The application of atomic absorption spectra to chemical analysis

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Summary—The theoretical factors governing the relationship between atomic absorption and atomic concentration are examined and the experimental problems involved in recording atomic absorption spectra are discussed. On the basis of the discussions, it is shown that such spectra provide a promising method of chemical analysis with vital advantages over emission methods, particularly from the viewpoint of absolute analysis. It is also suggested that the absorption method offers the possibility of providing a simple means of isotopic analysis.

1. Introduction

The application of atomic spectra to chemical analysis has proved so successful over such a wide field that there is a tendency to overlook some of the basic limitations of existing methods. In spite of the remarkable advances in technique which have resulted in press-button analyses of high precision at fantastic speeds, there has been practically no progress whatsoever in solving the fundamental problem of devising an absolute method, i.e., a method which will provide an analysis without comparison with chemically analyzed standards or synthetic samples of known composition. In routine analysis for production control this problem is of little consequence, since it is only necessary to have a limited number of standards, and in such work modern direct-reading methods leave little to be desired, except on the score of complexity of equipment and associated expense. When analyses of miscellaneous materials are required, the task of providing the required range of standards becomes insurmountable and the spectrochemical method then loses its accuracy, since accurate analyses generally necessitate the use of standards which are closely similar in composition to the sample for analysis. In some analyses it is also essential that the sample and standards be similar as regards physical condition. For example, the intensity of the spectrum of a metal or alloy may vary with the metallurgical history of the sample. This difficulty may be overcome by taking the sample into solution, but accurate and sensitive methods of analyzing solutions are only available for the limited range of elements, having a low excitation potential, which can be estimated by flame photometry. In this method, also, it is necessary to use standard solutions having compositions closely similar to that of the test solution.

The possibility of adapting any of the existing methods to absolute analysis does not appear to be promising. In the first place, there seems to be little prospect of developing a light source which is such that the emission spectrum of a given element is not affected by the presence in the atomic vapour of atoms of other elements. Secondly, even if these interelement effects were eliminated, there remains the problem of absolute intensity measurement and the associated problem

of determining the distribution of atoms over the various energy states. In practice there is the third difficulty that electrical discharges of the type now in use do not give a stable output of radiation; modern methods conceal these erratic variations in output by integrating, photographically or photoelectrically, the radiation over a period of several seconds. Finally, there are other problems arising from self-absorption and self-reversal, and from the fact that the processes of vaporization and excitation are not isolated from each other. A review of these and other aspects of source behaviour has been given elsewhere [1].

At the present stage of its development there is no doubt that the major obstacle to further progress in the technique of spectrochemical analysis is the occurrence of interelement effects, since if these could be eliminated it would be possible to use the same set of standards for the determination of any one element in any material. With existing emission methods the intensity of a given spectrum line due to one particular concentration of an element in different materials varies greatly. For example, PROKOF'EV [2] reports that for the same concentration of silicon the intensity of the silicon lines in the spark spectrum of steel is eight times as great as in brass, and in duralumin the intensity is even less. Many other examples of interelement effects have been published.

No satisfactory explanation of these effects has yet been given, nor can one be expected, since the phenomena occurring in the arc and spark discharges used as light sources are far too complex to permit of any theoretical analysis, and the approach to the subject seems likely to remain essentially empirical. It seems possible, however, to arrive at certain broad conclusions. Since interelement effects are usually of the same order of magnitude for different spectrum lines of a given element, corresponding to transitions between different energy states, they probably arise from changes in the concentration of atomic vapour rather than changes in the excitation conditions. However, such changes cannot occur in sources in thermal equilibrium at a constant temperature. Thus, if thermal equilibrium is assumed, then interelement effects must necessarily be due to a change in the temperature of the atomic vapour. Whilst the behaviour of the electrical discharges used in spectrochemical analysis shows that it is not justifiable to assume thermal equilibrium or to ascribe a temperature to the discharge, it is instructive to consider the effects of changes in temperature on a mass of atomic vapour in thermal equilibrium.

Consider the emission of a spectrum line due to the transition from an excited state j, of excitation energy E_j, to a ground state of energy $E_0 = 0$. Then if P_j and P_0 are the statistical weights for the excited state and ground state respectively, the number of atoms in the excited state, N_j, is related to the number of atoms in the ground state, N_0, by the relation

$$N_j = N_0 \frac{P_j}{P_0} e^{-\frac{E_j}{kT}} \tag{1}$$

and, neglecting self-absorption and induced emission, the intensity of the emitted line is proportional to N_j.

