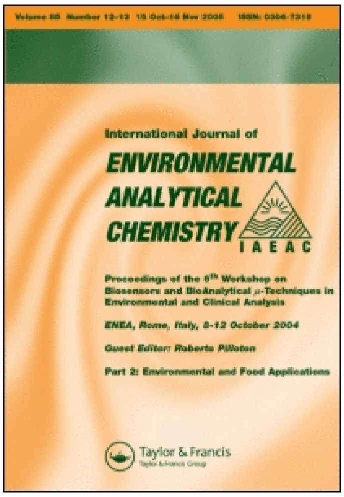

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Analytical Aspects of Photoelectron Spectroscopy†

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Photoelectron spectroscopy is a new technique for experimentally measuring the binding energies of electrons in molecules. The basic principles of the method are outlined and simple guidelines for the interpretation of u.v.-excited photoelectron spectra are laid down. The analytical potential and possible development of the method are briefly surveyed.

BASIC PRINCIPLES

Photoelectron spectroscopy is an experimental technique for measuring the binding energies of electrons in atoms and molecules. Thus, it is of fundamental importance and interest to the modern chemist, who has been weaned on molecular orbital theory. There are few chemically important techniques which do not find analytical usage, and it would be strange if such a major development as photoelectron spectroscopy proved an exception to the rule. It is therefore not surprising that it has attracted considerable attention since the independent pioneer studies of K. Siegbahn,[1,2] D. W. Turner[3] and Vilesov.[4]

The objects of this paper are to say (i) what the technique is, (ii) what its theoretical basis is, and (iii) how the method may be applied to analysis. An underlying theme is that much may be learned from the photoelectron spectrum without recourse to computers and theoreticians.

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The basic principles of the method and instrument are shown schematically in Figure 1. The method is based on an energy balance in reactions of the type

$$M + h\nu = M_n^+ + e_n \qquad (1)$$

where M is a sample molecule, $h\nu$ is a monoenergetic photon from the energy source and e_n is an electron from the nth orbital. This basic reaction, which occurs in the target chamber, refers to the ejection of just one electron, but it does not specify which electron. In fact, any electron whose binding energy is less than the photon energy may be ejected and this is indicated by the subscripts in equation (1). During the ionizing process the molecular ion may become vibrationally and rotationally excited to energies $E_{p(\text{vib})}$ and $E_{r(\text{vib})}$, respectively. Additionally, it will receive kinetic energy from the photon, but this can be neglected, and the kinetic energy of the molecular ion can be assumed to be that of the sample molecule. So if I_n is the energy required to ionize one electron from the nth orbital, i.e. the nth orbital ionization potential, the energy balance is given by

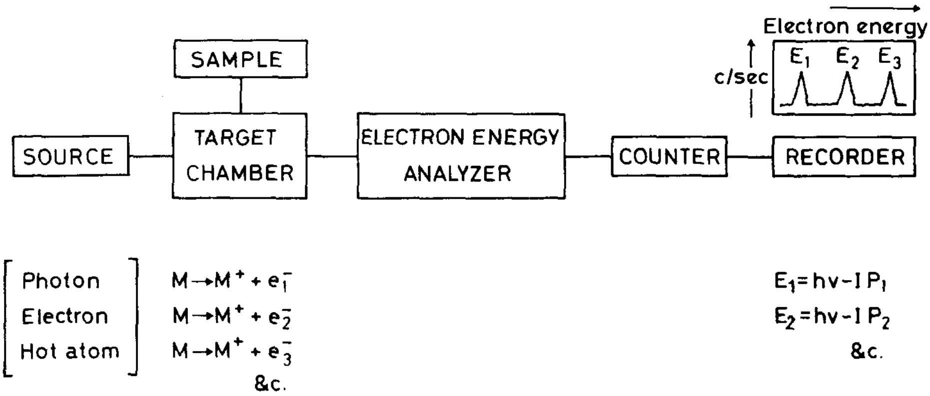


FIGURE 1 Schematic representation of photoelectron spectrometer and basic reactions.

$$\text{Energy of ejected electron} = E_{\text{elec}} = h\nu - I_n - E_{p(\text{vib})} - E_{r(\text{rot})} \qquad (2)$$

Since $I_n > E_{p(\text{vib})} > E_{r(\text{rot})}$ (I_n being typically 10–500 eV, E_{vib} being 0.1 eV and E_{rot} being 0.01 eV) this simplifies to

$$E_{\text{elec}} = h\nu - I_n \qquad (3)$$

For each value of n there may be several values of p and r so that a photoelectron spectrum consists basically of several bands (I_n) which may have fine structure ($E_{p(\text{vib})}$).

