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Electron capture negative ion mass spectroscopy (ECNIMS) has been performed on environmental chemicals and explosives. A trochoidal electron monochromator interfaced to a gas chromatograph and a quadrupole mass spectrometer allows compounds to be studied by this method. The method employed here differs from standard ECNIMS in that no reagent gas is used to moderate electron energies.

Several explosives were analyzed using this system, as were chlorinated compounds obtained from the lipid fraction of Arctic trout muscle. A miniaturized version of the system would be advantageous as a portable apparatus for field use. Among the required modifications would be the installation of cylindrical permanent magnets to replace the Helmholtz coils used for generating the magnetic field for the monochromator. Tests suggest that the trochoidal electron monochromator component of the system can be reduced in volume by a factor of 200 without an appreciable loss of energy resolution.
A System for Analyzing and Characterizing Environmental Chemicals and Explosives and a Proposal for its Miniaturization

by

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A System for Analyzing and Characterizing Environmental Chemicals and Explosives
and a Proposal for its Miniaturization

I. Introduction

A. Rationale and Overview

The ability to detect explosives and pesticides in small quantities has gained importance in recent years. Terrorist attacks have occurred against civilian aircraft over the last several years. There is also an increasing awareness in society that the environment of the world has become polluted with a variety of pesticides. Pesticides and explosive compounds have at least one characteristic in common. Both of these classes of compounds can readily capture electrons at very low energy. Pesticides such as heptachlor, hexachlorobenzene, and atrazine have been shown to undergo various electron attachment processes at low electron energy [1]. Explosives such as trinitrotoluene (TNT), PETN, and RDX are also known to undergo various electron capture processes at low electron energy [2]. The interaction of low-energy electrons with explosives is of vital concern. If a system could be designed which could detect explosives on the basis of their electron attachment energies, the airports of the world might operate more safely. The fact that pesticides and explosives display electronic attachment at very low energies is advantageous since it is in this energy region that the trochoidal electron monochromator works most efficiently.

Many basic electron attachment processes exist [3]. Two of these processes dominate at low electron energies. One possible interaction is that the molecule (AB) will undergo resonance electron capture to form the radical molecular anion. This
reaction can be written as

\[ AB + e^- \rightarrow AB^- \]"
This type of reaction can occur above about 7 eV. This is not a process which is of concern in the applications presented here. Ion pair production is not a resonance event like dissociative and nondissociative electron attachment. In ion pair experiments, production will be observed primarily as a background effect.

Electron affinity is generally defined as the energy difference between a neutral molecule at rest plus an electron at rest at infinity and the molecular negative ion [5a]. Both the neutral and the negative ion are assumed to be their ground electronic, vibrational, and rotational states in this definition. The electron affinity can be either positive or negative. When the electron affinity is negative, a related quantity called the vertical attachment energy (VAE) is defined as the difference in energy between the neutral molecule in its ground state plus an electron at rest at infinity and the molecular ion formed by the addition of the electron to the neutral. When the electron affinity is positive, a quantity called the vertical detachment energy (VDE) is defined as the minimum energy required eject the electron from the negative ion residing in its ground state. A molecule which has a positive electron affinity will tend to attach an electron and form a long-lived negative ion. If a molecule has a negative electron affinity, an electron may still attach to the molecule, but the resulting species will have a very short lifetime. In general, the lifetime of a species depends on the size of the potential barrier and the internal energy of the anion. Some examples of molecules which possess positive electron affinity are sulfur hexafluoride, polyhalohydrocarbons, polynuclear aromatics, and explosives.
Atomic helium, carbon monoxide, and diatomic nitrogen are examples of species which have negative electron affinity.

Low-energy electrons must interact with a molecule for various resonance electron capture experiments to be conducted. The experimental apparatus used in the experiments presented here involve two different methods of introducing sample molecules into path of the low energy electrons. The first of these was direct introduction of the sample on a solid probe at the exit aperture of the monochromator. This method allowed rapid determination of the resonant capture energies, but it was difficult to know how much material was actually interacting with the low-energy electrons.
the electrons. To allow for a more quantitative determination a gas chromatograph was interfaced to the system. This interface allows precise amounts of material to be introduced into the apparatus. After the sample had interacted with the electrons produced by the monochromator, the product species were analyzed by a quadrupole mass spectrometer. The basic experimental design is given in Figure 1.

Details on the principle of operation and the construction of the trochoidal electron monochromator will be presented in sections II and III.

B. Gas Chromatograph (GC)

The GC allows precise amounts of material to be inserted into the apparatus. The sample is injected into a region that is then heated. The top of the capillary column is kept at a low temperature which causes the sample to be thermally focused on the column [6]. The principle of thermal focusing is relatively simple. Keeping the column cool while the sample is hot creates a temperature gradient. The hot, fast-moving molecules of the sample arrive at the cold column and slow down. This allows any molecules which have not yet arrived at the column to arrive. When all the molecules have arrived in the cold region, the trailing molecules will be moving faster than the leading molecules since the leading molecules have been in the cold region for a longer period of time. The overall effect is a sharpening of the band which contains the sample.

A reasonably well defined distribution of sample is now heated and passed along the chromatographic column. The column supports both a stationary liquid
phase and a mobile gas phase. The inside of the column is coated with the stationary phase and a carrier gas is passed through the column to create the mobile phase. When the sample is introduced to the column, components which are more easily soluble in or have a stronger affinity for the stationary liquid phase will tend to spend more time in this phase. Those components of the mixture with a lesser solubility in or a lesser affinity for the stationary phase will tend to race ahead of the other components. The components which spend more time in the mobile gas phase will arrive at the end of the column first. In this manner, the separation of various components is achieved. Each of these components can now interact with the low-energy electrons produced by the monochromator.

C. Quadrupole Mass Spectrometer (QMS)

After the molecules interact with the electrons as described by equations (1), (2), and (3), the resulting products are analyzed through the use of a quadrupole mass spectrometer (QMS). The QMS consists of four rods arranged symmetrically as if they were running along the edges of a shoebox with a square cross section. Rods which are diagonally opposite from each other and separated by a distance $2r_0$ are coupled to one another electrically and to radio-frequency (RF) and direct-current (DC) voltage supplies. The theory of operation of the QMS is governed by the Mathieu equations [7]. The derivation of these equations is straightforward.

The potential applied to the electrodes is given by [8]
\[
\Phi = (U + V\cos\Omega t) \frac{x^2 - y^2}{r_0^2}
\] (4)

where \(U\) represents the potential due to the DC voltage and \(V\) is the maximum value of the RF supply at angular frequency \(\Omega\). To find the force on a singly charged ion of mass \(m\), the negative gradient of equation (4) must be taken. Performing this operation and using Newton's Second Law yields the equations of motion in the \(x\) and \(y\) directions. These expressions are given by

\[
m\ddot{x} + 2e(U + V\cos\Omega t) \frac{x}{r_0^2} = 0
\] (5)

and

\[
m\ddot{y} - 2e(U + V\cos\Omega t) \frac{y}{r_0^2} = 0.
\] (6)

To put these into the form of the Mathieu equations, let \(p = \Omega t / 2\), \(a = 8eU/mr_0^2\Omega^2\), and \(q = 4eV/mr_0^2\Omega^2\). In terms of these variables the equations of motion become

\[
\ddot{x} + (a + 2q\cos2p)x = 0
\] (7)

\[
\ddot{y} - (a + 2q\cos2p)y = 0.
\] (8)
In equations (7) and (8), the dots denote differentiation with respect to the variable p. Equations (7) and (8) are the Mathieu equations. It is these equations which govern the operation of the QMS.

