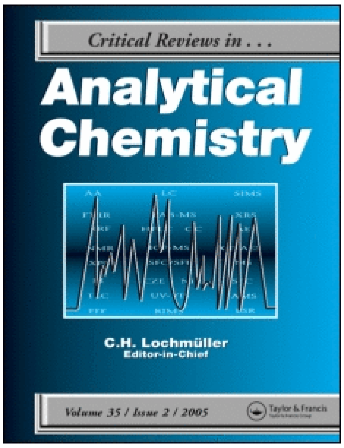

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ZEEMAN MODULATED ATOMIC ABSORPTION SPECTROSCOPY

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I. INTRODUCTION

The main area of application of the Zeeman effect to analytical spectroscopy lies in the Zeeman background correction technique recently developed for atomic absorption measurements. This specific area of application is the subject of the present paper.

Zeeman background correction will tolerate significantly higher spurious absorption backgounds than will continuum background correctors; it will also permit correction of a continuous or line background to be made irrespective of the spatial homogeneity or time dependence of the adsorbing medium. Zeeman background corrected instruments are insensitive to changes of source intensity, and thus they behave as true double beam spectrometers. Instrumental performance is obtained using a single source and with a single beam optical system, and hence the optical alignment of these instruments is always automatically optimized. The technique may be applied to essentially any line on which conventional single beam atomic absorption measurements can be made, with the same background correction efficiency irrespective of the spectral region in which the line lies. These characteristics represent powerful advances over existing background correction techniques, and are responsible for the rapidly increasing level of interest in the method which is currently apparent.

Recent reviews[1,2] have covered earlier work on Zeeman background correction as well as on related areas of application of the Zeeman effect in analytical spectroscopy. Areas where little new work has been reported since these reviews, such as the magneto-optic scanning of spectral lines, are not considered here except at points of specific interest. Where it is thought to be relevant, work described in previous reviews has been reexamined to permit comparison and judgment of later material to be made, and to provide some basis for a unified view of currently available technology.

II. SPECTROSCOPIC CHARACTERISTICS OF THE ZEEMAN EFFECT

The Zeeman effect in atomic spectroscopy describes the splitting of a single line into a multiplet upon application of an external magnetic field. The multiplet always consists of three groups of lines, containing one or more lines in each group. The separations between each group and between individual lines in each group are proportional to magnetic field strength until very high fields are reached. The number of lines actually observed and the state of optical polarization of those lines depend on the spectroscopic states involved in the transition considered and on the relative geometry of the optical and magnetic axes. In the absence of macroscopic effects, such as the perturbation of an emitting plasma by the magnetic field, the profile of each resolvable Zeeman multiplet component remains identical in form (although of lower amplitude) to the original zero field line. Zeeman splitting may be observed equally well with emission or absorption lines, and the discussion below applies equally to either mode unless otherwise stated.

A. Origin of the Zeeman Effect

The Zeeman effect arises because an atom, unless it is for example in a ^1S state, possesses a finite magnetic moment generated by the motions of its outer electrons (orbital motion coupled with electron spin). If the atom is in a ^1S state the electron distribution is spherically symmetrical and the resulting magnetic moment is zero.[3-6] An interaction energy exists between a finite atomic magnetic moment and an external magnetic field; thus the energy of the corresponding atomic state depends on the orientation of the atom in that state relative to the direction of the external field. Under zero field conditions all atomic orientations are of equal energy and are hence spatially degenerate.

The permitted relative orientations of the atom and external field are quantized. Their energies are characterized by the magnetic quantum number M_J (the z component of the total angular momentum vector J), which takes values J, J − 1 . . . − (J − 1), −J. Thus a total of 2J + 1 orientations are permitted. Their energies are given by

$$E = M_J g \beta H \qquad (1)$$

where E is the energy of the level characterized by M_J relative to the zero field level, H is magnetic field strength, g is the Landé factor (numerical values of g are given in Table 1), and β is the Bohr magneton. The latter two are given by

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \qquad (2)$$

$$\beta = \frac{h e}{4\pi m c} \qquad (3)$$

where J, L, and S are the usual symbols of Russell-Saunders coupling, and h, e, m, and c are Planck's constant, electron charge, and mass, and the velocity of light *in vacuo*, respectively. Equations 1 and 2 are approximations (although frequently very good ones). Equation 1 neglects quadratic terms[6] due to magnetically induced orbital distortions, whose influence can be seen experimentally at high field strengths for highly excited states.[6] Equation 2 is only valid for a Russell-Saunders coupling scheme, although analogous equations for other coupling schemes can be derived.[6] However the approximations implicit in Equations 1 and 2 are not important for the applications of the Zeeman effect discussed here, and they will not be considered further.

Since the possible values of M_J are equally positive or negative, Equation 1 shows that the magnetically perturbed energy levels are equally spaced and symmetrically distributed about the original degenerate zero field level (Figure 1): this symmetry is reflected directly in the corresponding and complete symmetry which is always seen in any Zeeman multiplet about the zero field line (Figure 2). Equation 1 also shows that a zero field transition which occurs between energy levels with J values of J_1, J_2 yields the possibility of splitting to give all lines arising from every possible combination of the $2J_1 + 1$, $2J_2 + 1$ sub-levels produced on application of the external field. Fortunately however this degree of complexity is not observed in practice, due to a rigid

TABLE 1

Lande g Values

S	J	L=0	1	2	3	4
1/2	L−1/2	—	2/3	4/5	6/7	8/9
	L+1/2	2	4/3	6/5	8/7	10/9
1	L−1	—	0/0	1/2	2/3	3/4
	L	—	3/2	7/6	13/12	21/20
	L+1	2	3/2	4/3	5/4	6/5
3/2	L−3/2	—	—	0	2/5	4/7
	L−1/2	—	8/3	6/5	36/35	62/63
	L+1/2	—	26/15	48/35	26/21	116/99
	L+3/2	2	8/5	10/7	4/3	14/11
2	L−2	—	—	0/0	0	1/3
	L−1	—	—	3/2	1	11/1
	L	—	5/2	3/2	5/4	23/20
	L+1	—	11/6	3/2	27/20	19/15
	L+2	2	5/3	3/2	7/5	4/3
5/2	L−5/2	—	—	—	−2/3	0
	L−3/2	—	—	10/3	16/15	6/7
	L−1/2	—	—	28/15	46/35	8/7
	L+1/2	—	12/5	58/35	88/63	14/11
	L+3/2	—	66/35	100/63	142/99	192/143
	L+5/2	2	12/7	14/9	16/11	18/13

From Kuhn, H. G., *Atomic Spectra*, 2nd ed., Hilger and Watts, London, 1964, 34. With permission.

adherence to the selection rules $\Delta M_J = 0, \pm 1$; $M_J = 0 \nleftrightarrow M_J = 0$ for $\Delta J = 0$.

The formation of a Zeeman multiplet for $J_1 = 3/2$, $J_2 = 1/2$ is shown in Figure 1 as an illustration of the above principles. The multiplet shown consists of an inner group of lines (π components) distributed symmetrically about the zero field frequency and centered between but separated from two outer groups (σ components). The π and σ components correspond respectively to transitions where $\Delta M_J = 0, \pm 1$. Individual component wavelengths, and hence the separation of any pair of lines in the multiplet, are given by Equations 1 to 3. The form of multiplet pattern shown in Figure 1 is a very general one. This generality is of prime importance to the analytical spectroscopist, since it is this which allows a correspondingly general range of applicability for the Zeeman background correction technique.

Two circumstances can arise to cause distortion of the multiplet pattern. The first is that some mixing of π and σ components can occur, due either to the effects of hyperfine splitting (dealt with at more length in Section I.E.) or to overlap between the $\Delta M_J = 0$ and $\Delta M_J = \pm 1$ transitions (e.g., Figure 2, $^2P_{3/2} - {}^2D_{3/2}$). The former situation is usually unimportant at the field strengths used in analytical spectrometers: the latter situation is uncommon, and in any case when lines of analytical use are affected (such as Al at 3093 Å) suitable alternative lines are normally available. Mixing of the π and σ groups in this way does not in fact reduce the efficiency of Zeeman background correction, but it does lower analytical sensitivity for reasons which are discussed later: lines showing such effects should therefore be avoided if possible.

An alternative circumstance can be envisaged, in which a line shows no Zeeman structure at all. In such a case Zeeman background correction could not be applied to that particular line. Such a situation would arise if the g values (Table 1) of both the upper and lower states involved in the transition were permitted to be zero. It seems, however, that transitions of this type are automatically forbidden, due to an inability

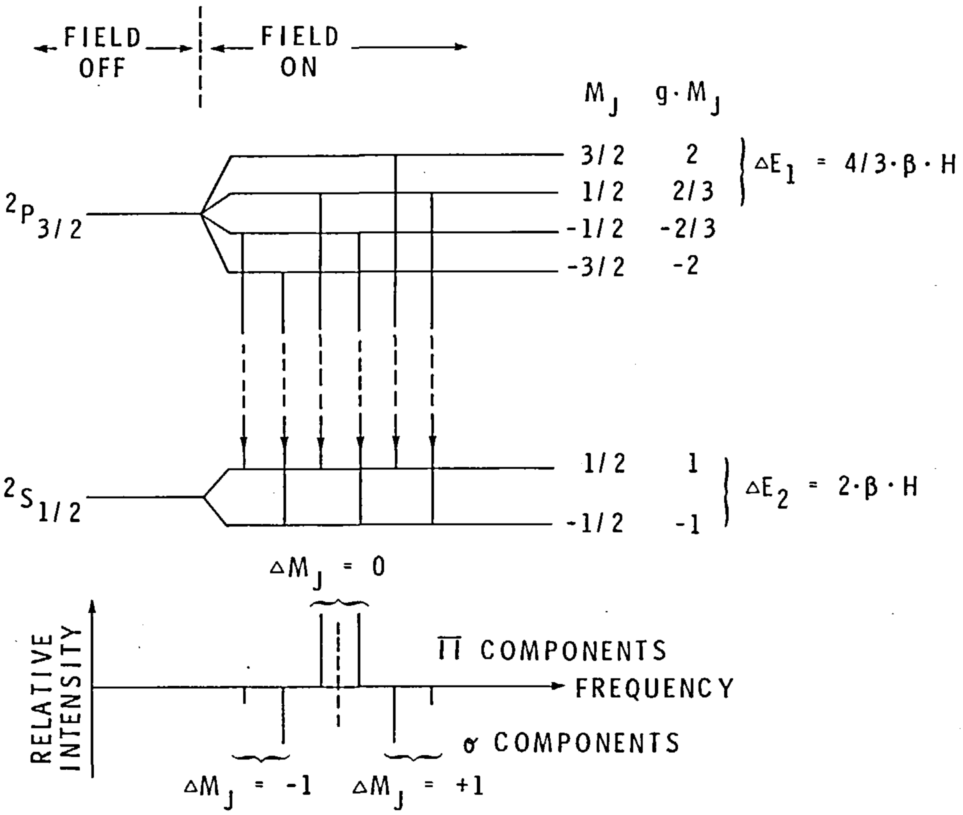

FIGURE 1. Zeeman multiplet arising from the splitting of $^2P_{3/2}$ and $^2S_{1/2}$ levels.

to satisfy the requirements of conservation of momentum during photon emission or absorption. (Indeed, no lines behaving in this manner have been reported experimentally to date.) There is no reason to suppose therefore that this circumstance reduces the generality wth which the Zeeman background correction technique can be applied in practice.