In order to illustrate the magnitude of N_j/N_0, the calculated values for resonance lines of various elements at different temperatures are given in Table 1.

Table 1. *Values of N_j/N_0 for various resonance lines*

Resonance line	Transition	P_j/P_0	N_j/N_0			
			$T = 2,000°K$	$T = 3,000°K$	$T = 4,000°K$	$T = 5,000°K$
Cs 8521 Å	$^2S_{1/2} - ^2P_{3/2}$	2	4.44×10^{-4}	7.24×10^{-3}	2.98×10^{-2}	6.82×10^{-2}
Na 5890 Å	$^2S_{1/2} - ^2P_{3/2}$	2	9.86×10^{-6}	5.88×10^{-4}	4.44×10^{-3}	1.51×10^{-2}
Ca 4227 Å	$^1S_0 - ^1P_1$	3	1.21×10^{-7}	3.69×10^{-5}	6.03×10^{-4}	3.33×10^{-3}
Zn 2139 Å	$^1S_0 - ^1P_1$	3	7.29×10^{-15}	5.58×10^{-10}	1.48×10^{-7}	4.32×10^{-6}

It will be seen that in nearly all cases the number of atoms in the first excited state is only a small fraction of the numbers of atoms in the ground state. The fraction only becomes appreciable at high temperatures for states of low energy. Since most elements have their strongest resonance line at wavelengths below 6,000 Å, and since we shall be concerned mainly with flames or furnaces having temperatures below 3,000°K, we may regard N_j as negligible compared to N_0. The fraction of atoms in higher excited states is much less than those given above, and thus ΣN_j is also negligible compared with N_0, and the latter can be considered as equal to the total number of atoms, N.

Thus, whilst the number of excited atoms varies exponentially with tempera-ture, the number of atoms in the ground state remains virtually constant and therefore the integrated absorption $\int K_\nu \, d\nu$ due to transitions from the ground state is independent of temperature. (This discussion only applies to atoms having a ground state well removed from the lowest excited state; the case of atoms having a multiplet ground state is discussed in Section 2.)

On the basis of the above discussion it would appear that atomic absorption spectra would have important advantages over emission spectra as a means of chemical analysis. It is therefore surprising to note that the research in this field has been devoted almost exclusively to emission spectra; the annual review [3] of progress in spectrochemical analysis is, in fact, given under the general title of "emission spectroscopy." Apart from the special case of estimating the contamina-tion of room and laboratory atmospheres by mercury vapour, the application of atomic absorption spectra to chemical analysis appears to have been confined to astrophysical work on the determination of the composition of the solar and stellar atmospheres.

The purpose of this paper is to examine the theoretical factors governing the relationship between atomic absorption and atomic concentration and to discuss the experimental problems involved in recording atomic absorption spectra. On the basis of these discussions, it is shown that such spectra provide a promising method of chemical analysis with vital advantages over emission methods, particularly from the viewpoint of absolute analysis. It is also suggested that the absorption method offers the possibility of providing a simple means of isotopic analysis.

2. Variation of atomic absorption with atomic concentration

The relationships between atomic absorption and atomic concentration, under various conditions, are fully discussed in several papers, mainly in astrophysical journals, and in standard reference books [4–6]. For the purpose of this discussion it is sufficient to consider only the most fundamental of these relationships. In this section the discussion will be further restricted by assuming that atomic absorption lines possess no fine structure; the case of isotopic hyperfine structure is discussed later in Section 4.

Consider a parallel beam of radiation of intensity I_{0_ν} at frequency ν incident on an atomic gas or vapour of thickness l cm. Then if I_ν is the intensity of the transmitted beam, the absorption coefficient K_ν of the vapour at frequency ν is defined by

$$I_\nu = I_{0_\nu} e^{-K_\nu l} \tag{2}$$

The dependence of K_ν on ν, i.e., the shape of the absorption line, is determined by the nature of the transition involved in the absorption and on the physical conditions such as temperature, pressure, and electrical fields, to which the atoms are subjected during the measurement.