This set of equations yields both stable and unstable solutions. If the trajectory is unstable for a particular choice of RF and DC voltages, the ion will collide with the electrode or exit between the electrodes and not arrive at the detector. If the solution is stable for these voltages, the ion will arrive at the detector. This is the basic filtering action of the quadrupole mass spectrometer.

The fundamental operation of the gas chromatograph and the quadrupole mass spectrometer has now been described. The only remaining implement of the system which need be presented is the trochoidal electron monochromator. It is the presentation of this device to which sections II and III shall be devoted.
II. Principle of Operation of an Electron Monochromator

The purpose of an electron monochromator is to produce monoenergetic electrons with a relatively small energy spread. One way of achieving this goal is to pass an electron through electric and magnetic fields which are perpendicular to one another. This type of device was first described by Stamatovic and Schulz in 1970 [9]. As described by Stamatovic and Schulz, the device analyzed was capable of producing electrons with specific energies with an energy width at half-maximum of 0.020 eV and a transmitted current of approximately $10^{-9}$ amperes.

An electron which traverses a configuration in which electric and magnetic fields are perpendicular to one another will undergo a trajectory which falls into a class of curves described mathematically as trochoids.

A. Equations of Motion for a Particle in a Crossed Field Monochromator

The equation of motion for a charged particle moving in electric and magnetic fields is generated using the Lorentz force law. In SI units

$$ F = e \left( E + v \times B \right), \quad (9) $$

where $F$ is the force on the particle, $e$ is the charge of an electron, $E$ is the electric field vector, $v$ is the velocity of the particle, and $B$ is the magnetic field vector. If Newton’s second law is applied to equation (9), the expression becomes
\[ ma = e \left( E + v \times B \right). \quad (10) \]

Now consider the case where the magnetic field is given by \( B = Bz \) and \( E = Ey \) where \( B \) indicates the magnitude of the magnetic field and \( E \) indicates the magnitude of the electric field which lies perpendicular to the magnetic field. If we parameterize the equations of motion in terms of a time, \( t \), \([10]\) we have as solutions

\[
x(t) = x_0 - A \sin(\omega t + \phi) + \frac{E}{B} t, \quad (11)
\]

\[
y(t) = y_0 + A \cos(\omega t + \phi), \quad (12)
\]

and

\[
z(t) = z_0 + \sqrt{\frac{2W_{||}}{m}} t + \left( \frac{eE_{||}}{2m} \right) t^2, \quad (13)
\]

where \( \omega = eB/m \) is the electron cyclotron frequency, \( W_{||} \) is the particle's kinetic energy parallel to the B field, and A, \( x_0 \), \( y_0 \), \( z_0 \), and \( \phi \) are integration constants to be determined by the initial conditions for given field strengths. If we consider a particle on the z-axis at time \( t=0 \) with a general velocity \((v_{ox}, v_{oy}, v_{oz})\) and \( E_{||}=0 \), then the equations of motion become

\[
x(t) = -A \left[ \sin(\omega t + \phi) - \sin\phi \right] + v_dt + x_o, \quad (14)
\]

\[
y(t) = A \left[ \cos(\omega t + \phi) - \cos\phi \right] + y_o, \quad (15)
\]
and

\[ z(t) = v_0 t, \quad \text{(16)} \]

where

\[ \tan \phi = \frac{-v_{0y}}{v_D - v_x}, \quad \text{(17)} \]

\[ A = \frac{v_{0z} - v_D}{\omega \cos \phi}, \quad \text{(18)} \]

and

\[ v_D = \frac{|E \times B|}{B^2} = \frac{E}{B}. \quad \text{(19)} \]

Analysis of equations (14), (15), and (16) shows that the particle will follow a trochoidal path, essentially a spiral-type motion. For the case \( \phi = 0 \) we see that the trajectory will be that of a cycloid in the x-y plane. If \( \phi \) is not zero, then this motion will be combined with uniform motion in the z direction given by \( v_{0z} \). The constant of integration \( A \) determines the amplitude of the cycloid and is seen to be proportional to \( E, B, \) and \( m/e \). In general, the particle will tend to spiral about a line in the x-direction which corresponds to the drift velocity, \( v_D \). At the exit of the monochromator, the direction of the electron's motion is still essentially the same as that of the magnetic field, but it is displaced from the z axis. It is this aspect of the trochoidal electron monochromator which allows it to be used as a device for selecting electrons of various energies. The displacement \( D \) from the incident axis is
proportional to the amount of time which the electron spends in the crossed-field region of the monochromator (Figure 2).

\[ D = v_D t \]  \hspace{1cm} (20)

where \( t \) is the time which the electron spends in the crossed-field region whose length is \( L \). This time is given by \( t = L / v_{0z} \). If we consider an electron entering the field with a kinetic energy given by
\[ W = \frac{1}{2} m v_{ox}^2, \quad (21) \]

then the time the electron spends in the crossed-field region can be expressed as

\[ t = L \left( \frac{m}{2W} \right)^{\frac{1}{2}}. \quad (22) \]

If equations (20) and (22) are combined we obtain

\[ D = \frac{v_D L}{v_{ox}} = v_D L \left( \frac{m}{2W} \right)^{\frac{1}{2}}. \quad (23) \]

The partial derivative with respect to \( W \) needs to be taken for the energy spread to be examined. This operation yields

\[ \frac{\partial D}{\partial W} = \frac{v_D L}{m} \left( \frac{m}{2W} \right)^{\frac{3}{2}}. \quad (24) \]

If we consider finite changes in displacement and energy spread rather infinitesimal elements, then the equation can be expressed as

\[ \frac{\Delta D}{\Delta W} = -\frac{v_D L}{m} \left( \frac{m}{2W} \right)^{\frac{3}{2}}. \quad (25) \]

If we multiply both sides of the equation by \( 2/D \) and insert the expression given in equation (23) for \( D \) on the right hand side of the equation then we have

\[ \frac{2\Delta D}{D} = -\frac{v_D L}{m} \left( \frac{m}{2W} \right)^{\frac{3}{2}} \frac{2}{v_D L \left( \frac{m}{2W} \right)^{\frac{1}{2}}} \Delta W. \quad (26) \]
When equation (26) is simplified, it leads to the following expression for the relative energy spread [11]:

\[
\frac{2 \Delta D}{D} = \frac{\Delta W}{W}.
\]

In this expression, \(W\) refers to the electron energy, \(\Delta W\) is the spread in the energy of the emerging electrons and \(\Delta D\) is the sum of the aperture diameters \(S_1\) and \(S_2\).

Some of the basic characteristics of the monochromator can be determined by analyzing equation (27). The left hand side of equation (27) is fixed by the construction of the monochromator. Thus, the right hand side must be equal to this constant for all possible values. Hence, if \(W\) is large, then \(\Delta W\) must be large as well. Since the lowest energy spreads are desirable, the monochromator should be run at low energies. There is an additional spread in the energy due to the electric field. A velocity spread is introduced into the incident beam due to the potential drop across the beam. The maximum potential drop across the beam is given by \(ES_1\) where \(S_1\) is the diameter of the entrance aperture (Figure 2).