B. The Normal and Anomolous Zeeman Effects

The formation of multicomponent π and σ groups by the type of process illustrated in Figure 1 is named the anomolous Zeeman effect (so-called because of the inability of classical theory to explain the multiplicity of lines observed). The appearance of an anomolous multiplet is thus a direct consequence (1) of the fact that both the upper and lower levels of the observed transition are split by interaction with the external field, and (2) that the magnitude of the splitting of the upper and lower levels is different (i.e., $\Delta E_1 \neq \Delta E_2$ in Figure 1) due to the corresponding differences in the variables of Equations 1 to 3. Anomolous multiplets are by far the most commonly encountered in practice.

A special case exists where the π and σ groups consist of one line each. This is the normal Zeeman effect. Consideration of Figure 1 shows the normal effect will be observed (1) if $\Delta E_1 = \Delta E_2$; and (2) if ΔE_1 or ΔE_2 is zero. Equations 1 and 2 show that condition (1) arises whenever $S_1 = S_2 = 0$ and hence $g = 1$: i.e., a transition between two singlet states. Some examples of ssch transitions are given in Table 1. A transition fulfilling condition (2) occurs if J_1 or J_2 is zero; the Hg 2537 Å intercombination line ($^3P_1 - {}^1S_0$) is perhaps one of the best known examples of this behavior.

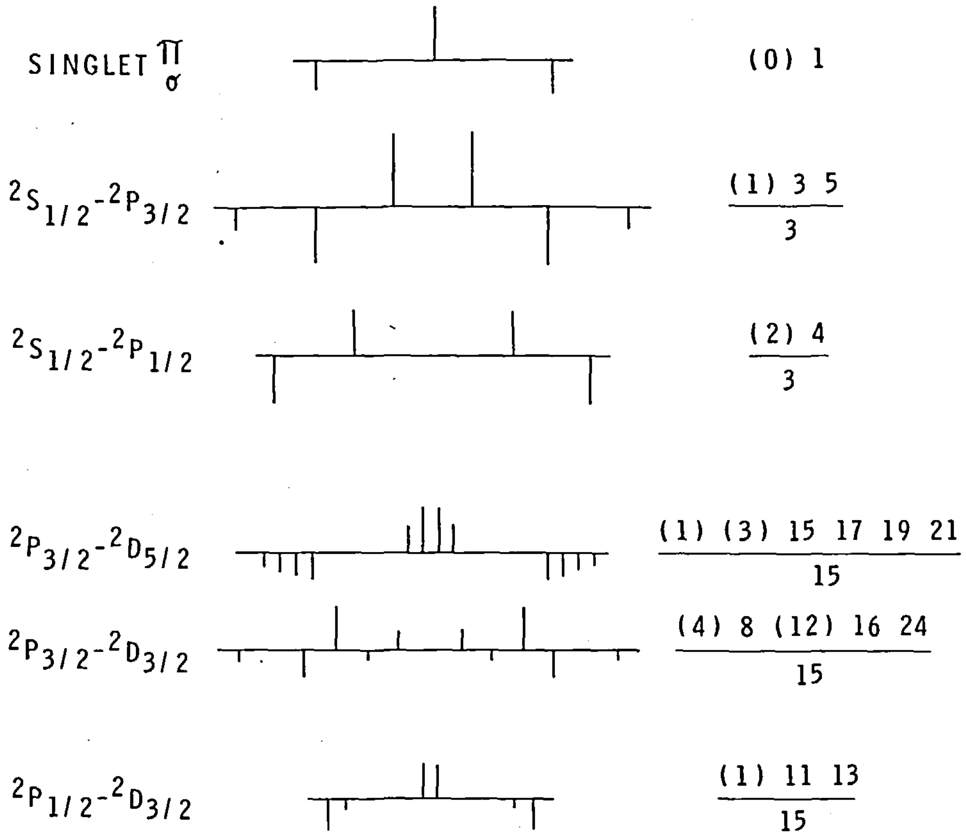

FIGURE 2. Zeeman patterns for doublet lines, with normal Lorentz triplet for comparison. The displacements of the components are given on the right as fractions of the normal effect; the numbers in brackets refer to π components. (From Kuhn, H. G., *Atomic Spectra*, 2nd ed., Hilger and Watts, London, 1964, 204. With permission.)

C. Polarization and Intensity of the Multiplet Components

A Zeeman multiplet may be observed along an optical axis either perpendicular or parallel to the axis of the applied field (transverse and longitudinal Zeeman effect, respectively). In the former case the π and σ components are linearly polarized with their electric vectors respectively parallel and perpendicular to the field axis. In the latter case only the two σ groups of the multiplet are observed, and they show right and left handed circular polarization. The sense of such circular polarization for the high or low frequency σ components depends on whether the magnetic field is directed towards or away from the observer. The polarization effects observed in the transverse and longitudinal modes arise from precessional and linear oscillations of an emitting (absorbing) dipole around and parallel to the field axis: their origins are discussed in detail elsewhere.[7]

The intensity (I) of any component or group of components observed in either the transverse or longitudinal Zeeman effect can be determined most easily from the correspondence principle. This requires that multiplet emission (absorption) observed *in toto* along a defined axis must show constant polarization and intensity as the magnetic field is reduced to zero. An extension of this requirement is that the total emission (absorption) energy of all lines beginning from any multiplet level (i.e., at any one value of M_J) is equal to the corresponding emission (absorption) energy from any other

TABLE 2

Experimental Z Values

Element	Wavelength (Å)	Transition	Z[a]	Z[b]	Z[31]	R
Ag	3281	$^2P_{3/2}$— $^2S_{1/2}$	1.1 (9)	2.2 (5)		0.05
Ag	3383	$^2P_{1/2}$— $^2S_{1/2}$		3.8 (7)		
Al	3093	$^2P_{3/2}$— $^2D_{3/2,5/2}$			2.7 (9)	
Au	2428	$^2P_{3/2}$— $^2S_{1/2}$	1.1 (9)			0.06
Cd	2288	$^1P_1$ — $^1S_0$	1.3 (9)			0.24
Cd	3261	$^3P_1$ — $^1S_0$	1.0 (6−9)			0
Cr	3579	$^7P_4$ — $^2S_3$	1.0 (7−9)			0
Cu	3248	$^2P_{3/2}$— $^2S_{1/2}$	1.4 (9)		2.7 (6)	0.29
Cu	3274	$^2P_{1/2}$— $^2S_{1/2}$	1.4 (9)			0.28
Fe	2483	$^5F_5$ — $^5D_4$			2.0 (8)	
Hg	2537	$^3P_1$ — $^1S_0$	1.5 (9)	1.5 (20)		0.35
K	7665	$^2P_{3/2}$— $^2S_{1/2}$	1.3 (9)			0.21
Mg	2852	$^1P_1$ — $^1S_0$	1.2 (9)	1.0 (>15)	<2.4	0.14
Mn	2795	$^6P_{7/2}$— $^6S_{5/2}$	1.1 (9)	1.7 (10)		0.10
Na	5890	$^2P_{3/2}$— $^2S_{1/2}$	1.2 (9)			0.15
Ni	2320	$^3G_5$ — $^3F_4$	1.0 (7−9)	1.4 (10)		0
Pb	2833	$^3P_1$ — $^3P_0$	1.2 (9)	1.3 (20)		0.17
Si	2516	$^3P_2$ — $^3P_2$			1.9 (8)	
Zn	2139	$^1P_1$ — $^1S_0$		1.0 (>15)	1.2 (7)	

Note: Numbers in parentheses are the field strengths in kilogauss at which Z was obtained.

[a] Data calculated from the experimental R values of Grassam et al.[23] The R values used are given in the last column. Z and R were related by assuming $K_{\parallel} = K_{zero\ field}$, which gives $Z = 1/1-R$. These values are minimum estimates of Z due to neglect of the change in $K_{\parallel}$ which occurs in practice.

[b] Data estimated from the experimental curves of Koizumi and Yasuda.[21]

level. An analogous statement also applies to terminating lines. Hence putting I_0 for the zero field intensity observed along the same axis as the appropriate multiplet,

$$\tfrac{1}{2}\sum_{\text{all } \Delta M = 0} I_\pi = \sum_{\text{all } \Delta M = +1} I_\sigma = \sum_{\text{all } \Delta M = -1} I_\sigma = \tfrac{1}{4} I_0 \qquad (4)$$

for the transverse effect,

$$\sum_{\text{all } \Delta M = +1} I_\sigma = \sum_{\text{all } \Delta M - 1} I_\sigma = \tfrac{1}{2} I_0 \qquad (5)$$

for the longitudinal effect,

$$\sum_{\text{all components}} I_\pi = \tfrac{1}{2} \sum_{\text{all components}} I_\sigma = \frac{1}{3} I_0 \qquad . \qquad (6)$$

considering the total emission energy of the multiplet over 4π steradians, and

$$2\left(\sum I_\sigma\right)_{M_1} + \left(\sum I_\pi\right)_{M_1} = 2\left(\sum I_\sigma\right)_{M_2} + \left(\sum I_\pi\right)_{M_2} \qquad (7)$$

where for example $(\Sigma\ I_\sigma)_{M_l}$ is the total σ emission intensity originating from (or terminating at) the $M_J = M_1$ level.

These equations are useful for determining signal magnitudes of Zeeman modulated spectrometers (Section V). Equations 4 and 5 are also of interest since it is their symmetry which permits Zeeman modulated signals to be independent of source intensity, *and thus leads to the double beam character of Zeeman background corrected instruments.*

Combined with the knowledge of multiplet symmetry about the zero field line, Equations 4 to 7 can be used to calculate individual component intensities for any multiplet. Examples of this use are given in various references texts.[5,6] However they are cumbersome to use with a complex multiplet and their representation as Equation 8 below is then preferable.