According to classical dispersion theory, the relationship between absorption and concentration is given by

$$\int K_\nu \, d\nu = \frac{\pi e^2}{mc} N_\nu f \tag{3}$$

where e is the electronic charge, m the electronic mass, c the velocity of light, N_ν the number of atoms per cm^3 which are capable of absorbing in the range ν to $\nu + d\nu$, and f, the oscillator strength, is the average number of electrons per atom which can be excited by the incident radiation. Equation (3) is not valid for strong absorption lines, since it assumes that the refractive index is of the order of 1 over the breadth of the absorption line.

For a resonance line due to a transition from a ground state which is well separated from the lowest excited state, N_ν can be considered as equal to N, the total number of atoms per cm^3 (see Table 1). If, however, the transition does not originate in the ground state, or if there is a multiplet ground state, then the number of atoms capable of absorbing is given by

$$N_\nu = N \frac{P_i e^{-\frac{E_i}{kT}}}{\sum P_j e^{-\frac{E_j}{kT}}} \tag{4}$$

where i denotes the initial state involved in the transition, and the summation in the denominator extends over all possible energy states. In practice, of course, the summation can be restricted to the low-lying levels.

In terms of transition probabilities the equation corresponding to equation (3) is

$$\int K_\nu \, d\nu = \frac{\lambda^2 P_j}{8\pi P_i} \cdot N_\nu A_{ji} \left(1 - \frac{P_i}{P_j} \frac{N_j}{N_\nu}\right) \tag{5}$$

where λ is the wavelength at the centre of the absorption line, P_i and P_j are the

statistical weights of the lower and upper states, respectively, involved in the transition, and A_{ji} is the Einstein coefficient of spontaneous emission for the $j \to i$ transition. N_j is the number of atoms in the upper electronic state, and will generally be negligible compared with N_ν, and in this case equation (5) reduces to the well-known relation:

$$\int K_\nu \, d\nu = \frac{\lambda^2 P_j}{8\pi P_i} \, N_\nu A_{ji} \tag{6}$$

In the general case N_ν is given by (4), but for resonance lines is equal to N. Similarly, if the transition from the jth to ith state is the only one which can occur, as in the case for resonance lines, $A_{ji} = 1/\tau$, where τ is the mean life of an atom in the excited state j.

Equations (3) and (6) provide simple relationships between absorption and concentration, and it is now necessary to investigate whether they can be applied to a practical method of spectrochemical analysis. Since the intensities of spectrum lines are usually expressed in terms of oscillator strengths, it is convenient to consider equation (3).

Firstly, it is necessary to know whether suitable absorption lines occur in regions of the spectrum which are amenable to measurement. In terms of sensitivity, it is obviously desirable to use the strongest resonance lines, and in general these will correspond to the strongest lines occurring in emission spectra. These are listed in a paper by MEGGERS [7], and reference to this shows that with the exception of the rare gases, hydrogen, mercury, the halogens and the metalloids, all elements have their most sensitive lines in the region 2,000–9,000 Å. Thus the lines for all the more common elements all lie in regions of the spectrum where measurements are simple to make.

The oscillator strengths of some of these lines have been determined, and are listed in Table 2. Theoretical calculation [8–14] of f-values is possible for atoms having simple electronic structures, but has not yet been carried out for heavy atoms having a complex structure. BATES and DAMGAARD [15] have described a simplified theoretical method and have published tables from which the absolute strengths can be rapidly obtained. The method has been shown to give accurate results for all transitions in the lighter simple systems, but there are insufficient experimental data to enable one to judge to what extent the method can be applied to the more complex electronic structures.

It is interesting to note that the oscillator strength for the strongest copper line is approximately the same as for the alkali metals, in spite of the fact that the closed 3d shell of the copper atom is not nearly so tightly bound as the inner electron shells of the alkali metals. By comparison with the f-values of other elements in Group 1, it seems probable that rubidium, silver, and gold will have f-values of the order of 0·7 for their strongest resonance lines. Similarly, the Group 2 elements Zn and Sr may be expected to have f-values of the order of 2 for their strongest lines.

It does not appear possible at the present time to make any corresponding estimates of the oscillator strengths of spectral lines of other elements, particularly those such as iron and cobalt, with complex electronic structures and multiplet

ground states. The possibility of determining approximate f-values for such elements by a simple experimental method is discussed in Section 4.

For those elements for which the oscillator strengths are known, the atomic concentration can be determined from the integrated absorption coefficient, using equation (3); the experimental problems involved in measuring such coefficients are discussed below.