Another contribution to the spread in the distribution of electron energies is the angular divergence of the incident beam. If we include the angular divergence, \(\gamma\), of the incident beam, then we must replace \(v_0z\) with \(v_0 \cos \gamma\) [12]. With this factor taken into account, equation (27) becomes:
If we include the additional energy spread due to the potential drop across the entrance aperture, then the expression for the width of the energy distribution at its base is given by

\[
\Delta D = \frac{\Delta W}{W} \cdot (28)
\]

This expression yields, within the limits of the first order approximation, theoretical values for the energy spread in a crossed field monochromator. It is worth reiterating that this is the width at the base of the energy distribution. Generally, the width at half maximum is measured, which will be less than the values which this expression would predict. Stamatovic and Schulz suggest dividing this expression by 2.5 to 3.5 to get an accurate expression for the full width at half maximum.

B. Comparison of Theory with Experiment

On the basis of equation (23), the energy of electrons passed by the electron monochromator can be predicted. This energy is given by

\[
W = \frac{1}{2} m \left( \frac{EL}{BD} \right)^2 . \quad (29A)
\]

All of the variables on the right side of equation (29A) are easily obtained from the design of the instrument. With \( m = 9.11 \times 10^{-31} \text{ kg} \), \( L = 1.9 \text{-cm} \), \( D = 3.19 \text{-mm} \), \( B = 1.30 \times 10^{-2} \text{ T} \), and \( E = 25 \text{ V/cm} \), a value of 3.73 eV is obtained for the energy
of the electrons being passed by the trochoidal electron monochromator. This result agrees with the following experimental data. To pass 0.03 eV electrons through the electron monochromator, an offset of approximately 4 eV is observed. This result is obtained by analyzing the electron attachment spectrum of hexafluorobenzene (C₆F₆) which will undergo electron attachment processes at 0.03 eV among others (see section III). There are several factors which may cause this offset to occur.

All of the voltages in the monochromator are held constant relative to the filament potential. In order for an electron to be emitted from the filament, the electron must acquire an energy which exceeds the work function of the filament material. (The concept of the work function will be explained more thoroughly in section V.) The work function of the filament used in the experiment analyzed above is 2.7 eV. Near-zero-energy electrons will tend to accumulate near the cathode. Since these electrons will proceed toward the monochromator very slowly, space charge effects are likely to occur. The space charge effect is likely responsible for much of the offset referred to above. The remainder of the offset is most likely due to contact potentials in the apparatus.

C. Determining the Kinetic Energy of the Electrons

The electrons entering the monochromator are emitted by a filament. The distribution of the thermal emission of the electrons is governed by a Boltzmann distribution. The electron monochromator passes electrons whose energies have a range given by equation (29). Electrons having energies greater than the work
function of the filament will be emitted. These electrons can now be accelerated into the monochromator region as necessary. If electrons other than those near zero energy are required, the filament potential must be augmented using a floating potential attached to the center of the filament. The floating potential can then be scanned to produce electrons with the required energies.
III. Design of a Complete System for Analysis of Environmental Chemicals and Explosives

A. Experimental Considerations

The design of the system is based on a design utilized by Illenberger and co-workers [13]. The sample is injected into a gas chromatograph (Hewlett-Packard 5710A) interfaced to one side of the electron monochromator. The other side of the electron monochromator is interfaced to the mass spectrometer (Hewlett-Packard 5982A). The electron optic components used to focus the electron beam were made of 99.999% pure molybdenum. The remaining components were made of 303 stainless steel with the exception of the filament holder which was made of oxygen-free high conductivity (OFHC) copper. The electrodes and the deflectors were machined with six equally spaced holes of 1.2-mm diameter on a 13-mm bolt center diameter. The thickness of the electrodes and the deflectors is 1.6-mm and 19-mm respectively. The holes around the perimeter of the electrodes and deflectors serve as seats for 1.6-mm diameter sapphire spheres (General Ruby and Sapphire, New Port Richey, FL). These spheres act not only to maintain the separation of the various electron optic components, but also as insulators. The monochromator and a 2% thoriated tungsten filament of 0.15-mm diameter are held together by two end plates. These plates are held together by four bolts. The complete assembly is spring-mounted on three supports to a six-inch flange in which a 20-pin feedthrough (Ceramaseal, New Lebanon, NY) is housed. The system is pumped by six-inch and
four-inch oil diffusion pumps. A base pressure of $10^{-8}$ torr is achieved under these conditions. Figure 3 shows the entire configuration.

![Figure 3: Schematic diagram of the gas chromatograph / electron monochromator / mass spectrometer system.](image)

The electrons are emitted by the filament and are then collimated by the four electrodes which precede the crossed-field region. The final three of these electrodes form an Einzel lens configuration. The four electrodes and the filament are offset 3.18-mm from the center of the ion chamber. This is the value of the variable $D$ referred to in section II. The apertures of the electrodes have diameters of 3.18-mm, 1.0-mm, 1.0-mm, and 1.0-mm in sequence. Two charged plates of length $L = 1.9$-cm serve to create the electric field $E$ necessary for the monochromator. A field of
about 0.4 V/cm is established, although this can be varied as needed. The magnetic field $B$ is generated by a pair of Helmholtz coils (Western Transformer, Portland, OR) external to the vacuum system. The two parallel coils are configured such that the separation between them is equal to their radius. This is the Helmholtz geometry, which creates a nearly uniform axial field at its center, where the monochromator is located. In the central field region the field is related to the current $I$ by $B = \frac{(4/5)^{3/2} \mu_0 NI}{R}$ in SI units, where $N$ is the number of turns per coil and $\mu_0$ is the permeability of free space. With $N = 96$ turns of double stranded #4 copper wire.

**Figure 4:** Configuration of Helmholtz coils with current $I$. The origin is located such that it is a distance $R/2$ along the $z$-axis from each coil. The distance $\rho$ is measured radially from the $z$-axis.
section of dimension 4.8-cm, however, and the thin-coil result must be integrated over these dimensions. The result of this integration yields a field-to-current ratio of \( \frac{B}{I} = 3.794 \) gauss/amp. A more detailed analysis of the Helmholtz coils will appear in the following section.

The electrons pass through the crossed field region and arrive at the exit aperture, which has a diameter of 1.0-mm. The set of three electrodes which follow the crossed field region also forms an Einzel lens configuration. The ions formed in the ion chamber are extracted by an electric field of approximately 0.7 V/cm. The ions are focused onto the mass spectrometer by the extraction optics. The ion detector consists of a Spiraltron electron multiplier (DeTech 450, Brookfield, MA) operated in pulse counting mode at 2-kV. The detector is preceded by conversion dynode which must be set at 5-kV for anion detection or -5-kV for cation detection. Hence two 5-kV power supplies are required (Bertan PMT-50A, Hicksville, NY). The role of the conversion dynode is to interact with the ion created in the electron attachment process. The ion collides with the dynode generating electrons which are then analyzed. Three additional electrodes function as an electron collector, which is useful for monitoring beam current. An electrometer monitors this intensity at the electron collector.