If $\Delta J = 0$ for the zero field line (i.e., $J \rightarrow J$ transition) relative component intensities originating at the multiplet level $M_J = M$ are given by:

$$I_\sigma = (J \pm M \pm 1)\,(J \mp M) \text{ for } M \rightarrow M \pm 1 \tag{8}$$

$$I_\pi = 4M^2 \qquad \text{for } M \rightarrow M$$

$$\text{For } J \rightarrow J + 1,$$

$$J_\sigma = (J \pm M + 1)\,(J \pm M + 2) \text{ for } M \rightarrow M \pm 1$$

$$I_\pi = 4\,(J + M + 1)\,(J - M + 1) \text{ for } M \rightarrow M$$

(The multiplet for $J \rightarrow J - 1$ can be represented as $J' + 1 \rightarrow J'$ and hence as $J \rightarrow J + 1$).

The relative intensities given by Equation 8 are readily converted to values relative to the intensity of the zero field line using Equations 4 to 6. Intensities at optical orientations other than exact longitudinal or transverse may then be determined if required by application of the law of Malus.[8]

Various different constant factors for Equation 8 are given in the literature, according, for example, as to whether the relative or total emission intensity is considered, and in the latter case whether the longitudinal or transverse effect is observed. When using such equations it is necessary to be clear on the exact conditions to which they apply.

Intensities calculated from Equation 8 are valid over the range of field strengths encountered in analytical work, but break down at high field strengths due to the Paschen-Back effect. Equations 4 to 6 are of a more general origin and may be applied at all field strengths.[4-6]

D. The Paschen-Back Effect

The accuracy of the discussion in Sections I.A. through I.C. rests on the assumption that the applied field causes only small perturbations of the energy levels observed. In this context such fields are referred to as "weak". However at high field strengths, particularly for states where L-S coupling is weak, it is sometimes feasible to generate a magnetic field so strong that the magnetic interaction exceeds the L-S coupling energy and thereby decouples L and S. This is the Paschen-Back effect, and the corresponding magnetic fields are referred to as "strong". Independently of the spectroscopic states involved a strong field multiplet always consists of a normal triplet, arising from the interaction between the external field and an atomic moment associated with electronic orbital motion only. Each line of the triplet is, however, split by a constant amount rather than by the field proportional splitting of the weak field case, due to perturbation from electron spin. Of necessity such Paschen-Back triplets would generally occupy a wavelength range of several Å if fully formed. In view of this magnitude the only element likely to show a Paschen-Back effect of analytical interest is Li, where the doublet splitting of the 6708 Å line is so small (0.15 Å) that a Paschen-Back transition commences at field strengths of a few kilogauss.[6] There is no quantitative data on the behavior of Zeeman modulated spectrometers to this effect; however it is known that the effect certainly does not prevent use of Zeeman background correction for the analytical determination of Li.[9,10]

The transition between an anomolous multiplet and a Paschen-Back triplet with increasing field strength is a gradual process. It is accompanied by changes in the relative intensities and positions of each multiplet component which for the most part cannot be calculated by the methods given above. Detailed calculations on these changes are given elsewhere.[4]

E. Hyperfine Splitting

Hyperfine splitting of an atomic line can occur due to nonzero nuclear spin, or due to multiple isotopic abundance. The effect of nuclear spin (quantum number I) on the Zeeman multiplet will be considered first.

As magnetic field strength is increased from zero, each hyperfine component of the original zero field line splits to form its own Zeeman multiplet. This situation only occurs at low field strengths, and the optical resolution of such multiplets is a matter of great difficulty; the situation is thus unlikely to concern the analytical spectroscopist, who is usually forced to atomize samples under conditions where line profiles are wide enough to obscure this initial situation. As the field strength is increased further a nuclear Paschen-Back effect (the Back-Goudsmit effect) occurs to decouple I, and thus transform the anomolous Zeeman splitting of each hyperfine component of the zero field line into a hyperfine splitting of each component of the ordinary, previously described Zeeman multiplet. This process commences at quite low field strengths, reflecting the narrow hyperfine splitting of a zero field atomic line. Thus for example the Back-Goudsmit effect of the Na ($I = 3/2$) $3^2S_{1/2} - 3^2P_{3/2}$ 5890 Å line is essentially complete at field strengths above about 1000 G.[11] At field strengths above that required to complete the Back-Goudsmit transformation, the Zeeman multiplet takes the form already described, except that high resolution measurement shows each multiplet component to be split into $2I + 1$ equally spaced components of equal intensity. This is the situation normally reached at the field strengths used in the present analytical spectrometers.

The hyperfine structure of a Zeeman multiplet component thus differs from that of the zero field line in regard to both intensity distribution and, often, the number of lines observed. These differences arise (1) because the hyperfine intensity distribution of the zero field line depends on the spatial degeneracy of the corresponding hyperfine levels, and this spatial degeneracy is lost in the external field, and (2) because the number of hyperfine components of the zero field line is determined by I-J coupling, which is lost in strong fields. It may be noted however that the actual wavelength ranges occupied by the hyperfine structure of any multiplet component and of the zero field line remain comparable.[6]

A more detailed description of the above behavior is obtained readily by coupling I and J, to give states characterized by the quantum number $F = J + I, J + I - 1 \ldots J - I$ ($J > I$). Each state shows $2F + 1$ fold spatial degeneracy, which is broken by an external field. The derivation of the resulting multiplet patterns, component intensities, etc., is in many respects analogous to that described above for states of $2J + 1$ fold spatial degeneracy. A full discussion of this topic can be found in the reference texts already cited.

The second and independent cause of hyperfine structure is multiple isotopic composition. At low resolution the Zeeman multiplets of each isotope appear identical for a given zero field line. However, at high resolution the equivalent multiplet lines of different isotopes are slightly frequency shifted from each other. The same effects are responsible for this as for the isotope shifts of the corresponding zero field lines, namely, the significantly different nuclear masses of different isotopes for light elements and an assymmetric distribution of nuclear charge for the heavy ones.[6]

Each line of a particular isotope shows a hyperfine structure characteristic of the nuclear spin of that isotope. Thus each isotope will, in general, show a different fine structure in addition to an isotopic frequency shift on all the lines of a Zeeman multiplet. The complete multiplet actually observed experimentally is obtained by summation of each isotopic contribution, combined in proportion to the appropriate isotopic abundance.

The hyperfine structure of a Zeeman multiplet can thus become extremely complex. It has been reported that this complexity can be still further increased in the case of an emission multiplet through self-absorption, which alters multiplet component intensities and in addition causes the appearance of extra lines.[12-14] The latter reports were based on the behavior of the emission multiplets observed from the alkali metals. Corresponding experimental measurements on other elements do not yet appear to have been carried out.

III. ZEEMAN BACKGROUND CORRECTION IN ATOMIC ABSORPTION SPECTROSCOPY

A. Terminology

No uniform terminology has yet been adopted in the literature on this subject, and it seems probable that this will remain the case until the main directions of development for Zeeman modulated instrumentation become more firmly established. The following terminology will be used in the present discussion.

Zeeman modulation (ZM) refers to any atomic absorption system in which a magnetic field is applied, across either the source or the atomizer. "Source modulation" and "atomizer modulation" refer to the application of the field across the source and atomizer, respectively, for the purposes of background correction. "Polarization modulation" refers to any method of selecting π and/or σ components by their particular optical polarization. "Magnetic modulation" refer to any method of distinguishing between π and σ components by use of an alternating magnetic field.

B. History

The first application of the Zeeman effect to atomic absorption spectroscopy appears to have been due to Schrenk et al.[15] who sought to increase the overlap between hollow cathode emission lines and analyte absorption lines by the application of a magnetic field across the hollow cathode lamp. Use of the Zeeman effect for background correction was suggested by Prugger and Torge in 1969,[16] and its specific application to atomic absorption measurements on Hg was demonstrated shortly afterwards by Hadeishi and McLaughlin.[17] The applicability of the technique to various other elements was later demonstrated by a number of different workers.[9,18-20] Early spectrometers were characterized by their use of laboratory-built sources specially designed to meet the unusual technical needs of ZM background correction. However Uchida and Hattori[19] in 1975, and Koizumi and Yasuda,[21] and Dawson et al. in 1976[22] developed the atomizer modulation techniques for flames and for electrothermal at-

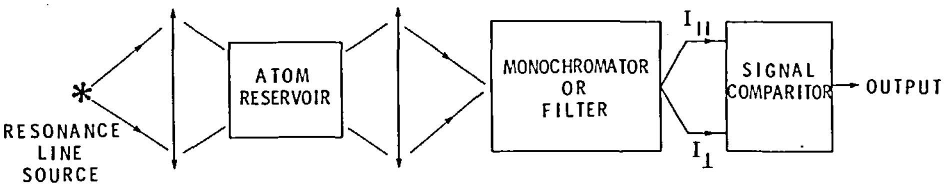

FIGURE 3. Block diagram of the optical arrangement common to all designs of ZM spectrometer.

omizers, respectively, which permitted use of conventional hollow cathode lamp sources. These developments were of the greatest significance, since for the first time they provided access to the powerful ZM background correction technique using routinely available spectroscopic equipment. This ability to utilize conventional equipment, and hollow cathode lamps in particular, appears likely to prove essential to any immediate widespread adoption of ZM background correction or routine application.

C. General Operating Principles of Zeeman Modulated Spectrometers

The symbols $I_{\parallel}$ and $I_{\perp}$ are used below to denote radiation which is linearly polarized in a plane parallel or perpendicular to the magnetic field axis. Thus for a transverse effect emission multiplet $I_{\parallel}$ and $I_{\perp}$ are equivalent to the total π and σ component emission, while for the corresponding absorption multiplet $I_{\parallel}$ and $I_{\perp}$ denote the polarization of incident radiation absorbed by the π and σ multiplet components.

The generalized schematic diagram in Figure 3 shows the major instrumental requirements common to all ZM spectrometers at the present time. The magnet and the modulation apparatus used to separate $I_{\parallel}$ and $I_{\perp}$ are not included, because their nature and position vary with individual instrumental designs. The nature and the relative merits of the various designs are discussed in later sections. In Figure 3 a monochromator or filter is used to isolate the line of interest, and the source is usually amplitude modulated to permit subsequent discrimination against atomizer emission at the source line frequency. This precaution is not always necessary (for example when the Zeeman modulation itself produces only AC analyte signals). The framework of the system is thus quite analogous to that of a conventional single beam instrument. This illustrates a major attractive feature of the ZM background correction technique: namely, that efficient double beam background corrected operation is achieved while retaining the convenience and automatic alignment implicit in the use of a single beam optical system. It also implies that conversion of existing instruments to ZM operation should be technically feasible.

