-height absorbance vs. rf power for Al in NBS SRM # 1412, Multicomponent Glass. ■ 4 Torr, ◆ 6 Torr, ▲ 8 Torr, + 10 Torr, × 12 Torr.

sample, with the result that the Delrin atomizer body could melt if one was not careful enough to avoid sputtering over extended periods of time. This conclusion is consistent with the observed dependence of the plasma in the atomizer vacuum line on the incident rf power. The results obtained indicate that at pressures less than 4 Torr, the power required to produce the optimum sensitivity would be less than 100 W rf with this rf atomizer. The use of small rf power is advantageous from the point of view of leakage of stray rf radiation. Other advantages of using small rf powers are the use of small power supplies and the required amount of cooling of the sample. Although the sample is in contact with the water-cooled cathode plate, a non-conductor is unable to transfer effectively the heat to the cold cathode plate as a conductor can.

The fundamental problem with this rf atomizer is, however the lack of a substantial dc bias potential on the cathode. Chapman [169] and Winchester et al. [67] have discussed the theoretical and experimental considerations, respectively, for rf sputtering sources. The dc bias potential that develops on the electrodes and therefore, the amount of sputtering that will occur at a given electrode in an rf sputtering system is inversely proportional to the area of the electrode in contact with the plasma, hence, the anode should be made extremely large compared to the cathode. The ratio of the anode/cathode areas of the rf atomizer has been determined to be ~ 9 , which is too small to allow a significant bias potential to be established on the cathode. The result is inefficient power coupling to the cathode, with the result that, as noted, most of the incident rf power is actually applied to the plasma rather than the cathode to produce atoms by cathodic sputtering. This explains why such large incident rf powers are

required to produce the small amount of cathodic sputtering observed. The results obtained with the present rf system are therefore not very reliable and are included only to show that non-conductors can be sputtered directly using rf sputtering, and that the development of an rf atomizer for atomic absorption spectrometry is in fact feasible and should be undertaken. The rf sputtering of solution residues was investigated using the rf atomizer. It was found that the efficiency of the present rf system is too low to permit substantial sputtering of a solution residue.

Another problem with the rf atomizer is that it has a complicated design with the presence of gas jets and the presence of multiple potential electrodes (any surface in contact with the plasma), such as the cathode, the anode, the arrester, the accelerator and the atomizer body. An attempt has been made to increase the ratio of the anode/cathode areas by replacing the central portion of the atomizer body with an anodized aluminum block; this will be referred to as the new rf atomizer. The ratio of the anode/cathode areas for the new rf atomizer is estimated to be ~ 55 . Power was applied direct to the cathode in the new rf atomizer. No results have been obtained with the new rf atomizer, and it is recommended that a simpler atomizer with all hard connections [170] be used for any future rf sputtering studies.

A problem that has been encountered when working with most of the non-conducting samples, particularly the brittle ones, is that they often break when tightly clamped to the atomizer cathode plate; if not tightly clamped they tend to leak. The cathode was therefore embedded in a resin, which seemed to work well, although it does require some sample preparation and hence, more time. An easier solution is to have

a sheet of a rigid backing material so that the pressure of the sample clamp is evenly distributed across the entire sample. A conductor is preferred for this purpose since it facilitates uniform rf power distribution over the sample cathode [170].

It was mentioned that the rf discharge established in the rf atomizer appeared to be more stable at lower pressures. Another problem encountered when working at higher pressures is shown in Figure 110. The absorbance profiles shown in Figure 110 are from the data for Figure 109. Figure 110a shows two absorbance vs. time profiles at 4 Torr for Al in NBS SRM # 1412 Glass. Profile a is for 50 W incident rf power and profile b is for 200 W incident rf power. There is a slight increase in noise with increasing incident rf power at a constant pressure. Figure 110b shows two absorbance vs. time profiles for Al in NBS SRM # 1412 Glass. Profile a is for 6 Torr, 50 W incident rf power, and profile b is for 10 Torr, 400 W incident rf power. Comparison of Figures 110a and 110b shows that the large increase in the noise is mostly probably due to the increased pressure and not to the increased incident rf power. Note that for Figure 110b, comparison of absorbance profiles for the two different pressures at 50 W incident rf power could not be done because of the large difference in sensitivity, as shown in Figure 109. Without exception, it has been found that the noise increases with increasing pressure, probably because of increasing instability of the discharge plasma at higher pressures. The characteristic concentration decreases (becomes better) with decreasing pressure, but the limit of detection decreases (becomes better) much more rapidly with decreasing pressure.

Table 39 gives the characteristic concentrations for various elements in NBS SRM

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Figure 110a - Peak-height absorbance vs. time for Al in NBS SRM # 1412, Multicomponent Glass. a) 4 Torr, 50 W incident rf power. b) 4 Torr, 200 W incident rf power.

Figure 110b - Peak-height absorbance vs. time for Al in NBS SRM # 1412, Multicomponent Glass. a) 6 Torr, 50 W incident rf power. b) 10 Torr, 400 W incident rf power.

Table 39 - Characteristic concentration for elements in NBS SRM # 1412, Multicomponent Glass.