Pulses from the detector are counted and stored in a multichannel analyzer. The data are acquired by sending the signal from the Spiraltron through a fast preamplifier (Ortec 9305), a main amplifier (Ortec 9302) which has been modified by the addition of a NIM-to-TTL pulse-shape converter (Paulus Engineering Co.,
Knoxville, TN), a ratemeter (Ortec 9349), and a multichannel analyzer (ACE-MCS) which is a plug-in board within a Hewlett-Packard Vectra 386/25 computer.

The electron energy distribution was calibrated using several compounds with generally accepted electron attachment energies. Sulfur hexafluoride has an electron attachment energy of 0.025 eV with a natural line width of 6 meV for the reaction \([14] \text{SF}_6 + e^- \rightarrow \text{SF}_6^-^-\). Nitrobenzene and hexafluorobenzene were used as calibrants for 0.025 eV electrons as well. The process \(\text{SF}_6 + e^- \rightarrow \text{SF}_5^- + F^-\) was used to calibrate 0.37 eV electrons [15]. \(\text{C}_6\text{F}_6 + e^- \rightarrow \text{C}_6\text{F}_5^- + F^-\) was used to calibrate at 4.5 eV [16].

B. Magnetic Field Due to Helmholtz Coils

The magnetic field for the monochromator is generated by a pair of Helmholtz coils (Figure 4). A coordinate system, with origin \(O\), is placed such that the upper loop resides at \(z = R/2\) and the lower loop at \(z = -R/2\). The magnetic field expressed in cylindrical coordinates [17] has components

\[
B_z = \frac{8 \mu_0 NI}{\sqrt{125} R} \left( 1 - \frac{144 z^4}{125 R^4} + \frac{432 z^2 p^2}{125 R^4} + \ldots \right) \tag{30}
\]

and

\[
B_\rho = \frac{8 \mu_0 NI}{\sqrt{125} R} \frac{72 z p (4 z^2 - 3 p^2 + \ldots)}{125 R^4}. \tag{31}
\]
These expressions are valid for small values of \( z \) and \( \rho \) as a result of approximations made in the expansion of the \( 1 / |r - r'| \) term. The component of the field in the \( \rho \)-direction vanishes on the axis where \( \rho \) is zero.

The third term in the expression for \( B_z \) also vanishes on the axis. The largest value which \( z \) can have between the coils is \( \pm R/2 \). For points between the coils, the largest that the \( z^4 \) term can be is \( 144 / (125 \times 2^4) = 0.07 \). It is apparent that the first term dominates. If only the first term is considered, the uniformity of the axial field to first order is very good since the first derivative of \( B_z \) is zero. In equation (31) a factor of \( \rho \) appears in the numerator. For small values of \( \rho \) off the axis, the field component is likewise small. These simple arguments serve to show that the field between the Helmholtz coils is very uniform. The expressions derived in section II governing the operation of the trochoidal electron monochromator assumed an uniform magnetic field. The effects of an inhomogeneous magnetic field has not been treated rigorously. The degree to which the field must be uniform for the monochromator to perform properly is not clear.

C. Performance of the Monochromator

There are three factors of particular interest in determining how well the monochromator performs. Factors of interest in this consideration are electron current, energy resolution, and the physical size of the apparatus.

In order to produce negative ions, the sample molecules injected must interact with the electrons produced by the monochromator. To ensure that analyte is
not unnessisarily wasted, there must be a sufficient current of electrons. The electron current which is transmitted through the monochromator is dependent upon the energy of the electrons which arrive at its entrance aperture. Only electrons which fall within the selected energy range will be transmitted through the monochromator. By altering the magnetic field, different electron currents may be obtained. The following graph (Figure 5) shows the electron current $I_e$ as a function of magnetic field strength $B$.

Electron Current vs. Magnetic Field Strength

![Graph showing electron current vs. magnetic field strength.](image)

**Figure 5:** Electron current vs. magnetic field strength.

To determine the energy resolution, the process of electron attachment to hexafluorobenzene was used. This process is generally accepted to have a null line
deduced that the energy resolution of the monochromator is $\Delta \varepsilon = \pm 0.5$ eV. The horizontal axis in Figure 6 includes negative electron energies. Naturally, it is not possible for a particle to have a kinetic energy less than zero. These values are included such that the entire peak is represented. Low energy resolution is primarily responsible for the need to include negative electron energies. In other figures in later sections, the natural line width of the resonance also contributes to the necessity of including negative electron energies.

Energy Resolution

![Energy Resolution Graph](image)

Figure 6: Electron energy spectrum for hexafluorobenzene. The first peak is used to measure the energy resolution. The full width at half maximum is 0.5 eV.
IV. Experimental Results

In section I, two methods of inserting various samples into the system were described. These two methods allow two different kinds of experiments to be performed. The first kind of experiment is one in which the electron energies are scanned. The second variety of experiments involve fixed electron energies but allow for a more quantitative analysis of the sensitivity of the apparatus to be shown.

A. Solid Probe Experiments

One way of introducing a sample into the apparatus is by putting the sample in solid form onto a probe. This probe is then inserted into the system. The filament voltage is varied to control the electron energy as all other components of the monochromator are held constant relative to the filament potential. A sweep of electron energy from 0 to 20 eV takes 3 milliseconds. Data are summed over successive runs to generate a complete spectrum.

One of the motivations for pursuing this line of study is to potentially develop a portable device capable of detecting explosives. One step in the development of such a device is a cataloging of the electron attachment energy spectra of explosives. Several such spectra appear here (Figures 7-12). All of these spectra exhibit low-energy electron attachment.

Pentaerythritol Tetranitrate (PETN) is shown in Figure 7. PETN is an
Figure 7: Electron attachment energy spectrum for PETN.

Figure 8: Electron attachment energy spectrum for TNT.

Figure 9: Electron attachment energy spectrum for Gulf Detagel.

Figure 10: Electron attachment energy spectrum for Ammonium Nitrate.

Figure 11: Electron attachment energy spectrum for DuPont Tovex.

Figure 12: Electron attachment energy spectrum for RDX.
Total Ion Yield PETN

![Graph of Total Ion Yield PETN](image)

Figure 7

Total Ion Yield TNT

![Graph of Total Ion Yield TNT](image)

Figure 8
Total Ion Yield Gulf Detagel

![Graph of Total Ion Yield Gulf Detagel](image)

**Figure 9**

Total Ion Yield Ammonium Nitrate

![Graph of Total Ion Yield Ammonium Nitrate](image)

**Figure 10**
Total Ion Yield Dupont Tovex

![Graph of Total Ion Yield Dupont Tovex](image)

Figure 11

Total Ion Yield RDX

![Graph of Total Ion Yield RDX](image)

Figure 12
explosive which detonates on percussion. It is more sensitive to shock than even 2,4,6-Trinitrotoluene (TNT) whose spectrum is shown in Figure 8. Gulf Detagel (Figure 9) is a blasting gel made by the Gulf company. Ammonium Nitrate (Figure 10) is a common fertilizer which can be adapted for use in explosive devices. DuPont Tovex, a low-velocity explosive used in construction and mining, is shown in Figure 11. 1,3,5-trinitro-1,3,5-triazocyclohexane (RDX) is an explosive developed by the military for their uses. All of the spectra with the exception of TNT seem to show a single electron attachment energy with the exception of TNT which has been studied further.