The monochromator bandpass is always sufficient to transmit all the Zeeman components of the line used. Thus ZM instruments are true double beam spectrometers, since they will permit a simultaneous comparison of $I_{\parallel}$ and $I_{\perp}$: a procedure which can yield a signal whose magnitude is independent of source intensity, due to the equality of $I_{\parallel}$ and $I_{\perp}$ already discussed. Variations in the relative transmission efficiencies of $I_{\parallel}$ and $I_{\perp}$ through practical optical components are readily compensated by use of a silica disc as a variable transmission polarizer.[23]

The principle of ZM background correction is indicated in Figure 4. For source modulated instruments $I_{\parallel}$ and $I_{\perp}$ are located predominantly at the center and in the wings of the zero field emission line, for the reasons already discussed in Section II. Thus $I_{\parallel}$ is always attenuated more than $I_{\perp}$ by atomic absorption occurring at the zero field line frequency. However any wavelength invarient background affects $I_{\parallel}$ and $I_{\perp}$ equally. Hence the ratio of $I_{\parallel}$ to $I_{\perp}$ measures atomic absorption irrespective of such a continuum background (Figure 4A). The reasons for using the ratio of $I_{\parallel}$ to $I_{\perp}$, and the effect of a wavelength dependent background on this ratio, are considered in Sections IV.F. and VI.B. below.

A finite multiplet width is required in practice to achieve the above situation, because (1) in practice the analyte absorption maximum is usually frequency shifted from the corresponding emission maximum by pressure broadening. The σ_+ or σ_- components of the emission multiplet have to be shifted through this absorption maximum before useful atomic absorption differences between $I_{\|}$ and $I_{\perp}$ become apparent. (2) The σ components must then be displaced well into the wings of the absorption profile in order to obtain optimum sensitivity (see Section V.B. below). The absorption profiles characteristic of the usual atmospheric atomizers typically require field strengths in the range 5 to 10 kG to optimally satisfy these requirements.

The case of atomizer modulation is the exact spectroscopic inverse of the above. The magnetic field across the absorbing atom cloud splits the absorption profile to the extent where the σ components lie beyond the source emission line. Hence $I_{\|}$ and IvT (which are necessarily of the same frequency in this configuration, in contrast to the source modulated case) are affected to a different extent by atomic absorption, but to the same extent by any background continuum absorption (Figure 4B). The same magnetic field strengths are required for atomizer as for source modulation, and the signal magnitudes of the two techniques are the same,[24] but their noise levels are different. The reasons for this behavior are considered in more detail later.

Thus it is clear that the generation of a Zeeman background corrected atomic absorption signal using either source or atomizer modulation is dependent only on the general form of the Zeeman multiplet, in which a π component envelope covering the zero field line frequency is centered between two σ component envelopes. The discussion of Section II shows this distribution to be quite general. It is expected therefore that ZM background corrected signals can be obtained with either modulation technique using any atomic line upon which conventional zero field atomic absorption is observed. This expectation has by now largely been confirmed experimentally: ZM measurements have to date been reported on over 40 different lines, and no evidence of an inability to use the technique has yet been found. Any reservations regarding the generality of the technique thus appear to have been satisfactorily answered.

IV. INSTRUMENTATION

The present discussion is directed towards spectrometers which have utilized the transverse Zeeman effect for background correction, since almost all the instruments described to date are of this type. There are two exceptions to this: a recent modification of a Varian spectrometer which permitted ZM correction to be obtained,[25] and a Hg detector, described by Hadeishi,[32] which is discussed in more detail below.

A. Polarizers

Use of linear polarizers occurs frequently in the following sections, and some mention of the types available and of their properties is felt to be worthwhile.

In general, transmission and polarization efficiency are not critical parameters for ZM instruments: poor polarizer characteristics reduce signal to noise ratios and can modify the shapes of calibration curves, but they do not affect background correction efficiency. As a rough guide, degradation of spectrometer sensitivity is likely to be detected if the extinction coefficient is greater than about 0.1, or if transmission efficiency falls below about 80% of ideality.

Dichroic polarizers,[21-23] prism polarizers,[10] and stacked quartz plate reflection polarizers[18] have all been used in practice. Quartz plate reflection polarizers show good transmission efficiency even at low wavelengths; their extinction coefficients are satis-

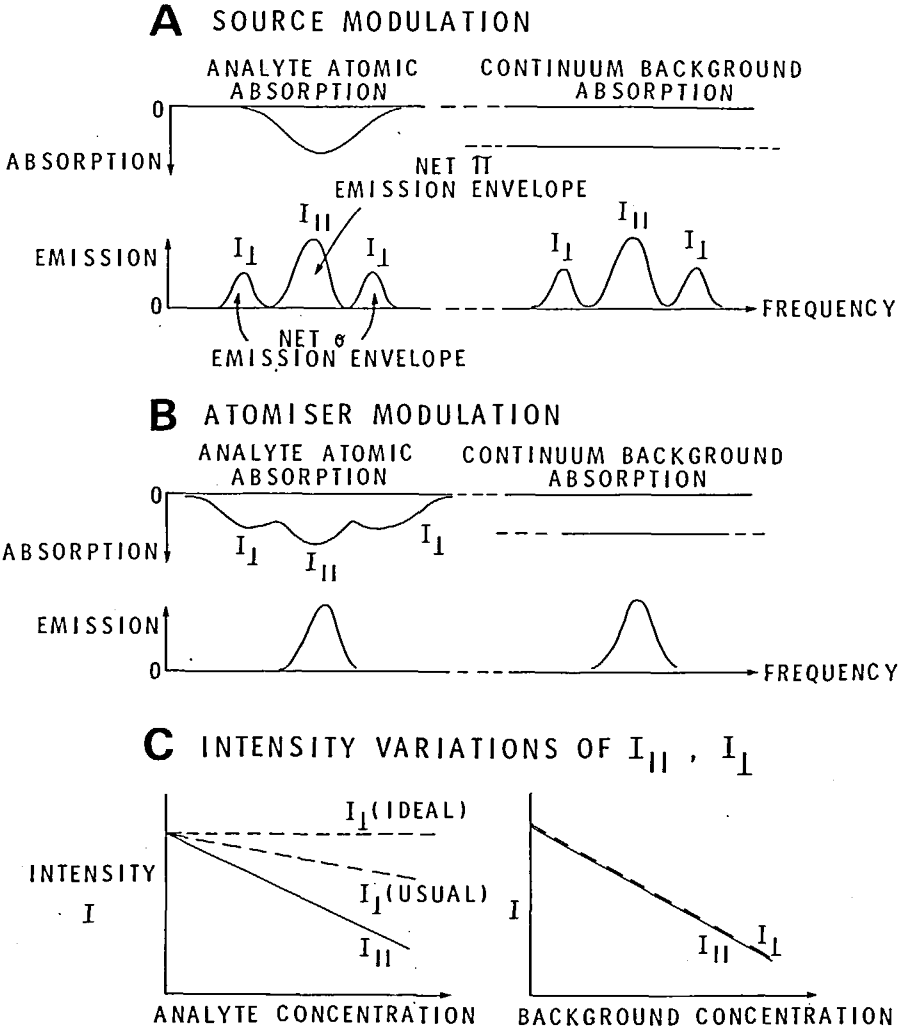

FIGURE 4. Schematic representation of the operation of a ZM spectrometer. (A) Spectroscopic overlap of a Zeeman emission multiplet with a broadened atomic line at the zero field frequency and with a continuum background. (B) Spectroscopic overlap of an emission line with a Zeeman absorption multiplet and with a continuum background. (C) Effect of the absorptions in (A) or (B) on $I_{\parallel}$ and $I_{\perp}$.The analogy between the profile envelopes of net π or σ character and the single π or σ component lines of the normal Zeeman effect is of use, since it permits a ready appreciation of the spectroscopic behavior of ZM spectrometers compared to their conventional background corrected counterparts.

factory, and their use also represents a very appreciable financial saving. However they must be mounted at their Brewster angle. A fixed Brewster angle set for one particular wavelength appears to give satisfactory results over the wavelength range usually required by analytical spectroscopists,[18] so that continual angular adjustment is not necessary. However precise alignment, usually of a combination photomultiplier and polarizer assembly at the monochromator exit slit, is required. This correspondingly complicates initial mechanical assembly.

Except for Wollaston quartz prism polarizers,[10] dichroic and prism polarizers show increasingly poor transmission efficiency at low wavelengths. The lines of Cd at 2288 Å, Pb at 2170 Å, and Zn at 2139 Å are particularly affected by this to the extent that

ZM Pb determinations now tend to be carried on the 2833 Å line, as was done with earlier conventional atomic absorption equipment[26] for similar reasons. In this context it should be pointed out that the choice of an optimum line for a ZM instrument is governed only partly by the usual zero field parameters of source intensity, 1% absorption sensitivity, line to background ratio, etc. The nature of the multiplet and the magnetic field available also affect analytical sensitivity (Section V.B.) so that for any particular element different optimum lines may exist for ZM and for zero field operation.[10,21] However the sensitivity changes associated with the use of ZM which cause this effect are quite small (Section V.B.) so that, although comprehensive data is not yet available, it seems likely that the number of elements thus affected is quite limited.

B. Magnets

The effects of magnetic field stability and homogeneity have not been investigated in detail. Nevertheless it is clear that variations in the former will affect long term signal stability and also the baseline stability of source modulated instruments, while poor field homogeneity is likely to reduce signal to noise ratios. However these parameters are probably not of critical importance. Drift in the average field strength of an electromagnet due to warm-up occurs quite slowly, and can in any case be controlled. Sensitivity data obtained with magnet pole face areas as low as 1 cm^2 suggest that sensitivity losses due to field inhomogeneity are quite small,[18] which accords with the rather broad range of optimum field strength reported for a number of elements.[21,23]

However, even if these factors are considered to be of only secondary importance, the selection of a suitable magnet still requires a compromise. This compromise must be resolved during instrument design by a clear definition of the purpose the instrument is required to fulfill. The need for compromise lies in the rather intense fields required, combined with the fact that the size of magnet needed to generate a given field strength increases as the volume contained between the pole pieces. Thus for source modulation special miniaturized sources must be used if magnet mass is to be kept down; conversely if hollow cathode lamps are to be used, an associated electromagnet mass of several hundred pounds is difficult (although not impossible)[25] to avoid. Atomizer modulation involves an analogous compromise: electrothermal atomizers can be used in conjunction with relatively small magnets, but use of long path flame atomizers is then precluded and flexibility in the choice of atomization conditions open to the analyst is lost. A possible exception to this may lie with atomic fluorescence measurements,[27-29] which in principle could permit flame atomizers to be used with small magnets. However this combination has not yet been investigated for analytical work.