The energies of the ejected electrons are measured and the experimentally obtained photoelectron spectrum is a plot of count rate (electron flux) against electron energy. Several instruments are calibrated for use with a specific source so that the plot is directly of count rate against ionization potential. Depending on the instrument and the worker the ionization potential may increase or decrease from left to right, therefore one must always note the convention employed when reading the literature.

It follows that the experimentally measured ionization potentials reflect the molecular orbital levels within a molecule which in turn reflect the electron distribution. This can be illustrated in a qualitative way by considering the HCl molecule. The occupied molecular orbitals, in order of increasing energy (decreasing ionization potential) are (i)–(iv) the scarcely modified 1s, 2s, 2p and 3s orbitals on chlorine, (v) the bonding orbital formed by H 1s and Cl 3p and (vi) and (vii) the degenerate, scarcely modified 3 2p "one pair" orbitals on chlorine. There are thus six ionization potentials which could be measured. Only two of these are less than 21.21 eV so that the photoelectron spectrum obtained with a helium 584 Å (21.21 eV) source will only show two bands (Figure 2) whereas one excited with a more energetic X-ray source will show six bands.

The source employed clearly has a bearing on the spectrum obtained. At present the two sources noted above are commonly employed and although photoelectron spectroscopy is a name applicable to both, photoelectron spectroscopy (PES) and electron spectroscopy for chemical analysis (ESCA) are often used to refer to u.v. and X-ray excitation, respectively. From many viewpoints u.v.-PES and X-ray-PES are preferable terms. The spectra

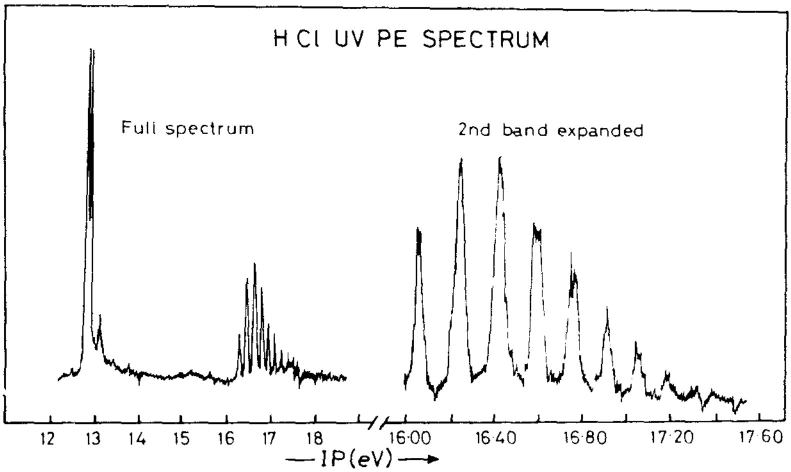


FIGURE 2 U.v.-PE spectrum of HCl (ref. 3).

obtained with the two sources differ in other respects also. The X-ray-excited spectrum extends over 1000 eV or more whereas a u.v.-excited spectrum spans only 10 or so eV. This results in much more clearly defined bands being obtained in a u.v.-PE spectrum. Further, the u.v.-PE spectrum originates from the valence shell molecular orbitals and thus provides direct information about molecular bonding. In particular, the spectrum may show the presence of π or lone-pair electrons, the positions and nature substituents or an isomeric form of the sample. Because many peaks in the X-ray-excited spectrum derive from essentially pure atomic orbitals, it is most useful for identifying the elements present in the sample molecule. Further, since the atomic orbitals are slightly modified on combination, it is often possible to deduce that atoms of an element are in non-equivalent positions within the molecule and to determine the proportion of atoms in a particular environment (Figure 3).

Most of the subsequent discussion will be qualitative, so it is worth considering one molecule which is simple enough to be subjected to full molecular orbital treatment. Water is such a molecule. The appropriate combinations of atomic orbitals which give rise to the molecular orbitals whose energies have been calculated (Table I) are shown in Figure 4. The X-ray and u.v.-PE spectra are shown in Figures 5 and 6.