Table 2. List of f-values

Resonance line	Transition	f	Reference
Li 6708 Å	$^2S_{1/2} - {}^2P_{3/2}$	0·50	[9]
Na 5890	$^2S_{1/2} - {}^2P_{3/2}$	0·70	[16]
K 7665	$^2S_{1/2} - {}^2P_{3/2}$	0·64	[17]
Cu 3247	$^2S_{1/2} - {}^2P_{3/2}$	0·62	[18]
Cs 8521	$^2S_{1/2} - {}^2P_{3/2}$	0·66	[19]
Be 2349	$^1S_0 - {}^1P_1$	1·82*†	[11, 13, 14]
Mg 2852	$^1S_0 - {}^1P_1$	1·74*	[13, 14]
Ca 4227	$^1S_0 - {}^1P_1$	2·28*†	[12, 13, 14]
Cd 2288	$^1S_0 - {}^1P_1$	1·20	[20]
Ba 5535	$^1S_0 - {}^1P_1$	2·10	[21]
Hg 1849	$^1S_0 - {}^1P_1$	1·19	[22]
Tl 2769	$^2P_{1/2} - {}^2D_{3/2}$	0·20	[23]
Cr 4254	$^7S_3 - {}^7P_4^0$	0·084	[24]
Ni 3415	$^3D_3 - {}^3F_4^0$	0·02	[25]
Fe 3720	$a^5D_4 - z^5F_5$	0·013	[29]

* Theoretical values.
† BIERMANN and TREFFTZ [13] state that these values should be corrected according to the method described in ref. 14. See also the values quoted in ref. 30.
Footnote. Since the purpose of this table is to indicate the order of the f-values for various lines, the values obtained by different observers are not included. They are discussed by KORFF and BREIT [26] and by MITCHELL and ZEMANSKY [4].

3. Experimental determination of atomic absorption coefficients

The shape of an atomic absorption line is determined by (a) the natural width of the line due to the finite lifetime of the excited state; (b) the Doppler contour due to the motions of the atoms relative to the observer; (c) pressure broadening, either by atoms of the same kind giving rise to resonance broadening or to foreign gases;

and (d) Stark broadening due to external electric fields or to neighbouring charged particles. The natural width of an atomic spectral line is of the order of 10^{-4} Å, and for the purposes of this discussion is negligible compared to the width due to other causes.

The Doppler width of a line is given by

$$D_\lambda = 1.67 \frac{\lambda}{C} \sqrt{\frac{2RT}{M}} \tag{7}$$

where R is the universal gas constant and M is the atomic weight. Typical values of D_λ are given in Table 3.

Table 3. Values of D_λ at various temperatures

Element	λ	M	D_λ		
			1,000°K	2,000°K	3,000°K
Na	5890	22·3	0·028 Å	0·039 Å	0·048 Å
Cu	3247	63·6	0·0092 Å	0·0013 Å	0·016 Å
Zn	2139	65·4	0·0060 Å	0·0085 Å	0·010 Å

If we assume that a temperature of 2,000°K is required to produce sufficient vapour, then the Doppler width is of the order of 0·01 Å. The accurate measurement of the profile of such a line would require a resolution of about 500,000, which is beyond the performance of most spectrographs. In addition, if it is desired to use photoelectric methods of intensity measurement, then it is scarcely feasible to use a continuous source, since the energy emitted over such a small spectral slit-width would be too small to give a high enough signal/noise ratio. In the past this difficulty has often been overcome by using the method of total absorption, in which the energy removed from the incident beam is measured. This method has the advantage that the measurement is independent of the resolution of the monochromator, but suffers from the disadvantage of giving a complicated relation between N and f, according to the region of the curve of growth in which the measurement is made. However, if the absorption is so strong that it is not possible to make an accurate measurement of the absorption coefficient, as in astrophysical work, then the curve-of-growth method is the only one available. The method has been successfully applied to the measurement of oscillator strength from furnace absorption spectra by KING [18] and by ESTABROOK [24, 25].

From the point of view of spectrochemical analysis, a more attractive method appears to be to measure the absorption coefficient at the centre of the line, using a sharp-line source which emits lines having a much smaller half-width than the absorption line. If the shape of the latter is determined entirely by Doppler broadening, we have [27]

$$K_{\max} = \frac{2\lambda^2}{D_\lambda} \sqrt{\frac{\ln 2}{\pi}} \cdot \frac{\pi e^2}{mc^2} Nf \tag{8}$$

where D is the Doppler width. Thus in this case also there is a linear relation between absorption and concentration.