Permanent magnets have been used for both source and atomizer modulation.[18-20] Their use gives significant reduction of size and weight and also eliminates the heat generated by electromagnets which can affect the performance of thermally sensitive apparatus such as hollow cathode lamps.[30] However electromagnets are probably preferable due to their ready control of field strength. Such control is essential if optimum sensitivity is to be obtained[24,31] and also for the correction of a wavelength-dependent background.[24]

C. Atomizers

There is no restriction on the choice of atomizer with source modulated instruments. Atomizers used with source modulation include air-acetylene and nitrous oxide-acetylene flames[18,19,31] and various long path furnaces designed to give simultaneous sample destruction and atom containment for Hg analyis.[17,32-34]

Atomizer modulated instruments have utilized total consumption burners and absorption tubes,[19] carbon rod atomisers[22] and graphite furnaces,[10,23] tantalum or molybdenum heaters,[21] and a dual chamber furnace designed to separate the analyte from a potentially interfering matrix.[35] This latter procedure is probably not essential to obtain accurately background corrected signals, but it can offer advantages in improved signal to noise ratios (since the analyte signal is no longer measured at the moment when source intensity is reduced by background absorption) and a reduction of vapor phase chemical interferences (to which ZM spectrometers are as sensitive as any other type of atomic absorption instrument). In addition, various types of ovens and furnaces[29,36,37] have been described which operated in fields of the strength required for ZM background correction. These devices were developed for the Zeeman scanning of line profiles, and have not been applied to the determination of analytical samples.

D. Sources

There is no restriction on the type of source used with atomizer modulated instruments; hollow cathode lamps are usually employed. Source modulated instruments require the use of magnetically stable lamps. Lamps showing suitable stability include microwave[38-41] and radio frequency[42-44] electrodeless discharge lamps, DC discharge lamps of specialized design,[45] vapor discharge lamps,[14,46] capacitively coupled hollow cathode sources,[47] and conventional hollow cathode lamps.[30] The latter three types all require radio frequency power supplies operating somewhere in the range 0.5 to 15 MHz: a frequency range which is high enough to give magnetic stability, but low enough to avoid the lack of sputtering ability reported for 100 MHz discharges.[43]

Hollow cathode lamps are probably the most satisfactory of these sources, for the following reasons. Vapor discharge lamps appear to work well, but are available for a limited number of elements. Capacitively coupled hollow cathode sources appear to show spectroscopic characteristics comparable to those of conventional hollow cathode lamps: indeed self-absorption was reported to be less for the former due to the pinched discharge used. They also have the advantage of being easily miniaturized for use with small magnets. However they have only been prepared for five elements up to the present time. Electrodeless discharge lamps show variability of performance;[43] this has been investigated in great detail by Jansen et al. for the specific case of Sr tubes.[48] Many also require thermal stabilization, which increases the complexity of the magnet assembly by the introduction of water cooling for the magnet yoke and thermal insulation of the pole faces.[10,35] DC discharge lamps must satisfy the condition that the magnetic and electric field axes be parallel.[45] For lamps designed to operate in a transverse field, the design restrictions thus imposed lead to poor intensity and stability unless rather complex assembly procedures are used.[49] Recently a variation on the original design which may overcome some of these problems was reported, which used the DC discharge as a source of sputtered atoms and a simultaneous 100 MHz discharge for excitation.[43]

Conventional hollow cathode lamps operated in the frequency range 1 to 10 MHz show stability in transverse magnetic fields, and their spectroscopic characteristics do not appear to be adversely affected relative to DC operation. However if high field strengths are required, then correspondingly large and massive magnets are usually needed. In addition, the transverse field causes partial focusing of the discharge along the cathode walls,[30] which may adversely affect lamp lifetime. Conventional DC driven hollow cathode lamps can be operated in longitudinal fields.[25] In this configuration the electric and magnetic axes are parallel in the neighborhood of the cathode, and the condition for magnetic stability of the discharge is therefore met provided the field is homogeneous.

E. Separation of $I_{\parallel}$ and $I_{\perp}$

Most ZM instruments described up to the present time have separated $I_{\parallel}$ and $I_{\perp}$

through their different linear polarizations, and then combined the corresponding signals to give a background corrected resultant as discussed in Section IV.F. below.

Simultaneous measurement of $I_{\parallel}$ and $I_{\perp}$ can be achieved by prisms[43] or by separate reflection polarizers mounted on mutually perpendicular axes.[18] Either prisms or reflection polarizers serve to direct $I_{\parallel}$ and $I_{\perp}$ along different directions onto different photomultipliers. Such systems can be difficult to align, and can also show reduced background correction efficiency due to different effective apertures for $I_{\parallel}$ and $I_{\perp}$.[18]

A more satisfactory technique which avoids such alignment problems is that of time shared measurement of $I_{\parallel}$ and $I_{\perp}$. This may be carried out by use of rotating polarizers aligned to transmit $I_{\parallel}$ and $I_{\perp}$ alternately,[10,22,23,44] or by the optically equivalent method of transmitting the combined $I_{\parallel} + I_{\perp}$ beam through a birefringent modulator and a fixed linear polarizer.[2,24,32,34] Birefrigent modulators cause a controlled, periodic rotation of the plane of polarization of the transmitted radiation (90° rotation in the present case): this causes the fixed polarizer to transmit $I_{\parallel}$ and $I_{\perp}$ in a correspondingly periodic manner. Suitable birefringent modulators used in analytical spectrometers include rotating retardation plates or quartz crystals,[43,44,49] and stress birefringent modulators. The latter devices consist of a silica block which is stressed electromechanically, either by clamping the block in the core of a pulse transformer[50] or piezoelectrically.[51-56] Units of the latter type are now commercially available.* Kerr and Pockels[57] cells may also be used for birefringent modulators. However compared to the mechanically stressed devices Kerr and Pockels cells suffer a number of optical disadvantages, summarized elsewhere,[50] while their main advantage over the former is a high switching frequency. This attribute does not appear to be of importance for ZM applications. Faraday rotation cells can also be built, but again they suffer disadvantages for ZM usage.[58]

Three alternative techniques have been described which do not involve a polarization sensitive separation of $I_{\parallel}$ and $I_{\perp}$.

Hadeishi and McLaughlin[17] have described an instrument in which a beam splitter, placed after the sample absorption cell, was used to produce two $(I_{\parallel} + I_{\perp})$ beams. The $I_{\parallel}$ component was removed from one beam by passing it through a resonance monochromator, and background correction was obtained by comparison between $(I_{\parallel} + I_{\perp})$ and $I_{\perp}$. No analytical data for the system was given.

An alternative instrument described by Hadeishi[32] for the analysis of Hg is of interest, since it made use of the longitudinal rather than the transverse Zeeman effect. In this instrument the σ_+ and σ_- multiplet components from an isotopically pure ^{198}Hg source were sequentially measured by a rotating quarter wave plate and fixed linear polarizer (a similar optical arrangement to that used in Zeeman line profile scanning techniques).[38-41] The absorption maximum of the natural Hg absorption profile is frequency shifted from the ^{198}Hg emission maximum by hyperfine effects and pressure broadening. Thus as the magnetic field across the source is increased, relative atomic absorption on the $\sigma+$ and σ_- components changes: hence in this method σ_+ and σ_- become analogous to $I_{\parallel}$ and $I_{\perp}$ of the transverse effect. The technique appeared to work well for Hg (data were given for seven standard reference materials with Hg concentrations in the 0.1 to 10 ppm range), but is likely to prove less satisfactory for general application. This is because it is not usually feasible to arrange an optimum asymmetry of an absorption profile on, say, σ_+ and a simultaneous and suitably low absorption on σ_-: thus sensitivity is reduced (indeed in the absence of pressure broadening and hyperfine structure such a system cannot respond to atomic absorption at all). The technique of using isotopically pure sources is of specific interest to ZM background correction for Hg, since it permits good sensitivity to be obtained without going to rather high field strengths, required with natural Hg sources due to the complex hyperfine structure of the latter.[10,59]

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* Morvue Electronics, Tigard, Oregon.

The third alternative to separate measurement of $I_{\parallel}$ and $I_{\perp}$ is modulation of the magnetic field itself, either across the source or across the atomizer.[19,41] Atomic absorption on the whole line then decreases as field strength increases and the σ components are displaced towards the wings of the absorption profile. An AC signal is thus obtained, at either the magnet modulation frequency or at a second harmonic thereof. Although no polarizers need be used with this method, better sensitivity is obtained if a single polarizer is used to absorb $I_{\parallel}$. The main advantage this technique offers is improved sensitivity for lines showing anomolous Zeeman splitting, since the atomic absorption measurement is made at zero field strength. However, if iron cored magnets are used modulation frequencies are restricted due to the high resulting inductance of the magnet winding, and sensitivity to a time dependent background may then be expected. In addition, careful mechanical design must be used at these low modulation frequencies to prevent vibration from affecting optical alignment. A commercial Hg analyzer has been built using this modulation technique.* Higher modulation frequencies can be obtained if the magnet core is omitted. This approach has been investigated recently using a water-cooled solenoid to generate a longitudinal field around a conventional hollow cathode lamp.[25]

F. Signal Processing

Only the combination of $I_{\parallel}$ and $I_{\perp}$ is considered here since an exactly analogous discussion can be applied to alternative measurement techniques, such as those using the longitudinal effect or magnetic modulation.

$I_{\parallel}$ and $I_{\perp}$ are equally affected by a continuum background, and simple subtraction of the corresponding signals provides an approximate correction (it should be noted that phase sensitive detection of birefringent or magnetically modulated signals invariably constitutes subtraction unless due precaution, such as simultaneous provision of automatic gain control to maintain a constant $I_{\perp}$ signal, is employed). However subtraction, although used quite widely,[17,18,22,23,32] is not the most effective technique available for the following reasons.

Put ${}^{o}I$ = intensity in the absence of absorption
${}^{b}K$ = background absorption coefficient of $I_{\parallel}$ or $I_{\perp}$
${}^{a}K_{\parallel}$ = atomic absorption coefficient of $I_{\parallel}$
${}^{a}K_{\perp}$ = atomic absorption coefficient of $I_{\perp}$
${}^{a}N$ = number of atoms in the absorption beam
${}^{b}N$ = number of particles causing background absorption

then

$$I_{\parallel} = {}^{o}I_{\parallel} \cdot \exp - ({}^{a}K_{\parallel} \cdot {}^{a}N + {}^{b}K \cdot {}^{b}N) \qquad (9)$$

and

$$I_{\perp} = {}^{o}I_{\perp} \cdot \exp - ({}^{a}K_{\perp} \cdot {}^{a}N + {}^{b}K \cdot {}^{b}N) \qquad (10)$$

where ${}^{o}I_{\parallel} = {}^{o}I_{\perp} = \frac{1}{2} \cdot {}^{o}I$, using Equation 4.