The agreement between theory and experiment is reasonable; it is well within the limits of theoretical error. The theoretical results are such that we

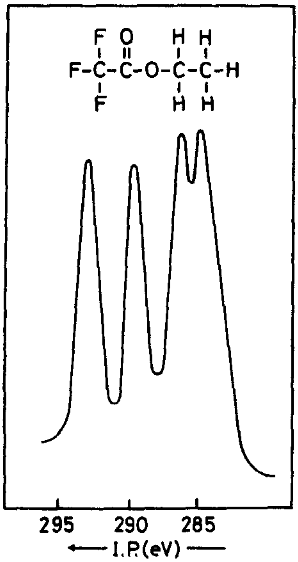


FIGURE 3 X-ray-PE spectrum of ethyl ester of trifluoroacetic acid.

TABLE I

Calculated and experimental ionization potentials for water

I.P. eV	1st ($1b_2$)	2nd ($3a_1$)	3rd ($1b_1$)	Ref.
Experimental	12.61	13.7	17.22	3
Calculated	11.79	13.2	18.55	5
	13.14	14.50	17.50	6
	14.18	16.19	19.82	7
	13.79	15.84	19.56	8
	10.94	12.92	17.22	9

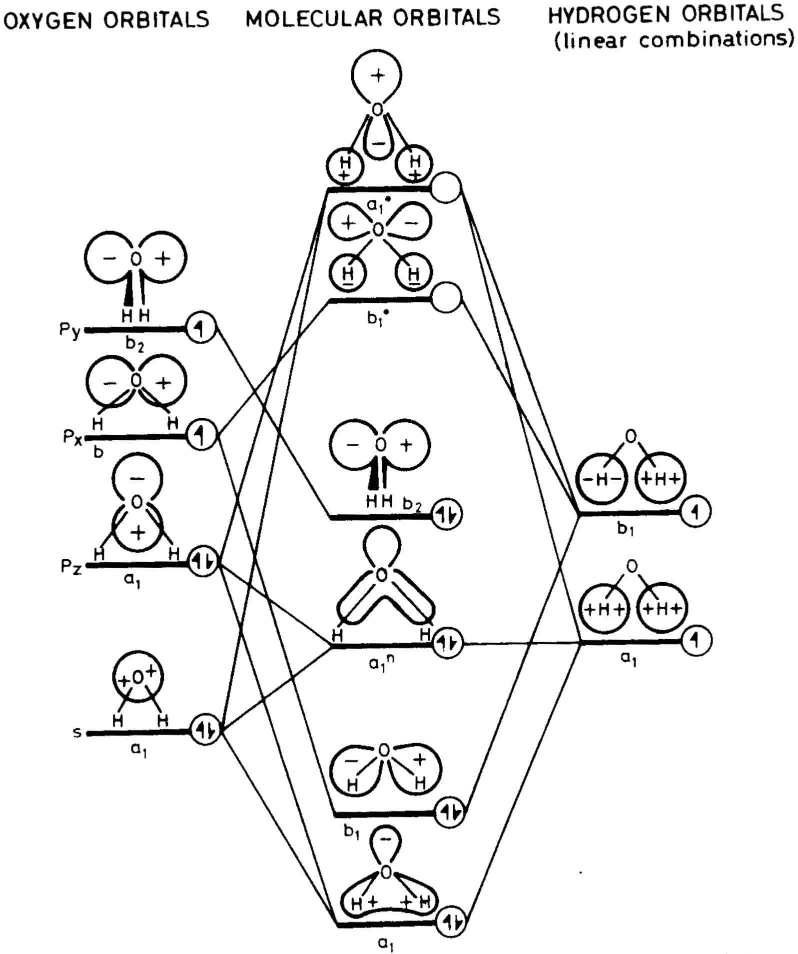
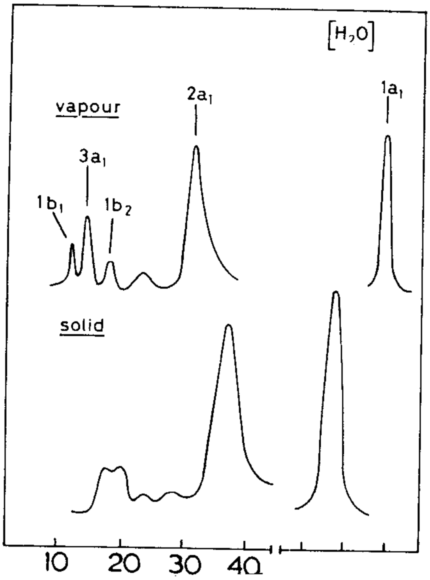


FIGURE 4 Combination of atomic orbitals of water to give molecular orbitals (Oxygen 2_p does not combine with the H 1s orbitals) and MO energy level diagram for water. Oxygen p_y is essentially non-bonding. (Royer, D. J., *Bonding Theory*, McGraw-Hill, 1968).