Figure 13 shows two spectra for TNT. For these experiments the NO₂ group in the para position was labeled with nitrogen 15. In these spectra the mass spectrometer was tuned to masses m/z = 46 and m/z = 47. By examining the two spectra, it is seen that the electron attachment energies of the ortho and para nitro groups are distinct processes. Once the energy for an electron attachment process is known, a second method of experimentation utilizing gas chromatographic techniques may be applied.

B. Introduction of Samples by Gas Chromatographic Inlet

Once an electron attachment energy has been found for a sample, the energy of the electrons allowed through the monochromator can be fixed at this value. By injecting the sample through the GC, a precise measurement of the mass of material
Figure 13: Electron attachment energy spectrum for TNT with the NO₂ in the para position labelled with ¹⁵N. The two processes are shown.
Figure 13

Chemical structures and electron energy plots.
sent through the apparatus is possible. The GC column passes all of the sample injected to the ion source where it interacts with the electrons coming from the monochromator. An examination of the resulting signal gives an indication of the sensitivity of the instrument.

Figure 14 shows how gas chromatography can be used to separate different components in a mixture. The data shown are for a mixture of 19.2 ng of RDX, 24.0 ng of nitrobenzene (NB) and 6.4 ng of TNT. An electron energy of 0.03 eV was used throughout the experiment. From Figure 14, it can be determined when a component will emerge from the GC column.

19.2 ng RDX + 24.0 ng NB + 6.4 ng TNT

![Gas chromatogram of a mixture of RDX, nitrobenzene(NB), and TNT for 0.03 eV electrons.](image)

**Figure 14:** Gas chromatogram of a mixture of RDX, nitrobenzene(NB), and TNT for 0.03 eV electrons.
Now a sample can be passed through the column and the electron energies can be scanned from 0 to 20 eV beginning when the sample arrives at the end of the column. An indication of the sensitivity of the instrument can be gained in this manner. Two such experiments are shown in Figures 15 and 16. Figure 15 shows the electron energy attachment spectrum for hexachlorobenzene (C₆Cl₆). It can be seen from the spectrum that for 5.4 ng of C₆Cl₆ a maximum of about 1100 anions can be detected. In figure 16, the electron attachment energy spectrum for 21.2 ng TNT is displayed.

5.4 ng Hexachlorobenzene

![Graph](image)

**Figure 15:** Electron energy attachment spectrum of 5.4 ng of C₆Cl₆.
A sample of fish oil provided by the Environmental Protection Agency (EPA) was analyzed by this method. The oil had been taken from fish located in Antarctica where the issue of the transport of pollutants was being studied. A portion of the resulting spectrum is shown in Figure 17. The spectrum in Figure 17 shows the yield of chloride ion. This provides an indication that chlorinated compounds have indeed arrived at the South Pole.

The ability of the system to analyze and provide some characteristics of explosives and environmental chemicals is clear. A smaller and equally efficient version of this device would be desirable for future work.
Figure 17: A section of a gas chromatogram of the lipid fraction of arctic trout muscle. Two main peaks are apparent. The peak at 260 seconds is HCB. The peak at 390 seconds is Cl₈-PCB. The remainder of the peaks are other PCB compounds and PCN compounds.
V. Proposed Modifications to a Trochoidal Electron Monochromator

Modifications to the electron monochromator are necessary for several reasons. First, it is desirable to enhance the electron current allowed through the monochromator. The size of the monochromator needs to be reduced as well. These two improvements will allow great flexibility in how the monochromator might be employed. Increased electron current will allow for inspection of very low levels of material. The reduced size will not only make the monochromator practical for an airport security setting, but may also allow the monochromator to be employed in other remote sensing experiments. All modifications made to the monochromator must produce electrons with reasonable energy resolution.

A. Electron Current

The ability to analyze minute quantities of material is desirable. It is imperative that as little of the analyte as possible be wasted. If there are an insufficient number of electrons present, it is possible that much of the analyte will not undergo electron attachment and, therefore, not be detected.

One way in which to enhance the electron current of the monochromator is by increasing the electron current emitted by the filament. There are two ways in which this goal might be accomplished.

The first way to increase the electron current is by using a filament with a lower work function. The work function of a substance is the amount of energy
required to remove one electron from a material. If the work function of the filament is decreased, then more electrons should be emitted from the material given the same surface composition and temperature. Tungsten with 2% thorium has a work function of 2.7 eV at an operating temperature of 2000 K [18]. Installation of a cerium hexaboride (CeB₆) filament should prove advantageous, as it has a lower work function of 2.4 eV and a normal operating temperature of 1800 K [19].

The second way which might be employed to increase the electron current passing through the electron monochromator is by increasing the flux of electrons emitted in the direction of the monochromator. This is another advantage of the CeB₆. The emitting surface is a disk of 1-mm in diameter. The thoriated tungsten filament currently employed is a piece of wire with a 0.15-mm diameter. The modification to a flat cathode should have the effect of emitting more electrons with velocities toward the monochromator. In that the CeB₆ filament is a disk, all of its surface area is parallel to the apertures of the electrostatic lenses. The surface area of the thoriated tungsten wire filament which is parallel to the apertures is obviously much less. Not only are more electrons going to be produced, but the direction in which they are emitted by the CeB₆ filament should enhance electron current through the monochromator.

B. Miniaturization

The present system has shown itself to be able to discern different compounds on the basis of their electron attachment energies [20]. Explosives are a class of
compounds of particular interest. If a monochromator is to be used in an airport
security setting, it must be of a reasonable size. At present the monochromator
occupies a volume of $3.67 \times 10^4 \text{ cm}^3$ neglecting electrical connections. This is
essentially the volume within the Helmholtz coils. A smaller size is desirable if a
portable device for use in airport security is to be created. There may be commercial
scientific applications which will require a smaller version of the present system as
well.

The greatest contribution to the volume occupied by the present apparatus is
associated with the Helmholtz coils. The coils produce a uniform field in the region
of the monochromator, but other alternatives for producing such a field exist. For
example, two cylindrical permanent magnets could be placed such that the axis of
their cylinders coincide, generating a field of sufficient strength in the region of
interest. If magnets of radius 3-cm were placed a distance of 30-cm apart, the
volume occupied by the monochromator would be reduced to approximately 200-cm$^3$.
This indicates a reduction by a factor of 200.

C. Energy Resolution

Both of these modifications must be made such that reasonable electron energy
resolution can be obtained. Recall that the distribution of electron energies is given
by (see section II)

$$
\Delta W = \frac{m}{e} \left( \frac{EL}{BD} \right)^2 \left( y^2 + \frac{S_1 + S_2}{D} \right) + ES_1 .
$$

(29)
Therefore, there should be little effect on the energy resolution due to the new filament on the basis of this equation. Equation (29) assumes that the magnetic field is uniform. If the field remains relatively uniform, then we expect this modification should have little effect on the energy resolution as well.
VI. Feasibility of Modifications

The remainder of this thesis will examine two questions: (1) whether
the installation of the CeB$_6$ filament is feasible and (2) whether the substitution of two
cylindrical magnets in place of the Helmholtz coils will be feasible.