Thus for small values of ${}^{a}K$, ${}^{a}N$,

$$(I_{\parallel} - I_{\perp}) \simeq \tfrac{1}{2} \cdot {}^{o}I \cdot (\exp - {}^{b}K \cdot {}^{b}N) \cdot ({}^{a}K_{\parallel} - {}^{a}K_{\perp}) \cdot {}^{a}N \qquad (11)$$

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* Scintrex Ltd., 222 Snidercroft Rd., Concord, Ontario.

while for small values of ${}^bK \cdot {}^bN$,

$$(I_{\|} - I_{\perp}) \simeq \tfrac{1}{2} \cdot {}^oI \cdot (1 - {}^bK \cdot {}^bN) \cdot (\exp[-{}^aK_{\|} \cdot {}^aN] - \exp[-{}^aK_{\perp} \cdot {}^aN]) \qquad (12)$$

From Equation 11 it is apparent that no background signal is observed as ${}^aN \rightarrow 0$. However Equations 11 and 12 show that signal magitudes when ${}^aN \neq 0$ are affected by a background absorption. Thus accuracy is lost as a result of the subtraction procedure.

A better technique is to measure the ratio of $I_{\|}$ to $I_{\perp}$. From Equations 9 and 10 $I_{\|}/I_{\perp} = \exp({}^aK_{\|} - {}^aK_{\perp}) \cdot {}^aN$; thus the ratio is always independent of a wavelength invarient background. Techniques for carrying out the ratio operation include analog division of the $I_{\|}$ and $I_{\perp}$ signals,[31] and the application of automatic gain control through variable gain amplifiers[20] or through photomultiplier voltage[10,21,43,44] to maintain a constant signal corresponding to $I_{\perp}$ (or to the total source intensity). An analysis of these procedures has been given elsewhere.[31]

The discussion above suggests that subtraction of the absorbances of $I_{\|}$ and $I_{\perp}$ should also be an adequate procedure. To be effective in practice, this requires accurate matching of the $I_{\|}$ and $I_{\perp}$ logarithmic amplifiers. At the present time there is no information to show whether such matching can be carried out sufficiently easily to offer a preferable alternative to the methods mentioned above.

V. CHARACTERISTICS OF ZEEMAN MODULATED SPECTROMETERS

A. Calibration Curves

Various workers have noted that the calibration curves produced by ZM spectrometers can show a maximum,[18,23] and this represents a disadvantage for analytical work in view of the reduction of linear working range and the potential ambiguity thus introduced.

This maximum is actually an artifact of the particular instrument concerned, rather than a characteristic of the ZM technique. The effect is observed only for high analyte concentrations with instruments in which signal processing leads to subtraction of $I_{\|}$ and $I_{\perp}$, and arises because the existence of high analyte concentrations violates the assumptions made when $I_{\|} - I_{\perp}$ is used as a measure of the background corrected analyte signal. The effect is illustrated in Figure 5, in which the signals $S_1 = I_{\|} - I_{\perp}$, $S_2 = 1 - I_{\|}/I_{\perp}$, and $S_3 = \log I_{\|}/I_{\perp}$ are plotted on a normalized scale. The signals S_1, S_2, S_3 were calculated directly from Equations 9 and 10 of Section IV.F. for ${}^bK = 0$ and $K_{\|}/K_{\perp} = 2.5$ Thus the curves of Figure 5 show only the features characteristic of the signal processing; they do not include any of the additional factors responsible for the shaping of atomic absorption calibration curves which are encountered in practice.[60]

In the absence of the effects discussed above, the experimental evidence currently available suggests the working ranges of ZM calibration curves may be a little better than with conventional instruments,[10] particularly in cases where the atomic absorption coefficient of $I_{\|}$ is reduced by anomolous Zeeman splitting or when the technique of

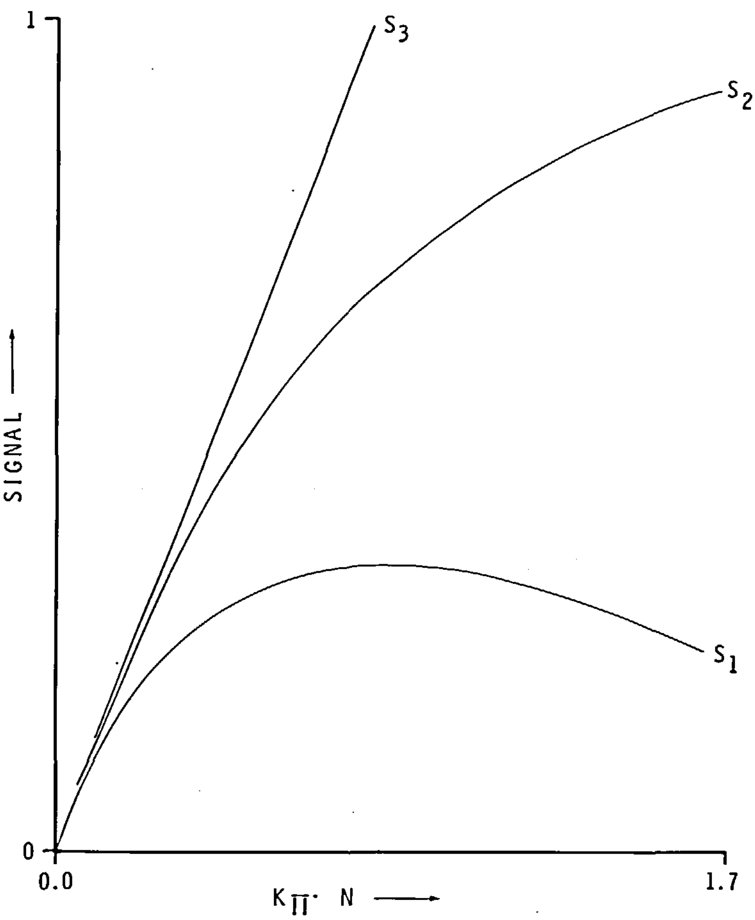

FIGURE 5. Calibration curves calculated from Equations 9 to 12.

magnetically induced optical rotation (Section VII.B.) is used. A technique for extending the useful working range of ZM calibration curves has been suggested[61] which is appilcable to most types of signal processing. In this technique single beam measurements are made on the σ components only of the multiplet. This permits the single beam atomic absorption coefficient to be reduced at will by increasing magnetic field strength. Background correction ability is lost with this method; however since it is automatic that only high analyte concentrations are involved this loss may not be critical. Concentration measurements up to 1200 ppm were obtained by this means.

B. Signal Magnitudes of ZM Spectrometers

In the discussion below the influence of factors such as atomization efficiency, sample delivery rate, absorption path length, etc. on an atomic absorption signal has been neglected; such factors will be assumed to affect all types of atomic absorption spectrometer equally.

The operation of an ideal background correction system should be such as to cause no reduction in the magnitude of genuine atomic absorption signals as a result of the background correction process. Unfortunately ZM spectrometers do not usually behave in this way, and their signal magnitudes and hence maximum analytical sensitivity are reduced in consequence. There are two main reasons for this lack of ideality: these are (1) the influence of anomolous Zeeman splitting and (2) the effect of hyperfine line structure. In order to discuss these effects quantitatively and to assess their combined influence on the signal magnitudes produced by ZM instruments, a parameter Z will be introduced. Z will be defined as the numerical ratio of the signal magnitude produced by an ideal background corrected spectrometer to that produced by a practical ZM instrument under equivalent conditions. Thus Z takes values from unity to infinity.

Anomolous Zeeman splitting raises Z values above unity for two reasons. The first is that, even allowing for frequency shifts due to pressure broadening, the separation of the π components from the zero field line frequency at the magnetic field strengths used in practice reduces the absorption coefficient of $I_{\|}$. Absorption coefficients for $I_{\|}$ have been measured for a number of lines at various field strengths.[18,21,23] The latest work reports[23] $I_{\|}$ atomic absorpton measured on 15 different lines to be within about 85% of the zero field absorption in all cases for field strengths up to 9 kG. However, values below 85% are known to exist,[21] in particular for field strengths much beyond 9 kG.

The second result of anomolous Zeeman splitting is that atomic absorption on $I_{\perp}$ is seldom negligible, since the field strength required to achieve negligible $I_{\perp}$ absorption usually also causes an unnecessary absorption loss on $I_{\|}$. Thus any signal processing technique involving subtraction or division of $I_{\|}$ and $I_{\perp}$ reduces the useful atomic absorption signal correspondingly.

The only circumstances where these effects are not apparent are when the line observed splits to give a normal triplet, or when magnetic modulation is used. In the former case $I_{\|}$ remains at the zero field frequency, and it is usually possible to apply a sufficiently strong field for atomic absorption on I_{σ} to be reduced to a negligible level. In the latter case atomic absorption measurements can be made under zero field conditions where the above effects are irrelevant. Finally, it is worth noting in the present context that identical Z factors occur where a given type of polarization selection of $I_{\|}$ and $I_{\perp}$ is used irrespective of whether source or atomizer modulation is employed.[24] The last two comments hold also in the presence of the hyperfine effects discussed below.

The effects of hyperfine splitting of ZM signal magnitudes are extremely difficult to discuss quantitatively, especially when the effects of source self-absorption and profile assymmetry due to pressure broadening are considered. This difficulty has already been noted by workers using the Zeeman line profile scanning technique,[38] and in fact has proved to be one of the reasons this method is not more generally applied. Intuitively, one might expect that the modification of hyperfine structure caused by the applied field is unlikely to lead to sensitivity enhancements. This supposition is supported to some extent by the fact that no Z values below unity have yet been reported. In addition, Grassam et al. recently described measurements in which absorption ratio of $I_{\perp}$ to I_{σ} were measured against field strength.[23] The resulting curves, in particular for the Cu 3248 Å and 3274 Å lines, showed anomolies attributable to hyperfine effects. These anomolies were such as to increase Z, although apparently to a lesser extent than the increases caused by anomolous Zeeman splitting. This technique appears to be a most useful way to obtain information regarding the sensitivity dependence of ZM spectrometers on the hyperfine splitting of the multiplet.

The only reported instance where a complex hyperfine structure can be utilized to advantage is the determination of Hg. In this case use of isotopically pure sources[17,20,32-34] can significantly enhance ZM signal magnitudes, particularly at low field strengths,[10,17,59] and also permits use of the longitudinal measurements already mentioned.

The quantitative influence on signal magnitudes of the effects discussed above can be assessed by empirical measurement of Z. Numerical values of Z, or related data, are available for a number of lines (Table 2). Optimum values of Z fall in the numerical range 1 to 3 and there is no reason to suppose that this range is not typical. Therefore it appears that, at optimum magnetic field strength, major sensitivity losses due to the behavior of either anomolous Zeeman splitting or of hyperfine component structure are not likely to be encountered. On the basis of this data, it is thought therefore that the analytical applicability of the ZM technique is unlikely to be more than marginally affected by the signal losses which are inherent to the method due to the above causes.