Element	Composition %	Characteristic concentration ppm
Al	3.99	170
B	1.40	290
Ba	4.20	3300
Ca	3.24	-
Cd	3.83	-
Fe	0.021	-
Li	2.09	-
Mg	2.83	-
Na	3.48	-
Pb	4.08	-
Si	16.53	900
Sr	3.85	-
Zn	3.58	10000

- A dash (-) means that the element in question could not be detected.

- Cu, Fe, Mn, Ni and Pb (about 450 ppm each) could not be detected in NBS SRM # 610, Trace Elements in Glass.

1412 Glass. The characteristic concentration is given in ppm by mass of the element present in the SRM. The characteristic concentrations range from the low hundreds of ppm (Al, B, Si) to the thousands of ppm (Ba, Zn). Approximately 450 ppm each of Cu, Fe, Mn, Ni and Pb could not be detected in NBS SRM # 610, Trace Elements in Glass. Table 40 gives the characteristic concentrations obtained for various elements in NBS SRM # 1263a Steel. The characteristic concentrations range from 1.3 ppm for Mo to 770 ppm for Mn, with most of the values being in the low to tens of ppm range. Of interest is the characteristic concentration for Al in steel, which is approximately an order of magnitude more sensitive than the characteristic concentration for Al in glass.

For the elements in Tables 39 and 40 that were not detectable, most were either present in too low a concentration for their detection, or the sensitivity of determination with the Perkin-Elmer hollow-cathode lamps was too low for their detection, or both. The Perkin-Elmer hollow-cathode lamps have been shown [158] to be less sensitive than the Westinghouse-type hollow-cathode lamps when used for atomic absorption spectrometry with atomization by cathodic sputtering in a glow discharge. It has also been shown that the sensitivity of atomic absorption spectrometry using cathodic sputtering atomization is highly dependent on the hollow-cathode lamp current [158]. This dependence has been confirmed for rf sputtering of Al in glass, as can be seen from Figure 111. For many of the elements in Tables 39 and 40 (specifically As, B, Ba, Ca, Li, Na, Si, Sn, Sr, Ti and Zn), the hollow-cathode lamp type and current were not optimized.

Table 41 gives the sputtering rates of glass (microscope slides) as a function of

Table 40 - Characteristic concentration for elements in NBS SRM # 1263a, Cr-V Steel.

Element	Composition %	Characteristic concentration ppm
Al	0.24	19
As	0.010	-
Co	0.048	-
Cr (dc)	1.31	76
Cr (rf)	1.31	46
Cu	0.09	280
Mn	1.50	770
Mo	0.030	1.3
Ni	0.32	35
Si	0.74	-
Sn	0.10	3.4
Ti	0.050	-
V	0.31	-

- A dash (-) means that the element in question could not be detected.

Figure 111 - Peak-height absorbance vs. hollow-cathode lamp current for Al in NBS SRM # 1412, Multicomponent Glass at 6 Torr, 100 W incident rf power.

Table 41 - Sputtering rates for glass and iron for 100 W.

Sample	Mode	Pressure Torr	Weight loss $\mu\text{g/s}$
Glass	rf	4	0.027
Glass	rf	6	0.018
Glass	rf	8	0.022
NBS SRM # 1265a, Electrolytic Iron	rf	8	0.16
NBS SRM # 1265a, Electrolytic Iron	dc	8	40.

pressure, and the sputtering rates, measured at 8 Torr, 100 W (dc and rf) for glass and for NBS SRM # 1265a, Electrolytic Iron. The sputtering rate of glass at 100 W incident rf power shows no obvious dependence on the pressure for the pressure range 4-8 Torr. The dc sputtering rate of glass is zero. Table 41 shows that the sputtering rate of glass is approximately an order of magnitude less than that of iron, which agrees with the difference in characteristic concentration for Al in steel and glass. However, the rf sputtering rate for iron is only 3.5% of the dc sputtering rate for iron under the same experimental conditions. This means that with the present rf instrumentation the rf sputtering efficiency is very low. It has been mentioned that the deficiencies of the present rf instrumentation make these values not very reliable. However, they do serve to show that the use of rf sputtering for atomic absorption spectrometry should be investigated further, since these values should be subject to considerable improvement with better instrumentation.

CONCLUSIONS

It has been shown that there are a number of severe matrix interferences in the atomic absorption spectrometric analysis of solution residues using the commercial Atomsource cathodic sputtering atomizer. Interferences can result from the presence of a matrix (such as NaCl) which readily arcs to give electrons which carry the discharge current without producing significant cathodic sputtering. The atomic absorbance profile is thus delayed until the matrix has dissipated to the point where the argon ions responsible for cathodic sputtering are again able to carry a substantial portion of the

discharge current. Interferences can also occur as a result of chemical reactions between the matrix and the cathode material. Peak-area absorbance has been shown to be much less subject to matrix interferences than peak-height absorbance. Preliminary results of the application of a cathodic sputtering atomizer employing rf sputtering to the direct analysis of conducting and non-conducting solids have been presented. The use of rf sputtering for the direct analysis of conducting and non-conducting solids by atomic absorption spectrometry has been shown to be feasible, despite severe limitations of the present rf instrumentation.

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