A. CeB$_6$ Filament

The installation of the CeB$_6$ filament is readily feasible. Filaments of such
material are currently manufactured by FEI Company of Beaverton, OR. Obtaining
the CeB$_6$ filament is not problematic. A potential problem which is not addressed by
equation (29) is that of space charge effects. Electrical interactions between electrons
passing through the monochromator were not considered in the development of
equation (29). If the interaction between the electrons is strong enough, the
trochoidal trajectory will be disrupted yielding a reduction in the electron current
passing through the apparatus. If space charge effects appear due to the installation
of the CeB$_6$ filament, improved performance might still be obtained. An option
would be to pulse the delivery of electrons to the monochromator. If enough time is
allowed between pulses, the electrons will be able to leave the monochromator region
before the next group of electrons arrives. In this manner space charge effects might
be circumvented.
B. Permanent Magnets

A second problem which was not addressed in the development of equation (29) was nonhomogeneity in the magnetic field. The treatment given in section II assumed that the magnetic field \( B \) was both unidirectional and of a single magnitude. If a less than uniform field is used, how uniform must it be to maintain the operation of the instrument? This is the question that must be answered if the feasibility of using permanent cylindrical magnets is to be determined.

Figure 18: Configuration of cylindrical permanent magnets. The magnets have length \( L \) and radius \( a \) with uniform magnetization \( M \), separated by a distance \( d \).

To generate a magnetic field for the monochromator, the use of two cylindrical permanent magnets has been proposed. The configuration of these
magnets is shown in Figure 18. The axial magnetic field generated by these two cylindrical magnets has been calculated (see Appendix) to be

\[
B_z^{ax} = 2\pi M\mu_0 \left[ \frac{d+2L-z}{\sqrt{a^2+(d+2L-z)^2}} - \frac{d+L-z}{\sqrt{a^2+(d+L-z)^2}} - \frac{z-L}{\sqrt{a^2-(z-L)^2}} + \frac{z}{\sqrt{a^2+z^2}} \right]. \tag{32}
\]

The off axis field is a considerably more difficult when the approach used to attain equation (32) is used. A good approximation for the radial field, however, is available. Given the axial component of the field it is possible to find the radial component by applying

\[\nabla \cdot B = 0. \tag{33}\]

In cylindrical coordinates this yields

\[
\frac{\partial B_z}{\partial z} - \frac{1}{\rho} \frac{\partial}{\partial \rho} (\rho B_\rho) = 0. \tag{34}
\]

In that \(B_z\) is not a function of \(\rho\), an ordinary differential equation can be generated. Solving this equation for \(B_\rho\) yields

\[
B_\rho = \frac{1}{2} \frac{\partial B_z}{\partial z} \rho. \tag{35}
\]

Substitution of the derivative of equation (32) with respect to \(z\) yields

\[
B_\rho = \pi M\mu_0 a^2 \left[ -\frac{1}{(a^2+(d+2L-z)^2)^{\frac{3}{2}}} + \frac{1}{a^2+(d+L-z)^2} - \frac{1}{(a^2+(z-L)^2)^{\frac{3}{2}}} + \frac{1}{(a^2+z^2)^{\frac{3}{2}}} \right]. \tag{36}
\]

Now expressions for the axial magnetic field and the radial field have been calculated. These results can now be compared to the Helmholtz fields presently in
use. Figure 19 shows a comparison of the magnetic fields generated by the Helmholtz configuration to the fields generated by the cylindrical permanent magnets. In the region where the monochromator is located the deviation is less than 10%.

**Axial Magnetic Fields**

Helmholtz and Permanent

![Graph showing magnetic field comparison](image)

**Figure 19:** Comparison of axial magnetic fields of Helmholtz coil configuration versus the permanent magnet configuration.

The radial contribution to the magnetic field is of concern as well. Figure 20 shows the variation of the radial component of the magnetic field for several values off the axis. For a point 2.5-cm off the axis, a radial component of no greater than 15 gauss is obtained. This factor is again on the order of 10% of the total magnetic field. Whether or not these deviations are too great remains to be seen.
A simple experiment was performed to simulate the inhomogeneity of the magnetic field that is created by the substitution of permanent magnets for the Helmholtz coils. Two cylindrical magnets were configured symmetrically such that they had a common $z$-axis as shown in Figure 18. A measurement of the radial field at a particular point near this configuration yielded 15 gauss. To introduce the inhomogeneity into the magnetic field, the two magnets were placed outside the vacuum system in the orientation shown in Figure 18. By superposition, the field at the monochromator should be the field generated by the Helmholtz coils plus the field generated by placing the magnets near the monochromator. The 15 gauss radial field is a good choice since this provides a radial component which is equal to the
maximum deviation of the field created by the permanent magnets relative to the Helmholtz configuration. Essentially a magnetic field has been created at the monochromator which is intended to mimic the field that two cylindrical magnets might generate. Hexafluorobenzene was leaked into the system via the solid probe for the pure Helmholtz configuration and then for the simulated permanent magnet configuration. The electron energy attachment spectra are shown in Figure 21.

Simulated Permanent Magnet and Helmholtz Fields

![Graph showing electron attachment energy spectra of C₆F₆ in magnetic fields. The magnetic field generated by Helmholtz coils (□) compared to the simulated permanent magnet field (■).]

**Figure 21:** Electron attachment energy spectra of C₆F₆ in magnetic fields. The magnetic field generated by Helmholtz coils (□) compared to the simulated permanent magnet field (■).

There are two important points to note here. First, a signal is still generated from the monochromator even though the field is not completely uniform. This is of perhaps the most importance in determining the feasibility of using permanent
magnets. If a beam of electrons cannot be obtained, then the modification is useless. Since a beam of electrons is indeed obtained, it can be concluded that this modification will be successful. Second, the peak shape and size are retained. The peak does, however, appear to shift when the simulated permanent magnetic field is used. This is not necessarily a problem since the data obtained can be calibrated to various standard values.
VII. Conclusions

The utility of the gas chromatograph / trochoidal electron monochromator / quadrupole mass spectrometer system has been shown to be effective in the analysis of both explosives, as demonstrated by Figures 7 - 12, and environmental chemicals, as demonstrated by the analysis of the Antarctic fish oil presented in Figure 17.

On the basis of the data presented in Figure 21, it can be concluded that the miniaturization of the trochoidal monochromator component of the system can be accomplished successfully by replacing the Helmholtz coils with cylindrical permanent magnets. The deviation of the magnetic field due to the permanent magnet configuration relative to the Helmholtz configuration was shown to be at most 10% in the region of the monochromator by Figure 20. Since the radial field introduced was 15 gauss and the contribution due to the Helmholtz field was 140 gauss, a 10% inhomogeneity was achieved. It can therefore be concluded that cylindrical permanent magnets can be used in place of the Helmholtz coils. The substitution of the permanent magnets for the Helmholtz coils was shown to reduce the overall size of the trochoidal electron monochromator by a factor of 200. The feasibility of installing a CeB₆ has also been established.

Pursuit of an effective method of detecting explosives and environmental chemicals continues. The analysis presented here promises hope for such a device one day.
References


[5a] Christophorou, p. 484.


[19] FEI Focus, Fall 1991, p.3.