C. Effect of Magnetic Field Strength on ZM Signal Magnitudes

The preceding discussion shows the quantitative dependence of Z on magnetic field strength to be generally of extreme complexity. Even qualitative predictions based on the substitution of the Landê factors of Table 1 into Equation 1 can be misleading, although correlation can be obtained in certain cases.[10,21,43] Thus the optimum field strength required for any particular line under given experimental conditions should always be determined experimentally. Conversely, the sensitivities of different lines towards ZM operation should only be quoted at the optimum field strengths characteristic of those lines with the particular spectrometer used.

Comprehensive empirical data relating to optimum field strengths have been published by Grassam et al.[23] and by Koizumi and Yasuda.[21] The former group have reported numerical values of the $I_{\perp}$ to $I_{\parallel}$ absorbance ratio for 12 elements over a range of field strengths from 0 to 9 kG. The latter workers calculated theoretical multiplet distributions for a large number of lines. Multiplets for all the lines examined were classified into eight different types of pattern, the pattern characteristic of any particular element being related to the position of that element in the Periodic Table. Experimental percentage transmission curves for $I_{\parallel}$ and $I_{\perp}$ vs. field strength were given for field strengths up to 20 kG for selected example lines from each pattern. These data provide excellent experimental evidence firstly for the general applicability of ZM background correction, and secondly for the validity of the remarks made above concerning the extent of the sensitivity losses characteristic of the ZM technique.

D. Noise Sources Characteristic of ZM Spectrometers

Two noise sources can occur with ZM spectrometers which must be corrected if optimum efficiency is to be obtained. The first of these is "Schlieren noise", which arises because thermal gradients around an atomizer cause $I_{\parallel}$ and $I_{\perp}$ to be transmitted with slightly different efficiencies;[62] thermal fluctuations therefore appear as noise on the spectrometer output. Such noise cannot be corrected on atomizer modulated instruments unless a modulated magnetic field is used rather than polarization separation of $I_{\parallel}$ and $I_{\perp}$. It can however be corrected readily on source modulated instruments by placing a birefringent modulator between source and atomizer, and using the associated linear polarizer to ensure the instrument only accepts radiation in a fixed plane of polarization.[31]

The second source of noise is "self absorption noise".[31] This occurs only in source modulated instruments, and arises because sputtered atoms tend to diffuse away from the exciting discharge, into a region where the magnetic field is reduced. Hence they tend to absorb $I_{\parallel}$ preferentially, which causes the net source output to be slightly polarized. The DC offset thereby induced in the spectrometer output can be compensated forby use of quartz reflection polarizers, angled to reflect a suitable fraction of $I_{\perp}$ out of the optical path.[31,59] However fluctuations in the degree of self-absorption cannot be thus compensated, and appear as noise or drift on the spectrometer output. No fully satisfactory technique has been developed to compensate for such noise, although various approaches have been tried.[31] However hollow cathode lamps are reported to show sufficient stability for self-absorption noise to be neglected for measurement periods up to about 100 sec.[31]

It has been reported that the field strengths giving a maximum self-absorption signal from a hollow cathode lamp are lower than those giving an optimum analyte response.[30] A flame atomizer was used, and the effect was attributed to the absorption profile in the lamp being narrower than that in the flame. The effect can be used to give further partial discrimination against self-absorption noise.

E. Relative Analytical Sensitivity of ZM and Continuum Background Corrected Instruments

Comparisons in the following two sections are drawn specifically between ZM and continuum (D_2 or H_2) corrected spectrometers. However quite analogous comparisons exist for the less common situation where correction is made using a nonresonance line[63-65] or with a xenon-mercury continuum.[66]

It has been pointed out that, provided the ZM associated noise described above is overcome, a ZM spectrometer can give better detection limits than a conventional continuum corrected instrument.[31] Two reasons given for this are (1) the excellent ZM background correction capability permits use of higher sample delivery rates before errors due to background absorption become apparent and (2) since extraneous noise due to source intensity or background absorption fluctuations is corrected, ZM spectrometers should be signal to noise (S:N) limited by photon noise:[67,68] i.e., all other factors being corrected, the S:N ratio improves as the square root of source intensity. This is a minimum noise level below which no true absorption instrument will go with existing methods of data processing. Consequently ZM instruments show the long term stability, noted by several workers,[10,18,23] which permits use of correspondingly long integration times to improve S:N ratios.

It must be emphasised that the above comments do not necessarily mean that ZM spectrometers are automatically more sensitive than continuum corrected instruments. For pure analyte solutions condition (1) no longer need apply to the latter, provided the (occasionally serious) effect of solvent background[69,70] is not important. In this case double beam continuum corrected instruments are also capable in principle of satisfying condition (2), in which case their sensitivity will be comparable or better than that of a ZM spectrometer, according to the value of the Z factor of the latter. Thus the relative sensitivities of these instruments depend upon the particular analytical situation considered: i.e., the nature of the sample matrix, type of atomization used, the properties of the analyte, the spectroscopic line used, etc. A general conclusion that can be given however is that at worst the S:N ratio of a ZM spectrometer will be lower than that of a continuum corrected instrument by the factor Z. As background correction becomes increasingly important the sensitivity differences between the two become smaller, until finally the ZM instrument becomes the more sensitive. This relative dependence becomes more marked as sample delivery rates are increased. The pattern is well illustrated by the data of Koizumi and Yasuda,[43] who found that Cd and Pb could be determined directly in blood serum and urine with ZM correction, but that prior ashing was necessary with D_2 correction. Analogous data have also been given by Grassam et al.[23]

It is implicit in the above comparison that the instruments concerned show the same source intensity, that the intensities of sample and reference beams are exactly matched (these correspond to $I_\parallel$ and $I_\perp$ in the ZM case, and matching is thus automatic), and that optical transmission losses are comparable. Such a comparison is reasonable between ZM and continuum corrected instruments: it is however more complicated for alternative devices such as those using wavelength modulation of laser[71] or continuum sources.[72-78] No generalized comparison will be given here, other than to point out that any alternative background correction device must show a parameter analogous to Z and that various equations have been derived which therefore permit a theoretical S:N comparison to be made once this parameter is known.[31,67,68]

F. Comparative Sensitivity Parameters for ZM Spectrometers

It is apparent from the discussion above that a strong need exists for the introduction of a parameter suitable for relating the sensitivity of ZM spectrometers both to each other and to non-ZM instruments. There is no general consensus on this matter in the literature: workers have tended to derive comparative factors suited to their own particular experiments as the need arose. The Z factor used here is the same factor used by the author to relate the detection limits of a ZM spectrometer to the conventional 1% absorption sensitivity figures of non-ZM instruments.[31] This is not to suggest that Z necessarily merits wider adoption; merely that it happens to be convenient in the present discussion.

Other comparison factors used include the "R" factor of Dawson et al.[22,23] defined as the ratio of atomic absorption on $I_\perp$ to that on $I_\parallel$. This parameter was used to determine the dependence of ZM signal magnitudes on field strength for various elements:[23] it is also very suitable for comparing the signals of different ZM instruments at low analyte concentrations. However R is less easy to use directly to compare ZM and non-ZM spectrometers, due to its lack of any ground zero counterpart.

The use of the 1% absorption sensitivity on $I_\parallel$ as an equivalent to the conventional 1% absorption sensitivity has also been suggested.[35] this is probably less satisfactory however since it neglects the (often significant) effect of atomic absorption on $I_\perp$.

The above parameters all interrelate ZM signal magnitudes at a defined field strength, and fulfill a more or less similar purpose to the conventional 1% absorption sensitivity concentration. They are undoubtedly useful since they permit comparison to be made without specifying the associated noise levels, which can be a (sometimes arbitrary) function of the particular instrument design. If the effects of noise are to be included the best comparative parameter is a defined S:N ratio, as pointed out by Hadeishi and McLaughlin.[35]

It is to be hoped that some standardization of a comparative technique suitable for ZM spectrometers will be reached before the now rapidly expanding use of these instruments causes a further proliferation of terms.

VI. BACKGROUND CORRECTION EFFICIENCY

A. Comparison of Zeeman Modulation and Continuum Corrected Spectrometers

The power of the ZM background correction technique has been demonstrated under various stringent absorption conditions, including smoke,[18] NaCl vapor,[35] and the vapors produced by the ashing of matrices such as blood serum,[22,23,44] fishmeal,[35] and urine.[10,44] In a very convincing series of experiments Grassman et al.[23] demonstrated the superiority of ZM over D_2 correction with such testing background media. These workers developed apparatus which could display simultaneously the signals from an atomizer modulated ZM system and from a conventional D_2 background corrector. When applied to the detection of Pb in serum measured at 2833 Å the ZM system corrected a background of 2 absorption units to within .005 absorption units; this was at least a factor of five better than the correction obtained from the D_2 corrector even after careful alignment. This magnitude of ZM correction, and the observations concerning the relative efficiency of D_2 correction, agree well with the data reported by Koizumi and Yasuda.[44] In view of the combined evidence now available, the superior efficiency of the ZM over D_2 background correction must be regarded as proven.

The superiority of ZM correction for a continuous absorption background probably arises for two main reasons. The first is that the sensitivity to optical alignment characteristic of continuum correctors is not apparent with a ZM instrument. Thus the "sample" and "reference" beams are generated in the same optical volume of the same source and travel identical optical paths; hence optical alignment of the two beams is always automatically optimized. The second reason is that the atoms responsible for emitting "sample" and "reference" beams are not segregated in the source. Thus the relative spatial distribution of $I_{\parallel}$ and $I_{\perp}$ in the wavefronts traveling through the optical system is homogeneous. Therefore, a continuously absorbing medium affects $I_{\parallel}$ and $I_{\perp}$ equally, even when that medium shows nonuniform longitudinal and/or lateral distribution through the optical path, and even when that nonuniformity is time dependent.

Consideration will now be given to the relative background correction efficiency of atomizer and source modulation. For a wavelength invarient background the correction efficiency of both systems can be readily shown to be identical.[24] The correction efficiency is limited only by the accuracy with which $I_{\parallel}$ and $I_{\perp}$ are measured and by the linearity of signal processing circuits. It is worth noting however that unless the response times, as well as the gain, of the circuits used to handle the $I_{\parallel}$ and $I_{\perp}$ signals are accurately matched, even a moderate background absorption which changes rapidly with time can generate a transient which may be indistinguishble from a genuine pulse signal. Errors due to this cause are characteristic of electrothermal rather than flame atomizers.