If such a sharp-line source is used, it is now no longer necessary to use a spectral slit-width of the same order as the half-width of the absorption line. The require-ment now is the ability to isolate a selected line from other lines emitted by the source. Thus spectrographs having the same resolution as those used in conventional emission methods are adequate. In many cases it may be sufficient to use filters.

Various methods of producing such sharp-line sources are available. In our work it has been found convenient to use hollow-cathode discharge tubes, and it has proved possible to make sealed-off tubes about the size of a photomultiplier tube.

There is one other experimental difficulty. In many cases vaporization of the sample will result in the emission of radiation at exactly the wavelength where it is desired to make the absorption measurement. This difficulty can be overcome by modulating the incident radiation before it reaches the atomic vapour and amplify-ing the output of the detector by an amplifier tuned to this modulation frequency. Thus the radiation emitted by the atomic vapour, which is not modulated, produces no signal at the output of the amplifier.

So far it has been assumed that the line shape is determined solely by Doppler broadening, and this is sensibly true if the vapour is produced by a vacuum furnace, such as that used by KING, and if the vapour pressure is so small that resonance broadening is negligible. Another convenient method of vaporizing the sample is to atomize a solution of the sample into the air supply of a Meker burner, as in emission methods of flame photometry. In this case there is broad-ening due to foreign gases, and, although we have not made accurate measurements for the flame we have used, its magnitude is probably of the same order as that due to thermal motions. Once the broadening due to pressure is known, the corresponding correction to equation (8) can be applied, using the tables published by ZEMANSKY [28]. As an example, if the pressure broadening width is equal to the Doppler width, the maximum absorption is 43 per cent of that due to Doppler broadening alone.

IV. Discussion

The above discussion of atomic absorption spectra has indicated the attractive possibilities of using them for chemical analysis and of developing a method which will provide a useful complement to emission methods and in many cases may well supersede them. One of the main attractions of this absorption method is that, theoretically, it is expected to be much less susceptible to interelement effects. In so far as effects observed in emission are due to variations in the distribution of atoms over the various excited states, they would have no counterpart in absorption where this is due to a transition from the ground state. Similarly, absorption will not be critically dependent on the temperature of the atomic vapour, since the Doppler width only varies as $T^{1/2}$, whereas small changes in temperature produce large changes in the intensity of the emitted radiation. In addition, the integrated absorption coefficient is independent of wavelength, in marked contrast to the emission intensity, which will vary according to Planck's law.

Whilst the discussion has been limited to the ideal case of a vapour in thermal equilibrium, in practice there may be effects due to a sheath of cool vapour. But whereas in emission spectroscopy this causes self-reversal which reduces the peak intensity, in absorption it will contribute to the absorption and will in no sense reduce the sensitivity. Incidentally the self-reversal observed in emission spectra provides a good indication of the sensitivity of the absorption method. Another cause of deviation from thermal equilibrium is chemiluminescence; this may well produce a number of excited atoms, which is comparable with that due to thermal excitation, but will not produce any significant change in the number of unexcited atoms. Thus the effects on the absorption spectrum are negligible compared to those on the emitted radiation.

On the experimental side, the important advantage of the absorption method lies in the fact that the measurement of the absorption coefficient consists of measuring the ratio of two intensities, which is much simpler to achieve than the measurement of emission intensities in absolute units.

The possibilities of absolute analysis have been discussed and the use of a relative absolute method may also be noted. For example, if the sample solution is atomized into a flame, then a calibration for one element would serve to deduce the approximate calibration of other elements, provided the oscillator strengths are known. In this connection it would appear that, using standard solutions, this method could be used to determine oscillator strengths, at least to within an order of magnitude.

Finally, the absorption method may prove suitable for isotopic analysis. If sources emitting spectra of only one isotope are used, then an analysis for this isotope can be obtained directly, since the oscillator strength is the same for each component of the hyperfine structures of the excited level. If no pure isotope is available, then sources having different concentrations of isotopes may be used. Alternatively, an isotopic filter containing the vapour of one or more isotopes may prove satisfactory.

The results of some preliminary experiments have been in full accord with the conclusions arrived at in this paper, and future papers by J. P. SHELTON and the author will describe the construction of an atomic absorption spectrophotometer and its application to various analytical problems.

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