Other References:


Appendix
Magnetic Field Calculations

To calculate the magnetic field due to a permanent magnet from first principles, consider Maxwell’s equations for magnetostatics:

\[ \nabla \cdot B = 0 \quad (A.1) \]
\[ \nabla \times H = J \quad (A.2) \]

For a hard ferromagnet, the material can be treated as if a magnetization, \( M(x) \), is specified and the current is such that \( J = 0 \). Since \( J = 0 \), equation (A.2) becomes

\[ \nabla \times H = 0 \quad (A.3) \]

Since the curl of the gradient of any quantity is always zero, \( H \) can be expressed as the gradient of a magnetic scalar potential

\[ H = -\nabla \phi_m \quad (A.4) \]

In ponderable media the magnetic field \( B \) is given by

\[ B = \mu_0 (H - M) \quad (A.5) \]

Hence, the magnetostatic Poisson equation is generated

\[ \nabla^2 \phi_m = -\rho_m \quad (A.6) \]

with an effective magnetic charge density
\[
\rho_m = -\nabla \cdot M .
\] (A.7)

For present considerations, the ferromagnet is treated as if it has a particular magnetization \( M(x) \) within a volume \( V \) and it is assumed that it falls to zero at the surface, \( S \), of the magnet. If we define an effective magnetic surface charge density \( \sigma_m \) as

\[
\sigma_m = \mathbf{n} \cdot M
\] (A.8)

where \( \mathbf{n} \) is the normal directed outward from the surface, the solution to equation (A.6) becomes

\[
\phi_m = -\int \frac{\nabla' \cdot M(x')}{|x-x'|} d^3x' + \oint_S \frac{n' \cdot M(x') \ da'}{|x-x'|} .
\] (A.9)

For the case where the magnetization is uniform throughout the volume, the first term in equation (A.9) vanishes since the divergence of \( M(x') \) is zero. Consider specifically the configuration of two cylindrical permanent magnets of radius \( a \) and length \( L \) with bulk magnetizations \( M_z \) and \(-M_z \) respectively oriented symmetrically with a common z-axis (see Figure A1). Here \( z \) is a unit vector in the z direction.

First consider each of the magnets separately. If a magnet with bulk magnetization \( M_z \) is placed at the origin of a coordinate system with the z-axis coincident with the cylinder's axis, the effective magnetic surface charge density on the upper and lower surfaces of the magnet are related by
\[ \sigma_u = \hat{n} \cdot \mathbf{M} = \hat{z} \cdot \mathbf{M} = M = -\sigma_I. \quad (A.10) \]

So the effective magnetic surface charge on the top of the cylinder, \( \sigma_u \), is exactly the opposite of the effective magnetic surface charge on the bottom of the cylinder, \( \sigma_I \).

Since we are assuming that the magnetization is uniform throughout the volume of the cylinder, the first term in equation (A.9) is indeed zero. Now consider the second permanent magnet placed a distance, \( d + L \), from the origin. This allows the distance between the inner surfaces of the magnets to be described by the variable \( d \).

The effective magnetic surface charge is similar to that of the first magnet, with the inner surface having a magnetic charge density equal to \( \sigma_I = -M \) and the outer surface having \( \sigma_u = M \). First the calculation of the magnetic field on the \( z \)-axis between the magnets will be presented. Following the axial derivation, the more difficult to calculate off-axis field will be found.

A. Axial Field of Two Cylindrical Magnets on a Common Axis

With the geometry as shown in Figure 18 in section VI, the magnetic scalar potential on the \( z \)-axis at a point some distance \( z \) from the origin is given by
\[ \phi_m = 2\pi \int_0^a \frac{\rho_u'd\rho_u'}{\sqrt{(d+2L-z)^2+\rho_u'^2}} - 2\pi \int_0^a \frac{\rho_i'd\rho_i'}{\sqrt{L-z)^2+\rho_i'^2}} \]

\[ + M \int_0^a \frac{\rho_u'd\rho_u}{\sqrt{(z-L)^2+\rho_u^2}} - M \int_0^a \frac{\rho_i'd\rho_i}{\sqrt{(z-L)^2+\rho_i^2}}. \] (A.11)

Performing the integration over \( \phi \) and \( \phi' \) yields

\[ \frac{\phi_m}{2\pi M} = \int_0^a \frac{\rho_u'd\rho_u'}{\sqrt{(d+2L-z)^2+\rho_u'^2}} - \int_0^a \frac{\rho_i'd\rho_i'}{\sqrt{(d+L-z)^2+\rho_i'^2}} + \int_0^a \frac{\rho_u'd\rho_u}{\sqrt{(z-L)^2+\rho_u^2}} - \int_0^a \frac{\rho_i'd\rho_i}{\sqrt{(z-L)^2+\rho_i^2}}. \] (A.12)

The remaining integrals are straightforward. Hence we have

\[ \phi_m = 2\pi M \left[ \sqrt{\rho_u^2+(d+2L-z)^2} - \sqrt{\rho_u^2+(d+L-z)^2} + \sqrt{\rho_u^2+(z-L)^2} - \sqrt{\rho_u^2+z^2} \right] \] (A.13)

\[ \phi_m = 2\pi M \left[ a^2+(d+2L-z)^2 - a^2+(d+L-z)^2 + a^2+(z-L)^2 - a^2+z^2 \right]. \] (A.14)

Equation (A.14) represents all of the contributions to the potential at a point on the axis at a distance \( z \) from the origin. On the z-axis \( H_\rho = H_\phi = 0 \) by symmetry.

Hence

\[ H = -\frac{\partial \phi_m}{\partial z} \hat{z} \] (A.15)

and therefore,
\[ H = 2\pi M \left[ \frac{d+2L-z}{\sqrt{a^2+(d+2L-z)^2}} - \frac{d+L-z}{\sqrt{a^2+(d+L-z)^2}} - \frac{z-L}{\sqrt{a^2+(z-L)^2}} - \frac{z}{\sqrt{a^2+z^2}} \right] \hat{z}. \] (A.16)

Since the field of interest is external to the magnets themselves (i.e., \( M = 0 \) here), equation (A.5) becomes \( B = \mu_0 H \) (SI units) in this region. Hence equation (A.16) becomes

\[ B = 2\pi M\mu_0 \left[ \frac{d+2L-z}{\sqrt{a^2+(d+2L-z)^2}} - \frac{d+L-z}{\sqrt{a^2+(d+L-z)^2}} - \frac{z-L}{\sqrt{a^2+(z-L)^2}} - \frac{z}{\sqrt{a^2+z^2}} \right] \hat{z}. \] (A.17)

which provides a complete description of the magnetic field along the axis of the cylindrical magnets.