B. Effect of a Wavelength-Dependent Background

When the background signal shows a wavelength dependence over the multiplet both source and atomizer modulated instruments can give a spurious response. This situation arises for example when two atomic lines occur in close proximity.[79] The probability of such spectral overlap occurring is proportional to the bandpass of the instrument concerned, and is therefore usually greater with D_2 than with ZM correction. In general the magnitude of such interferences is different for source and atomizer modulation, since interference in the former arises because of absorption variations across the analyte emission multiplet, while in the latter interference arises because of varying absorption of the emission line across the absorption multiplet of the interferant. The effect is discussed quantitatively elsewhere.[24] No details are currently available on the magnitude of such interference effects for atomizer modulated instruments. Line interferences have been examined experimentally between the Hg and Co lines at 2536.49 Å and 2536.52 Å and between the Fe and Pt lines at 2719.03 Å and 2719.04 Å using a source modulated instrument, however, and suitable correction techniques for these interferences are reported to be available.[24] This report concluded that the techniques developed were likely to be useful for other interference systems, and were also likely to be equally applicable to atomizer modulated instruments. In view of the known sensitivity of continuum background correction to line interferences[70,80] it appears probable that the superior ease of use and efficiency of ZM background correction apparent for a continuum background is observed to an even greater extent with line interferences.

In view of the discussion given above it will be apparent that comments made in the literature, to the effect that atomizer modulation permits background correction to be carried out at exactly the same wavelength as that used for the atomic absorption measurement,[10,21-23] must be interpreted judiciously. Such comments do not mean that all background effects are automatically eliminated by use of atomizer modulation, nor do they mean that the background rejection capability of atomizer modulation is necessarily superior to that of source modulation. The relative effectiveness of the two configurations depends entirely upon the absorption profile of the particular interferent and the nature of the Zeeman structure which that profile happens to show.

VII. FURTHER DEVELOPMENTS

A. Atomic Fluorescence

Koizumi and Yasuda have mentioned the possible extension of the ZM technique to provide scatter correction in atomic fluorescence measurements.[43] Techniques of measuring ZM atomic fluorescence have already been described for the Zeeman scanning of emission profiles;[27-29] however no analytical application of these techniques has yet been developed. The technology required by fluorescence measurements appears little different from that associated with the absorption equipment described above, and it seems probable that effective ZM atomic fluorescence scatter cancellation can be achieved. The problems of molecular fluorescence interference appear analogous to those of line interferences in the absorption mode, in which case a possible ZM correction can be foreseen here as well.

An interesting potential advantage of ZM atomic fluorescence measurements is the reduction of magnetic field strengths achievable by use of the Hanle effect. The Hanle effect describes the magnetic depolarization of the fluorescence excited by a polarized source[7] on application of an external magnetic field.

The effect relies on the external magnetic field being sufficiently strong to break the spatial degeneracy of atomic energy levels, and this requires lower field strengths than those required to also induce measurable frequency shifts in the associated Zeeman multiplet components. Hanle effect measurements are usually made at low pressure[81-83] to avoid the collisional depolarization apparent in atmospheric atomizers. However Chenevier and Lombardi have reported successful measurements of a Hanle dispersion curve for the Cd 2288 Å line in an atmospheric air-acetylene flame.[84] Similar data have also been reported by Evdokimov et al.[85] It is not clear how general this phenomenon might be, nor how useful it might prove analytically, and more data would be of interest.

B. Magnetically Induced Optical Rotation (MIOR)

MIOR is a recent approach to ZM background correction:it is instrumentally similar to the techniques described above, but is spectroscopically quite different.

In the MIOR technique linearly polarized light from a resonance line source is passed through an atom reservoir located in a longitudinal magnetic field. The situation is thus instrumentally analogous to an atomizer modulated ZM spectrometer utilizing the longitudinal Zeeman effect. However a MIOR instrument differs in that a second linear polarizer is placed after the atom reservoir, the two polarizers being crossed to prevent transmission of the resonance line to the detector. The presence of analyte atoms in the atom reservoir causes rotation of the plane of polarization of the incident radiation to occur (Faraday effect), and light is then transmitted through the second polarizer.

The origin of this effect lies in the relative frequency shift of the circularly polarized σ components of the analyte absorption multiplet, which gives rise to a difference in the refractive index of the absorbing medium for right handed and for left handed circular polarizations of incident radiation. Full details are discussed elsewhere,[7,86] and only a brief summary of the properties of the phenomenon will be given here.

The degree of polarization rotation observed at an emission frequency ν and absorption frequency ν_0 is approximately proportional to $(\nu - \nu_0)^{-2}$. It is also dependent on the vapor phase atom concentration of the analyte, the magnetic field strength and the path length of the absorption cell.

The spectroscopic selectivity of the technique arises from the refractive index discontinuity observed at ν_0. The sharpness of this discontinuity reflects the narrowness of the emission and absorption lines used, so that in practice the selectivity of MIOR and of atomic absorption spectroscopy are comparable. However species showing a wide band absorption at the source emission line do not give rise to large values of $(\nu - \nu_0)^{-2}$, and thus do not cause polariztion rotation; hence, unlike atomic absorption, MIOR is not sensitive to the presence of such species. Therefore the technique shows an automatic and inherent "background correction" facility.

Three MIOR spectrometers have been described up to now;[87-89] full details are only available on two of these[87,89] at the time of writing. These latter instruments were used for the detection of Hg vapor. In the most recent version,[89] the atom reservoir comprised a 30-cm tube carrying a 3000 turn solenoid driven at 60 Hz and giving a maximum field strength of 900 G, which illustrates the ability of MIOR to utilize lower field strengths than conventional ZM spectrometers and therefore to permit use of correspondingly less cumbersome magnet assemblies. This in turn makes it technically easier to employ AC modulation of the magnetic field. The optical system consisted of an Hg electrodeless discharge source mounted at the focus of a collimating lens to produce an approximately parallel beam through the atom reservoir. Calcite prism polarizers were used which, in conjunction with the collimated optical system, gave an extinction coefficient of the order of 10^{-5}. A good extinction coefficient is more important with pMIOR than with conventional ZM to obtain a good S:N ratio, for reasons indicated below. The Hg 2537 Å line was isolated by a Hg line filter and the signal detected by a lock-in amplifier, using the magnetic modulation for its reference, in a normal fashion.

A theoretical analysis of the instrument showed the output signal to contain frequencies of 60 and 120 Hz due to the magnetic modulation (higher harmonics also occur, but are of successively lower amplitude). The simultaneous 60 and 120 Hz signals were observed in practice, and use of the ratio of these signals, rather than either one alone, as a measure of Hg concentration appeared to give an unusual extension to the linear working range of calibration curves. The background rejection capability of the instrument was tested with benzene and with acetone vapor, and its lack of sensitivity to these appeared to be fully comparable to that of a conventional ZM instrument. MIOR background rejection of smoke and of NaCl vapor generated by the electrothermal atomization of 25,000 μg/mℓ NaCl solutions has also been reported.[86]

The analytical sensitivity of MIOR is a matter of interest, since S:N ratios of the technique are determined by different factors from those associated with conventional ZM spectrometers. MIOR signals are stronger for lines which split to give an anomolous multiplet rather than a normal triplet, for reasons discussed elsewhere.[7] In addition, the technique is not inherently limited by photon noise due to the source. The pS:N ratio at a given analyte concentration is governed by source intensity and photomultiplier dark noise, in much the same way as with atomic fluorescence: however unlike atomic fluorescence the S:N ratio of MIOR increases with absorption path length. Experimental detection limits so far reported for MIOR are given in Table 3, and can be seen to compare quite favorably with the corresponding values obtained with conventional ZM spectrometers. Preliminary studies thus appear to indicate that the technique is an effective approach to ZM background correction, and that further data should prove to be of interest.

VIII. CONCLUSIONS

The technique of Zeeman modulated background correction has received independent examination from several groups of workers under some extremely testing experimental conditions. From the data thus obtained it is evident that the background correction efficiency of the method is very significantly superior to that of the continuum background correction systems currently in wide routine use. In addition, and unlike

TABLE 3

Comparison of MIOR and ZM Detection Limits

	Detection limit, g		Sample size	
Element	MIOR	ZM[10]	MIOR	ZM[10]
Cd[86]	5×10^{-13}	3×10^{-13}	5 μℓ	20 μℓ
Cu[86]	3×10^{-11}	1×10^{-11}	5 μℓ	20 μℓ
Hg[87]	4×10^{-12}	1×10^{-10}	1 mℓ vapor	20 μℓ
Pb[86]	5×10^{-11}	4×10^{-12}	5 μℓ	20 μℓ

continuum correctors, the ZM technique can be applied to any wavelength the analyst may require without regard to the intensity balance of sample and reference beams, since these intensities are always automatically optimized by the equality of $I_{\parallel}$ and $I_{\perp}$. Furthermore, the ZM technique is immune to degradation of performance caused by misalignment, since alignment is always exactly optimized in a properly designed instrument by the automatic and homogeneous coincidence of sample and reference beams. These features represent an in-built degree of efficiency and reliability which clearly recommends the technique for routine application.

No theoretical or experimental reason has emerged to show why the advantageous characteristics of ZM background correction should not be observed for any element upon which conventional atomic absorption measurements can be made. Consideration of the relative analytical sensitivities of conventional and ZM background corrected spectrometers suggests that in the worst cases a ZM spectrometer may lose a factor of about three relative to a continuum corrected instrument. (Even this factor is not inherent to the ZM technique, but arises because of the polarization selectivity of existing instrumental designs.) Furthermore, the relative sensitivity of the former improves as the magnitude of the background which is to be corrected increases. Thus in practice the ZM spectrometer can frequently be expected to show comparable or superior sensitivity to a continuum corrected instrument. To the present, only a limited amount of experimental evidence has been reported upon which to judge this expectation: however the evidence which is available supports it in a most convincing manner. It is felt therefore that a comparison of the analytical sensitivities of ZM and continuum corrected spectrometers does not markedly favor the latter.

Hence it is concluded that the adoption of ZM rather than continuum background correction for routine analytical use must be regarded as a highly desirable objective, since such a development can be expected to lead to improved accuracy and precision of analytical data at a minor cost of some small sensitivity losses in a few cases. The techniques required to so utilize the Zeeman effect are mostly very recent, and further developments both in existing types of equipment and in alternative and possibly more effective ways of applying the Zeeman effect must be anticipated. Therefore it is probable that a spectrometer design which combines optimum instrumental simplicity, flexibility, and performance has not yet been achieved. However it is also very clear that efficient ZM spectrometers suitable for reliable routine operation can be built now, by use of the technology already developed for existing instrumental designs. It is to be hoped that such technology will be employed to provide a greater commercial availability and to ensure a correspondingly wider usage of these instruments in the future.

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