[H₂O]
vapour
1b₁
3a₁
1b₂
2a₁
1a₁
solid
10
20
30
40

is in the 1 position its p-orbitals or π-system can interact with π_2 but not with π_1. Hence π_2 is no longer degenerate with π_1 and two bands appear in the spectrum. If the substituent has a degenerate pair of p- or π-orbitals, e.g. 3p on chlorine, only one of the pair will have the correct symmetry to interact with the benzene π_2 and so this pair will lose its degeneracy also. This type of interaction is perfectly general and has been observed for p-π[12,15] and p-p systems such as ethanedithiol (Figure 8), dichloropropanes and halohydrins,[13] and π-π systems such as norborandiene.[16] The extent of splitting is governed by comparability of energy and extent of overlap of the orbitals concerned. The extent of mixing is often revealed by the shape of the bands in the PE spectrum. Effects are usually additive; for example, the *cis*-dichloropropene spectrum shows p-p interaction superimposed on p-π,[15] and electronegativity and inductive effects are usually additive as in the halohydrins.[13]

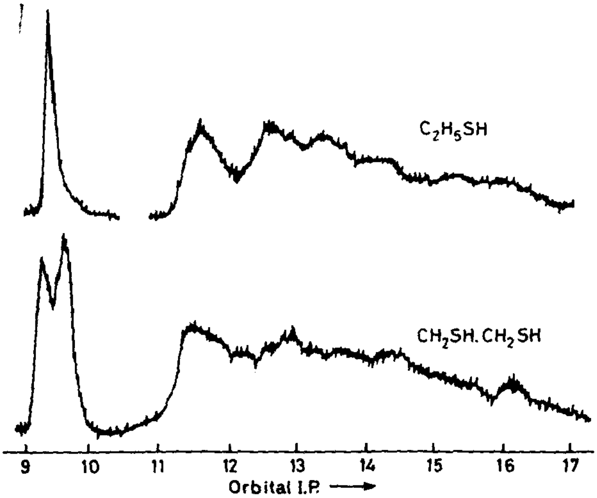


FIGURE 8 U.v.-PE spectrum of ethanethiol and 1,2-ethanedithiol showing splitting of S 3p lone-pair orbitals by interaction.

Rule 3 means that examination of compounds containing halogens, phosphorus, nitrogen, oxygen, and sulphur by u.v.-PES is often rewarding.

QUALITATIVE ANALYSIS

In principle, and, as Siegbahn's group have demonstrated, in fact, X-ray-PES is very useful for qualitative analysis. The presence of all elements except hydrogen can be detected with certainty, approximate elemental analysis can be obtained and a correlation diagram, such as Figure 7, may permit structural identification. It is usually possible to say which one of several possible isomeric configurations is correct. There are several problems: it is not easy to be certain of the absolute value of the binding energy because of surface charges on the sample and in the target chamber; it is not always easy to resolve peaks due to the same atoms in a non-equivalent environment; and neighbour effects may result in a wide range of binding energy (chemical) shifts for the same atom, e.g. Hercules has examined 50 compounds containing quaternary nitrogen and found a spread of 5 eV for the nitrogen peak.[17]

Qualitative analysis by u.v.-PES is also an attractive proposition. The work of Turner's group has shown that the spectra of different compounds, even closely related ones, are quite distinct.[3] Our own work has only served to confirm this (Figures 9 and 10). As yet there is no equivalent approach to group frequencies used in infrared spectroscopy or the chemical shifts of n.m.r. spectroscopy, but it is probable that generalizations will emerge, and indeed some are suggested in Figure 10.