At the midpoint between the two magnets the field is of interest. Knowledge of the field at this point will give a reasonable indication of how the field may behave at nearby points. Using equation (A.17), the field at this point (\( z = L + d/2 \)) is found to be

\[ B = 2\pi M\mu_0 \left[ \frac{2L+d}{\sqrt{a^2+(L+d/2)^2}} - \frac{d}{\sqrt{a^2+(d/2)^2}} \right] \hat{z}. \] (A.18)

Equation (A.18) can be used to determine a value for \( M \) given a desired field strength.
B. Off-Axis Field of Two Cylindrical Magnets with a Common Axis

The off axis field is significantly more difficult to calculate. The starting point is again equation (A.9):

\[ \phi_m = -\int_V \frac{\nabla \cdot M(x')}{|x-x'|} d^3x' + \int_S \frac{n \cdot M(x')}{|x-x'|} da'. \quad (A.19) \]

Equation (A.19) is first applied to a single disk with uniform magnetization. After the field created by this disk is calculated, the remainder of the field can be found by superposition. Once again, if the magnetization is uniform throughout the magnet, then the first term vanishes. Let \((r', \theta', \phi')\) describe a point on the upper face of the cylindrical magnet. The contribution to the potential at the point \((r, \theta, \phi)\) will be given by substitution into equation (A.9). From the law of cosines

\[ \frac{1}{|r - r'|} = \frac{1}{\sqrt{r^2 + r'^2 - 2rr'\cos\gamma}} \quad (A.20) \]

where

\[ \cos\gamma = \cos\theta\cos\theta' + \sin\theta\sin\theta'\cos(\phi - \phi'). \quad (A.21) \]

Since our origin is at the surface of the magnet and all of the potential is due to contributions from that plane, we know that \(\theta' = \pi / 2\). Furthermore, the way we choose to orient our coordinate system is of little significance. Hence, we choose to orient it such that \(\phi = 0\). Thus we can reduce equation (A.21) to
Finally, the total expression for the off-axis potential can be written

\[
\phi_m(r, \theta) = M \int_0^a r' dr' \int_0^{2\pi} \frac{d\phi'}{\sqrt{r^2 + (r')^2 - 2rr'\sin\theta \cos\phi'}} .
\]  

\[\text{(A.23)}\]

To calculate this integral, a trigonometric substitution must be made. In particular,

\[
\cos(2\alpha) = 1 - 2\sin^2 \alpha \quad \text{(A.24)}
\]

must be applied. The integral becomes

\[
\phi_m(r, \theta) = M \int_0^a r' dr' \int_0^{2\pi} \frac{d\phi'}{\sqrt{r^2 + (r')^2 - 2rr'\sin\theta(1 - 2\sin^2(\frac{\phi'}{2}))}} .
\]  

\[\text{(A.25)}\]

which can be expanded to yield

\[
\phi_m(r, \theta) = M \int_0^a r' dr' \int_0^{2\pi} \frac{d\phi'}{\sqrt{r^2 + (r')^2 - 2rr'\sin\theta + 4rr'\sin\theta \sin^2(\frac{\phi'}{2})}} .
\]  

\[\text{(A.26)}\]

If a new variable \( \chi \) is defined such that
\[ \chi = \frac{\phi' - \pi}{2} \quad \Rightarrow \quad d\phi' = 2d\chi \quad (A.27) \]

and a second variable \( \kappa \) is defined such that

\[ \kappa^2 = \frac{4rr'\sin\theta}{r^2 + (r')^2 + 2rr'\sin\theta} \quad (A.28) \]

then the integral in equation (A.26) can be rewritten as the following:

\[ \phi_m(r, \theta) = M \int_0^a \frac{2r'dr'}{\sqrt{r^2 + (r')^2 + 2rr'\sin\theta}} \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \frac{d\chi}{\sqrt{1 - \kappa^2\sin^2\chi}}. \quad (A.29) \]

Since the \( \sin^2\chi \) function is even, the second integral in equation (A.29) can be expressed as

\[ \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \frac{d\chi}{\sqrt{1 - \kappa^2\sin^2\chi}} = 2\int_0^{\frac{\pi}{2}} \frac{d\chi}{\sqrt{1 - \kappa^2\sin^2\chi}}. \quad (A.30) \]

This allows equation (A.29) to be rewritten as

\[ \phi_m(r, \theta) = M \int_0^a \frac{4r'dr'}{\sqrt{r^2 + (r')^2 + 2rr'\sin\theta}} \int_0^{\frac{\pi}{2}} \frac{d\chi}{\sqrt{1 - \kappa^2\sin^2\chi}}. \quad (A.31) \]

The second of these integrals is now in the form of a complete elliptic integral. A series solution to this is known to be (Dwight 773.1, p. 180)
If terms up to $\kappa^2$ are included, then our expression for the potential becomes

$$
\phi_m(r, \theta) = 2M\pi \int_0^a \frac{r'dr'}{\sqrt{r^2+(r')^2+2rr'\sin\theta}} + 2M\pi r\sin\theta \int_0^a \frac{(r')^2dr'}{(r^2+(r')^2+2rr'\sin\theta)^{3/2}}. \quad (A.33)
$$

Now we only have to evaluate the radial integrals. All of these integrals can be determined (Dwight 380.011, p. 75 and Gradsteyn, I. S. and Ryzhik, I. M., 2.261 and 2.264, p.83). Substitution yields the following expression for the potential:

$$
\phi_m^{\text{off axis}} = 2\pi M[ \sqrt{R} - r\sin\theta[ \ln(2\sqrt{R} + 2r' + 2r\sin\theta) ]^a_0 ]
$$

$$
+ 2\pi M r\sin\theta \left[ -\frac{(2\cos^2\theta - 2\sin^2\theta)r' - r\sin\theta}{2\cos^2\theta \sqrt{R}} + \ln(2\sqrt{R} + 2r' + 2r\sin\theta) \right]^a_0 \quad (A.34)
$$

where

$$
R = (r')^2 + r^2 + 2rr'\sin\theta. \quad (A.35)
$$

When the endpoints are inserted and evaluated, the off axis potential is finally found

$$
\phi_m^{\text{off axis}} = 2\pi M[ \sqrt{R(a)} - r + r\sin\theta \left( \frac{2a(\cos^2\theta - \sin^2\theta) - r\sin\theta}{2\cos^2\theta \sqrt{R(a)}} + \sin\theta \right) ] \quad (A.36)
$$
where

\[ R(a) = a^2 + r^2 + 2ar \sin \theta. \quad (A.37) \]

This is the magnetic scalar potential of a disk centered at the origin with the axis of the disk coincident with the z-axis. The disk has a uniform magnetization \( M \) in the z direction. Since the physical configuration of concern is that of a pair of cylindrical magnets, the expression for the potential and the resulting expressions for the magnetic field are most naturally expressed in cylindrical coordinates. Converting equation (A.36) to cylindrical coordinates yields

\[
\phi_M(\rho,z) = 2\pi M \left[ \sqrt{X} - \sqrt{Q} + \frac{\rho}{2z^2} \left( \frac{2a(z^2 - \rho^2) - \rho Q}{\sqrt{X}} \right) + \frac{\rho^2}{\sqrt{Q}} \right] \quad (A.38)
\]

where

\[
X = a^2 + \rho^2 + z^2 + 2a\rho \quad (A.39)
\]

and

\[
Q = \rho^2 + z^2. \quad (A.40)
\]

To generate an expression for the magnetic fields, the gradient of equation (A.38) must be taken. In cylindrical coordinates, this is given by

\[
B = -\mu_0 \nabla \phi_M = -\mu_0 \frac{\partial \phi_M}{\partial \rho} \hat{\rho} - \mu_0 \frac{\partial \phi_M}{\partial z} \hat{z}. \quad (A.41)
\]
Performing the operations suggested by equation (A.41) yields a complete description of the magnetic field for points off the axis of symmetry. This expression is valid for a single positively charged magnetic surface. The problem as presented in the previous section indicates that four surfaces must be considered. The result generated by equation (A.41) can be used to find the contributions due to the remaining surfaces. By substituting $\pm M$ for $M$ and $z - x$ for $z$ into equation (A.41), an expression for the contribution to the potential from any surface with magnetization $\pm M$ located a positive distance $x$ from the origin can be obtained. Using linear superposition will then yield a complete description of the magnetic field between the magnets.