QUANTITATIVE ANALYSIS

The area under a peak in an X-ray-PE spectrum is proportional to the concentration of the corresponding element in the sample. The proportionality factor depends both on the element and the orbital from which ionization is being observed. Thus a calibration curve is required. From the few studies made, it seems an adequate method down to a concentration level of about 1%.[18] We have studied the possibility of using u.v.-PES for quantitative analysis.[19] Our preliminary results show that it is quite feasible, but that the sampling systems of the present generation of instruments will have to be modified before it will be a method of choice. The basic problem lies in getting a representative portion of the sample into the target chamber. Because of (*a*) the differences in the volatilities of the components of a mixture, and (*b*) the possibility of the sample molecules undergoing reactions on the way to or within the target chamber, one cannot be certain that the spectrum observed is the spectrum believed to have been observed.

ANALYSIS OF MIXTURE

We are currently studying the spectra of mixtures in detail with two specific questions in mind: (i) Can one strip out the spectra of components known to be present in the mixture to leave either the spectrum of an unknown component or a base line? (ii) Are these secondary reactions in the target chamber, which vitiate the assumption that a spectrum of a mixture is the sum of the

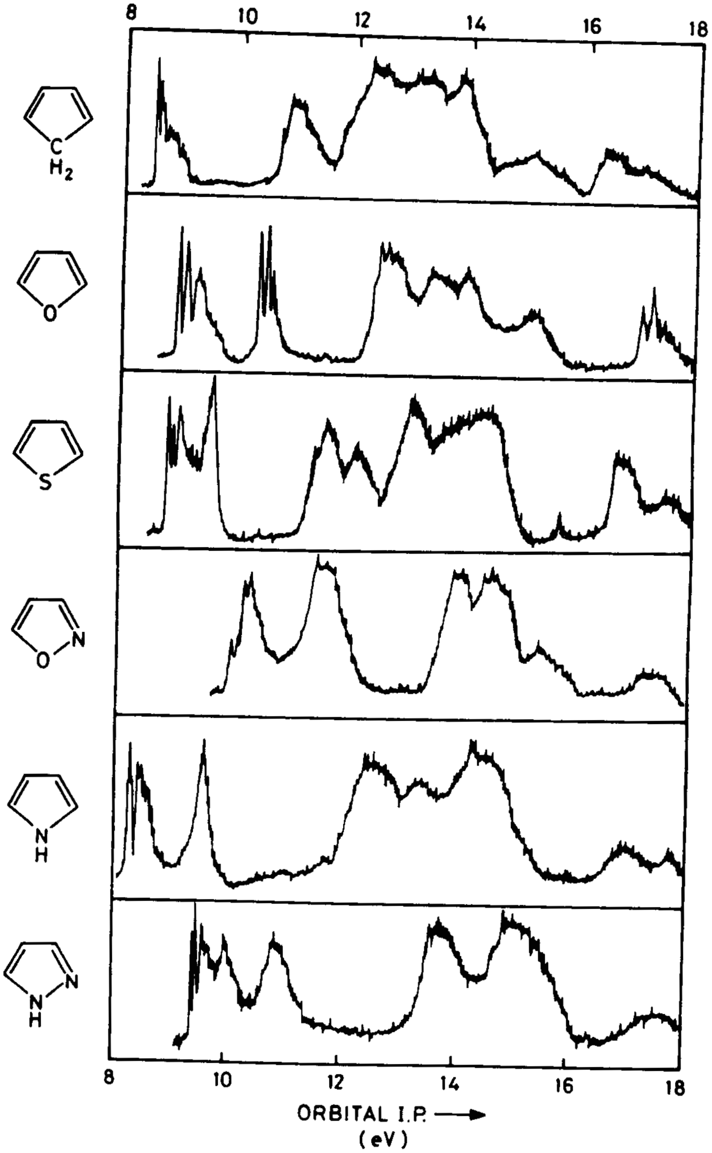


FIGURE 9 U.v.-PE spectra of a number of 5-membered heterocyclic compounds.

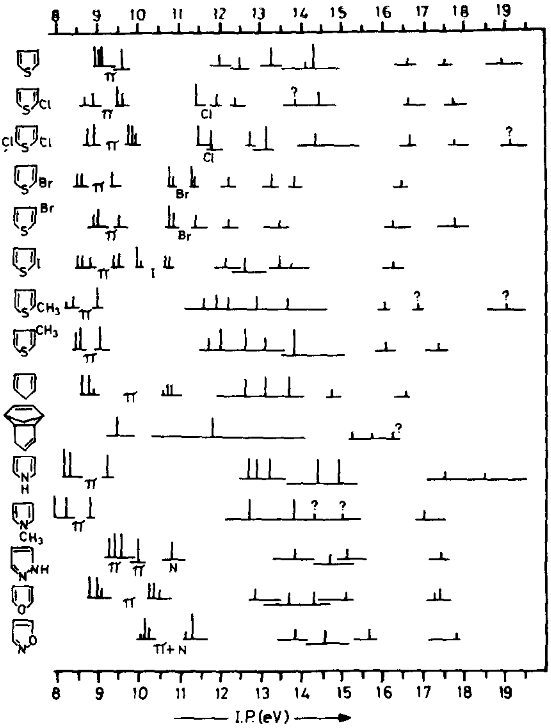


FIGURE 10 Correlation diagram for spectra of 5-membered heterocyclic and related compounds. The horizontal lines indicate peak width at half peak height; the vertical lines indicate strong, medium or weak intensities.

spectra of its components? The second question is obviously related to the first. At present it seems that secondary reactions can cause spectra run under different conditions to be variable, but that the differences are not great enough to make the spectrum stripping exercise a waste of time. On the contrary, the resolution of a spectrum of a mixture of PCl_5, $POCl_3$ and HCl into the spectra of its components can be achieved in a most convincing manner.[20] This work was carried out by hand calculation, but we are now sorting out the appropriate computer program to apply the technique routinely. Already, we have seen several instances where we anticipate that spectrum stripping will lead to improved results. For example, a typical "pure" pesticide sample contains some impurity. If we assume a mixture of three components, A, B, and C, of decreasing volatility and if we further assume that A is a readily recognizable impurity such as H_2O or HCl, then we obtain initially a spectrum of A+B+C; on further pumping A is removed to give a spectrum of B+C. Finally we pump until the successive spectra obtained are identical and we assume they are due to pure C. Stripping of A and C from the first spectrum then gives the spectrum of B.

SENSITIVITY

At present, not much is known about the sensitivity of the method. X-ray-PES seems to require microgram amounts of sample. We have used milligram amounts in our u.v.-PE spectrometer, but only a minute fraction of the sample actually reaches the target chamber. It is reasonable to argue that by analogy with mass spectrometry and argon GLC detectors that spectra should be obtainable on microgram amounts or less.

We are at present assembling the pieces to test the hypothesis that it should be possible to obtain a spectrum from the effluent of a GLC column.

COMPARISON WITH OTHER METHODS

No method has yet been devised which will take any sample, automatically process it and print out its elemental analysis, identity, and features of structural interest. Photoelectron spectroscopy is not going to alter this position. Like other spectroscopic methods its results complement those obtained from other methods. We have argued for example that the u.v.-PE spectra of 2- and 3-bromothiophene provide information which is a valuable addition to that provided by infrared and mass spectroscopy.[21] We have also been told, informally, by experts in the field that some of our spectra of phosphorous-containing compounds provide useful information, which is not so readily obtained by other techniques.

Nevertheless it is reasonable to ask: What specifically does photoelectron spectroscopy have to offer the analyst? I would suggest the following:

(i) X-ray-PES can identify all the elements presents within the sample except hydrogen.

(ii) X-ray-PES can provide sufficient information to make the identification of a compound probable.

(iii) U.v.-PES provides a unique spectrum of a compound, which will serve for qualitative identification.

(iv) U.v.-PES seems clearly to show up isomeric variations.

(v) U.v.-PES shows inter-electronic interactions within a molecule.

(vi) Elements such as O, N, P, S, and halogens are often identifiable from the u.v.-PE spectrum.

(vii) Both methods are more sensitive than n.m.r. and infrared but not so sensitive as mass spectrometry.

We can reasonably expect, over the next few years, improvements in instrumentation, which will allow the rapid handling of small samples of diverse compounds. We can also hope that our understanding of spectra will improve to the point where we may readily infer the presence of atoms and groups within the sample molecule. So far only a few pesticides or related compounds have been examined, but our studies of heterocycles,[21] ethylene halohydrins,[13] and organophosphorus compounds[20] and Eland's study of mercury compounds, such as dimethyl mercury,[22] indicate that there is considerable scope for the application of the technique to pesticide analysis.

It is worth recalling that n.m.r., infrared and mass spectrometry were all fairly crude techniques ten years after their discovery. We must also bear in mind that photoelectron spectroscopy is basically a tool for probing electrons and most molecules have electrons.

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